DEVELOPMENT OF METHODS
FOR DETERMINATION
OF ADSORPTION KINETICS
AT METAL ELECTRODES

A Thesis Submitted to
the College of Graduate Studies and Research
in Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy
in the Department of Chemistry
University of Saskatchewan
Saskatoon

by

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Development of methods for determination of adsorption kinetics at metal electrodes

Adsorption at metal electrodes is usually a very fast process and it plays a most important role in many areas of industry. The thermodynamics of the process are well known for many systems. However, there is currently no good method that allows a determination of very fast kinetics of adsorption to be made. Previously, many attempts at evaluation of kinetic parameters of adsorption were made, but in most cases, due to the inadequacy of the experimental methods used, the parameters obtained were much lower than expected.

This thesis aims at providing the means for determining the kinetics of adsorption at metal electrodes. The methods herein described are based on two different experimental techniques. These techniques are: i) fast cyclic voltammetry (FCV, potential sweep rate up to 100000 V/s) and ii) high frequency AC and FFT SW (Fast Fourier Transform Square-wave) voltammetry (frequency up to 50 MHz) at ultramicroelectrodes (5 or 6.25 μm in radius). A theoretical description of the adsorption process for both kinds of experiments is presented. A simulation program was written to provide a better understanding of the process and to elucidate the development of methods for determining the kinetics of adsorption.

Thermodynamic and kinetic descriptions of the process are based on the Frumkin adsorption isotherm. Both the equilibrium constant and the adsorption rate constant are treated as functions of potential and the electrode coverage. Comparison of results for different systems is presented as an analysis of the dependence of the adsorption rate constant on the equilibrium constant.

FCV proved to be useful in the evaluation of kinetics of chemisorption (standard rate constant in the range of $10^6$ s⁻¹) but the results for adsorption of aliphatic alcohols were unreliable.

High frequency AC methods allowed the determination of kinetics of physical adsorption. It was found that the activation energy of the adsorption process can be expressed as a linear combination of the electrical component of the standard free energy of adsorption (a major contribution) and the energy of lateral interactions (a
minor contribution). At the zero charge potential the rate constant reaches the maximum value of $(4.6 \pm 0.3) \times 10^9$ s$^{-1}$. 
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Abstract

Adsorption at metal electrodes is usually a very fast process and it plays a most important role in many areas of industry. The thermodynamics of the process are well known for many systems. However, there is currently no good method that allows a determination of very fast kinetics of adsorption to be made. Previously, many attempts at evaluation of kinetic parameters of adsorption were made, but in most cases, due to the inadequacy of the experimental methods used, the parameters obtained were much lower than expected.

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1. Introduction

The adsorption of organic substances at metal electrodes has been investigated for a long time [1, 2]. The process is interesting due to its application in areas like electroanalysis [2], electro-organic synthesis, polymerisation [3,4], photo processes [5], electrocatalysis and inhibition of electrode processes [6].

Adsorption on electrodes is most often considered from the thermodynamic point of view, with the assumption that adsorption equilibrium is achieved quickly. Although equilibrium of the adsorption process of most organic substances is attained within $10^{-6}$s it is often important to be able to determine the value of the adsorption rate constant. Although thermodynamic properties of the system may be favourable, the kinetics of the process may indicate that the system is inadequate for the intended purpose. This can be understood if the rates of both adsorption and desorption processes are considered. If both rates are high, but the adsorption rate is considerably larger than the desorption rate constant, then the corresponding equilibrium constant will also be high. Consideration of adsorption thermodynamics alone may lead to an erroneous choice of the system in such cases. It has to be stressed that when a stable deposited monolayer is desired the exchange of the monolayer components between solution and interface should be avoided. For example, although the thermodynamic parameters characterising adsorption of different corrosion inhibitors are well known, this information isn't adequate for the evaluation of their inhibiting properties. Such an evaluation would require its kinetic description as well. Methods used in attempts to determine such kinetics [7] proved to give unsatisfactory results.
More examples of such systems, showing the need for a development of methodology allowing determination of adsorption kinetics, will be given below.

Many surfactants assemble spontaneously into organised monolayers if their solutions are brought into contact with the substrate. This property may be used to modify the surfaces if the head group interacts with the substrate. In addition, if a tail group is carefully selected self assembled monolayers could be used to produce desired physico-chemical properties [8]. Self-assembled films can be used as platforms for electronic and optical devices, chemical sensors, lubricants, model biological membranes and catalysts [9]. They can also be utilised in the investigation of electron transfer mechanisms at the electrode/electrolyte interface. Some examples of self-assembling monolayers include sulphur containing compounds on gold and platinum [10,11], isocyanates on platinum [12] and pyridine derivatives on platinum [13]. The property of organosulphur derivatives to form monomolecular films on many metal surfaces has found application in many areas of chemistry. For instance, xanthates are used in ore flotation [14]. The two-dimensional structures of these films can be controlled to a greater extent if their deposition is performed under electrochemical conditions. Again, the determination of the kinetics of such a process is desirable for selection of optimum systems.

The adsorption processes are important also because of their effect on other electrode processes. The adsorbed surfactants influence the electrode kinetics through several different mechanisms. The electrode process may be inhibited because of the blocking of the electrode surface, the change of the potential in the outer Helmholtz plane (oHp), or the change of the activation energy for the charge transfer step [15]. Again the complete analysis of the effect of surfactants on the examined process requires a consideration of surfactant adsorption kinetics.
Another example of adsorption processes important in industry is the application of organic coatings. They can be deposited on metal surfaces when the polymerisation process is initiated electrochemically. This method has many advantages over those traditionally used [16]. The polymerisation is initiated by the radical-type oxidation processes of adsorbed substances, which leads to a chain growth [17]. In a similar way as for other adsorption processes the kinetics of the initial adsorption step have a significant influence on the overall process, and the investigation of the kinetic properties of the system may lead to a better understanding of the examined process.

Electro catalysis is another area where the adsorption kinetics are of great importance. The study of the electrocatalysis taking place in direct fuel cells with small organic molecules shows that the anodic oxidation of the reactant to CO₂ occurs through two possible pathways [18]. The first pathway leads through the formation of reactive intermediates, while the second one goes through dissociative adsorbates. The latter possibility arises from the interactions of the reactant molecules with the electrode surface. This adsorption process takes place at potentials at which oxygen adsorption does not occur, leading to the poisoning of the surface. An example of such self-poisoning may be the electrooxidation of formic acid on Pt electrode [18]. The electrode loses its activity almost completely after a scan to positive potentials. The dissociative adsorption of organic molecules includes many steps, from which the first and the most important seems to be the adsorption of the reactant at the electrode surface. Full understanding of the self-poisoning phenomenon includes the investigation of the kinetics of this process.

Until now there has been no method developed that would allow the determination of the kinetics of fast adsorption processes at electrodes. The methods used so far are most commonly based on the examination of the dependence of the electrode coverage on the adsorption time. This imposes a
limit on the highest accessible rate constant, which is much lower than the value expected for the adsorption of organic substances (ca. $10^6$ s$^{-1}$). This indicates that there is a need for a universal method of the determination of kinetics of adsorption to be developed. The aim of this work is to develop a theory describing the kinetics of physical and chemical adsorption processes and to create and test methods of determination of these kinetics. This work presents two methods based on cyclic voltammetric and AC experiments on ultramicroelectrodes, that can be successfully used in the determination of kinetics of adsorption process for both physical and chemical adsorption. The theoretical description of the adsorption limited by the kinetics of the process, together with the simulation program based on this description provides the long needed basis for further development in this area.
2. Theoretical

2.1 Double layer.

Before any theoretical considerations of the adsorption processes taking place at an electrode immersed in electrolyte solution can be made, the properties of the double layer formed at the interface have to be taken into account.

The double layer can be presented schematically as in Fig. 2.1. The layer adjacent to the electrode is occupied by solvent molecules and/or any specifically adsorbed substances. This forms the inner Helmholtz plane (iHp). Solvated ions or molecules can approach the electrode only to a certain distance, called the outer Helmholtz plane (oHp), determined by the thickness of the solvent layer and the size of the adsorbed molecules. The number of ions in the oHp is controlled by ion diffusion and their electrostatic interactions with the charged electrode. For a detailed description of this dependence see references [19 - 21].

Because of the separation of the charge at the electrode and in solution a potential gradient is observed in the double layer (see Fig. 2.1). At all times charge at the electrode, \( q_m \), is equal to the total charge on the solution part of the interface composed of the charge of any ions in the oHp, \( q_{oHp} \), and of any specifically adsorbed ions, \( q_{ads} \).

\[
q_m = q_{oHp} + q_{ads} = zF\Gamma_+ + zF\Gamma_-
\]

(2.1)

where \( z \) is the charge of the ion, \( F \) is the Faraday constant and \( \Gamma_+ \) and \( \Gamma_- \) are the cation and anion relative surface excesses. A comparison of the experimental charges corresponding to cations and anions at the solution part of the interface with those calculated theoretically assuming
Fig. 2.1. Schematic model of the double layer. Solvated cations construct the outer Helmholtz plane (oHp). The centre of specifically adsorbed ions at the electrode surface corresponds to the inner Helmholtz plane (iHp). Potential profile in the double layer given below. $\Phi_m$, $\Phi_e$ and $\Phi_{iHp}$ are the potential of the electrode, of the bulk of the solution and in iHp, respectively.
that all the charges reside only in the diffuse part of the double layer (ΩHp being the minimum distance of the ions from the electrode), allows a detection of specific adsorption. Specific adsorption of ions or neutral molecules cannot be explained solely by electrostatic interactions with the oppositely charged electrode. In many cases (especially for specific adsorption of anions) the adsorption takes place despite the repulsive electrostatic forces. The process can be understood only if all kinds of interactions between the adsorbate, the electrode material, solvent molecules, other molecules present in the solution and other adsorbing molecules are taken into account. Fig. 2.2 is an illustration of the change in the properties of the double layer caused by an adsorption process. It shows the potential profile across the double layer for different electrode potentials (and hence different degree of anion adsorption) for a mercury electrode in contact with 0.3 M NaCl aqueous solution [20].

It has to be remembered that the adsorption of organic substances at the electrode surface is not always caused by an affinity to the electrode material or any electrostatic interactions, but in some cases by the solvophobicity of these compounds, leading to their expulsion from the solution to the interface, where the interactions with the solution components are minimised. Even though no specific interactions with the electrode surface take place, the presence of organic molecules can be easily determined, because of the changes in the thickness of ΩHp, leading to the changes in the double layer capacitance values.

2.2 Thermodynamics of adsorption.

In the previous section it was indicated that the extent of adsorption is determined by the interactions between all the components present in the double layer and in the bulk of the solution. The concentration of the adsorbate, \( i \), at the electrode surface (measured by the relative surface excess, \( \Gamma_i \), surface concentration, \( c_i \) (expressed in mol×cm\(^{-2}\)), or the degree of
Fig. 2.2. Potential profiles in the double layer for mercury in contact with 0.3 M NaCl in water at 25°C. Potentials given in respect to the potential of zero charge in NaF.
electrode coverage, \( \theta \) can be determined by different electrochemical and non-electrochemical methods (e.g. radiochemical, spectroscopic, ellipsometric, microbalance, etc.), some of which will be described in later sections. Once the concentration of the adsorbate at the electrode surface is known, the relationship between this value and the bulk concentration can be determined. It has to be remembered that, as in any other system, all the species at the interface have to be in equilibrium with those in the bulk of the solution. From these considerations the isotherms describing the electrode coverage as a function of the bulk concentration and the availability of an electrode surface for adsorption (expressed as 1-\( \theta \)) can be derived in terms of the adsorption energy. Some of the most commonly used isotherms are presented in Table 2.1.

Adsorption equilibrium at the electrode/solution interface can be presented in a way first proposed by Vetter and Schultze [22-27]:

\[
M(-OH_2)_\nu + S_{aq}^* \rightleftharpoons M - S^{z+\lambda} + \nu e^- + \nu H_2O_{aq}
\]  

(2.2)

where \( \nu \) is the number of water molecules replaced at the electrode surface by one adsorbate molecule, \( S, M \) represents the electrode, \( z \) is the charge of the adsorbate, \( \lambda \) is the number of electrons transferred between the electrode and the adsorbate, which can be a fractional number. There is a difference between the adsorption process in which specific interactions occur between the adsorbate and the electrode material (electrosorption process) and the redox reaction at the electrode surface. In the case of adsorption the electrons involved in the process are not totally transferred from or to the electrode, but remain shared to a different degree between the electrode metal and the adsorbate, whereas in the case of the redox process (any discharge process at the electrode) electrons are transferred and the product and the electrode remain separated. In the case of an electrosorption process the electrons shared between the electrode and the adsorbate form a chemical bond, which in the same way as any bond formed
Table 2.1. Adsorption isotherms. Equations were given in this form to keep the formalism used in the thesis. $K$ is the adsorption equilibrium constant, $c_i$ and $c_o$ are concentrations of adsorbate in iHp and oHp, respectively, expressed in mol/cm$^2$, $\theta$ is the electrode coverage, $v$ is the number of solvent molecules replaced by one adsorbate molecule and $g$ is the interaction parameter.

<table>
<thead>
<tr>
<th>Name</th>
<th>Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry</td>
<td>$K = \frac{c_i}{c_o}$</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$K = \frac{c_i}{c_o(1-\theta)}$</td>
</tr>
<tr>
<td>Virial</td>
<td>$K = \frac{c_i}{c_o} \exp\left(\frac{2g\theta}{RT}\right)$</td>
</tr>
<tr>
<td>Temkin</td>
<td>$K = \frac{1}{c_o} \exp\left(\frac{2g\theta}{RT}\right)$, for 0.2&lt;\theta&lt;0.8</td>
</tr>
<tr>
<td>Frumkin</td>
<td>$K = \frac{c_i}{c_o(1-\theta)} \exp\left(\frac{2g\theta}{RT}\right)$</td>
</tr>
<tr>
<td>Generalised Frumkin</td>
<td>$K = \frac{c_i}{c_o(1-\theta)^v} \exp\left(\frac{2g\theta}{RT}\right)$</td>
</tr>
</tbody>
</table>
between different elements, can be polarised to a certain degree, depending on the difference in the properties of the elements involved. The charge transfer from the adsorbate molecule to the electrode and *vice versa* depends on the Fermi level of the electrode metal and on the ionisation potential and electron affinity of the adsorbate. The extent to which the electrons are transferred between the electrode and the adsorbate may be described by another term introduced by Vetter and Schultze, namely the electroosorption valency, $\gamma$. The authors propose to express the electroosorption valency at $E_{pzc}$ (the zero charge potential), $\gamma_N$, as a function of the geometric factor, $g_f$, charge of the adsorbate, $z$, charge transfer, $\lambda$, and dipole terms of the desorbed water molecules, $\kappa_{w}$, and the adsorbate molecules, $\kappa_s$:

$$\gamma_N = g_f z - \lambda(1 - g_f) + \kappa_s - \nu \kappa_w$$  \hspace{1cm} (2.3)

The dipole term $\kappa_s$ depends on the dipole moment, $m_i$, the thickness of the double layer, $l_i$, and the angle from the surface normal at which the molecule is adsorbed, $\phi$:

$$\kappa_s = \frac{m_i}{l_i} \cos \phi$$  \hspace{1cm} (2.4)

where $e$ is the charge of the electron, and subscript $i$ indicates the adsorbate molecule.

The geometric factor, $g_f$, describes the extent of the adsorbate penetration into the double layer, which may be represented as a function of the electrode potential, $\Phi_m$, the potential in the adsorption layer (i.e., iHp), $\Phi_{ad}$, and the potential in the bulk of the solution, $\Phi_s$:

$$g_f = \frac{\Phi_{ad} - \Phi_s}{\Phi_m - \Phi_s}$$  \hspace{1cm} (2.5)

The $g_f$ value cannot be precisely determined, but it was estimated by Schultze and Koppitz [25] based on the results for ionic systems to be ca. 0.4.
Electrosorption valency may be represented as an analogue of the charge transferred in the electrode process, \( z \). It should be recalled that a derivative of the chemical potential of the electroactive substance, \( \mu_s \), with respect to the electrode potential, \( E \), is proportional to the number of electrons exchanged in the process:

\[
\left( \frac{\partial \mu_s}{\partial E} \right)_{a_m} = z F
\]  

(2.6)

where \( F \) is the Faraday constant, and \( a_m \) is the activity of the electrode metal.

The electrosorption valency may be represented by a similar equation:

\[
\gamma = -\frac{1}{F} \left( \frac{\partial \sigma_m}{\partial E} \right)_{\Gamma_i} = \frac{1}{F} \left( \frac{\partial \mu_s}{\partial E} \right)_{\Gamma_i} = \frac{1}{F} \left( \frac{\partial \Delta G_{ads}}{\partial E} \right)_{\Gamma_i}
\]

(2.7)

where \( \sigma_m \) is the charge density on the electrode, \( \Delta G_{ads} \) is the Gibbs energy of adsorption, and \( E \) is the potential difference across the interface.

Generally, electrosorption valency may depend on the electrode potential which may be expressed by the equation:

\[
\gamma = \gamma_N - \frac{1}{F} \int_{E_{mc}}^{E} \left( \frac{\partial C}{\partial E} \right)_{\Gamma_i} dE
\]

(2.8)

where \( C \) is the capacitance at a constant coverage.

The Gibbs energy of adsorption may be obtained by the integration of equs. (2.7) and (2.8):

\[
\Delta G_{ads} = \Delta G_{ads}^2 + \gamma_N FE - \int_{E_{mc}}^{E} \left( \frac{\partial C}{\partial E} \right)_{\Gamma_i} dEdE
\]

(2.9)

There is a strong difference between the adsorption process of aliphatic and aromatic compounds. The observed effects caused by the adsorption of aliphatic compounds depend mainly on the chain length, and the character of the functional group, which determines the orientation of the adsorbed molecule and the thickness of the double layer. Reorientation of the adsorbed molecules is observed only in a few cases. In the case of aliphatic,
neutral molecules, not interacting chemically with the electrode, \( z = 0 \) and \( \lambda = 0 \). This leads to a conclusion that \( \gamma_N \) should vary linearly with \( \kappa_s \) (see eqn. (2.3)), as \( \kappa_w \) may be assumed to be almost constant. In the case of molecules interacting chemically with the electrode metal \( (\lambda \neq 0) \), a deviation from the straight line dependence is observed. These effects were reported by Koppitz et al. [28].

The behaviour of aromatic compounds adsorbed at the electrode surface seems to be more complex [26, 27]. The reorientation process becomes quite common, as there are several possible orientations, favoured at different potentials. A detailed examination of this process was performed by Rolle and Schultze [26] for the adsorption of phenol at mercury. Fig. 2.3 presents the possible orientations of phenol at the electrode surface, which were taken into account by the authors. Only orientations B and C were concluded to represent the process taking place at the electrode in case of aromatic compounds. Notice that organic molecules reside in the iHp, while water and ions form the oHp. Orientation B is characterised by similar properties to those of adsorbed aliphatic molecules as there is no charge transfer between the electrode and the adsorbate. A different situation is observed when the molecules are adsorbed in orientation C, where the bonding via the \( \pi \) system is observed.

The electrosorption valency for aromatic compounds adsorbed in the flat orientation at the electrode, \( \gamma_N \) is in the range of \(-0.2\) to \(+0.07\), whereas all flatly adsorbed aliphatic molecules display a value of the electrosorption valency 0.04. This wide range of the electrosorption valency in case of aromatic compounds indicates that there is a charge transfer from the molecule to the electrode, which varies widely for different compounds \((\lambda > 0)\).

The estimation of \( \lambda \) for the adsorption of phenol was presented in [26]. The authors determined the value of the electrosorption valency from the dependence of the charge on the electrode on the electrode coverage for
Fig. 2.3. Schematic representation of various possibilities of adsorbed phenol at mercury.
different potentials. The slope of this dependence had two values for
different electrode coverages, indicating that the molecules were adsorbed at
two different orientations. They concluded that the flat orientation is
favoured at lower coverages, while the perpendicular one is favoured at
higher values of the electrode coverage. As $z = 0$ for both orientations, the $g\kappa$
term in eqn. (2.3) vanishes. In case of a flat adsorption of a phenol molecule
$\kappa_\parallel$ is zero, as the dipole vector is perpendicular to the electric field. The
dipole term in eqn. (2.3) corresponding to adsorbed water molecules was
evaluated to be -0.015. The number of water molecules replaced at the
electrode surface by one adsorbate molecule was determined from molecular
models to be 2 for the perpendicular and 4 for the flat orientation. As $\gamma_N$ for
the flat orientation was determined to be -0.06, taking all the values needed
in eqn. (2.3) as given above (and $g_\parallel = 0.4$), $\lambda$ is calculated to be ca. 0.2. In a
similar way, as $\gamma_N$ for the perpendicular orientation was 0.05, and $\kappa_\parallel$ in this
case can be assumed to be 0.04 cos$\varphi$, $\lambda$ is ca. zero, in accordance with earlier
predictions, since $\pi$ system is separated from the electrode by the hydrogen
atoms which reduces the electronic interaction to almost zero.

The importance of charge transfer in the case of flatly adsorbed aromatic
molecules can be determined by the analysis of the first ionisation potential,
$I$, of the $\pi$ electrons. If $I < 9$ eV, then the charge transfer contributes
significantly to the electrosorption valency, and the dependence can be
expressed as $d\lambda/dI = -0.40 \, V^{-1}$ [27].

An even more complex behaviour than that in the case of organic
neutral molecules is encountered when ionic organic molecules are
adsorbed. Blomgren and Bockris [29] and Conway and co-workers [30, 31]
demonstrated that not only are the organic ions adsorbed, but the
adsorption of neutral organic molecules and inorganic anions also takes
place at the electrode. In such cases the electrosorption valency has to be
described by an equation taking into account the contribution of other
adsorbed species (especially organic ions). Rolle and Schultze [27] showed that the charge transfer in the case of anilinium ion (RNH$_3^+$) is about 0.05, which is a smaller value than that for neutral aniline (0.19). In a similar way the charge transfer for benzoate is higher (0.36) than that in the case of neutral benzoic acid (0.09), which can be explained by a higher electron density in case of the anion. The adsorption of aromatic cations was explained as being caused by π-electron interactions at positive potentials and by electrostatic interactions at negative potentials.

The energy of adsorption reflects complex interactions between the adsorbate and all other components of the system (including the electrode and the solvent). For perpendicularly adsorbed aromatic molecules the maximum adsorption energy (-18.5 kJ/mol for phenol [26]) is similar to that for aliphatic compounds (-16 kJ/mol for butanol), whereas for flatly adsorbed aromatic compounds it is slightly larger (about 7 kJ/mol more negative for a flat than for a perpendicular orientation of phenol). It was shown by Bockris [32] that the energy of adsorption of flatly adsorbed organic molecules, Δ$G'_{ads}$, may be obtained from the equation:

$$ΔG'_{ads} = ΔG'_{ads}^\pi - ΔνΔG_w + ΔG_r$$  \hspace{1cm} (2.10)

where $ΔG'_{ads}$ is the energy of adsorption for a perpendicularly adsorbed molecule, $ΔG_r$ is the free adsorption energy due to π bonding and $ΔνΔG_w$ is the energy needed for desorption of Δν water molecules during the change of orientation of an adsorbate molecule from perpendicular to flat relative to the electrode surface. Using this equation and taking the energy of water desorption as equal to -21 kJ/mol [32], the energy of the π bonding can be evaluated as -50 kJ/mol.

The thermodynamic properties of the electrosorption of aliphatic compounds were summarised by Koppitz et al. [28]. The adsorption of most of the aliphatic compounds may be successfully described by the Frumkin isotherm (for equation see Table 2.1) [1, 33-35]. The values of the interaction
parameter, \( g \), for most aliphatic compounds lie in the range of \(-\frac{RT}{2}\) to \(-3\frac{RT}{2}\) (\(-1.24\) to \(-3.72\) kJ/mol). The interaction parameter measures the energy of lateral interactions required to remove one solute molecule from a solute filled monolayer and one solvent molecule from a solvent filled monolayer and to exchange their positions; it reflects the adsorbate-adsorbate, solvent-solvent and adsorbate-solvent interactions. The standard Gibbs energy of adsorption at zero coverage, \( \Delta G_{w}^{\circ} \), reflects the free energy required to remove one adsorbed water molecule from the water monolayer \((-U_{w} - zw_{ww})\) and to replace it by one adsorbate molecule \((U_{s} + zw_{ws})\). \(-U_{w}\) and \(U_{s}\) are the energies needed to overcome any external forces during a desorption of one water molecule and the energy gained during an adsorption of one adsorbate molecule, respectively, whereas \(-zw_{ww} + zw_{ws}\) expresses a difference between the energy spent on overcoming water-water interactions and gained on creation of water-adsorbate interactions.

As was already mentioned above, most of the organic substances [36] are characterised by a negative value of the interaction parameter, \( g \). This indicates that the lateral interactions, adsorbate-adsorbate and solvent-solvent, are more attractive than interactions between adsorbate and solvent molecules. As a consequence the adsorption process becomes more favoured as the electrode coverage increases. The Langmuir isotherm (obtained from the Frumkin isotherm when \( g = 0 \)) would be observed when all the lateral interactions are either very small or equal for both the adsorbate and the solvent.

If the difference in the size between organic and water molecules is taken into account, the generalised Frumkin isotherm results:

\[
K = \frac{c_{i}}{c_{o}(1-\theta)} \exp\left(\frac{2g\theta}{RT}\right)
\]  

(2.11)

\( c_{i} \) and \( c_{o} \) are the concentrations of the adsorbate at iHp and oHp, respectively, expressed in mol/cm\(^2\); \( \nu \) represents the number of water
molecules desorbed from the electrode surface in order for one adsorbate molecule to be adsorbed and $K$ is the adsorption equilibrium constant. Note that the interaction parameter in the generalised Frumkin isotherm has a slightly different value than in the case of the Frumkin adsorption isotherm. This is caused by the requirement that $\nu$ consecutive adsorption sites are occupied by one adsorbate molecule, leading to geometric constraints. It was observed [36] that the generalised Frumkin isotherm doesn't describe the experimental data any better than the Frumkin isotherm. In an attempt to explain this seemingly illogical phenomenon it was postulated [1, 37, 38] that the adsorbate molecule displaces small clusters of water molecules (formed due to hydrogen bonds) of the same size as the adsorbate. Guidelli [36] proposed this theory, taking into account not only the possibility of H-bond formation, but the local order as well. These attractive interactions cause the water molecules to aggregate and occupy a maximum of adjacent sites permitted by the thermal diffusion. As a consequence the probability of the adsorbate to displace $\nu$ water molecules from the electrode surface is greater than $(1-\theta)^\nu$, and tends to be expressed by $(1-\theta)$ value.

It was observed that the interaction parameter is a quadratic function of the electrode charge [39] with a minimum negative value for the charge of maximum adsorption. This seems to be due to the H-bonding between the adsorbed water molecules and to attractive dipole-dipole interactions between adjacent water dipoles [36]. For increasingly negative values of the electrode charge the number of H-bonds does not change, but the increasing value of the electric field causes the water dipoles to rotate and as a result repulsive interactions take place. As the overall attractive interactions between adsorbed water molecules decrease, the value of $g$ becomes less negative. For positive values of the electrode charge a different effect causes the interaction parameter to become more positive. Water molecules are interacting with the electrode through oxygen atoms and they become
chemisorbed, which leads to a breaking of the H-bonds within the monolayer. The latter effect is also responsible for the deviation from the Frumkin isotherm at positive electrode potentials [39].

It was estimated from the adsorption energy dependence on the electrode charge [40, 41] that the number of water molecules displaced from the electrode by one adsorbate molecule is 2.5 for n-butanol, 3.5 for n-pentanol, 4 for n-hexanol, 4.5 for n-heptanol, and 5.5 for n-octanol, which is in a good agreement with the experimentally determined surface area occupied by one n-alcohol molecule (taking the area for one water molecule as close to 0.10 nm$^2$). It was also noted that an increase in the H-bonding should be observed as $\nu$ value increases, which would lead to a more negative value of the interaction parameter. This was shown to be true for tertiary aliphatic alcohols, which occupy a larger area than n-alcohols, and display a more negative value of the interaction parameter [42].

When the adsorbate is a neutral, non-polar molecule, the adsorption process is totally determined by the properties of the water monolayer, as the adsorbate doesn't interact either with other adsorbate molecules or with the electric field. As a result, a maximum adsorption occurs when the desorption of water molecules requires the least energy. When the desorption of water molecules has to be taken into account, two factors will influence the extent of the process: the energy required to break H-bonds within the water monolayer, and the energy needed to overcome electrostatic interactions of water dipoles with the electric field. The energy needed to break H-bonds when the desorption of water molecules takes place is partly recovered due to a rearrangement of water molecules surrounding the adsorbed solute molecule, leading to an increase in the number of H-bonds. As a consequence, the main contribution to the energy needed during adsorption of neutral, non-polar substances comes from the electrostatic interactions of adsorbed water dipoles with the external electric
field. These interactions are smallest for small negative values of the electrode charge.

The properties of the electrode metal also have to be taken into account. Both the bulk solvent and the bulk metal undergo a certain reorganisation when they are brought into contact. The solvent dipoles tend to assume a preferential orientation at the electrode surface, even if the charge at the electrode is zero. The valence electrons of the metal, when brought into contact with a solution, spill over the surface of the metal, leading to a formation of the surface dipole, whose negative end is always directed towards the solution. This is caused by the existence of unbalanced forces acting on both electrons and ion cores at the metal interface. The effect of these unbalanced forces is negligible in the latter case as lattice interactions keep ion cores in place. This model is known as "jellium". Different metals forming electrodes are characterised by a different degree of electron spillover. This property explains the differences in the properties of different metal electrodes. The electron density profile at the electrode/solution interface may be represented schematically as in Fig. 2.4. For negative charge on the electrode the electron spillover toward the solution occurs to a larger degree, while for a positive electrode charge the degree of spillover is much smaller. The electron spillover towards the solution leads to a net positive charge in the bulk of metal (indicated as a positive background in the figure). Electron spillover creates an electric field that opposes the spillover itself. The range of this field is very small, and vanishes at a distance from the electrode of 1-2 Å. As a result this field acts only on the first lattice plane of water and adsorbate molecules. If an adsorbate dipolar molecule is adsorbed at a negatively charged electrode with the positive end towards the electrode, then the effect of this electric field produced by electron spillover causes the molecule to be expelled from the adsorbed state. An opposite effect is observed when the molecule is adsorbed with its negative end toward a negatively charged electrode. This description of the
Fig. 2.4. Schematic picture of jellium in contact with a three-dimensional lattice of water molecules, in which the first lattice plane also contains monomeric dipolar solute molecules. The electron density profile is shown at zero charge (−), as well as at a positive (+) and at a negative (−) charge. Taken from [36].
electron spillover explains the difference in the adsorption of aliphatic alcohols [43, 44] and thiourea [45] on Hg and Ga electrodes. It is worth mentioning that, as the bulk electron density in Ga is two times higher than in Hg, the electron spillover in the case of Ga is also expected to be higher, as well as the local electric field generated by it. Aliphatic alcohols are adsorbed with the OH group towards solution. The short range electric field created by the electron spillover acts only on the terminal $H^\delta^+ - C^\delta^-$ dipoles, facing the electrode with its positive end. As a consequence of a higher electron spillover and a higher resulting electric field on Ga electrode, the adsorption of alcohols on this electrode is smaller than on a mercury electrode. In case of thiourea the negative end of $C^\delta^+ - S^\delta^-$ dipoles is directed towards the electrode and an opposite effect is observed (a higher adsorption at Ga than on Hg electrode).

2.3 Kinetics of adsorption.

In the previous section a description of different effects on the adsorption thermodynamics of different substances on metal electrodes was discussed. The kinetics of the adsorption process at the metal electrodes is in many ways analogous to the kinetics of a discharge process at the electrode. There are, however several differences that have to be taken into account during a theoretical description of the process.

The amount of the substance adsorbed at the electrode is controlled by its diffusion from the bulk of the solution to the electrode surface (or rather oHp) and by the adsorption and desorption rate constant, $k_a$ and $k_d$, respectively. The interface during the adsorption process may be schematically represented as in Fig. 2.5. As the Frumkin adsorption isotherm successfully describes adsorption of most organic substances the rate constant of adsorption and desorption processes may be expressed with the equation based on this isotherm:
Fig. 2.5. Schematic illustration of an electroosorption process. iHp and oHp are inner and outer Helmholtz planes, respectively. A represents the adsorbate and Sol the solvent molecule. Adsorption/desorption step is represented as a transfer of adsorbate molecules between iHp and oHp with rate constants $k_a$ and $k_d$. 

23
\[ k_s(E, \theta) = k_s(E) \exp \left( -\frac{2G^s\theta}{RT} \right) = k_s \exp \left[ -\alpha \frac{\gamma(E)F}{RT} (E - E^o) - \frac{2G^s\theta}{RT} \right] \] (2.12)

\[ k_d(E, \theta) = k_d(E) \exp \left( \frac{2(g - g^s)\theta}{RT} \right) = k_d \exp \left[ (1 - \alpha) \frac{\gamma(E)F}{RT} (E - E^o) + \frac{2(g - g^s)\theta}{RT} \right] \] (2.13)

where \( \alpha \) is the charge transfer coefficient, \( E^o \) is the standard potential and \( k_s \) is the standard rate constant of the adsorption/desorption process, expressed in \( s^{-1} \). Since the rate constant of the process depends not only on the potential, but on the electrode coverage as well, an additional term expressing this dependence is included in the kinetic equation. The activated complex interaction parameter, \( g^s \), takes into account the interactions between the adsorbed molecules in the ground and in the activated states, which increase the energy barrier for both adsorption and desorption process by \( 2g^#\theta/RT \). The resulting adsorption rate may be expressed as follows:

\[ \frac{dc_i(t)}{dt} = k_s(E)c_e(t)[1 - \theta(t)] \exp \left( -\frac{2G^s\theta(t)}{RT} \right) - k_d(E)c_i(t) \exp \left( \frac{2(g - g^s)\theta(t)}{RT} \right) \] (2.14)

or

\[ \frac{dc_i(t)}{dt} = k_s(E, \theta)c_e(t)[1 - \theta(t)] - k_d(E, \theta)c_i(t) \] (2.15)

In the literature [46, 47] kinetic equations for adsorption are usually written with a symmetry factor, \( \chi = g^#/g \), which in general form can be represented as:

\[ \chi = \left( \frac{\partial \Delta G_{ad}^s}{\partial \theta} \right)_E = \left( \frac{\partial \Delta G_{ad}}{\partial \theta} \right)_E \] (2.16)

where \( \Delta G_{ad}^s \) is the activation energy of the adsorption process.
Gileadi [46] suggested that \( \chi \) should be equal to the symmetry factor, \( \alpha \), which by analogy to reduction-oxidation reactions can be defined as:

\[
\alpha = \left( \frac{\partial \Delta G_{ads}^\circ}{\partial \theta} \right)_{\theta} = \left( \frac{\partial \Delta G_{ads}^\circ}{\partial \Delta G_{ads}^\circ} \right)_{\theta} \tag{2.17}
\]

However, since the first derivative is calculated at a constant potential and the second one at a constant coverage, there is no reason to assume that they should be equal. Typically, \( \alpha \) is between 0 and 1 but the experimental results presented in the discussion part of the thesis show that \( \chi \) can be significantly larger than 1. Furthermore, in some special cases \( \Delta G_{ads} \) may be independent of the coverage \( (g = 0) \) which leads to an undefined \( \chi \). Because of that the symmetry factor, \( \chi \), is not used in the above kinetic equations.

Most of the adsorption kinetic measurements performed so far have been based on the analysis of the dependence of the electrode coverage on time. This method of the evaluation of adsorption kinetics is limited to relatively slow processes. In most cases adsorption was carried out for a measured time with a subsequent determination of the electrode coverage. In many cases the method used for the electrode coverage determination put a limitation on the highest accessible adsorption rate constant. Most of the organic substances are adsorbed in a time scale shorter than \( 10^{-6} \text{ s}^{-1} \) [e.g. 50 and 51]. The adsorption rate constants obtained by different authors [52-71] were much lower indicating that the reported values of rate constants correspond to processes different than adsorption. In most cases the investigated processes were controlled either by mass transport to the electrode, or the measured rate constant corresponded to a different process, taking place at the electrode surface and changing the electrode coverage. One of the probable explanations of very small adsorption rate constants obtained in these experiments is that the investigated process was an
adsorbate reorientation, not adsorption. In most of these papers the measurements were limited either to one potential, or, at best, to just a few potential values. Again, it is well known that adsorption at the electrode surface changes dramatically with a change of the electrode potential, which in turn makes a determination of this dependence essential in any serious examination of the adsorption process. Until now the most thorough examination of the kinetics of adsorption processes was performed by Lorenz and Möckel [50] and Armstrong [51]. In both cases methods were used that took advantage of a very short time parameter characteristic for AC techniques. However, the technical instrumentation available in the 1950s and 60s wasn't advanced enough to allow accurate determination of the adsorption rate constants of the examined substances. Even if the available frequencies (1 MHz used in some measurements by Armstrong) were high enough for kinetic experiments, the electrodes commonly employed at that time were not small enough to allow measurements at high frequencies or to record cyclic voltammograms at high potential sweep rates. Nevertheless, these studies opened a new approach in this area. Unfortunately, they were seemingly forgotten by those who dealt with this problem later. This is especially surprising since the problems mentioned above should no longer be a barrier, due to technological progress. Recently, a method of fabricating ultramicroelectrodes was developed [73-75], and they are now commonly used in many kinetic measurements. The advantages associated with the application of ultramicroelectrodes will be discussed later. The development of electronics in the last thirty years has been extensive and this has positively influenced the progress in the electronic equipment used in electrochemistry. A short literature review showing attempts made so far to determine adsorption kinetics will be presented below.

The first attempts to measure the kinetics of the adsorption process at electrodes were made over 40 years ago. Frumkin and Melik-Gaikazyan [48] in 1951 and then Melik-Gaikazyan [49] in 1952 considered the dependence
of the impedance obtained for the adsorption process on the kinetics of the process. Unfortunately the adsorption rate constant values determined for the adsorption of n-amyl alcohol from 1 M KCl solution were dependent on the frequency used, changing from $1.4 \times 10^2$ to $1.1 \times 10^6$ s$^{-1}$ for the corresponding frequency range of 20 to 200000 Hz. The equipment used was a simple AC bridge. The frequencies employed in these measurements were limited by the technical possibilities at that time and, as it will be shown later, they were too small for the accurate determination of the adsorption rate constants of alcohols.

In 1956 Lorenz and Möckel [50] published a paper that for many years set a standard in this area. The frequencies employed by them were again only up to 100 kHz, and the adsorption rate constant evaluated for different aliphatic alcohols, cyclohexanol, benzyl alcohol, phenol, methylethyl ketone, chloroform and butyric acid was determined to be larger than $10^5$ s$^{-1}$. Mixed diffusion and kinetic control was assumed. The dependence of certain impedance components for different frequencies was analysed with the assumption of various rates of diffusion and adsorption, corresponding to pure diffusion, pure kinetic and mixed control.

In 1967 Armstrong et al. [51] studied the kinetics of the adsorption process of n-butyric acid and cyclohexanol from 2 M KCl solution at a mercury electrode. The frequencies used in these experiments are impressive, as they range from 100 Hz to 1 MHz. The cell resistance was evaluated at relatively low frequencies (300 Hz to 500 kHz) at the potentials at which the adsorption process was absent. The authors argued that the use of a very high frequency in the evaluation of the cell resistance may lead to the oversight of some processes changing the cell resistance, like electrode shielding, or electrolyte penetration. The authors concluded that up to 150 kHz there was no deviation from a pure diffusion control for both substances studied. This led them to the conclusion that the adsorption rate
constant must be higher than $10^6 \text{s}^{-1}$. At the same time, they imposed the upper limit on this value to be $10^{10} \text{s}^{-1}$, corresponding to the rotational relaxation time of the molecule. The authors attributed the discrepancy between their results and those of Lorenz and Möckel [50] to an incorrectly evaluated cell resistance in the latter case, due to the determination of this value from extrapolation to high frequencies.

In the most recent literature the problem of kinetic control of the adsorption process seems to be gaining some interest. Nevertheless, very often the methods used seem to be not adequate for the attempted task, and in most cases only very limited information is obtained. It seems surprising that such measurements are not performed with the use of increasingly more sophisticated methods, involving ultramicroelectrodes and electrochemical methods characterised by a very short time parameter. These methods include high frequency AC voltammetry and cyclic voltammetry with a very high potential sweep rate, commonly used in the determination of kinetics of electrode processes. In the following part a short review of the recent literature regarding this problem will be presented.

In many papers examining the adsorption kinetics the experimental methods used do not allow determination of high rate constants. These methods are characterised by a high time parameter (e.g. polarography or slow sweep rate cyclic voltammetry). In most cases no attempt is made to determine the adsorption rate constant but a method is given that allows one to distinguish between diffusion and kinetic control of the process. For example, in 1985 Komorsky-Lovric' and Lovric' [52] considered a kinetic control of the adsorption of the electrode reaction product. The authors used polarography to obtain experimental data and gave a method of distinguishing between kinetic and diffusion control of the adsorption of the product at the electrode. No direct evaluation of the corresponding adsorption rate was attempted. As well, no rate determination was
attempted in case of the work of Miller and Doll [53] who investigated the adsorption of two polypeptides (alamethicin and mellitin) at a mercury electrode. The degree of the electrode coverage was determined from the decline of the differential capacitance accompanying the adsorption process. The authors conclude that in the case of alamethicin the process is diffusion controlled as the capacitance, \( C \), can be represented by the equation:

\[
C = \theta C_m + (1 - \theta)C_o
\]  

(2.18)

where \( C_m \) is the capacitance of the surface covered by the condensed monolayer, and \( C_o \) is the capacitance when no adsorption takes place. The effect of mellitin adsorption kinetics on the overall process was also evaluated from the change of the double layer capacitance with time. The changes of capacitance with time indicated that at higher electrode coverages the adsorption process was slowed down, probably due to the repulsion between positively charged adsorbing molecules. Stamford et al. [60] claimed to measure the adsorption rate constant from cyclic voltammetric experiments recorded for a potential sweep rate equal to 300 V/s. This allowed the measurements of rate constants up to 5 s\(^{-1}\), which is actually a rate of diffusion for an adsorption process.

Many authors have determined the rate of adsorption by analysing the change of the electrode coverage, \( \theta \), with time, \( t \). In many cases the adsorption process is carried out for a measured time with a subsequent oxidation of the adsorbed substance. This method may introduce some inaccuracy in the evaluation of \( \theta \) vs. \( t \) dependence and hence in the determination of the adsorption rate constant. Recently, a very interesting paper [54] describes the kinetics of a dissociative adsorption of formic acid on platinum electrodes. The series of processes taking place at the electrode surface may be presented as follows:

\[
\text{HCOOH} + \text{Pt} \rightleftharpoons \text{PtHCOOH}_{ads}
\]

(2.19)

\[
\text{PtHCOOH}_{ads} \rightarrow \text{PtCO}_{ads} + \text{H}_2\text{O}
\]

(2.20)
\[ \text{PtCO}_{\text{ads}} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- + \text{Pt} \] (2.21)

The oxidation reaction (2.21) was used to determine the amount of formic acid adsorbed at the electrode. The value of the adsorption rate for the adsorption potential -0.030 V at Pt(100) electrode was calculated to be \(1.24 \times 10^{-10}\) mol cm\(^{-2}\) s\(^{-1}\) (about 0.25 s\(^{-1}\)). Another example of the determination of the dependence the electrode coverage on time from the charge corresponding to the oxidation of adsorbed substances is the work of Tirado \textit{et al.} [57]. The authors investigated the kinetics of the adsorption process of self-assembling molecules. The Langmuir isotherm was used in the formation of kinetic equations with the assumption that the rate of the desorption process is negligible:

\[ \theta = 1 - \exp(-k_a C_b t) \] (2.22)

A different dependence was expected for a fast adsorption process controlled by the mass transport or diffusion:

\[ \theta = 2\pi^{-1/2} \left( \frac{C_b}{\Gamma_{\text{max}}} \right) (D t)^{1/2} \] (2.23)

where \(D\) is the diffusion coefficient, and \(\Gamma_{\text{max}}\) is the maximum surface excess. In the case of the examined adsorption of osmium complexes of the type [Os(bpy)\(_2\)LCl\(^+\)], where bpy is 2,2'-bipyridine and L are different organic ligands, the adsorption process was better described if a kinetic control was assumed. The measured adsorption rate constants were found to change with the bulk concentration with values ranging from 700 to 10000 M\(^{-1}\)s\(^{-1}\) (corresponding to a half reaction time, \(\tau_{0.2}\), for 0.1 M solution of \(7 \times 10^{-6}\) to \(1 \times 10^{-4}\) s), without a defined dependence on the bulk concentration.

Another method used for the determination of electrode coverage was based on the suppression of hydrogen evolution caused by adsorption of some substances. Drazic' \textit{et al.} [55] examined the kinetics of adsorption of Cl\(^-\) and Br\(^-\) ions and of 2-naphthol-3,6-disulphonic acid (NDSA) during the cathodic polarisation of an iron electrode in 0.5 M H\(_2\)SO\(_4\) solution. These substances
behave as inhibitors of the corrosion process. Adsorption of halogen ions and many organic substances inhibit the evolution of hydrogen [56]. It was observed [55] that both Cl\(^-\) and Br\(^-\) ions followed the Temkin isotherm. The kinetic equation corresponding to this isotherm (with the assumption that the desorption rate is negligible) can be represented as [55]:

\[
\frac{d\theta}{dt} = k_a C_b \exp\left(-\frac{2\beta g \theta}{RT}\right)
\]  

(2.24)

where \(C_b\) is the bulk adsorbate concentration and \(\beta\) is the transfer coefficient (assumed to be equal 0.5). The integration of this equation gives the dependence of \(\theta\) on time:

\[
\theta = \left(\frac{RT}{2g\beta}\right) \ln\left(\frac{2g\beta k_a C_b}{RT}\right) + \left(\frac{RT}{2g\beta}\right) \ln t
\]  

(2.25)

The slope of the dependence of \(\theta\) on \(\ln t\) permits the evaluation of the interaction parameter, \(g\), while the intercept allows the determination of \(k_a\) at zero coverage. As an example of the results obtained in these systems, the values for the adsorption of both ions at -350 mV were as follows:

i) for Br\(^-\) ion \(g = 40.8\) kJ/mol and \(k_a = 0.61\) mol\(^-1\)dm\(^3\)s\(^{-1}\) (corresponding to the half reaction time, \(\tau_{1/2} = 0.11\) s for 0.1 M Br\(^-\) solution).

ii) and for Cl\(^-\) ion \(g = 22.9\) kJ/mol and \(k_a = 3.4\times10^{-5}\) mol\(^-1\)dm\(^3\)s\(^{-1}\) (corresponding to \(\tau_{1/2} = 2.0\) s for 0.1 M Cl\(^-\) solution).

In case of NDSA a kinetic equation based on the Frumkin adsorption isotherm was used. As it differs from the one used in this thesis (see eqns. (2.14) and (2.15)) it is presented below:

\[
\frac{d\theta}{dt} = k_a \nu(1-\theta)^\nu C_b \exp\left(-\frac{g\theta}{RT}\right) - k_d \theta \exp\left(\frac{g\theta}{RT}\right)
\]  

(2.26)

This equation seems to be based on an oversimplified model, as the authors arbitrarily separate the effect of interactions in the adsorbed state between an adsorption and desorption process, assuming that this is symmetrically divided between the two processes. The estimation of the values of \(k_a\) and \(k_d\)
was obtained by computerised curve fitting, with the assumption that \( \nu = 3 \).

The results for the NDSA adsorption at the electrode potential -350 mV were as follows:

\[ g = -6.2 \text{ kJ/mol}, \ k_a = 1.6 \times 10^{-2} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1} \] (corresponding to \( \tau_d = 4.3 \text{ s} \) for 0.1 M solution) and \( k_d \approx 10^{-3} \text{ s}^{-1} \).

The same kinetic equation used for the determination of the kinetics of adsorption of Cl\(^-\) ion led to the determination of both adsorption and desorption rate constants:

\[ g = 11.4 \text{ kJ/mol}, \ k_a = 2.7 \times 10^{-2} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1} \] (corresponding to \( \tau_d = 2.6 \text{ s} \) for 0.1 M Cl\(^-\) solution) and \( k_d = 6 \times 10^{-7} \text{ s}^{-1} \).

The kinetic parameters presented above [55] seem to be very small. An explanation of this effect may be obtained if we consider the properties of the electrode used and the implications of the method employed in the determination of the adsorption/desorption rate constant. During cathodic polarisation of the iron electrode a process of electromechanical desorption, characterised by the "peeling off" of the subsequent layers of the electrode takes place, causing an additional "desorption" (independent of the electrochemical properties of the system) or rather a mechanical removal of the adsorbed substances from the electrode surface. As the kinetics of the process were evaluated from the dependence of the electrode coverage on time, and the electrode coverage was influenced by both an electrochemical process and a purely mechanical removal of the adsorbed layer from the electrode, the observed rate constant was a complex function of both of these processes and didn't allow any conclusions regarding the rate of the adsorption process itself. The process may be looked at as caused by the hydrogen evolution, leading to the removal of small pieces of iron into the solution, together with the adsorbed layers of examined substances. A choice of a different method to determine the kinetic parameters would be helpful in the evaluation of the kinetics of adsorption alone.
The kinetics of the flavin adenine dinucleotide (FAD) adsorption from 1 M H₂SO₄ solution at platinum electrodes was investigated by Podlovchenko et al. [58]. Potentiodynamic sweeps were used to obtain kinetic information. As in the case of work reported in reference [55], the suppression of hydrogen evolution was a measure of the adsorption process. A Temkin adsorption isotherm was assumed and the equation describing the rate of adsorption, \( v_a \), was represented as follows:

\[ v_a = k_a C_b \exp(-\alpha f \theta) \]  

(2.27)

where \( f \) is the inhomogeneity factor. The adsorption rate constants obtained were 6.1 × 10⁻² cm/s (2.0 × 10⁶ s⁻¹) and 6.0 × 10⁻³ cm/s (1.95 × 10⁵ s⁻¹) for electrode potentials of 0.5 V and 0.1 V, respectively. The difference in the adsorption rate constant between the two potentials was attributed to a higher hydrogen coverage at the lower potential.

In many cases researchers have examined the rate of the electrode processes following adsorption, not of the adsorption itself. The work of Chen et al. [59] is an example of the application of fast cyclic voltammetry for the determination of kinetics of such a process. The authors evaluated the rate constant of the examined process from the peak separation for different scan rates. In such a case the kinetic parameters can be determined from the peak separation, because both peaks are proportional to sweep rate, in the same way as the charging current. This is contrary to the case of electroosorption, for which only the desorption peak increases proportionally to the sweep rate. This implies that the described method cannot be used when chemisorption is examined. A similar situation was encountered in the case of the work performed by K. Scott [61] who determined the rate of the electrode process following the adsorption.

The kinetics of the adsorption processes at electrodes have been investigated not only with electrochemical methods but with other methods, sensitive to changes in the electrode coverage, as well. Some of them include
the use of an electrochemical quartz crystal microbalance [62-65], ellipsometry [66-69], surface acoustic wave [70], and radiochemistry [71]. Some examples of the application of these techniques in the determination of adsorption kinetics will be discussed below.

The quartz crystal microbalance (QCM) is a very useful tool in the investigation of the adsorption process, as the response is directly proportional to the amount of the substance adsorbed at the electrode. Some complications arising from the possibility that other processes take place at the electrode surface simultaneously with the investigated adsorption process may be taken into account if the QCM measurements are performed together with electrochemical measurements, thus shedding more light on the nature of the process. Before the application of this technique in the study of adsorption kinetics will be described, a paper [72] examining the thermodynamics of the adsorption of bromide and iodide ions on gold electrode will be discussed, as an introduction to this technique. The authors performed in situ measurements with the gold working electrode attached to the QCM. The electroosorption valency was determined from the dependence of the charge obtained from electrochemical measurements corresponding to the adsorbed layer on the electrode coverage, calculated from the QCM response. The values found were 1.01 for iodide and 0.39 for bromide. The results seem to be reasonable if the fact that bromide is more electronegative than iodide and hence tends to attract electrons more strongly is taken into account. The method is very straightforward and seems to be a very promising tool in the investigation of an adsorption process.

Lacour et al. [63] presented a comparison of the application of QCM and double layer capacitance measurements in the determination of kinetics of an adsorption process. The experiments were performed for the adsorption of bovine serum album onto a gold electrode. The electrochemical
measurements involved a determination of the impedance, related to the double layer capacitance, at 3 s intervals (frequency 825 Hz). The experimentally obtained curves of the double layer capacitance and the electrode mass change (caused by an adsorption process) as a function of time were fitted with an exponential function of a form:

\[ f(t) = a_o + a_1 \exp(-1/\tau_1) + a_2 \exp(-1/\tau_2) \]  

(2.28)

where \( a_o, a_1 \) and \( a_2 \) are constants and \( \tau_1 \) and \( \tau_2 \) are time parameters.

The two methods (QCM and capacitance measurements) were applied simultaneously at the vibrating interface. In the case of the results obtained with QCM the mass change followed initially a sharp decline, which after about 40 s stopped and the curve began to follow an exponential rise. Such an effect was not observed in the case of electrochemical measurements. The authors explained this anomaly by the hydrodynamic perturbations which followed the protein addition. This phenomenon prevented the application of this method in the determination of rate constants corresponding to time parameters lower than 40 s. The initial time interval was not included in the further analysis. Although the above effect was not observed in case of electrochemical measurements, the same part of the experimental results was excluded from further analysis in order to make the comparison of these two methods more reliable. It was noted that when the whole time scale (including the 0 - 40 s interval) was analysed in the case of double layer measurements, the fitting of the capacitance dependence to time required an introduction of an additional time constant, \( \tau_0 \). Determination of this constant from QCM measurements was impossible, as the initial time interval was unavailable for analysis. Nevertheless, the difference in other parameters caused by an introduction of the additional time constant was not significant, and didn't cause a big discrepancy between the results obtained with both methods. The time parameters determined in this paper for the adsorption at -1080 mV were (\( \tau_0 = 12 \) s) \( \tau_1 = 81 \) (105) s and \( \tau_2 = 668 \)
(695) s for electrochemical measurements and $\tau_1 = 83$ s and $\tau_2 = 615$ s for the measurements performed with QCM. The values in brackets are given for the analysis including the initial time interval. The paper showed that QCM can be successfully used for the determination of adsorption kinetics only when the process is slow, whereas the electrochemical method (although higher frequencies would be required to measure high adsorption rate constants) seems to be much superior in this respect.

Another paper dealing with the determination of adsorption kinetics implementing QCM [62] described the self-assembling adsorption of ferrocenylundecanethiol at gold substrate, deposited onto the quartz crystal. The kinetic measurements were performed without any potential applied to the electrode, followed by a transfer of the gold electrode with the adsorbate layer to an electrochemical cell and subsequent electrochemical measurements. The observed quartz crystal frequency steeply decreased after the addition of the adsorbate, and after that a gradual decrease was observed. The initial adsorption rate was determined to be $3.33 \times 10^{-11}$ mol cm$^{-2}$s$^{-1}$ (7.4$\times$10$^2$ s$^{-1}$), followed by a slower adsorption with the rate equal to $3.33 \times 10^{-13}$ mol cm$^{-2}$s$^{-1}$ (7.4$\times$10$^4$ s$^{-1}$). The authors attributed the slow adsorption following the fast initial process to the enhanced packing of the adsorbate molecules. Cyclic voltammetry on the modified gold electrode was carried out simultaneously with the QCM frequency measurements. The value of the electrode coverage obtained from the integration of current was in agreement with the value determined previously from the QCM frequency measurements. The frequency recorded during a potential scan decreased upon oxidation of ferrocene and returned to the initial value on the reverse scan of potential. Since the frequency decrease is a measure of the mass gain, it indicates that the formation of ferrocenium cation was accompanied by the uptake of an anion. In both of the above papers [62, 63] the reported adsorption rate constants are very small and the results
indicate that QCM may be used as a tool in the determination of adsorption kinetics only if the corresponding adsorption rate constant is very small.

Thomas et al. [70] investigated the gas phase adsorption kinetics of n-alkylthiols on gold. The surface acoustic wave (SAW) technique used in these experiments is very sensitive to the presence of surface-confined adsorbates as a result of the short range of the wavelength (high frequency), reaching to only one layer on the surface. The perturbations of SAW are directly proportional to the mass changes. The corresponding changes in the electrode coverage may be calculated and its dependence on time monitored in order to determine kinetic parameters. The adsorption kinetics of the examined alkylthiols fit into a simple first order Langmuir rate law. The values obtained for CH₃(CH₂)₈SH and CH₃(CH₂)₁₃SH were 6.0×10⁻² s⁻¹ and 8.3×10⁻⁴ s⁻¹, respectively.

Yang et al. [66] investigated the adsorption of acetylenic alcohols from H₂SO₄ solution on iron using in situ time resolved automatic ellipsometry. The use of a Fourier transform automatic rotating analyser ellipsometer allows the minimum time measurements in the range of milliseconds. During the adsorption process the measured parameter was changing with time in such a way that two plateaus were observed, the first one corresponding to a relatively fast adsorption process (time parameter for the adsorption of 6×10⁻⁴ M 1-octyn-3-ol from 0.01 M H₂SO₄ at potential -0.4 V in the range of 1 - 2.5 min.), and a second one slightly slower (the same conditions, time parameter 6 - 10 min.). At higher concentrations an additional plateau was observed. The first plateau seemed to correspond to orientational changes, while the subsequent one was due to multilayer formation. The observed kinetics are not kinetics of an adsorption process but of the reorientation of the adsorbed molecules at the electrode surface. When the reorientation from the partly upright (pu) to the upright (u) state
takes place, the corresponding change in the electrode coverage may be presented as:

$$\frac{d\theta_u}{dt} = k_{a,pu}\theta_u + k_{a,u}C_b(1 - \theta_u - \theta_{pu})$$ (2.29)

or after some rearrangements, assuming that the overall process is controlled by the reorientation step:

$$\tau = -\frac{1}{k_{a,pu}}\ln C_b + \text{const}$$ (2.30)

where $k_{a,pu}$ and $k_{a,u}$ are the rate constants for reorientation of the $pu$ configuration, and adsorption from solution in the $u$ configuration, respectively. The slope of the last dependence gives the value of the reorientation from the $pu$ to $u$ configuration rate constant, which is $2\times10^{-3}\text{ s}^{-1}$ in case of 1-octyl-3-ol.

Finally, radiochemical methods also find their application in the determination of adsorption kinetics. The study of the adsorption of an organic solvent N,N-dimethylformamide (DMF), commonly used in electrochemistry, on platinum electrode was performed by Szklarczyk and Sobkowski [71]. The authors observed that the addition of DMF leads to the formation of an irreversible oxidation peak and the suppression of the hydrogen adsorption. The solvent adsorbs at the electrode, and can be removed from its surface by a subsequent oxidation at sufficiently high anodic potentials. The electrode coverage was obtained as a function of time from radiometric measurements. The best fit of experimental data was obtained when the Langmuir type kinetic equation was employed:

$$\frac{d\theta}{dt} = k_a(1 - \theta)^2 = k_a^0(1 - \theta)^2 \exp\left(\frac{n\beta E F}{RT}\right)$$ (2.31)

where $k_a^0$ is the adsorption rate constant at $E = 0\text{ V}$, and $n\beta$ in this equation corresponds to $-\alpha\gamma$ in the equations used in this work (see eqns. (2.12) and (2.13)), although the authors do not state this explicitly. The adsorption rate constant at $E = 0\text{ V}$ determined from the data obtained in the potential
range of 0.21 to 0.45 V was 14 s\(^{-1}\) and in the range of 0.05 to 0.21 V was \(9.4 \times 10^{-3} \text{ s}^{-1}\). The values of \(n\beta\), corresponding to the same potential ranges as above, were -0.14 and 0.19, respectively. The change in \(n\beta\) sign indicated that different adsorption mechanisms were observed in the two potential ranges, which would explain a difference in the measured adsorption rate.

There is a considerable lack of consistency in the theoretical description of kinetics of an adsorption process. Unlike in the case of kinetics of an electron transfer at the electrode, each author seems to develop their own description scheme, which in turn causes the results reported in different papers to be almost incomparable. This is due to the fact that this area of electrochemistry, although started over 30 years ago, is still in the stage of infancy. The work presented in this thesis, and in the papers based on it [76, 77], is an attempt to provide a uniform description of adsorption kinetics. The theoretical model used here (see eqns. (2.12) to (2.15)) is based on the Frumkin isotherm, which, as was shown above, describes the adsorption of organic substances very well. The kinetic equations are formed through an analogy to those used in the description of ordinary electrode kinetics. The system is readjusted to account for differences in the properties of the systems examined. In the case of normal electrode processes (simple charge transfer reactions) product and reactant are either in the solution, and then it is reasonable to find a dependence of the rate of the process on the bulk concentration, or one or both of them are deposited or adsorbed at the electrode surface. In the latter case, to maintain the same standard of data description, the same dependence is sought, and hence, the units of the process are expressed in \(\text{cm} \times \text{s}^{-1}\). In case of an adsorption process the product remains at the electrode surface in all cases. It seems appropriate to express the dependence of the adsorption and desorption rate on the surface concentration, even though the adsorption of the substance takes place from the oHp. The substance in the oHp may be treated as
remaining at the "surface" corresponding to the oHp, as only the substance present in the o Hp can be adsorbed. The concentration of the substance in the o Hp (obtained with the aid of the convolution algorithm) may be easily recalculated into a concentration expressed in surface units, if the concentration value is multiplied by the thickness of a solvent layer (corresponding to the thickness of the first layer in the diffuse part of the double layer, eqn. (4.1)). As a consequence the rate constant units most suitable for adsorption are s⁻¹.

Another advantage of the model used in this thesis over those presented above is that it takes into account a unique characteristic of the adsorption process, namely the effect of a partial charge transfer between the adsorbed molecule and the electrode metal and the influence of the interactions of the adsorbed substance and solvent dipoles, as well as the penetration of the substance into the double layer (through the geometric factor, g) on the overall process. In none of the papers presented above have the authors considered the uniqueness of the adsorption process, namely, including the electrosorption valency into the equations describing the kinetics of the adsorption process. It is especially surprising since the combination of electrochemical and non-electrochemical methods (sensitive to the changes in the mass of the electrode) used by many of the authors to determine adsorption kinetics is especially useful in the simultaneous determination of the electrosorption valency (see [72]).

Another characteristic, making the theoretical system used in this work to describe kinetics of adsorption superior to those presented above, is that it takes into account not only the interactions between the substances present at the electrode surface (through the interaction parameter, g) but also those observed when the adsorbate is in its activated state (through the interaction parameter, g'). The latter parameter is not present in the
thermodynamic description of the process, but is taken into account when the kinetics is considered.

As was shown in the literature review, most of the authors used simple, Langmuir or Temkin type kinetic equations to describe the process. In most cases the analysis of data was based on the assumption that the rate of the desorption processes is negligible. This assumption, unless proven to be true, is not acceptable, especially when account is taken of the fact that the desorption process is much faster than adsorption at certain potentials. It will be shown later, that the rate of desorption process can be considerably fast, even if the adsorption is the predominant process. As well, such an assumption limits the potential range that can be examined with the proposed method.

It was shown above that there is a need for a uniform description of adsorption kinetics and for a methodology allowing the kinetics of adsorption processes to be determined. This thesis aims at meeting this demand.

2.4 Characteristics of different metal electrodes.

The reproducibility of the electrode surface area and the need for a well known description of this surface is very important in any kinetic measurements. It was noticed by many authors that the problems in the quantitative interpretation of the double layer capacitance measurements in case of solid electrodes may be caused by the crystallographic non-uniformity of the electrode surface [78, 79]. This in turn leads to a requirement for the use of single crystal electrodes when the kinetic parameters are to be determined. A short review will be presented of the characteristics of different metal electrodes, as the investigation of the dependence of adsorption kinetics on the properties of the electrode is important to a complete understanding of the process.
The problem of electrode heterogeneity caused by a simultaneous existence of several crystallographic orientations can be overcome if single crystal electrodes are employed. The technology of obtaining such electrodes is now well developed and commonly used by many electrochemists [80, 81]. There are two types of single crystal electrodes used in electrochemistry. These are either single crystal faces or films of given crystallographic orientation. The latter are obtained by depositing a thin film of preferentially oriented metal on other supports, like mica [82] or sodium chloride [83].

In the case of electrodes obtained by the growth of single crystals further processing is necessary to obtain a well defined surface of a desired crystallographic orientation. The processing includes cutting, mechanical and electrochemical or chemical polishing, and a final surface preparation, i.e. high temperature annealing or sputtering of the same metal to diminish the surface defects. When the desired single crystal electrode is separated it has to be embedded into an isolating material (teflon in most cases) to ensure that only the surface of interest remains in contact with the solution. This is followed by a series of experiments to confirm the crystallographic orientation of the surface and a lack of any surface defects. This includes X-ray, electron diffraction and LEED used to determine the crystallographic orientation; optical microscopy and electron microscopy used to examine the physical state of the surface; Auger spectroscopy used to determine the chemical composition of the surface layer. As an alternative technique the single crystal is not put into an isolating material but, after the crystallographic surface of a desired orientation is obtained through cutting and polishing, the electrode is immersed in the surface layer of solution and pulled up so that only the solution in the created meniscus remains in contact with the preferred crystal face. This eliminates the need for isolating other walls of the electrode.
Ex situ experiments have to be followed by in situ electrochemical measurements, necessary to determine whether the electrode's behaviour is correct in electrochemical conditions. Even after all these procedures are successfully completed problems associated with the characteristic properties of solid electrodes still remain. Some of them are the edge effect, the precision of crystallographic orientation and defects in a metal surface. All of the above mentioned effects change the surface and lead to a crystallographic anisotropy, which makes any quantitative analysis difficult.

As this thesis deals with the development of methodology for the determination of adsorption kinetics a short review of papers examining adsorption at different metal electrodes will be presented. The investigation of the adsorption phenomena on single crystal electrodes is increasingly popular [84-86]. The examination of the adsorption process at different metal electrodes is not limited to electrochemical methods but involves many non-electrochemical in situ techniques, sensitive to the changes in the properties of the adsorbed substances. Raman and infrared spectroscopy as well as second harmonic generation and electronreflectance spectroscopy are employed in the determination of the orientation of an adsorbate and the nature of the bond existing between an adsorbate molecule and the electrode metal [87-91]. An excellent tool for the determination of the properties of adsorbate covered electrode surfaces is scanning tunnelling microscopy (STM) [92]. The electrochemical methods can be successfully used for the thermodynamic and kinetic description of the system. Both groups of methods complement each other, allowing a more complete characterisation of the adsorption process.

In addition to the possible problems associated with the preparation of single crystal electrodes, surface reconstruction may occur when an electrode is exposed to a potential scan. Such an effect is for instance
observed in the case of gold single crystal electrodes [93-95]. This in turn alters the observed electrochemical response especially when a slow potential scan is applied to the electrode. Such a change in the properties of the electrode surface is difficult to account for and introduces additional uncertainties when the examined process is not already well understood.

Mercury is characterised by a well defined, uniform surface, and thus is an electrode metal of choice in any new study. The aim of this work is not to show a complete characteristic of the kinetic behaviour of different substances in different conditions (different solvents, electrolytes and electrodes) but to develop a method that would allow such investigations in the future. Because of that, to avoid any unnecessary complications arising from the use of more complex systems, the experiments described in this work were confined to mercury and amalgam electrodes. This helps to avoid any unnecessary complications of the analysed system, and makes it easier to understand the observed effects.

2.5 Characteristic properties of ultramicroelectrodes.

Until the 1970s the electrodes commonly employed in electrochemistry had a linear dimension in the range of millimetres. The technical developments in electronics in the last thirty years made possible an accurate determination of very small currents. This in turn has enabled electrochemists to reduce the size of the electrodes to the range of micrometers, associated with the flow of a current at a level of nA. This step in electrochemistry opened many new possibilities. Some of them include measurements in vivo [96, 97], experiments in high resistivity media [98], in very small volumes of solution (even in one drop) [99, 100] and under high potential sweep rate conditions [101]. The advantages associated with the use of ultramicroelectrodes are an increased temporal resolution, increased current density and decreased sensitivity to the solution resistance [102].
Charging current is a source of many limitations in electrochemical techniques. With no faradaic or adsorption process at the electrode surface, the system can be described by an equivalent circuit composed of the solution resistance, \( R_s \), and the double layer capacitance, \( C_{dl} \), in series. In such a case for potential sweep methods only the charging current, \( i_c \), is observed [102]:

\[
i_c = vC_{dl} + \left( \frac{E_i}{R_s} - vC_{dl} \right) \exp\left( -\frac{t}{R_sC_{dl}} \right)
\]  

(2.32)

where \( v \) is the potential sweep rate, \( E_i \) is the initial potential and \( t \) is the time passed from the beginning of the experiment. In most cases it can be assumed that the second term is negligible, and as a consequence charging current is directly proportional to the potential sweep rate and to the double layer capacitance:

\[
i_c = vC_{dl}
\]  

(2.33)

When an electroactive species is present in solution, the resulting current adds to the charging current. As the charging current doesn't depend on the analyte concentration for high concentrations of supporting electrolyte and is especially high at short times, the limitation resulting from its existence is particularly pronounced in diluted solutions and when high potential sweep rates are employed. This effect is significantly reduced when ultramicroelectrodes are used. As the double layer capacitance is proportional to the electrode area, its value is much lower in the case of ultramicroelectrodes. This makes it possible to carry out measurements in very dilute systems and for high potential sweep rates (or generally when short time parameters characterise the technique employed) with ultramicroelectrodes. An additional reduction of the effect of the charging current is obtained when pulsed voltammetric techniques are employed. The faradaic current characterised by spherical diffusion of the analyte in the
case of ultramicroelectrodes is much less dependant on time than in case of standard size electrodes. This makes pulse techniques even more successful.

Another effect limiting the use of electrochemical techniques is the solution resistance and the corresponding potential drop, \( iR_s \), caused by the total current flow in the system. This effect can significantly distort electrochemical data, especially if a solution has a high specific resistivity, \( \rho \), or high potential sweep rates are employed (leading to high charging currents). The solution resistance of a spherical electrode can be described by the equation:

\[
R_s = \frac{\rho}{4\pi r_o}
\]  

(2.34)

where \( r_o \) is the electrode radius. In the case of ultramicroelectrodes a decrease in the current (proportional to \( r_o^2 \)) leads to a reduction of the ohmic drop, \( iR_s \), while an increase in the solution resistance (proportional to \( r_o \)) causes an increase of the ohmic drop. The overall effect leads to a decrease in the ohmic drop with a decrease in an electrode radius. This makes measurements in highly resistive media possible (even when no supporting electrolyte is added and the concentration of the analyte is small [103]). This has led to the use of many organic solvents, previously inaccessible to electrochemistry due to the high resistivity of their solutions.

Even though the effect of the ohmic drop is significantly reduced in case of ultramicroelectrodes, it cannot be totally ignored, especially if very fast electrochemical techniques are used. A high value of the charging current leads to an increase in the ohmic drop value. Nevertheless, the conditions accessible with ultramicroelectrodes are far superior to those used in the case of traditional electrodes. The possibility of recording curves for very high potential sweep rates is very desirable if fast electrode reaction rate constants (both electroreduction/oxidation and adsorption processes) are to be determined.
A problem commonly encountered when ultramicroelectrodes are employed is that the sealing of the wire forming an electrode into the isolating material is not perfect. As a result, the solution leaks into the created space and the observed capacitance is much higher than expected for the electrode. This causes the charging current to increase significantly, and quite often makes any analysis of the recorded curves impossible. It is very important to test the properties of the electrode prior to its use in electrochemical experiments, in order to avoid problems associated with an imperfect fabrication of the electrode. Such tests must include recording of capacitance curves in order to determine the electrode area and the corresponding roughness factor. It is difficult to obtain a totally smooth electrode surface when solid ultramicroelectrodes are employed (see section 2.4). The problem seems to be somewhat simplified when mercury electrodes are used. In most cases mercury ultramicroelectrodes are prepared on other metal supports. The metal of choice is gold, as it is well wet by mercury and a deposition of mercury is easily achieved, leading to the formation of perfect hemispherical electrodes. The deposition of mercury can be performed electrochemically, which makes the control of the amount of mercury possible. As mercury forms uniform and smooth surfaces it is easy to predict the surface area of the electrode from the deposited amount of mercury. Mercury ultramicroelectrodes have all the advantages of ultramicroelectrodes described above and, in addition, their usage ensures a reproducibility of the surface not obtained with other kinds of ultramicroelectrodes.

Another problem commonly encountered when work with ultramicroelectrodes is attempted is a much higher diffusion of solution contaminants to the electrode caused by the small electrode dimensions. In addition, the amount of contaminants necessary to block the electrode surface is much lower than for bigger electrodes. Extra care has to be taken to ensure a high purity of all the solutions used.
The advantages of working with ultramicroelectrodes outweigh all the problems. The application of these electrodes makes possible measurements at conditions previously inaccessible and allows determination of very fast kinetics of electrode processes. Because of the possibility of recording experiments characterised by very short time parameters when ultramicroelectrodes are employed, kinetic experiments presented in this thesis were performed with these electrodes.

2.6 Characteristics of the electrochemical methods used.

Throughout this work most of the experiments were performed using ultramicroelectrodes, except for a few cases when the thermodynamic characteristic of the examined system was sought. Because of that the description of the methods used will be limited to the case of ultramicroelectrodes since the theoretical description in case of traditional electrodes is well known. Two main groups of electrochemical methods were used for the determination of kinetic parameters of adsorption, namely cyclic voltammetry (FCV) at high sweep rates and AC methods, including AC voltammetry and a method invented in this laboratory, Fast Fourier Transform (FFT) Square Wave Voltammetry (SWV). The last method will be described in the experimental part as the method itself is a part of this thesis.

2.6.1 Cyclic voltammetry at ultramicroelectrodes.

As was mentioned above, the behaviour of ultramicroelectrodes under cyclic voltammetric conditions is different from that of traditional electrodes. The difference comes from the fact that due to the small size of the electrodes diffusion to the electrode is much faster. The current, \( i \), at an ultramicroelectrode at a constant potential more negative than the formal
potential may be presented as a function of time, $t$, using an equation similar to the Cottrell equation [20]:

$$i = nFAD_{ox}C_{ox,b}\left(\frac{1}{(\pi D_{ox}t)^{1/2}} + \frac{1}{r_0}\right)$$

(2.35)

where $n$ is the number of electrons exchanged in the process, $D_{ox}$ is the diffusion coefficient and $C_{ox,b}$ is the bulk concentration of the oxidised form. For short times the first term in the above equation is predominant and a linear diffusion is observed. When the time increases the time dependant term approaches zero and the observed current is time independent, limited by a much faster spherical diffusion of the substance to the electrode (see Fig. 2.6). In this case the dimensions of the electrode are much smaller than the diffusion layer thickness. The observed spherical diffusion to the electrode leads to the steady-state response. The corresponding flux of the reactants to the electrode is much greater than in the case of linear diffusion. This feature is useful when small concentrations of electroactive substance are employed. Spherical diffusion to the electrode is observed when the second term in eqn. (2.35) is at least ten times higher than the first term, hence when $D_{ox}t/r_0$ is equal to 31.4. This corresponds to a time parameter of 0.25 s or larger for a 5 μm ultramicroelectrode. The dependence between the time parameter, $t$, and the potential sweep rate, $v$, may be expressed as:

$$t = \frac{RT}{vnF}$$

(2.36)

This indicates that for the process to be controlled by spherical diffusion to the electrode, the sweep rate in cyclic voltammetric experiments should be 103/n mV/s or smaller.

Mass transport to ultramicroelectrodes can be approximated by linear diffusion if the time parameter, corresponding to the potential sweep rate used, is short enough. Following the same argument as above the first term
Fig. 2.6. Current changes with time for a potential-step experiment at planar and spherical electrodes, evaluated for \( D = 10^{-6} \text{ cm}^2\text{s}^{-1} \) and electrode radius \( 5 \times 10^{-4} \text{ cm} \). \( C_0^* \) is the bulk concentration of the electroactive substance. Taken from [102].
of eqn. (2.35) should be ten times higher than the second one. When the electrode radius is 5 \( \mu \text{m} \), the corresponding time parameter required for the process to be controlled by linear diffusion has to be lower or equal to 0.08 ms, or the potential sweep rate higher or equal to 321/n V/s.

In the case of CV experiments under steady state conditions (low potential sweep rate, spherical diffusion to the electrode) the limiting current controlled by diffusion, \( i_* \), is independent of potential and for a hemispherical electrode may be described by the equation:

\[
i_* = 2\pi \gamma n F D_{ Ox } C_{ Ox,b } \quad (2.37)
\]

Under these conditions the reverse wave is almost identical to the forward one as the diffusion of the reaction product away from the electrode is also fast due to very small dimensions of the electrode.

A different situation is encountered when the potential sweep rate is high. The time dependent term in eqn. (2.35) is predominant and the current value depends on potential in the same way as for standard size electrodes. For a comparison of cyclic voltammograms obtained under both conditions see Fig. 2.7.

As was already mentioned above the charging current increases proportionally to the potential sweep rate, while the faradaic current is proportional to the square root of this value. As a consequence when high sweep rates are employed the charging current tends to become higher than the faradaic current, which puts a limit on the highest potential sweep rates accessible even when ultramicroelectrodes are utilised. The current associated with the desorption of a substance from the electrode surface is directly proportional to the potential sweep rate in the same way as the charging current. This indicates that the cyclic voltammetric peak associated with the desorption process can be successfully analysed at much higher potential sweep rates than the peak corresponding to a faradaic
Fig. 2.7. Cyclic voltammograms for reduction of 1 mM Ru(NH$_3$)$_6^{3+}$ in an aqueous 0.1 M trifluoroacetate solution at a hemispherical mercury ultramicroelectrode 5 µm in radius at slow and fast scan rates. Taken from [102].
process involving diffusion of the reactant from the bulk of solution to the electrode.

For kinetic parameters of the process to be determined the rate of diffusion has to be fast enough not to impose a limit on the overall rate of the process. As the diffusion rate, \( v_d \), may be represented as a ratio of the diffusion coefficient of the substance, \( D \), to the thickness of the diffusion layer, \( \delta \):

\[
v_d = \frac{D}{\delta}\tag{2.38}
\]

and the diffusion thickness depends on the properties of the electrode and the method used, the applicability of the method for the determination of kinetic parameters may be evaluated. The diffusion thickness in case of a steady state process may be assumed to be equal to the electrode radius, \( r_e \), whereas in case of fast-sweep-rate cyclic voltammetry it depends on the time parameter characterising the method used (depending on the potential sweep rate employed). A conclusion from these considerations is that in order for the rate of diffusion to be equal to \( 3 \text{ cm s}^{-1} \) (if the diffusion coefficient is assumed to be \( 6 \times 10^{-6} \text{ cm}^2\text{s}^{-1} \) and \( n \) equal to 1) the electrode radius has to be \( 0.02 \mu\text{m} \) in the case of the steady state and the potential sweep rate should be \( 120000 \text{ V s}^{-1} \) for fast CV experiments. The two possibilities will be considered below.

The advantages of the usage of ultramicroelectrodes at high potential sweep rates were already discussed above. The possibility of obtaining CV curves at high potential sweep rates is especially important if the kinetics of fast processes taking place at electrodes is to be determined. The application of CV for the determination of an electron transfer kinetics is quite common. The first attempt to use fast cyclic voltammetric curves obtained at ultramicroelectrodes was made in 1981 by Robinson and McCreery [104]. The interesting aspect of this work is that in order to avoid the need of monitoring the fast changing current, and to reduce the effect of the
charging current, the authors observed the changes taking place at the electrode surface by employing absorption spectroelectrochemistry. The application of high potential sweep rates in cyclic voltammetric measurements is significantly increasing. It has been shown that the CV curves at high potential sweep rates can be used to determine heterogeneous electron transfer rate constants exceeding 2 cm s\(^{-1}\) [105, 106]. There are experiments reported in literature, where the potential sweep rate used was as high as 1.7 - 2 MV/s [101, 107].

The current density is very high when ultramicroelectrodes are employed. This leads to an increased influence of electrode kinetics on the recorded signal when the system is under steady state conditions [108]. As was shown above, the determination of kinetic parameters under steady state conditions requires the use of much smaller electrodes than in case of fast cyclic voltammetric experiments. This area of electrochemistry is very enticing. The kinetic parameters can be determined from curves obtained at very low potential sweep rates, as the response at steady state conditions is independent of the potential sweep rate used. However, this apparent advantage is counterbalanced by a risk of significant experimental errors. The fabrication of very small electrodes required for the determination of high electron transfer rate constants is very difficult. It was shown [109] that due to the difficulty of precisely determining the electrode properties the observed effects caused by an imperfect sealing of the electrode may be erroneously attributed to a high reaction rate. As an example of the discrepancy between results obtained at so-called nanodes (radius of the electrode in the range of nanometres) under steady state conditions and at ultramicroelectrodes for high potential sweep rates or from high frequency AC voltammetric curves, see Table 2.2 [110-114]).

In case of the adsorption process the determination of its kinetics from steady state curves is not possible. The advantage associated with the fast diffusion of the analyte to the electrode is counterbalanced by the fact that
Table 2.2. Comparison of the results of heterogeneous charge transfer kinetics determination with different experimental methods. Examined process: Fe(Cp)$_2$ → Fe(Cp)$_2^+$ + e.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$k_3$ / cm s$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M TBAPF$_6$ in ACN, 0.7 μm Au ring, steady state</td>
<td>0.09±0.05</td>
<td>[110]</td>
</tr>
<tr>
<td>0.6 M TEAP in ACN, 5 μm Pt disk, ultrafast CV</td>
<td>0.95±0.4</td>
<td>[111]</td>
</tr>
<tr>
<td>0.3 M TBAP in ACN, 16 Å Pt, steady state</td>
<td>220±120</td>
<td>[112]</td>
</tr>
<tr>
<td>0.1 M TBAP in ACN, 5 μm Pt, AC voltammetry</td>
<td>2.6±0.5</td>
<td>[113]</td>
</tr>
<tr>
<td>0.5 M TBABF$_4$ in ACN, 1 μm Pt, SECM</td>
<td>3.7±0.6</td>
<td>[114]</td>
</tr>
</tbody>
</table>

Symbols used: Fe(Cp)$_2$ - ferrocene, TBA$^+$ - tetrabutyl ammonium cation, TEAP - tetraethyl ammonium perchlorate, TBAP - tetrabutyl ammonium perchlorate, TBABF$_4$ - tetrabutyl ammonium tetrafluoroborate, SECM - scanning electrochemical microscopy
the amount of the substance that can adsorb at the electrode surface is very insignificant because of the very small electrode area. This results in a signal (adsorption/desorption current in case of CV curves) that cannot be analysed due to its very minute value. In addition, an adsorption process is not a steady state process as the concentration of the adsorbate at the electrode surface changes with time until an equilibrium is reached.

Because of the above problems associated with steady state CV, the experiments in this work were limited to high potential sweep rate cyclic voltammetric curves.

2.6.2 AC voltammetry at ultramicroelectrodes

Most of the AC voltammograms have been recorded at conventional size electrodes. This limits the highest frequency that can be employed, and limits the kinetic parameters that can be determined with this method. Only recently have ultramicroelectrodes been used to obtain kinetic parameters of fast charge transfer processes with the use of the AC voltammetric technique [113, 115-119].

The relationship between different properties of the system and the shape of the AC voltammogram is less obvious than in the case of cyclic voltammetric curves. This has resulted in a much smaller interest in these techniques in comparison to DC techniques. Although the data processing is more complicated, the richness of the information obtained is more than rewarding. The possibility of a simultaneous determination of the solution resistance, the double layer capacitance and the admittance not only provides the tools for the determination of kinetic parameters but it also allows a monitoring of any electrode imperfections. A simple procedure allows for correction of the results for the solution resistance and the double layer capacitance, which is very complicated in the case of cyclic voltammetric curves [120]. The difference mentioned above arises from the fact that in the case of AC experiments the time parameter, corresponding to
the frequency used, is constant, whereas in the case of cyclic voltammetry the corresponding parameter, depending on the potential sweep rate value, changes with time due to changes in the ohmic drop value [121]. Another advantage of AC methods is that the reduction of noise is easily achieved when a lock-in amplifier and a system of filters are used.

The comparison of results obtained at standard size electrodes with AC and DC methods shows that AC methods are better suited for the determination of fast charge transfer kinetics. This is especially true when ultramicroelectrodes are used. AC measurements involve recording of the total impedance as a function of potential for different frequencies. The use of a phase sensitive lock-in amplifier allows the determination of a real and imaginary part of the total impedance. The equivalent circuit corresponding to the charge transfer process at mercury hemispherical electrode can be presented as in Fig. 2.8, where \( C \) is the stray capacitance, \( R_s \) is the solution resistance, \( R_a \) is the activation resistance, \( Z_w \) is the Warburg impedance and \( R_{m} \) is the non-linear mass transport impedance, both associated with the mass transport to the electrode. Stray capacitance develops on wires connecting the working electrode to a current transducer and between the wires and solution. When very small electrodes and high frequencies are employed, the alternating current passes mainly through the stray capacitance [122]. This effect can be taken into account if the stray capacitance is determined in an independent electrochemical experiment. The solution resistance and the impedance associated with the double layer capacitance can be subtracted from the total impedance as discussed above. The resulting impedance is called the faradaic impedance and it is composed of the activation resistance and the mass transport impedance. As the activation resistance is inversely proportional to the rate constant of the process, its determination is necessary to be able to obtain kinetic parameters characterising the process.
Fig. 2.8. Equivalent circuit for a redox process at a hemispherical electrode; $R_s$ solution resistance, $C_s$ stray capacitance, $C_{dl}$ double layer capacitance, $R_a$ activation resistance, $Z_W$ Warburg impedance and $R_{nl}$ non-linear mass transport impedance.
A theoretical description of the process taking place at hemispherical mercury electrodes under high frequency AC conditions was presented by Baranski [122]. The effect of different parameters on the precision of the kinetic parameter determination was examined with a simulation program. It was shown that the use of ultramicroelectrodes in AC measurements allows the determination of rate constants about 10 times higher than is possible with standard size electrodes, and that under special conditions (e.g. high supporting electrolyte conductivity) rate constants up to 100 cm/s can be measured.

Baranski and Winkler [115] used AC voltammetry at ultramicroelectrodes to determine the kinetic parameters of the electro-oxidation of ferrocene in different solvents using frequencies up to 50 kHz. The results show a systematic dependence on the properties of the system examined and seem to be self consistent. This indicates that AC voltammetry at ultramicroelectrodes can be successfully employed in the determination of kinetics of electrode processes.

To predict the behaviour of a system using AC techniques, an equivalent circuit composed of capacitors and resistors is sought. In the case of an adsorption process such a system may be presented as in Fig. 2.9. When the effect of the solution resistance and the double layer capacitance are subtracted, the resulting impedance is composed of the activation resistance, the Warburg impedance and the pseudocapacitance. The Warburg impedance expresses the limitation of the process caused by slow mass transport to the electrode. If the concentrations used are high enough the value of this impedance is negligible and doesn't influence the total impedance of the system. The value of interest in kinetic measurements is the activation resistance which is inversely proportional to the rate of the process. In order for this value to be determined the pseudocapacitance has to be eliminated from the total impedance. There are different methods leading to the extraction of the activation resistance and hence the rate of
Fig. 2.9. Equivalent circuit of the cell in case of adsorption process. $C_s$ - stray capacitance, $C_{dl}$ - double layer capacitance, $R_s$ - solution resistance, $Z_W$ - Warburg impedance, $Z_c$ - pseudocapacitive impedance, $R_a$ - activation resistance.
the process from impedance data, however they won't be discussed here, as they are very specific to the system used. In this work a method of determining kinetic parameters from impedance data was developed and will be presented in the experimental part of the thesis. So far, there have been no reported attempts of determining kinetics of an adsorption process with the use of ultramicroelectrodes and AC voltammetry.

An advantage of AC methods over cyclic voltammetry is that in the first case equilibrium conditions exist at the electrode due to a slow potential sweep. At the same time a small, few millivolt, high frequency potential excitation allows a determination of kinetics of the process at different potentials. This indicates that one experiment is sufficient to provide information about both thermodynamic and kinetic properties of the system. When cyclic voltammetry is used, two experiments are required to obtain the same information. This may lead to some errors, as the process takes place at different potentials for a low and high potential sweep rate.

In AC experiments a lock-in amplifier may be used in order to determine an in-phase and out-of-phase component of the circuit current at a corresponding frequency. A determination of the frequency dependence of the analysed signal requires recording of several curves at different frequencies. As an alternative, FFT SWV may be used. In this case one experiment provides the signal corresponding to the whole spectrum of frequencies. It is analysed through a FFT technique and it is separated into its component frequencies.

When high frequencies are involved special attention must be paid to the properties of the electronic system used in data acquisition. Very often the sensitivity of the current transducer changes with frequency which could lead to wrong impedance values and hence to wrong kinetic parameters. Also the open circuit admittance of the current transducer used may be different than zero. Another problem may arise at high frequencies due to the finite value of the current transducer's input impedance. The
behaviour of the system should be carefully examined and a correction of the data for the observed effects performed. This can be done through a carefully designed calibration procedure. In most cases it involves a recording of the in phase and out of phase components of the admittance at all frequencies used in experiments for a system of resistors and capacitors. The values obtained are stored in computer memory and compared with those predicted theoretically. The resulting difference is then used to correct experimental results.

It was shown above that high frequency AC experiments at ultramicroelectrodes are well suited for the determination of fast kinetics of electrode processes. Because of that this technique was used in this thesis for the determination of adsorption kinetics. A more detailed description of the system used will be presented in the experimental part of the thesis.

2.7 Simulation of experimental data

The simulation of experimental data is especially important when a new method of data analysis is developed. The simulation allows testing of the accuracy of the method, as the values introduced to the program may be compared with those obtained from the analysis. Contrary to the experimental data the parameters describing the simulated curve are well known, which makes it an ideal tool in testing of new analysis methods. In addition, once the method is developed, a comparison of experimental and simulated curves, obtained for the same parameters as those determined from analysis, allows a determination of possible imperfections of the method or shows that the examined system is more complex than that for which the method was developed. Simulation is also of great help when the influence of different parameters on the behaviour of the system is sought. It's difficult to find examples of all the possible performances in real systems, which makes such an examination difficult. Once the interesting
properties corresponding to certain parameters are observed, examples can be sought and explained.

Simulation is also of great help when the best conditions for analysis are to be determined. Baranski [122] examined different parameters affecting the accuracy of the determination of kinetic parameters of a charge transfer process from AC experiments recorded at ultramicroelectrodes. The simulation program allowed him to conclude that the greatest accuracy in the determination of kinetic parameters can be achieved when either high frequencies (100 kHz) and electrodes of a medium size (ca. 5 μm in radius) or low frequencies and very small electrodes (radius in the range of nm) are used (see Fig. 2.10). At high frequencies a serious limitation arises from a high value of stray capacitance. In the low frequency region both stray and double layer capacitance are negligible, which leads to a frequency independent total impedance. In this case AC voltammograms become derivatives of the steady state DC voltammograms. However, the use of very small electrodes may lead to significant errors resulting from a contamination of the electrode surface during a long data acquisition period. Similarly, as in the case of cyclic voltammograms, medium size ultramicroelectrodes seem to give more reliable results. This kind of electrode was used in AC experiments described in this thesis.

When the examined process is very complex and no analytical determination of the examined parameters is possible, very often a series of simulation curves is obtained and the best fit to the experimental data is sought. This is a method commonly used when the kinetics of the electron transfer process coupled with higher order chemical reactions are being determined [123-126].

So far there is no simulation program successfully describing both physical and chemical adsorption. A. Leverenz and B. Speiser [127] wrote a simulation program for an adsorption process, but the conditions considered were quite different from those characteristic of an electrosorption process.
Fig. 2.10. Simulated random errors for the determination of $R_a$ shown as a function of frequency and electrode radius (logarithmic scale). $k_e = 10$ cm/s, $\rho = 33 \, \Omega \, \text{cm}$, $\alpha = 0.5$, $E = E^0$, $C_{dl} = 10 \, \mu\text{F/cm}^2$, $C_b = 10 \, \text{mM}$, $D = 10^{-5} \, \text{cm}^2/\text{s}$, $C_s = 1 \, \text{pF}$. Taken from [122].
First of all the adsorption equilibrium was assumed to be maintained at all times. This excluded the possibility to investigate the influence of the adsorption rate constant on the curve shape. Another assumption made was that the amount of adsorbed molecules doesn’t change with potential, which obviously doesn’t correspond to the experimental reality. No possibility of the limitation of the process by diffusion was taken into account. The model describes physical adsorption well, for which the observed currents are not limited by diffusion, but fails in the case of chemisorption.

A book devoted to simulation programs in electrochemistry [128] was written in 1980. In the chapter entitled "Adsorption Kinetics" theoretical information is given that has to be considered during simulation of adsorption. There is, however, no indication that the considered process may be limited by the adsorption rate. The author assumed that the adsorption step was much faster than the diffusion of the substance to the electrode and that an equilibrium between the adsorbing substance in the oHp and the iHp existed at all times. A possibility of a kinetic limitation of the adsorption process was taken into account by Feldberg [129] who gave a theoretical description of the adsorption process at the electrode surface in such a case. However, no work taking into account all the parameters affecting adsorption process was reported.

Adsorption kinetics were considered by Delahay and Mohilner [130] with the assumption that the Temkin isotherm is obeyed. A mass transport problem associated with the adsorption process for coulstatic charging was examined by Delahay [131]. A series of other papers dealing with the problem of adsorption at electrodes was published [132-134], however none of them presents a simulation program fully describing the dependence of the properties of the system on different parameters, when the overall process is limited by the adsorption step.

The simulation program corresponding to the electrosorption process will be described in the experimental part of this thesis. It takes into
account the change of the electrode coverage with potential, limitations caused by diffusion and by a slow adsorption/desorption process.
3. Experimental

3.1 Chemicals used

All solutions were prepared from double distilled deionised water (Corning Mega-Pure system MP-6A and D-2). L-Cysteine, thioglycol, penicillamine, mercaptopropionic acid, L-cysteine ethyl ester, propan-2-ol, n-propanol, n-butanol, ethyl methyl ketone, butyric acid and n-pentanol were of analytical grade and all were used as received. All other chemicals used were also of analytical grade. Cyclic voltammetric experiments were performed in 1 M H$_2$SO$_4$ and KOH supporting electrolyte solutions to ensure a high conductivity of the media and to reduce the ohmic drop effect, which is difficult to take into account in these experiments and can significantly distort the data obtained at high potential sweep rates. In the case of AC experiments the effect of the ohmic drop can be eliminated through the simple procedure of subtracting the solution resistance from the total impedance. This allowed recording of AC voltammograms in solutions characterised by a much lower conductivity (such as 1 M Na$_2$SO$_4$ or 1 M K$_2$SO$_4$). In all cases special care was taken to avoid contamination of solutions used as this is a significant problem when ultramicroelectrodes are employed. Before experiments all solutions were deaerated for about 10 minutes with oxygen-free argon.

3.2 Electrodes used

A three electrode system in a conventional electrochemical cell was used in all experiments. In all kinetic measurements the working electrode was a 5 or 6.25 μm in radius mercury ultramicroelectrode. The electrodes were fabricated in this laboratory. The procedure involved sealing of the gold wire
(Goodfellow Metals Ltd. for 5 μm and Alfa Εsler for 6.25 μm gold wire) into a soft glass tubing, of inner diameter ca. 1 mm and outer 7 mm. The gold wire was first put into the tube which was then sealed at one end in a gas burner flame. A vacuum pump was connected to the opposite tube end to ensure a better sealing. The end of the capillary containing the wire was then inserted into a vertical furnace and kept at 750°C for several minutes to soften the glass and allow sealing of a part of the wire. A lead was made by connecting a copper wire to the gold wire with the aid of a silver conductive epoxy (Johnson Matthey). Then the electrode tip was cut and the electrode polished with 220, 400 and 600 grade carborundum paper and finally, with 0.3 μm alumina. Fig. 3.1 schematically presents such an electrode used in cyclic voltammetric experiments.

In case the of AC experiments the above described electrode was slightly modified to ensure a better performance under these conditions. In the case of AC experiments a limitation in the accuracy of data acquisition is caused by the difficulty of controlling the value of the stray capacitance, corresponding to the connecting wires and the charge build-up between the wire forming the working electrode and the solution surrounding the electrode walls. To reduce this problem the working electrode was placed in a metal shield, covered with an insulator (see Fig. 3.2). In addition the metal shield was grounded which led to a reduction of the stray capacitance value and also ensured a constant value of this parameter in all experiments. Through a calibration procedure described below (section 3.3.1), the stray capacitance can be taken into account and eliminated from the recorded signal.

Mercury hemispherical ultramicroelectrodes were prepared just prior to the use both for cyclic voltammetric and AC experiments. Mercury was electrochemically deposited from 0.1 M Hg₂(ClO₄)₂ in 1 M HClO₄ solution (prepared by dissolving Hg₂O in HClO₄) onto the gold disk ultramicroelectrode. The amount of deposited Hg was controlled by
Fig. 3.1. Diagram of an ultramicroelectrode used in CV measurements.
Fig. 3.2. Diagram of an ultramicroelectrode used in AC measurements.
monitoring the charge passing during the controlled potential electrolysis. The potential during electrolysis was more positive than -700 mV versus Hg|Hg$_2^{2+}$ to prevent hydrogen evolution. The mercury electrode was cleaned by washing it after deposition in concentrated H$_2$SO$_4$. The electrode prepared in such a way usually gave reproducible results for about 5 experiments. After that it was washed in concentrated sulphuric acid to remove adsorbed impurities. After about 20 experiments the electrode was repolished and a new mercury hemisphere was deposited.

When ultramicroelectrodes are employed a serious problem arises because of an increased rate of mass transport to such electrodes. This leads to a very fast poisoning of the electrode surface, caused by an adsorption of impurities from solution onto the electrode surface. It has to be stressed that this problem is not an effect of negligence on the part of the experimenter but is to be expected when work with ultramicroelectrodes is attempted. The level of impurities present in analytical grade reagents is high enough to cause such an effect. The procedure described above involving the washing of the electrode surface in concentrated sulphuric acid and a deposition of a new mercury hemisphere every few experiments is a consequence of this problem. In the initial studies with ultramicroelectrodes different approaches leading to the reduction of this effect were tested. One such example is a "shock" procedure, where a very positive potential (ca. 2000 mV) was applied to the electrode for a very short time. Oxidation processes taking place at the electrode seemed to cleanse the electrode surface (Fig. 3.3). However, the processes occurring at such positive potentials are difficult to control. This led to a choice of a less aggressive procedure of cleansing the electrode in a concentrated sulphuric acid.

As a means of testing whether the results obtained at ultramicroelectrodes are correct (not distorted by an adsorption of impurities) cyclic voltammograms were obtained for the solutions studied at a traditional size mercury electrode and then compared with those obtained
Fig. 3.3. Comparison of CV curves obtained on a newly deposited (solid line) mercury hemispherical electrode (25 μm in radius) and on the same electrode after an application of a potential "shock" (dashed line) (2000 mV for 500 ms followed by -1200 mV for 100 ms). Experimental conditions: $3 \times 10^{-5}$ M cysteine in 0.5 M NaOH; reference electrode Ag|AgCl|sat. NaCl; potential sweep rate 250 V/s.
at ultramicroelectrodes. A static mercury electrode (SMDE), EG&G Model 303 was used in these experiments. The working electrode surface area was 0.011 cm$^2$. The same electrode was also used in some AC experiments, when thermodynamic parameters of the adsorption process were determined.

In all experiments platinum foil of an area ca. 1 cm$^2$ was used as an auxiliary electrode. The reference electrode in CV experiments was Ag$\mid$Ag$_2$SO$_4$(s)$\mid$1 M H$_2$SO$_4$ (404 mV vs. SSCE) while in AC experiments it was Hg$\mid$Hg$_2$SO$_4$(s)$\mid$1 M K$_2$SO$_4$. Unless otherwise stated potentials are given in respect to one of these reference electrodes. Since the surface area of the reference electrode was about 1 cm$^2$, small currents passing through the cell did not polarise the reference electrode interface. However, the junction between the reference electrode and the cell had a resistance of about 1200 $\Omega$. In order to eliminate this undesirable resistance the reference electrode was connected to the auxiliary electrode via a 10 $\mu$F capacitor. Note, that in typical cyclic voltammetric experiments at sweep rate 100 kV/s the lowest frequency component of the waveform has a frequency of about 50 kHz. At this frequency the 10 $\mu$F capacitor has an impedance of 0.32 $\Omega$. Therefore, fast changing currents pass through the external capacitor and then through the auxiliary electrode/solution interface. Electrical charges generated with fast experiments at ultramicroelectrodes are very small (typically less than 1 nC). Such charges can be easily absorbed by the double layer of the auxiliary electrode without causing any appreciable change in the potential across the auxiliary electrode/solution interface. It should be emphasised that in electrochemical experiments with ultramicroelectrodes the use of a potentiostat makes sense only if a positive feedback iR compensation is employed, otherwise it is a useless device which introduces additional noise and data distortion.
3.3 Electronic set-up

Electronic circuit in CV experiments. The experimental set-up is presented in Fig. 3.4. In data acquisition an 8 bit CompuScope 220 (Gage Applied Sciences, Inc., Montreal, Canada) card was employed. This card contained a 256 kbyte memory buffer and allowed sampling of current at a maximum rate of 40 MHz. A potential scan was generated with a 12 bit arbitrary waveform generator card (WSB100 from Quatech, Inc. Akron, USA). This card can produce a waveform composed of up to 32768 data points at a maximum rate of $2 \times 10^7$ points per second. A current transducer used in experiments (Fig. 3.5) was made with a Burr-Brown OPA621 operational voltage amplifier characterised by the gain bandwidth product of 600 MHz. The voltage gain resulting in the circuit presented in Fig. 3.5 was ca. 50. The resistance of the variable resistor connected to the non-inverting gate of the amplifier was selected so that a full current range, allowing the greatest resolution, could be used. The ohmic drop at the current transducer was equal to the ratio of the range selected (100 mV or 200 mV per range) to the gain of the amplifier (50) giving the value of 2 or 4 mV. The maximum sweep rate accessible with this set-up was 100000 V/s. Data acquisition and processing was controlled by a computer program operating under Microsoft Windows, written in this lab.

Electronic circuit in AC experiments. The electronic circuit used in AC measurements included an EG&G Lock-in amplifier model 5202 with the frequency range of 0.1 to 50 MHz, a Tektronix model SG503 high frequency generator, an IBM compatible personal computer (80486, 66 MHz CPU), a custom built potentiostat and an ac current transducer. The diagram of the circuit is shown in Fig. 3.6. The DC potential of the working electrode is controlled by a potentiostat comprising an OP07 operational amplifier. Resistors $R_1$ and $R_2$ (both 47 kΩ) and capacitors $C_1$ and $C_2$ (both 0.1 μF) act as low pass filters and limit the time constant of the potentiostat circuit to
Fig. 3.4. Diagram of the experimental setup used in electrochemical CV measurements. ADC is a CompuScope 220 card used for data acquisition, and DAC is an arbitrary waveform generator card.
Fig. 3.5. Diagram of the current transducer used in CV experiments. OPA 621 is an operational amplifier and ADC is a CompuScope 220 card used for data acquisition.
Fig. 3.6. Diagram of an electronic set-up used in AC experiments. Ref. stands for a reference and Aux. for an auxiliary electrode. Values of resistors and capacitors are given in text.
about 5 ms. This time constant is sufficient for DC sweep rates up to 0.2 V/s. Since DC currents passing through ultramicroelectrodes at such low sweep rates are smaller than 1 nA, the potential drop on a 47 kΩ resistor is negligibly small (<0.05 mV). The AC generator provides high frequency sinusoidal potential which is used as a reference signal for the lock-in amplifier and as a modulation signal (5 mV p-p) for the electrochemical cell. AC current produced by this modulation signal passes through the capacitor \( C_i \), the auxiliary electrode, solution, the working electrode and the current transducer. The capacitor \( C_i \) only slightly adds to the overall impedance of the AC circuit (about 16 Ω at the lowest frequency used) but provides a very high impedance for the DC current. The capacitance of the auxiliary electrode is more than 10 μF, therefore it produces a negligible impedance at frequencies larger than 0.1 MHz. The AC current transducer is made of a OPA621 (Burr-Brown) operational amplifier, which has the gain-bandwidth product of 600 MHz. The AC current causes a potential drop on \( R_i \) resistor (100 Ω). This potential is then amplified about 30 times by OPA621 and passed to the lock-in amplifier. Capacitance \( C_i \) (about 21 pF) includes the capacitance introduced by shielding of the working electrode (see Fig. 3.2) and the capacitance of the coaxial cable connecting the working electrode to the current transducer. Although this capacitance contributes to a decrease in the current transducer sensitivity at frequencies above 20 MHz, the shielding is advantageous from the viewpoint of the measurement accuracy. The measuring circuit was controlled by the microcomputer equipped with a PCL818 data acquisition card (from B&C Microsystems Inc.). An analog output of this card was used to generate a DC potential sweep, and two analog input channels were used to record the in-phase and out-of-phase response of the lock-in amplifier. The data acquisition and data processing program was devised in this laboratory using Microsoft's Visual Basic and Visual C++. 

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Experimental setup for high frequency FFT SWV. In high frequency FFT SWV experiments an electronic circuit similar to the one for FCV experiments (Fig. 3.4) was used. However, in the case of FFT experiments a different data acquisition card was employed (12 bit CompuScope 1012, Gage Applied Sciences, Inc., Montreal, Canada). This card allowed sampling of current at a maximum rate of 20 MHz and contained a 512 kB memory buffer. Principles of the technique are described in section 4.2.1. In all high frequency FFT SWV experiments 32 current points per square-wave cycle were sampled and used in the Fourier Transformation.

3.3.1 Calibration of the AC circuit.

A block diagram of the AC circuit is shown in Fig. 3.7. An unknown impedance of the electrochemical cell, \( Z_e \), is in parallel with the open circuit admittance, \( Y_{oo} \), and in series with the serial impedance, \( Z_s \). The open circuit admittance includes the stray capacitance (\( C_s \)) of the working electrode in parallel with the \( R_1 \) resistor (see Fig. 3.6) and the crosstalk impedance, \( Z_{ct} \). This last element accounts for a flow of current between the AC generator and the lock-in amplifier via ground loops and electromagnetic coupling. The serial impedance is comprised of the current transducer input impedance (mainly \( R_2 \) in parallel with \( C_s \) as shown in Fig. 3.6), in series with the capacitor \( C_I \), resistor \( R_4 \) and an inductance of connecting wires, \( L_t \). In addition, a complex frequency-dependent sensitivity of the current transducer, \( S(\omega) \), has to be taken into account. Admittance of the cell (\( Y_c \)) can be calculated from an admittance recorded by the lock-in amplifier (\( Y_m \)) only if \( S(\omega) \), \( Y_{oo} \) and \( Z_s \) are known. A standard calibration procedure was used to determine these parameters. During calibration the electrochemical cell was replaced with a low inductance carbon film resistor (1/4 watt). At each frequency measurements were carried with two standard resistors \( R_{el} \) and \( R_{ez} \) as well as with an open circuit. The resistance of the first resistor
Fig. 3.7. Block diagram of an AC circuit. $Z_x$ is the impedance of the cell, $Z_{oc}$ open cell impedance and $Z_s$ serial impedance. Other circuit elements are the same as in Fig. 3.6.
was comparable with the expected solution resistance of the electrochemical cell and the second resistor had a resistance about two times larger. Resistors were connected to the current transducer with special leads which had inductance and shielding capacitance similar to those of the working and auxiliary electrodes used in the electrochemical cell. Calculations involved solving appropriate complex variable equations.

Unfortunately, this calibration procedure was inaccurate for frequencies higher than 10 MHz. This was likely caused by some errors in the orthogonality of the lock-in amplifier, too simplistic a treatment of the crosstalk impedance in Fig. 3.7, and perhaps by a harmonic distortion caused by the circuit. Consequently, calibration above 10 MHz was done by measuring the impedance of 14 standard circuits composed of resistors, capacitors and inductors. The least square multiple regression method was then used to calculate 6 regression parameters \( \alpha_0, \alpha_1, \alpha_2, \beta_0, \beta_1, \beta_2 \) which are defined as follows:

\[
Z'_r = \alpha_0 + \alpha_1 Z'_m + \alpha_2 Z''_m
\]

(3.1)

\[
Z'_s = \beta_0 + \beta_1 Z'_m + \beta_2 Z''_m
\]

(3.2)

where: \( Z'_m \) and \( Z'_s \) are the measured and expected real impedances, \( Z''_m \) and \( Z''_s \) are the measured and expected imaginary impedances.

3.3.2 Optimum surface area of working electrodes in AC measurements.

During either a calibration or measurement an effort was made to keep the stray capacitance (\( C_s \)) and inductance (\( L_l \)) of the connections as similar as possible. But matching of different circuits can never be perfect. The differences between the stray capacitance and inductance of circuits used in the calibration and in the measurement are assumed to be \( \Delta C_s \) and \( \Delta L_l \), respectively. Practice shows that it is difficult to obtain \( |\Delta C_s| \) smaller than 0.2 pF and \( |\Delta L_l| \) smaller than 3 nH. If \( Z_{xe} \) is the impedance of the cell
already corrected for \( Y_{oc}, S(\omega) \) and \( Z_s \), then the true cell impedance, \( Z_c \), could be calculated by subtracting \( \Delta C_s \) and \( \Delta L_L \):

\[
Z_c = \frac{1}{Z_{sc} - j\Delta L_L \omega - j\Delta C_s \omega} = Z_{sc} \frac{1 - \frac{j\Delta L_L \omega}{Z_{sc}}}{1 - jZ_{sc} \Delta C_s \omega - \Delta L_L \Delta C_s \omega^2}
\]  

(3.3)

Normally \(|Z_{sc} \Delta C_s \omega|\) and \(\Delta L_L \Delta C_s \omega^2\) are much smaller than 1 and \(Z_s\) is close to \(Z_{sc}\), consequently eqn. (3.3) can be approximated by:

\[
\Delta Z_s = Z_s - Z_{sc} = j(Z_s)^2 \Delta C_s \omega - j\Delta L_L \omega
\]

(3.4)

Since \(\Delta C_s\) and \(\Delta L_L\) are independent, random sources of errors, the overall relative uncertainty of a measurement can be estimated as:

\[
\frac{\Delta Z_s}{Z_s} = \sqrt{\left(|Z_s| \omega \Delta C_s \right)^2 + \left(\frac{\omega \Delta L_L}{Z_s}\right)^2}
\]

(3.5)

Eqn. (3.5) predicts that there is an optimum cell impedance for which a maximum accuracy can be achieved. When the cell impedance becomes larger (or smaller) than the optimum value the relative error increases due to an uncertainty in the stray capacitance (or in the inductance). An approximate 2% accuracy of measurement can be obtained at 50 MHz if the absolute impedance of the cell is between 100 and 600 \(\Omega\). In order to study dynamics of the double layer, the contribution from the reactance of the double layer capacitance to the overall cell impedance should not be less than 20% at this frequency. It follows that the capacitance of the electrode should be between 5 and 160 pF. Assuming that an average double layer capacitance is 20 \(\mu F/cm^2\), we can estimate limits for the working electrode surface area as \(2.5 \times 10^{-7}\) to \(8 \times 10^{-6} \text{ cm}^2\). In this work hemispherical mercury ultramicroelectrodes 5 \(\mu m\) or 6.25 \(\mu m\) in radius (1.6 \times 10^{-6} \text{ or } 2.45 \times 10^{-6} \text{ cm}^2 \text{ in surface area}) were used. With such electrodes it is possible to carry out measurements in highly conducting electrolytes without an electronic \(iR\)
compensation. The solution resistance of a hemispherical electrode [102 p. 308] is given by:

$$Z_s = \frac{\rho}{2\pi r_0}$$  \hspace{1cm} (3.6)$$

where \( r_0 \) is the electrode radius and \( \rho \) is the specific resistivity of solution.

The reactance of the double layer is:

$$Z_{dl} = -\frac{1}{2\pi \varepsilon_0 \omega C_{dl}} j$$  \hspace{1cm} (3.7)$$

where \( C_{dl} \) is the double layer capacitance of the electrode per unit surface area.

At 50 MHz the absolute impedance of a 6.25 \( \mu \)m hemispherical electrode in aqueous 3.74 M H\(_2\)SO\(_4\) and 1 M K\(_2\)SO\(_4\) is expected to be about 315 and 3100 \( \Omega \), respectively. The phase angle under the same conditions should be about -12\(^\circ\) and -1.2\(^\circ\), respectively. It is clear that the conductivity of the second solution is not sufficient for carrying out measurements at 50 MHz.
4. Results and Discussion

4.1 Cyclic Voltammetry Methods

As was already discussed in the theoretical part of this thesis two different kinds of methods were employed in the studies of the kinetics of adsorption at metal electrodes. The first part of this work was devoted to the development of methods allowing the determination of adsorption kinetics from CV curves. This chapter will present the results of this work.

4.1.1 Simulation Method

It is essential in the case of research directed at the development of a new method of data analysis to ensure that the behaviour of the system is well understood and that all the interdependencies between the shape of experimental curves and the examined properties are well accounted for. Before any experiments were analysed, the properties of the system were carefully examined with the aid of a simulation program. Since, as was already stated in the theoretical part, there was no simulation program reported in the literature adequate for the system of interest, such a program was developed. This chapter will describe the basic assumptions made during development of this program and will show the dependence of the shape of CV curves on different properties of the system.

The Frumkin adsorption isotherm, discussed in the theoretical introduction, was assumed to describe the relationship between the concentrations in the iHp and oHp (Table 2.1) when an equilibrium is maintained. In such a case the concentration of the adsorbed species at the oHp can be calculated from mass transport equations that normally require
a concentration to be expressed in moles per unit volume, $C_o$. Calculation of $c_o$ from $C_o(0)$ (concentration of the adsorbate in the oHp expressed in number of moles per volume) is straightforward. If $C_o(0)$ is small (usual case), the mole fraction of adsorbing substance in solution is $C_o(0) \times V_{sol}$ (where $V_{sol}$ is the molar volume of solvent) and the mole fraction of adsorbate at the oHp can also be expressed as $c_o A_{sol} N_A$ (where $A_{sol}$ is the surface area occupied by a solvent molecule, and $N_A$ is the Avogadro constant). Since mole fractions of the adsorbate calculated in both ways must be equal, therefore:

$$c_o = C_o(0)V_{sol}/(A_{sol}N_A) = C_o(0)\rho_{sol}$$

(4.1)

where $\rho_{sol}$ is the diameter of a solvent molecule.

The adsorption and desorption rate constants in the simulation program were taken as functions of potential:

$$k'_a(E) = k_e \exp \left[ -\alpha \frac{\gamma(E)F}{RT}(E - E^o) \right]$$

(4.2)

$$k'_d(E) = k_e \exp \left[ (1 - \alpha) \frac{\gamma(E)F}{RT}(E - E^o) \right]$$

(4.3)

by an analogy to an ordinary electron transfer process.

The charge transfer coefficient, $\alpha$, and the electroosorption valency, $\gamma$, were assumed to be either constant or linear functions of potential.

In computations the entire potential range (from the initial potential, $E_{ini}$, to the vertex potential, $E_{ver}$, and back to $E_{ini}$) was divided into $n_p$ potential steps. Consequently, the triangular potential wave-form normally used in cyclic voltammetric experiments was approximated by a staircase function with a step height, $\Delta E$, a duration, $\delta t$, and the step number, $l$.

$$\Delta E = 2 \times (E_{ver} - E_{ini})/n_p$$

(4.4)

$$\delta t = \left| \Delta E \right|/\nu$$

(4.5)

where $\nu$ is the potential scan rate.
The solution near the electrode was divided into layers (boxes) of thickness $\delta x$:

$$\delta x = \sqrt{D \delta t / D_m}$$  (4.6)

where $D$ is the diffusion coefficient of adsorbed species and $D_m$ is a dimensionless constant (the model diffusion coefficient) which must be less than or equal to 0.5 [20 p. 657, 129]. The distribution of concentration near the electrode was calculated using a finite difference equation [20 p. 657, 129] derived from the Fick's diffusion law. The change in concentration of the adsorbed substance in the box closest to the electrode (box 0, starting at oHp) is calculated as:

$$C_0(0) := C_0(0) + D_m \times [C_0(1) - C_0(0)]$$  (4.7)

and in subsequent boxes as:

$$C_0(n) := C_0(n) + D_m \times [C_0(n+1) - 2C_0(n) + C_0(n - 1)]$$  (4.8)

where index $n$ represents the box number.

Note that the above expressions represent an assignment (not equivalence), i.e., $C_0(n)$ on the left hand side of the expression is not equal to $C_0(n)$ on the other side. Computations were carried out for $N = 6 \times \sqrt{D_m l}$ boxes. Eqns. (4.7) and (4.8) are valid for linear symmetry of diffusion; algorithms needed to calculate mass transport for spherical symmetry of diffusion are given in the literature [129]. Both methods of diffusion were included in the simulation program.

The potential across the interface, $E(l)$, was calculated as the sum of the applied potential, $E_a(l)$, and the ohmic drop:

$$E(l) = E_a(l) + R_s I'$$  (4.9)

where $R_s$ is the solution resistance and $I'$ is a current obtained by a consecutive approximation method described later.

In numerical simulations, mass transport and kinetic processes are usually treated separately. The change in concentration of adsorbed substance, $\delta \chi_i$, can be calculated by solving a kinetic equation based on the
Frumkin adsorption isotherm (eqn. (2.14)). Lateral interactions between the activated complex and adsorbed molecules in their ground state are taken into account in this equation. Such interactions, described by the parameter \( g^\# \), increase the energy barrier for both adsorption and desorption processes by \( 2g^\# \theta/RT \). In the simulation program it is easier to separate the effect of the electrode coverage and the electrode potential on the adsorption/desorption rate constant, whereas when experimental curves are considered such a separation is difficult if not impossible. Because of that, in the kinetic equations given in the theoretical part of this work, potential and electrode coverage dependent rate constants were considered, while in the simulation program a different approach was chosen.

Eqn. (2.14) is difficult to solve analytically because \( \theta \) depends on time. However, since a change of potential during \( \Delta t \) is very small, the change in \( \theta \) is also very small (less than 0.01); furthermore, a typical interaction parameter is within \( \pm 2RT \). Consequently, the exponential terms can be approximated as:

\[
\exp\left(\frac{2b\theta(t)}{RT}\right) = \exp\left(\frac{2b}{RT} \left[ \theta_i + \Delta \theta(t) \right] \right) \approx \exp\left(\frac{2b\theta_i}{RT}\right)
\]  

(4.10)

where \( \theta_i \) is the electrode coverage at the beginning of the period \( \Delta t \), and \( b \) is either \( -g^\# \) or \( g^\# \). Simplification according to eqn. (4.10) means that in the numerical simulation exponential terms are approximated by staircase functions, with \( \theta_i \) calculated from \( c_i \) at the beginning of each period, \( \Delta t \). Pre-exponential terms \( (1-\theta, c_i \) or \( c_o \) cannot be approximated in the same way because that would lead to unstable simulations for electrode coverages approaching 1 or 0. Note, that in such cases even a small inaccuracy in the determination of \( c_i \) can lead to a change of sign in the pre-exponential terms, whereas the same inaccuracy is negligible in the case of exponential terms. As a consequence, the time dependent pre-exponential terms are changing continuously within the time period \( \Delta t \). Solution to eqn. (2.14) can be
obtained assuming that the total number of moles of adsorbate at the electrode and in box(0) is constant during the time period $\delta t$. At the beginning of each $\delta t$ period the concentration in box(0), $C_0(0)$, is calculated from the mass transport eqn. (4.7). The total number of moles of an adsorbate taking part in the electrode process (at iHp and oHp), $m_i$, is given by:

$$m_i = A c_i^0 + A \delta x C_0(0)$$  \hspace{1cm} (4.11)

where $A$ is the surface area of the electrode and $c_i^0$ is the surface concentration of an adsorbate at iHp (expressed as a number of moles per electrode area) from a previous iteration ($c_i^0 = c_i(\ell - I)$).

Based on eqns. (4.1) and (4.11), a relation between concentrations of an adsorbate at the oHp and the iHp during one time period is given by:

$$c_i(t) = \frac{\rho_{mol}}{\delta x} \left[ \frac{m_i}{A} - c_i(t) \right]$$  \hspace{1cm} (4.12)

Combining eqns. (2.14) and (4.12) leads to the following expression:

$$\frac{dc_i(t)}{dt} = a[c_i(t)]^2 + bc_i(t) + c$$  \hspace{1cm} (4.13)

where $a = \frac{k_a(E, \theta) \rho_{mol}}{\delta x c_{max}}$; $b = -\frac{k_a(E, \theta) \rho_{mol}}{\delta x} - \frac{m_i k_a(E, \theta) \rho_{mol}}{\delta x A c_{max}} - k_d(E, \theta)$; $c = \frac{k_a(E, \theta) \rho_{mol} m_i}{\delta x A}$

The quadratic expression on the right hand side of this equation can be represented as a product of first order polynomials, which leads to the following expression:

$$\left( \frac{1}{c_i(t) - x_1} - \frac{1}{c_i(t) - x_2} \right) dc_i = \sqrt{\Delta} dt$$  \hspace{1cm} (4.14)

where $\Delta = b^2 - 4ac$; $x_1 = \frac{-b - \sqrt{\Delta}}{2a}$ and $x_2 = \frac{-b + \sqrt{\Delta}}{2a}$
Integration of eqn. (4.14) from 0 to $\delta t$ gives the following solution:

$$
\ln \left[ \frac{(c_i - x_i)(c_i - x_j)}{(c_i^\circ - x_i)(c_i^\circ - x_j)} \right] = \sqrt{\Delta} \delta t
$$

(4.15)

where $c_i^\circ$ is the concentration of an adsorbate in the iHp at the beginning and $c_i$ at the end of the time interval, $\delta t$. The concentration of an adsorbate at the iHp calculated from this expression is given by the formula:

$$
c_i = (\mathcal{K} \times \mathcal{Q} - \mathcal{P}) / (1 + \mathcal{K})
$$

(4.16)

where:

$$
\mathcal{P} = (\Delta + b) / (2 \times a); \quad \mathcal{Q} = (\Delta - b) / (2 \times a);
$$

$$
\mathcal{K} = \exp \left[ (-\Delta \times dt) \times (A + c_i^\circ) / (B - c_i^\circ) \right]
$$

The concentration calculated in this way for each time interval allows the determination of current as a function of potential. Current is calculated by taking into account the change in the amount of adsorbed species and the charging current:

$$
I'(l) = -\gamma FA(c_i - c_i^\circ) / \delta t + AC_{dl}[E(l) - E(l - 1)]
$$

(4.17)

where $A$ is the surface area of the electrode, $F$ is the Faraday constant and $C_{dl}$ is the double layer capacitance. In order to properly evaluate the ohmic drop calculations described by eqns. (4.9) to (4.17) are repeated 5 times for each time interval, $l$. The last value of $I'(l)$ is taken as a good approximation of the current in a given time interval.

The initial coverage of the electrode can be set at any value between 0 and 1. In experiments the bulk concentration of an adsorbate is usually very small and a desired initial coverage is obtained by a pre-concentration lasting several seconds. Alternatively, the initial coverage can be calculated assuming an equilibrium between the bulk solution and the electrode at the initial potential. The second option is more suitable for a simulation of an
electrosorption processes involving a large bulk concentration of an adsorbate.

The simulation program described above takes into account both mass transport to the electrode (diffusion of the analyte from the bulk of the solution to the oHp and vice versa) and the rate of the adsorption/desorption process. If a high adsorption rate constant or a small potential scan rate is entered into the program, the resulting simulated cyclic voltammogram is controlled by diffusion. When a small adsorption rate constant and/or a high potential sweep rate are chosen, the shape of the resulting curve is determined by the rate of the process (see Fig. 4.1). Note that as the adsorption process is expected to be fast (adsorption rate constant above $10^6$ s$^{-1}$) the obtained voltammograms show that the process is reversible (controlled by diffusion rate) at potential sweep rates as high as 1000 V/s, and becomes irreversible (controlled by the rate of adsorption) for potential sweep rates around 100000 V/s. This again stresses the need for the use of ultramicroelectrodes in experiments designed to determine the kinetics of an adsorption process, as such high sweep rates are inaccessible using standard size electrodes.

This simulation program successfully describes both physical and chemical adsorption at the electrode. As was stressed in the theoretical introduction both processes can be described in a similar way, the only difference being that in the case of chemisorption there is a partial charge transfer between the adsorbing substance and the electrode material ($\lambda \neq 0$), while in case of physical adsorption no charge transfer is observed ($\lambda = 0$). As a consequence, a very low value of the electrosorption valency at the potential of zero charge corresponds to a process of physical adsorption. When the electrosorption valency is close to 1, this indicates a covalent bond between the adsorbing substance and the electrode material (this will be explained in detail in section 4.1.3.1.1). In the case of physical adsorption,
Fig. 4.1. Simulation of CV curves controlled by diffusion of the adsorbate (1000 V/s) and by kinetics of the adsorption process (100000 V/s). Conditions: $A = 1.60 \times 10^{-6}$ cm$^2$, area per adsorbate molecule $2.12 \times 10^{-16}$ cm$^2$, solvent molecule radius $3.07 \times 10^{-8}$ cm, $g = -2000$ J/mol, $g' = -1000$ J/mol, $h_s = 6.00 \times 10^6$ s$^{-1}$, $\alpha = 0.5$, $E^o = -800$ mV, $C_0 = 1.00 \times 10^{-6}$ M, $D = 1.00 \times 10^{-5}$ cm$^2$s$^{-1}$, $\gamma = -0.93$, $\alpha_{ni} = 0.6$, $E_{pc} = -430$ mV, $R_s = 0$, $C_{dl} = 20$ $\mu$F/cm$^2$, linear diffusion.
where no charge transfer takes place between the adsorbing substance and the electrode, the electrosorption valency is different than zero, although much smaller than in the case of chemisorption. This is caused by the fact that the electrosorption valency is a measure of the charge flow in the external circuit, caused not only by the charge transferred to or from the electrode, but also by the transfer of ions and dipoles within the double layer. In the case of physical adsorption the electrosorption valency strongly depends on potential. If for example, \( \gamma(E) = \gamma_N + \gamma_1(E - E_{pzc}) \) [26], then the standard free energy of adsorption will be a quadratic function of potential:

\[
\Delta G^\circ_{\text{ads}} = \Delta G^\circ_{\text{pzc}} - \gamma_N F(E - E_{pzc}) - \gamma_1 F(E - E_{pzc})^2
\]  

(4.18)

In this case cyclic voltammograms will show two adsorption and two desorption peaks. Voltammograms simulated for \( \gamma_N = -0.1, \) \( \gamma_1 = 2 \text{ V}^{-1} \) and different bulk concentrations of an adsorbate are shown in Fig. 4.2. As can be seen, they display the above described property. Such curves can be obtained in aqueous electrolytes containing, for example, long chain aliphatic alcohols. They are for identical conditions with the exception that the bulk concentration was the only parameter changed. It can be seen that two sets of adsorption/desorption peaks are placed symmetrically in respect to the zero charge potential, which is reasonable if we consider the quadratic dependence of the energy of adsorption on potential, with the minimum value at the potential of zero charge. It can also be observed that for higher concentrations the adsorption/desorption process is shifted to potentials further from the potential of zero charge, while in the case of lower bulk concentrations the process takes place at potentials closer to this potential. This indicates that as the bulk concentration increases, the energy of adsorption also increases due to the effect of an equilibrium between the adsorbing substance in the iHp and the oHp (see Table. 2.1, Frumkin isotherm). It can also be seen that as the bulk concentration decreases the adsorption peak becomes much smaller than the desorption peak. This indicates that the adsorption process is limited by the rate of diffusion to the
Fig. 4.2. Simulated cyclic voltammograms for γ dependent on potential. Conditions: \( A = 0.016 \, \text{cm}^2 \), area per adsorbate molecule \( 2.12 \times 10^{-15} \, \text{cm}^2 \), \( \rho_{sol} = 3.07 \times 10^{-8} \, \text{cm} \), \( g = -2350 \, J/\text{mol} \), \( g^{\#} = 0 \), \( k_s = 1 \times 10^6 \, s^{-1} \), \( \gamma_0 = 0.1 \) at \( E_{pzc} \), \( \gamma_l = 2 \, \text{V}^{-1} \), \( \alpha = 0.5 \), \( \nu = 1 \, \text{V/s} \), \( \Delta G_{ads,pzc}^0 = -34.2 \, \text{kJ/mol} \), \( D = 6 \times 10^{-6} \, \text{cm}^2 \, \text{s}^{-1} \), \( C_{dl} = 25 \, \mu \text{F} \), equilibrium coverage, linear diffusion. Bulk adsorbate concentration: \( 1.02 \times 10^{-1} \, \text{M} \) (a), \( 2.56 \times 10^{-2} \, \text{M} \) (b), \( 6.40 \times 10^{-3} \, \text{M} \) (c), \( 1.60 \times 10^{-3} \, \text{M} \) (d), \( 2.00 \times 10^{-4} \, \text{M} \) (e).
electrode. These curves were obtained with the assumption that an equilibrium exists at the initial potential between the amount of adsorbed substance and the substance in the bulk of solution. This explains the fact that as the bulk concentration decreases the charge corresponding to the desorption peak decreases as well. Note also that as the bulk concentration increases (hence, the potentials at which the process takes place is shifted farther from the potential of zero charge) the peaks become sharper. This may be understood if we consider a phenomenon described in the later part of this chapter, namely that the width of the peak decreases as the electrosorption valency increases. In the case of physical adsorption the electrosorption valency increases with the increasing difference between the electrode potential and the potential of zero charge. Hence, it is expected that in the case described above the electrosorption valency at the potentials at which adsorption/desorption peaks are observed is higher than in case of lower bulk concentrations of an adsorbate. This explains the difference in the peak width in both cases.

The standard free energy of chemisorbed ions or molecules depends almost linearly on potential and in such a case only one desorption/adsorption peak is observed in the polarizable potential range of the working electrode. The effect of an adsorbate concentration on voltammograms simulated for $\gamma$ independent of potential and equal to -0.93 is shown in Fig. 4.3. All the curves were obtained for identical conditions (standard rate constant, the charge transfer coefficient, electrosorption valency, formal potential, etc.). The only parameter being changed was the bulk concentration of an adsorbate. Area of adsorption peaks decreases as the concentration of adsorbing species decreases which indicates that the rate of adsorption depends on diffusion from the bulk solution. The charge associated with the desorption peak is constant for all these curves as the initial coverage is kept constant. Another property that changes with the change in bulk concentration is the potential of an adsorption and
Fig. 4.3. Simulated voltammograms for different adsorbate bulk concentrations with no dependence of the electrosorption valency on potential. Conditions: $A = 1.6 \times 10^{-6} \text{cm}^2$, area per adsorbing molecule $2.12 \times 10^{-15} \text{cm}^2$, $\rho_{\text{sol}} = 3.07 \times 10^{-8} \text{cm}$, $k = 6 \times 10^6 \text{s}^{-1}$, $\alpha = 0.5$, $\nu = 1000 \text{V/s}$, $E^\circ = -800 \text{mV}$, $D = 1 \times 10^{-5} \text{cm}^2/\text{s}$, $\gamma = -0.93$, $R_\text{s} = 0$, $C_d = 20 \mu\text{F/cm}^2$, $g = -2000 \text{J/mol}$, $g' = -1000 \text{J/mol}$, linear diffusion, equilibrium initial coverage. Adsorbate bulk concentration as indicated.
desorption peak. Both peaks move toward more positive potentials as the bulk concentration decreases. Such behaviour should be expected if we take into account an equilibrium between species in the iH·p and the oH·p (Table 2.1, Frumkin isotherm).

As was already stated above the simulation program successfully takes into account the effect of the electroosorption valency on the shape of the cyclic voltammograms, giving curves typical of physical and chemical adsorption. A typical value of the electroosorption valency in case of chemical adsorption is close to ±1, corresponding to a covalent bond between an adsorbed substance and the electrode material. Fig. 4.4 presents two voltammograms obtained for the electroosorption valency equal to +0.93 and -0.93. A negative value of the electroosorption valency indicates that electrons are transferred from the adsorbate to the electrode, while a positive electroosorption valency corresponds to the transfer of electrons from the electrode material to the adsorbate. It can be seen from Fig. 4.4 that, in the case of a negative electroosorption valency, the adsorption process takes place at more positive potentials, with a desorption of the substance as the potential becomes more negative. The opposite effect is observed for a positive electroosorption valency. It can be easily explained if we consider that a transfer of electrons from the adsorbate to the electrode is preferred at more positive potentials and becomes unfavourable as the electrode potential becomes more negative. In a similar way the transfer of electrons from the electrode to the adsorbing substance is to be expected when the electrode potential is negative, and becomes energetically unfavourable as the potential is shifted in the positive direction. In the case of physical adsorption the electroosorption valency changes with potential. The value depends on the transfer of ions caused by the adsorption of organic molecules rather than on the transfer of electrons to or from the adsorbate. If one considers cyclic voltammograms simulating the process of physical adsorption (Fig. 4.2), the two sets of adsorption and desorption peaks
Fig. 4.4. Simulated voltammograms for different electrosorption valency independent of potential. Conditions: $A = 1.6 \times 10^{-6}$ cm$^2$, area per adsorbing molecule $2.12 \times 10^{-15}$ cm$^2$, $\rho_{sol} = 3.07 \times 10^{-8}$ cm, $k_s = 6 \times 10^5$ s$^{-1}$, $\alpha = 0.5$, $\nu = 1000$ V/s, $E^o = -800$ mV, $C_{ini} = 1.00 \times 10^6$, $D = 1 \times 10^{-5}$ cm$^2$/s, $\gamma = -0.93$ or 0.93, as indicated, $R_s = 0$, $C_{dl} = 20$ $\mu$F/cm$^2$, $g = -2000$ J/mol, $g^* = -1000$ J/mol, linear diffusion, equilibrium initial coverage.
correspond to a negative (peaks at more negative potentials) and to a positive (at more positive potentials) electroosorption valency. The simulation program can also be used to study the effect of different diffusion modes to an ultramicroelectrode. Fig. 4.5 presents the comparison of the effect of sweep rate on cyclic voltammetric curves expected for a hemispherical ultramicroelectrode when linear or spherical diffusion is assumed. In both cases the desorption peak height is proportional to the potential sweep rate, while the adsorption peak height to the square root of the sweep rate. In all cases shown in this figure the desorption/adsorption process is reversible. In the case of linear diffusion to the electrode the ratio of the adsorption to desorption peak height ($I_a/I_d$) reaches a constant value as the bulk concentration of an adsorbate approaches 0 (compare Fig. 4.3). In such a case the height of the adsorption peak depends on the concentration of the adsorbate near the electrode generated during the desorption process. This limiting value of $I_a/I_d$ is independent of the sweep rate (as long as the process is reversible), but it depends on the reversal potential, the initial electrode coverage, the electroosorption valency and the interaction parameter. For spherical diffusion the adsorption peak disappears completely at low sweep rates if the bulk concentration of an adsorbate approaches zero. This arises from a faster mass transport of the desorbed molecules away from the electrode under spherical diffusion conditions.

The shape of the voltammogram reflects the properties of the adsorbing system. This dependence was investigated using simulated curves, because it is much easier to understand and explain the effect of different parameters using such curves. Examined properties include the width of the peak, separation of adsorption and desorption peaks, the effect of a sweep rate and the electrode coverage.

The width of the stripping (desorption) peak depends on the electroosorption valency and on the interaction parameter (Fig. 4.6). The influence of the interaction parameter on the peak width increases with an
Fig. 4.5. Comparison of cyclic voltammograms calculated for spherical (right) and linear (left) diffusion and different sweep rates assuming a reversible electrosorption process. Conditions: $A = 1.6 \times 10^{-2} \text{cm}^2$ (linear diffusion) or $1.6 \times 10^{-6} \text{cm}^2$ (spherical diffusion), $D = 6 \times 10^{-6} \text{cm}^2/\text{s}$, area per adsorbate molecule $2.12 \times 10^{-15} \text{cm}^2$, $\rho_{\text{sol}} = 3.07 \times 10^{-8} \text{cm}$, $g = -3650 \text{ J/mol}$, $\gamma = -0.95$, $\delta E = 0$, $E^* = -700 \text{ mV}$, $\theta_{\text{ini}} = 0.45$, $C_b = 5 \times 10^{-7} \text{ M}$, $C_{\text{dl}} = 25 \mu\text{F}$, $R_s = 0$. Potential sweep rate: 1638 V/s (a), 102 V/s (b), 6.4 V/s (c), 0.4 V/s (d). Current divided by a dimensionless number equal to sweep rate expressed in V/s.
Fig. 4.6. Effect of $\theta_{ini}$ on shape of reversible curves. Simulated conditions: $A = 1.6 \times 10^{-2} \text{cm}^2$, linear diffusion, $D = 6 \times 10^{-6} \text{cm}^2/\text{s}$, area per adsorbate molecule $2.12 \times 10^{-15} \text{cm}^2$, $\rho_{sol} = 3.07 \times 10^{-8} \text{cm}$, $g = -3000 \text{ J/mol}$ (right) and $3000 \text{ J/mol}$ (left), $\gamma = -0.95$, $\delta y/\delta E = 0$, $E^o = -700 \text{ mV}$, $v = 10 \text{ V/s}$, $C_b = 5 \times 10^{-7} \text{ M}$, $C_{dl} = 25 \mu \text{F}$, $R_s = 0$. $\theta_{ini} = 1 \ (a)$, $0.8 \ (b)$, $0.6 \ (c)$, $0.4 \ (d)$, $0.2 \ (e)$, $0.1 \ (f)$. 
increase in the initial coverage of the electrode. In the case of numerically calculated cyclic voltammograms, the calculation of the average width of the peak, \( \bar{w} \) (which can be defined as the charge associated with the peak divided by the peak height, \( I_{\text{max}} \), and multiplied by the sweep rate) is very easy:

\[
\bar{w} = \frac{\gamma}{I_{\text{max}}} \int_{E_i}^{E_f} I(t)dt
\]  

(4.19)

Integration limits are selected in such a way that the total charge associated with the peak can be obtained. The normalised average peak width \( \left( \frac{\gamma |F|}{RT} \bar{w} \right) \) obtained from curves simulated for a linear symmetry of diffusion was plotted against \( \theta \) in Fig. 4.7 (a). It was assumed that the concentration of an adsorbate near the electrode generated during the desorption process is significantly larger than its bulk concentration. The average peak width depends linearly on \( \theta \) (for \( 0<\theta<0.6 \)) with the intercept equal to \( 3.29 \times RT/(\gamma |F|) \). Therefore, one can determine the electro sorption valency from the average peak width extrapolated to zero coverage. The slope of \( \frac{\gamma |F|}{RT} \bar{w} \) versus \( \theta \) contains information about the interaction parameter. The plot of \( |\gamma|F/RT \frac{d\bar{w}}{d\theta} \) versus \( 2g/RT \) is shown in Fig. 4.7 (b).

The relation can be represented by an empirical quadratic equation

\[
\gamma = 9.62 \times 10^{-3} x^2 + 9.20 \times 10^{-1} x + 1.44
\]

which can be used to determine the interaction parameter. Curves used in the analysis should be free of ohmic drop and recorded at sufficiently low sweep rates to insure a reversible process. The above equations can be used to describe electrosorption processes at ultramicroelectrodes, if the sweep rate is not be lower than about \( 200 \times RT Da^2/(\gamma F) \) (\( a \) is the smallest dimension of the electrode). Under such conditions non-linear diffusion to the ultramicroelectrode is negligible.

The desorption peak potential (Fig. 4.8) extrapolated to zero coverage
Fig. 4.7. (a) Dependence of peak width \( w \) on initial coverage for a reversible process in the case of linear diffusion. Interaction parameter changed from 3000 J/mol (top curve) to -3000 J/mol (bottom curve).

(b) Slope of peak width versus initial coverage as a function of interaction parameter for linear diffusion.
Fig 4.8. Desorption peak potential, $E_d$ versus $\theta_m$ for $g$ varied from -3000 J/mol (bottom curve) to 3000 J/mol (top curve) for linear diffusion.
\((E_d, \theta = 0)\) depends only on the standard potential, \(E^\circ\), sweep rate and the adsorbate diffusion coefficient. The following semiempirical relation was derived for linear diffusion from a mathematical analysis of the problem and verified by numerical simulations:

\[
E_{d, \theta = 0} = E^\circ + 0.46 \frac{RT}{\gamma F} + \frac{RT}{\gamma F} \ln \left( \frac{1}{\rho_{\text{sol}}} \sqrt{\frac{D}{u}} \frac{RT}{\gamma F} \right)
\]  
(4.20)

In this equation \(\nu\) is the sweep rate, \(D\) is the diffusion coefficient and \(\rho_{\text{sol}}\) is the diameter of a solvent molecule (the presence of \(\rho_{\text{sol}}\) arises from eqn. (4.1)). Eqn. (4.20) can be used for the determination of the standard potential of the adsorption process. Note that these equations were derived assuming that: the electrosorption valency is independent of potential, the adsorption process is reversible, there is no ohmic drop, and the bulk concentration of an adsorbate is negligibly small. The last condition means that the maximum concentration of an adsorbate at the electrode produced during the desorption process must be at least 100 times higher than its bulk concentration. The reversible desorption peak potential, \(E_d\), is also affected by the electrode coverage if the interaction parameter, \(g\), is not equal to zero. In principle, this relation could be used to determine \(g\). However, the dependence of \(E_d\) on \(\theta\) is relatively small, non-linear, and most importantly, it is strongly affected by the ohmic drop.

The influence of adsorption kinetics may be noticed when the sweep rate in cyclic voltammetric experiments or simulations is varied over a wide range (see Fig. 4.9). The separation of adsorption and desorption peaks is independent of the sweep rate up to a certain value, then it increases with the sweep rate. This indicates that at sweep rates high enough the process becomes irreversible and kinetic parameters of the process can be determined from cyclic voltammograms. The critical sweep rate above which the process becomes irreversible depends on the standard rate constant and the \(\alpha\) coefficient. Estimates of the kinetic parameters presented here are
Fig. 4.9. Effect of sweep rate on reversibility of the adsorption process. Simulated conditions: $A = 1.6 \times 10^{-6} \text{ cm}^2$, $D = 6 \times 10^{-6} \text{ cm}^2/\text{s}$, spherical diffusion, area per adsorbate molecule $2.12 \times 10^{-15} \text{ cm}^2$, $\rho_{\text{sol}} = 3.07 \times 10^{-8} \text{ cm}$, $g = 1000 \text{ J/mol}$, $g^{\#} = 500 \text{ J/mol}$, $k_a = 2 \times 10^5 \text{ s}^{-1}$, $\alpha = 0.65$, $\gamma = -0.95$, $\delta \gamma / \delta E = 0$, $E^\circ = -700 \text{ mV}$, $C_b = 5 \times 10^{-7} \text{ M}$, $C_{\text{dl}} = 25 \mu\text{F}$, $R_s = 0$, $\theta_{\text{ini}} = 0.1$. Sweep rate: $1 \times 10^6 \text{ V/s}$ (a), $6.6 \times 10^4 \text{ V/s}$ (b), $4.1 \times 10^3 \text{ V/s}$ (c), $256 \text{ V/s}$ (d), $16 \text{ V/s}$ (e), $1 \text{ V/s}$ (f). Current divided by a dimensionless number equal to sweep rate expressed in V/s.
based on the analysis of the desorption peak potential, because for small initial coverages the adsorption peak is very small in comparison to the charging current (see Fig. 4.9) and the determination of its maximum potential may be erroneous. In Fig. 4.10 the desorption peak potential \(E_d\) obtained from simulated curves is plotted against the logarithm of the normalised sweep rate \(\bar{v} = |\gamma| \frac{F}{RT} \nu\). The plot shows two distinctly different slopes in the reversible and irreversible regions. The cross-point of these two slopes corresponds to the potential, \(E_{d,c}\), and the normalised sweep rate, \(\bar{v}_c\). Numerical calculations show that if the initial electrode coverage is small \((\theta_i \leq 0.1)\) then \(\bar{v}_c\) approximately describes the rate constant of the desorption process at the potential \(E_{d,c}\). Therefore, the standard rate constant of the adsorption/desorption process can be estimated as:

\[
k_s \approx \bar{v}_c \exp \left[ - \frac{(1 - \alpha) \gamma F}{RT} (E_{d,c} - E^*) \right]
\]  

(4.21)

For totally irreversible desorption processes the average width of the peak depends on the symmetry of the electron transfer activation barrier (\(\alpha\) coefficient) and on the \(\frac{2(g - g^*) \theta}{RT}\) factor. Since the second factor varies with the electrode coverage, both \(\alpha\) and \((g - g^*)\) can be determined from the dependence of the irreversible peak width on \(\theta_i\). In Fig. 4.11 the effect of \(\theta_i\) and \(g^*\) on the shape of cyclic voltammetric curves is shown. The relation between the normalised peak width \((\alpha |\gamma| \frac{F}{RT} \bar{w})\) and the initial electrode coverage for a linear symmetry of diffusion is shown in Fig. 4.12 (a). The normalised peak width depends linearly on \(\theta_i\) (for \(0 < \theta_i < 0.6\)). The intercept is equal to 2.71 \((2.71RT/|\gamma| F)\) for an unnormalised peak width) and the slope depends on the \((g - g^*)\) parameter. The plot of \(\alpha |\gamma| F / RT \frac{d\bar{w}}{d\theta}\) versus
Fig. 4.10. The desorption peak potential versus the normalised sweep rate ($\tilde{\nu} = \frac{\nu F}{RT}$). Conditions as in Fig. 4.9. The cross-point of two limiting slopes obtained for low and high sweep rate regions is used to estimate the adsorption rate constant.
Fig. 4.11. Effect of $\theta$ on shape of irreversible curves for $g \cdot g^\# = -3000$ J/mol (left) or $g \cdot g^\# = 3000$ J/mol (right). Conditions: $g = -2000$ J/mol, $g^\# = 1000$ J/mol (left) or $-5000$ J/mol (right), $A = 1.6 \times 10^{-6}$ cm$^2$, spherical diffusion, $D = 6 \times 10^{-6}$ cm$^2$/s, area per adsorbate molecule $2.12 \times 10^{-15}$ cm$^2$, $\rho_{sol} = 3.07 \times 10^{-8}$ cm, $k_s = 3.7 \times 10^5$ s$^{-1}$, $\alpha = 0.65$, $E^\circ = -700$ mV, $\nu = 1 \times 10^6$ V/s, $C_b = 5 \times 10^{-5}$ M, $\gamma = -0.95$, $\delta \gamma / \delta E = 0$, $R_s = 0$, $C_{du} = 25$ $\mu$F. Initial coverage: 0.1 (a), 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e), 1 (f).
Fig. 4.12. (a) Relation between the normalized peak width and the initial electrode coverage for $(g - g^*)$ varied from 3000 J/mol (top curve) to -3000 J/mol (bottom curve).
(b) Slope of peak width versus initial coverage curve as a function of $2(g - g^*)/RT$. 
\(-2(g - g^\#)/RT\) is also shown in Fig. 4.12 (b). The relation can be represented by an empirical quadratic equation \( y = 2.43 \times 10^{-2} x^2 - 7.12 \times 10^{-1} x + 4.40 \times 10^{-5} \).

The relations described above allow a quick determination of thermodynamic and kinetic parameters of an adsorption/desorption process from cyclic voltammetric experiments obtained with ultramicroelectrodes at a wide range of sweep rates. However, these relations are valid only under specific conditions, which sometimes may be difficult to reach in experimental reality. In particular it may be difficult to obtain totally irreversible cyclic voltammograms that are undistorted by the ohmic drop for fast electrosorption processes. A different, more universal method of determining kinetic parameters from cyclic voltammetric curves will be presented in section 4.1.2. This method was also developed based on the use of simulated curves. The approach used during the development of this method is more analytical, being based on equations describing the adsorption process (Frumkin adsorption isotherm). The simulated curves are used in this case to verify the method and not, as above, to enable the determination of empirical dependencies existing between the shape of the curves and the properties of the system. This method seems to be more reliable than the previous one and it was used in the determination of kinetic parameters for real systems.

4.1.2 Method of data analysis.

From the previous discussion of the dependence of the shape of cyclic voltammograms on the potential sweep rate it can be concluded that at sufficiently low potential sweep rates an equilibrium exists between the adsorbate in the iHp and the oHp, while for high potential sweep rates the process is expected to be controlled by the kinetics of an adsorption/desorption process and described by eqns. (2.12) and (2.13). The equation describing the dependence of the desorption current on the adsorption and desorption rate constant:
\[ i_d = \gamma FA\left\{ k_d(E,\theta)c_i - k_d(E,\theta)c_{so}(1-\theta) \right\} \]  \hspace{1cm} (4.22)

\[ i_d = \gamma FA\left\{ k_d'(E)c_i \exp\left[ \frac{2(g-e^\theta)}{RT} \right] - k_d'(E)c_{so}(1-\theta)\exp\left[ \frac{-2g^\theta}{RT} \right] \right\} \]  \hspace{1cm} (4.23)

can also be represented by an equation showing the origin of the observed current for the departure of the system from an equilibrium:

\[ i_d = \gamma FAk_d(E,\theta)c_i\left\{ 1 - \frac{k_a(E,\theta)}{k_d(E,\theta)} \frac{c_{so}(1-\theta)}{c_i} \right\} \]  \hspace{1cm} (4.24)

Taking into account the relationship between the concentration of an adsorbate in the iHp and the charge transferred between an adsorbed substance and the electrode, \( q \):

\[ q = \gamma FAC_i \]  \hspace{1cm} (4.25)

the following equation can be obtained:

\[ i_d = k_d(E,\theta)q\left\{ 1 - \frac{k_a(E,\theta)}{k_d(E,\theta)} \frac{c_{so}(1-\theta)}{c_i} \right\} \]  \hspace{1cm} (4.26)

Remembering that the ratio of the adsorption and desorption rate constants is the equilibrium constant and that the ratio of concentrations is equal to the reaction quotient, \( Q_{ads} \), it can be seen that the desorption current is a measure of the departure of the system from equilibrium:

\[ i_d = k_d(E,\theta)q\left\{ 1 - \frac{K(E,\theta)}{Q_{ads}} \right\} \]  \hspace{1cm} (4.27)

and hence can be used in the determination of the kinetics of the process. This expression leads to an equation describing the dependence of the desorption rate constant on the desorption current:

\[ k_d(E,\theta) = \frac{i_d}{q} \frac{Q_{ads}}{Q_{ads} - K(E,\theta)} \]  \hspace{1cm} (4.28)

Curves recorded at low potential sweep rates are characterised by an equilibrium between an adsorbate in the iHp and in the oHp and the reaction quotient is equal to the equilibrium constant. Larger values of the desorption current observed for high potential sweep rate experiments
originate from an increasing departure of the system from equilibrium and allow the determination of the desorption rate constant. Analysis of eqn. (4.28) indicates that the determination of the kinetics of the process from curves recorded at sufficiently high potential sweep rates is possible if the equilibrium rate constant and the concentrations in the iHp and the oHp are known as functions of potential.

It was stated above that at sufficiently low potential sweep rates an equilibrium exists between an adsorbate in the iHp and the oHp. It indicates that these curves may be used to determine the equilibrium rate constant, \( K(E, \theta) \), if the concentrations in the iHp and the oHp are known. This information can be obtained from the desorption current using integration and convolution transformations. First, background current has to be subtracted. This can be done by fitting the background current before and after the peak to a 3rd order polynomial expression by the least squares method - see Fig. 4.13 (A). Then the polynomial expression is used to estimate the background current under the peak. This is a convenient method but not very accurate; errors may be significant if desorption currents are small. For this reason only the middle part of the curve (80% in terms of surface area) was used for the determination of thermodynamic and kinetic parameters (Fig. 4.13 (B)).

Integration of the desorption peak gives the charge, \( q \), due to adsorbed species in the iHp (Fig. 4.13 (B)), which is related to \( c_\ell \) through eqn. (4.25). In case of linear diffusion the convolution transformation [20 p. 236] needed to calculate concentration of an adsorbate in the oHp is given by:

\[
C_o(0) = C_b + \frac{1}{\gamma FA \sqrt{D}} \int_0^\infty \frac{i_a(\tau)}{\sqrt{\pi(t-\tau)}} d\tau
\]

(4.29)
Fig. 4.13 (A). Background correction for the desorption peak by a 3rd order polynomial curve fitting (details in text). Curve (a) represents a cyclic voltammogram recorded for the desorption/adsorption of thioglycol from 1 M H$_2$SO$_4$ with a Hg/Au ultramicroelectrode (5 µm in radius). The initial coverage was 0.69 and the sweep rate was 1000V/s. Curve (b) represents estimation of the background current and curve (c) the desorption peak after the background current subtraction.
Fig. 4.13 B. (a) - integration of curve (c) from Fig. 4.13 A. (b) - convolution of curve (c) from Fig. 4.13 A.
Part of the curves between dashed vertical lines was used in the analysis.
where $C_b$ is the bulk concentration of adsorbate and $C_o(0)$ is its concentration close to the electrode surface (just outside the double layer) (see Fig. 4.13 (B)).

For spherical (outside the sphere) diffusion the convolution transformation is [135, 136]:

$$C_o(0) = C_b + \frac{1}{\gamma FA r} \int_0^\infty i_d(\tau) \left[ \left( \pi \frac{D \times (t-\tau)}{r^2} \right)^{1/2} \frac{r^2}{D \times (t-\tau)} \right] \exp \left( \frac{D \times (t-\tau)}{r^2} \right) \text{erfc} \sqrt{\frac{D \times (t-\tau)}{r^2}} d\tau$$

(4.30)

where $r$ is the electrode radius.

Since both the integration and the convolution treat current as a function of time (not potential), the correction for uncompensated solution resistance can be easily introduced into calculations [20, 135].

The concentration of an adsorbate at the electrode surface obtained by the convolution is expressed in mol/cm$^3$. In order to calculate $c_o$ in mol/cm$^2$ this concentration must be multiplied by the diameter of a solvent molecule, $\rho_{sol}$, (compare eqn. (4.1)). In addition the effect of the diffuse layer potential, $\varphi_2$, must be taken into account, then:

$$c_o = C_o(0) \rho_{sol} \exp(-zF\varphi_2/RT)$$

(4.31)

where $z$ is the charge on the adsorbate molecule in solution.

In the present analysis the effect of $\varphi_2$ potential was neglected because of high concentrations of the supporting electrolyte used in all experiments.

Note, that the ratio of $c_o$ to $c_i$, needed to calculate the equilibrium constant, is independent of $\gamma$, as long as $\gamma$ is independent of potential.

The degree of coverage, $\theta$, is determined from the ratio of the charge associated with the adsorbed substance, $q$, to the charge associated with a monolayer of an adsorbed substance, $q_m$. Both quantities can be obtained by an integration of experimental curves. The charge corresponding to a monolayer is estimated by analysing the dependence of the charge associated with the desorption peak on the concentration of the adsorbate in
solution and on the preconcentration time. Again, the degree of coverage
determined in this way is unaffected by $\gamma$, if $\gamma$ is independent of potential
and $\theta$. In case of simulated curves the maximum charge was estimated from
the area, $A_o$, occupied by the adsorbed molecule:

$$q_m = \frac{\gamma FA}{A_o N_A} \quad (4.32)$$

This equation can also be used in the case of experimental curves if the
area corresponding to one adsorbed molecule is known.

The ratio of concentrations of the adsorbate in the iHp and the oHp
determined in the above way is a function of potential and the electrode
coverage, and in the case of the Frumkin adsorption isotherm it can be
expressed as:

$$\ln K(E, \theta) = \ln \frac{c_{eq}^i}{c_{eq}^o (1 - \theta^{eq})} = -\frac{\Delta G_{ads,pc}^o}{RT} - \frac{\gamma F}{RT} (E - E_m) - \frac{2g\theta^{eq}}{RT} \quad (4.33)$$

The multiple linear regression method [137], (left hand side of
expression (4.33) versus $E$ and $\theta^{eq}$) allows the determination of the standard
energy of adsorption, the electroosorption valency and the interaction
parameter. An attempt to extract such parameters from simulated curves
showed that values obtained from one curve differ substantially from values
entered into the simulation program. This problem arises from the fact that
for the middle part of the stripping peak there is an almost linear
correlation between $\theta^{eq}$ and potential. To avoid this problem parameters
have to be determined from a simultaneous analysis of several curves
obtained for different initial coverages. Errors in the determination of the
interaction parameter can be minimised by a proper selection of curves for
the analysis. Curves obtained for very low initial coverages are expected to
give rather poor agreement between the determined and the actual
parameter, because in such conditions interactions are small and their
influence on the curve shape is insignificant. For high coverages
interactions should be substantial, but in experimental reality the assumed
model (Frumkin isotherm) is not always exactly obeyed, and uncertainty in the determination of \( c_{\text{max}} \) (a monolayer surface coverage) may contribute significantly to overall errors. In conclusion, stripping curves obtained for the initial coverages in the middle range (perhaps 0.1 to 0.8) are expected to give the most accurate values of thermodynamic parameters.

If thermodynamic parameters of the adsorption process are known then currents observed in high sweep rate voltammetric experiments can be used to calculate the rate constant of the desorption process as a function of potential (see eqn. (4.28)). Note that the concentrations needed for these calculations were obtained in the same way as for the case of slow sweep rate experiments (using convolution and integration algorithms).

The desorption rate constant may be expressed as a function of potential, the electrode coverage, the electro sorption valency and the charge transfer coefficient, \( \alpha \):

\[
k_{d}(E, \theta) = k_{d}^{0} \exp \left[ \frac{2(g - g^*) \theta}{RT} \right] \exp \left[ (1 - \alpha) \frac{\gamma F}{RT} (E - E_{pzc}) \right] \quad (4.36)
\]

where \( k_{d}^{0} \) is the rate constant of desorption at the zero charge potential, \( E_{pzc} \), with a zero electrode coverage.

Therefore, by the least squares regression method (\( \ln k_{d} \) versus \( E \)) it is possible to determine \( \alpha \) and \( k_{d}^{0} \exp [2(g - g^*) \theta / RT] \).

A similar expression can be written for the rate of adsorption:

\[
k_{a}(E, \theta) = k_{a}^{0} \exp \left[ \frac{-2g^* \theta}{RT} \right] \exp \left[ - \alpha \frac{\gamma F}{RT} (E - E_{pzc}) \right] \quad (4.35)
\]

Then, if \( \gamma \) and \( \alpha \) are independent of potential, the standard potential, \( E^{\circ} \), and the standard rate constant, \( k_{a}^{0} \), can be calculated. The standard potential is chosen as a potential for which adsorption and desorption rate constants are equal (standard energy of adsorption is equal to zero). Therefore:
\[ E^o = E_{pce} - \frac{\Delta G_{adv,pce}^o}{\gamma F} \]  

(4.36)

and

\[ k_s = k_s^* \exp \left[ -(1 - \alpha) \frac{\Delta G_{adv,pce}^o}{RT} \right] \]  

(4.37)

If the interaction parameter of the activated complex, \( g^* \), and the interaction parameter, \( g \), are equal to zero then the determined \( k_s^0 \exp[2(g-g^\#)\theta/RT] \) rate constant is equal to the desorption rate constant at the potential of zero charge. The error introduced by a wrong choice of the adsorption isotherm was tested. Table 4.1 presents results of the analyses of cyclic voltammograms simulated for a Frumkin isotherm \((g \neq 0, \ g^* = 0)\) obtained with the assumption that the Langmuir isotherm is obeyed. As expected, such analysis produces correct results for low coverages, where the interactions between the adsorbed molecules are very small, but fails at higher coverages, due to increasing interactions, affecting the shape of analysed curves.

Similarly as in the case of the determination of thermodynamic parameters a multiple regression method can be used to obtain kinetic parameters. The dependence of the desorption rate constant on potential and the electrode coverage can be presented by the equation:

\[ \ln k_d(E, \theta) = (1 - \alpha) \frac{\gamma F}{RT} (E - E^o) + \frac{2(g - g^\#)\theta}{RT} + \ln k_s \]  

(4.38)

A multiple regression with respect to potential and the electrode coverage allows the determination of the charge transfer coefficient, the activated complex interaction parameter and the standard rate constant. As before, to ensure a reliable result a series of curves has to be analysed.

The method described above for the determination of thermodynamic and kinetic parameters from experimental curves based on the multiple regression method presents some risk of creating systematic errors. The
Table 4.1. Results of analysis carried out with the assumption of Langmuir isotherm for voltammograms simulated according to Frumkin isotherm. Parameters used in simulations: $E^o = -800$ mV, $\gamma = -0.8$, $g = -2000$ J/mol, $k_s = 5 \times 10^6$ s$^{-1}$, $\alpha = 0.4$.

<table>
<thead>
<tr>
<th>initial coverage</th>
<th>formal potential / mV</th>
<th>electrosorption valency</th>
<th>standard adsorption rate constant / s$^{-1}$</th>
<th>charge transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>-811.7</td>
<td>-0.79</td>
<td>6.66$\times 10^6$</td>
<td>0.37</td>
</tr>
<tr>
<td>0.1</td>
<td>-796.8</td>
<td>-0.83</td>
<td>4.75$\times 10^6$</td>
<td>0.38</td>
</tr>
<tr>
<td>0.2</td>
<td>-785.5</td>
<td>-0.87</td>
<td>3.54$\times 10^6$</td>
<td>0.38</td>
</tr>
<tr>
<td>0.5</td>
<td>-779.1</td>
<td>-0.92</td>
<td>2.52$\times 10^6$</td>
<td>0.33</td>
</tr>
<tr>
<td>1</td>
<td>-781.6</td>
<td>-0.93</td>
<td>1.53$\times 10^6$</td>
<td>0.18</td>
</tr>
</tbody>
</table>
equilibrium constant depends on the electrode potential and coverage. At the same time there is an almost linear dependence of the electrode coverage on potential, which makes it difficult to separate the effects of the independent variables on the value of the dependent variables. In addition, the potential acting at an electrode is influenced by the ohmic drop, which depends on the value of the current. The current value depends on the amount of the substance being desorbed. This means that there is a complex dependence of the equilibrium constant on many interdependent parameters. A similar situation is encountered in the case of kinetic parameters. To avoid these complications it may seem more reasonable to employ a different approach to the determination of the thermodynamic and kinetic parameters of the process.

In the above method a series of several curves was employed in one analysis to ensure a better description of the system with the Frumkin isotherm. Curves obtained for different coverages may correspond to different experimental conditions (e.g. a slightly different potential range) and this in turn may introduce an error into the determination of the kinetics of the process. It seems reasonable to find an equation describing the dependence of the equilibrium constant on as many parameters as possible (in most cases potential and the electrode coverage are adequate) for one experiment and then to use this dependence to calculate the equilibrium constant required for the determination of kinetic parameters. It should be stressed that the parameters describing the equilibrium constant determined in this way may not have any clearly defined physical meaning, but would provide the best description of the experimental value, and hence enable the most accurate determination of kinetic parameters.

For the sake of interpretation, the most desirable description of the system is obtained when as small a number of parameters as possible successfully predicts the change of the examined property. In the case of an adsorption process the system would be simplified if the equilibrium
constant could be represented with the Langmuir adsorption isotherm (see Table 2.1). The Langmuir adsorption isotherm assumes that there are no interactions between the molecules of adsorbed substance, and hence the resulting equilibrium constant is independent of the electrode coverage. This means that in such a case a simple one parameter regression (with respect to potential) is adequate for the determination of all required parameters. Application of this analysis would significantly reduce the possibility of errors caused by the inability to separate the effect of different parameters on the property of interest with the multiple regression method. The results of this one-parameter analysis should not be, however, accepted blindly. If the electrosorption valency calculated in this way depends on the electrode coverage, this would indicate that the examined system is not properly described by the Langmuir isotherm, and that a more complex analysis should be attempted. In a similar way the method of choice in the determination of kinetic parameters of the adsorption process would be based on the assumption that there are no interactions between the activated complex and the adsorbed molecules \((g^* = 0)\). The adsorption rate constant calculated from one experiment, with the equilibrium constant described with as many parameters as possible, may then be analysed as a function of potential. Again this assumption should be verified by analysing the dependence of the charge transfer coefficient and the standard rate constant on the initial coverage. The existence of such a dependence would indicate interactions of the activated complex with adsorbed molecules and a more complex analysis based on the Frumkin adsorption isotherm should be employed.

In the case of interactions between adsorbed molecules (either attractive or repulsive) the electrosorption valency (determined with the assumption that the Langmuir isotherm is obeyed) changes with the electrode coverage (see Fig. 4.14) and its change depends on the form and strength of the interactions. If the analysis of the electrosorption valency dependence on the
Fig. 4.14. Dependence of electrosorption valency (obtained with the assumption that the Langmuir adsorption isotherm is obeyed) on electrode coverage for different interaction parameters (values as indicated on graph). Curves simulated for $\gamma = -1$. 
initial coverage indicates the existence of interactions between the adsorbed molecules, then the relation between the determined parameters and those corresponding to the Frumkin adsorption isotherm should be sought. In the case of large bulk concentrations of the adsorbate, $c_0$ can be assumed to be constant throughout the experiment. The dependence of the equilibrium constant on potential and the electrode coverage can be expressed in the case of the Frumkin isotherm as:

$$\ln \frac{\theta c_{\text{max}}}{c_0(1 - \theta)} = -\frac{\gamma F}{RT}(E - E^*) - \frac{2g\theta}{RT} = -\gamma \bar{E} - \bar{g} \theta$$

(4.39)

where $\bar{E}$ and $\bar{g}$ are the normalised potential and the normalised interaction parameter, respectively. If both the interaction parameter and the electroosorption valency are potential independent then the potential derivative of the logarithm of the equilibrium constant would be:

$$\frac{d}{d \bar{E}} \ln \left[ \frac{\theta c_{\text{max}}}{c_0(1 - \theta)} \right] = -\gamma - \bar{g} \frac{d \theta}{d \bar{E}} = -\gamma_L$$

(4.40)

where $\gamma_L$ is the electroosorption valency determined with the assumption that the Langmuir isotherm describes the system. After further calculations the expression for the dependence of the electrode coverage on the normalised potential can be obtained:

$$\frac{d \theta}{d \bar{E}} = -\frac{1}{\gamma} \frac{1}{\theta(1 - \theta) + \bar{g}}$$

(4.41)

and after comparison with eqn. (4.40) the dependence between the electroosorption valency determined from the Langmuir adsorption isotherm and the Frumkin adsorption isotherm can be found:

$$\gamma = \gamma_L [1 + \bar{g} \theta(1 - \theta)] \equiv \gamma_L [1 + \bar{g} \theta_{\text{ave}} (1 - \theta_{\text{ave}})]$$

(4.42)

where $\theta_{\text{ave}}$ is the average electrode coverage during a desorption process.

As there are two unknown parameters in this equation (the electroosorption valency and the interaction parameter) they should be
sought through a method of trial and error as the best set of parameters describing the dependence of the electrosorption valency on the electrode coverage. This can be done with the aim of the simulation program, already described above. Simulated curves with known electrosorption valency and interaction parameter can be analysed with the assumption that the Langmuir adsorption isotherm is obeyed and the resulting electrosorption valency dependence on the electrode coverage can be compared with the experimental result. The best set of values would be assumed to describe the process.

A similar approach can be taken for the determination of the kinetic parameters of the process. If the charge transfer coefficient depends on the electrode coverage, then the values corresponding to the Frumkin adsorption isotherm should be determined. The adsorption rate constant depends on potential and the electrode coverage as follows:

$$\ln k_a = -\alpha L \gamma_L E - \bar{g}^* \theta = -\alpha_L \gamma_L E$$  \hspace{1cm} (4.43)

where $\bar{g}^*$ is the normalised interaction parameter of the activated complex and $\alpha$ is the charge transfer coefficient determined with the assumption that the Langmuir adsorption isotherm is obeyed. It follows after differentiation with respect to potential and taking into account eqn. (4.41) that:

$$\alpha_L \gamma_L = \alpha \gamma + \bar{g}^* \frac{d \theta}{d E} \gamma \frac{(1 - \theta)}{1 + \bar{g} \theta (1 - \theta)}$$  \hspace{1cm} (4.44)

As for the determination of the thermodynamic parameters, the best set of kinetic parameters is selected with the use of the simulation program.

It was shown above that the separation of the effect of the electrode coverage and of potential on both kinetic and thermodynamic parameters is difficult. As both the adsorption rate constant and the equilibrium constant depend on potential and the electrode coverage, some useful information can
be obtained from considering the dependence of the adsorption rate constant on the equilibrium constant, expressed through the symmetry factor, $\xi$:

$$
\xi = \frac{\Delta \ln k_a}{\Delta \ln K_a} = \frac{\partial \Delta G_{ad}^a(E, \theta)}{\partial \Delta G_{ad}^a(E, \theta)}
$$

(4.45)

As the symmetry factor depends on the interactions at the electrode surface (expressed through $\chi$, eqn. (2.16)) and on the symmetry of the energy barrier, $\alpha$, it can be expressed as:

$$
\xi = \alpha + \bar{g}\theta(1-\theta)(\alpha - \chi)
$$

(4.46)

The determination of this parameter doesn't require the separation of the effects of the electrode coverage and potential, making the analysis of data much simpler. At the same time it provides a means of comparison of results obtained for different systems. Substances characterised by similar kinetic properties are characterised by similar symmetry factors, which means that the plots of the dependence of the logarithm of the desorption rate constant on the logarithm of the equilibrium constant form a set of parallel lines.

The next section will present the application of the above methods of data analysis to experimental systems. A comparison of experimental curves with those obtained from simulation for the parameters obtained from the analysis will also be presented as a means of verification of the method developed.

4.1.3 Kinetics of adsorption of thiocompounds

4.1.3.1 Chemisorption at mercury ultramicroelectrodes

Mercury ultramicroelectrodes were prepared in the way described in the experimental part of the thesis through an electrochemical deposition of mercury hemisphere at a gold electrode. Because of the large potential sweep rates required to determine the rate of the process and the resulting large current leading to an increased value of the $iR$ drop, the solutions
examined were chosen to ensure that the solution resistance is as small as possible. Most of the experiments described in this chapter were performed in 1 M KOH or 1 M H₂SO₄ supporting electrolyte solution. These solutions have a much higher conductivity than the solutions of salts. Another advantage is their high purity, especially important when the work with ultramicroelectrodes is attempted. Even a very small concentration of impurities results in a very fast contamination of ultramicroelectrodes due to their small size and an increased diffusion rate to the electrode surface.

4.1.3.1.1 Adsorption of thioglycol from acidic and basic solutions

Adsorption of thioglycol at mercury electrodes, which is thermodynamically favourable at positive potentials, is usually accompanied by the oxidation of mercury and the formation of soluble Hg(-S-R)_n complexes. This process causes a significant interference at concentrations of thioglycol higher than about 1 mmol/L. In this work CV (cyclic voltammetric) experiments were carried out for concentrations of thioglycol varying from 8×10⁻⁶ to 6.4×10⁻⁵ mol/L. In order to accumulate a desired quantity of the adsorbate on the electrode cyclic voltammetric experiments were preceded by a short pre-concentration (0.1 to 7 s) at the initial potential and then a potential scan was started in the direction of negative potentials. After reaching the vertex value, the potential was reversed and a part of the thioglycol released from the electrode surface was re-adsorbed. Between experiments the electrode was held at a sufficiently negative potential to prevent an accumulation of thioglycol on the surface.

Peaks associated with an adsorption/desorption of thioglycol occur at different potentials in acidic and basic solutions. In 1 M H₂SO₄ the process takes place at potentials more positive, and in 1 M KOH, at potentials more negative relative to the zero charge potential (Fig. 4.15). The potential of zero charge, E_pzc, of mercury electrode in the absence of specific adsorption is about -426 mV vs. SSCE (sodium chloride saturated calomel electrode).
Fig. 4.15 A. Cyclic voltammograms obtained for desorption/adsorption of thioglycol from 1 M KOH solution on Hg/Au ultramicroelectrode (5 µm in radius).

Sweep rate was 1000 V/s. Initial coverage of the electrode with thioglycol was: a. 0.83; b. 0.55; c. 0.33; d. 0.15; e. 0.004.
Fig. 4.15 B. Cyclic voltammograms obtained for desorption/adsorption of thioglycol from 1 M KOH solution on Hg/Au ultramicroelectrode (5 μm in radius). Sweep rate was 100000 V/s.

Initial coverage of the electrode with thioglycol was: a. 0.54; b. 0.51; c. 0.33; d. 0.19; e. 0.06.
Fig. 4.15 C. Cyclic voltammograms obtained for the desorption/adsorption of thioglycol from 1 M H₂SO₄ solution on a Hg/Au ultramicroelectrode (5 μm in radius). Sweep rate was 1000 V/s.

Initial electrode coverage with thioglycol was: a. 0.57; b. 0.49; c. 0.35; d. 0.21.
Fig. 4.15 D. Cyclic voltammograms obtained for the desorption/adsorption of thioglycol from 1 M H₂SO₄ solution on a Hg/Au ultramicroelectrode (5 µm in radius). Sweep rate was 100000 V/s.

Initial electrode coverage with thioglycol was: a. 0.74; b. 0.63; c. 0.42; d. 0.15; e. 0.06.
The difference in the desorption/adsorption peak potentials originates from the energy required to remove a proton from the thioglycol molecule in acidic solutions. The desorption peak potential for thiocompounds decreases linearly with an increase in pH, for \(0 < \text{pH} < 10\), and it is practically independent of pH for \(\text{pH} > 10\) [138]. Since the pK_a of thio-groups (R-S-H) is about 10, the above results clearly indicate that thiocompounds are adsorbed on mercury without a proton being attached to the sulphur.

Thermodynamic parameters of the adsorption were determined from cyclic voltammograms recorded at 1000 V/s. In both solutions the electroosorption process was at equilibrium under these conditions. Curves recorded at 100000 V/s were used for obtaining kinetic information. At this sweep rate the process becomes quasi-reversible (Fig. 4.15 (D)), and an increase in the adsorption and desorption peak separation may be easily noticed. Fig. 4.15 (A) presents cyclic voltammograms recorded in basic solution for different initial electrode coverages with thioglycol. As the surface concentration increases, a second cathodic peak appears at slightly more positive potentials. The position of this peak doesn't change with an increase in the sweep rate. This peak may result from a fast reorientation of the adsorbed molecules at the surface caused by the change in the electrode potential. The occurrence of this peak was a source of some uncertainty in the background subtraction used in data analysis. In addition, KOH solutions seem to be more contaminated than H_2SO_4 solutions which leads to a lower reproducibility and more scatter in the kinetic parameters for alkaline solutions.

Desorption peaks observed in the acidic solution are much sharper than those in the basic solution. For both acidic and basic solutions the desorption peak width changes with the electrode coverage (Fig. 4.16). However, slopes of the curves are different in these two cases. The desorption peak width is strongly influenced by the electroosorption valency and by the interaction parameter. If one assumes that the electroosorption
Fig. 4.16. The desorption peak width as a function of electrode initial coverage. Experimental points were obtained from voltammograms recorded for 1 M KOH (▲) and 1 M H₂SO₄ (○) solutions containing thioglycol at concentration varying from 8×10⁻⁶ to 8×10⁻⁵ mol/L with a Hg/Au ultramicroelectrode (5 μm in radius). Potential sweep rate was 1000 V/s. Solid lines represent data obtained from voltammograms simulated for the following parameters: \( E^0 = -600 \text{ mV} \), \( \gamma = -1.02 \) (curve a) or \( \gamma = -0.94 \) (curve b), \( g = 2436 \text{ J/mol} \) (curve a) or \( g = -3676 \text{ J/mol} \) (curve b) and other parameters are the same as in the experiments.
valency is independent of the electrode coverage, then the relation presented in Fig. 4.16 can only be explained by interactions between the adsorbed molecules. Opposite dependence on the electrode coverage indicates that there are opposite interactions between the adsorbed thioglycol molecules in basic and in acidic solutions. The experimental data in Fig. 4.16 are compared with peak widths obtained from curves simulated for positive and negative interaction parameters. The results suggest that there are attractive interactions between adsorbed thioglycol molecules in the acidic solution and repulsive interactions in the basic solution.

The data analysis presented above is based on the assumption that the electrosorption valency does not depend on potential. The dependence of the electrosorption valency on potential can mainly originate from a change of the double layer capacitance with the electrode coverage at a constant potential [25]. For thioglycol in basic solution the double layer capacitance was practically independent of the electrode coverage, while in the acidic solution the changes in double layer capacitance are clearly visible but also small (Fig. 4.17). It should be added that the analysis of voltammograms recorded at low sweep rates doesn't indicate any clear dependence of the electrosorption valency on potential in either acidic or basic solutions.

All the recorded voltammograms were analysed according to the two methods previously described in section 4.1.2 with the assumption of the Langmuir (no interactions between adsorbed molecules and hence $g = 0$) and Frumkin isotherms. The electrosorption valency calculated according to the Langmuir isotherm from low sweep rate experiments is shown in Fig. 4.18. In 1 M H$_2$SO$_4$ $\gamma$ decreases with initial coverage of the electrode, while in 1 M KOH it increases. This clearly must result from neglect of the interaction parameter. The electrosorption parameter determined from the analysis based on the Frumkin isotherm is -0.94 and -1.02 in acidic and basic solution, respectively. Linear extrapolation of the results obtained with the assumption of the Langmuir isotherm to the zero coverage gives
Fig. 4.17. Double layer capacitance of the static mercury electrode (0.011 cm$^2$) at frequency 0.65 kHz in 1 M $\text{H}_2\text{SO}_4$ solution containing thioglycol at concentration varying from $8 \times 10^{-6}$ to $8 \times 10^{-5}$ mol/L. Initial electrode coverage with thioglycol was: 0.85 (■), 0.73 (○), 0.56 (●), 0.37 (○), 0.18 (□).
Fig. 4.18. Electrosorption valency determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M H₂SO₄ (■) and 1 M KOH (□). Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
very similar values. The electrosorption valency is related to the partial charge transfer coefficient, $\lambda$, via an approximate equation [25] in which terms corresponding to the contributions from dipole moments of solvent and adsorbate molecules and the potential dependence of electrosorption valency were omitted, as they are expected to be negligibly small:

$$\frac{\gamma}{z} \approx g_f - (1 - g_f) \frac{\lambda}{z}$$  \hspace{1cm} (4.47)

where $g_f$ is the geometric factor assumed to be close to 0.16 in aqueous solutions [25]. If $\gamma/z$ is close to 1, $\lambda/z$ must be close to -1 regardless of the value of the geometric factor. This indicates that in both solutions the bond formed between sulphur and mercury has a purely covalent character.

Analysis of data with the assumption of the Frumkin isotherm also allows the determination of the interaction parameter. In case of adsorption from acidic solution it is negative (-3680 J/mol) and from basic solution it is positive (2450 J/mol). These results indicate that attractive interactions occur between the adsorbed thioglycol molecules in acidic solution and repulsive interactions occur in the basic solution.

The standard energy of adsorption determined at the potential of zero charge (-426 mV vs. SSCE) is much more negative in 1M KOH (-46.6 kJ/mol) than in 1M H₂SO₄ solution (2.93 kJ/mol).

The method of fast data analysis presented in the section 4.1.1, based on the analysis of the peak width, was also tested for the determination of thermodynamic parameters of adsorption. In this method the dependence of the desorption peak width and the peak potential is analysed as a function of the electrode coverage. As was stressed above, this method isn't accurate as it doesn't take into account factors that influence the characteristics of the desorption peak such as the ohmic drop and the spherical symmetry of diffusion. The analysis of the experimental data with the aid of this method was performed only for sake of comparison. The results obtained differ slightly from those presented above but they are acceptable as a simple
estimate. The electrosorption valency obtained from the average peak width extrapolated to zero electrode coverage was -1.14 and -1.09 for 1 M KOH and 1M H₂SO₄, respectively. The interaction parameter estimated from the change in the average peak width with initial electrode coverage was 4800 J/mol in 1 M KOH and -2300 J/mol in 1M H₂SO₄. The standard free energy of adsorption at the zero charge potential calculated from eqn. (4.20) was -44.3 kJ/mol and 1.4 kJ/mol for 1 M KOH and 1M H₂SO₄, respectively.

The simple method for the determination of kinetic parameters (the alpha coefficient, the activated complex interaction parameter and the standard adsorption rate constant) based on the analysis of peak width is applicable only to irreversible processes and it cannot be used for the adsorption of thioglycol since at the highest sweep rate of 100000 V/s the electrode process is quasi reversible. Consequently, kinetic parameters were determined only by the convolution method described in the previous section. That method takes into account the rates of both forward and backward processes as well as the resistance polarisation of the solution.

The kinetic parameters determined for the adsorption of thioglycol from 1 M KOH and 1 M H₂SO₄ (with the assumption that \( g^* = 0 \)) are presented in Table 4.2. In the case of adsorption from basic solution the charge transfer coefficient has an average value of 0.47±.03 and does not correlate with the initial coverage (the regression coefficient is 0.14). The standard rate constant decreases with an increase of the electrode coverage. The least squares linear regression of \( \ln k_s \) versus \( \theta \) has a slope of -2.3±.3, intercept of 15.8±.14 and the regression coefficient 0.85. The value of the standard rate constant extrapolated to zero coverage is \( 7.6 \times 10^6 \, \text{s}^{-1} \).

The results in Table 4.2 show that the standard rate constant for the adsorption of thioglycol from acidic solution is independent of the electrode coverage; \( \ln k_s \) versus \( \theta \) relation has a slope of 0.07±.09, and an intercept of 15.13±.05. The value of the standard rate constant extrapolated to zero
Table 4.2. Kinetic parameters obtained for the electrosorption of thioglycol from 1 M KOH and 1 M H$_2$SO$_4$ solution at Hg/Au ultramicroelectrode (5 μm in radius) obtained with the assumption that $g^e = 0$. Sweep rate was 100000 V/s. Concentration of thioglycol varied from $8\times10^{-6}$ mol/L to $8\times10^{-5}$ mol/L and pre-concentration time (at -300 mV for basic, and 150 mV for acidic solution) varied from 0.1 to 6.4 s. Thermodynamic parameters determined according to the Frumkin isotherm from voltammograms recorded at 1000 V/s were: $\Delta G_{s,k,pzc}^\circ = -46.6$ kJ/mol ($E^\circ = -901.2$ mV vs. SCE), $\gamma = -1.02$, $g = 2450$ J/mol for basic, and $\Delta G_{s,k,pzc}^\circ = 2.9$ kJ/mol ($E^\circ = -393$ mV vs. SCE), $\gamma = -0.94$, $g = -3678.9$ J/mol for acidic solution.

<table>
<thead>
<tr>
<th>Initial coverage $\theta$</th>
<th>Standard rate constant, $k_s$ [s$^{-1}$]</th>
<th>Charge transfer coefficient $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KOH</td>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>0.056</td>
<td>0.15</td>
<td>4.99$\times10^6$</td>
</tr>
<tr>
<td>0.12</td>
<td>0.19</td>
<td>5.73$\times10^6$</td>
</tr>
<tr>
<td>0.25</td>
<td>0.24</td>
<td>4.65$\times10^6$</td>
</tr>
<tr>
<td>0.27</td>
<td>0.34</td>
<td>4.02$\times10^6$</td>
</tr>
<tr>
<td>0.34</td>
<td>0.58</td>
<td>3.45$\times10^6$</td>
</tr>
<tr>
<td>0.49</td>
<td>0.72</td>
<td>2.45$\times10^6$</td>
</tr>
<tr>
<td>0.52</td>
<td>0.74</td>
<td>2.93$\times10^6$</td>
</tr>
</tbody>
</table>
coverage is $3.7 \times 10^6$ s$^{-1}$. The charge transfer coefficient determined for this solution increases with the electrode coverage; the $\alpha$ versus $\theta$ relation has a slope of $0.24 \pm 0.02$, an intercept of $0.56 \pm 0.01$ and the regression coefficient is 0.94. All statistical calculations presented above were done for a data set two times larger than the one shown in Table 4.2. The observed change in kinetic parameters with the electrode coverage arises from the fact that the rate of the adsorption process, as defined by eqn. (4.38), is a function of both the potential and the electrode coverage. As was already stated before, the effect of these two parameters is difficult to separate as the electrode coverage is a function of the electrode potential. An attempt to determine the effect of these two parameters on the adsorption/desorption rate constant can be done with a multiple regression method based on equation (4.38) showing the dependence of the rate constant on the electrode coverage and the potential.

Two series of 15 experiments done in 1 M KOH and 1 M H$_2$SO$_4$ were analysed according to eqn. (4.40) (experimental conditions as in Table 4.2). The results of the regression analysis are shown in Figs. 4.19 and 4.20, and the kinetic parameters are listed in Table 4.3. It may be significant that the difference between interaction parameters of the activated complex in the acid and base is exactly the same as the corresponding difference between the interaction parameters of the product in these media, i.e., $g_a' - g_s' = -5936 \pm 120$ and $g_a - g_s = -6130 \pm 80$ J/mol.

The analysis of the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant allows the determination of the symmetry factor, discussed in the previous chapter. In the case of thioglycol adsorption from acidic solution the symmetry factor was determined to be 0.53, while for its adsorption from basic solution it was found to be 0.52. Both values are similar indicating a similar nature of the process in both solutions. Fig. 4.21 shows the dependence of the logarithm of
Fig. 4.19. Desorption rate constant as a function of potential and electrode coverage. Based on 15 voltammograms recorded for desorption of thioglycol from a Hg/Au ultramicroelectrode (5 μm in radius) in 1 M H₂SO₄. Sweep rate was 100000 V/s. Initial electrode coverage with thioglycol varied from 0.1 to 0.7. $\alpha$ and $g^*$ parameters were determined by the multiple linear regression.
Fig. 4.20. Desorption rate constant as a function of potential and electrode coverage. Based on 15 voltammograms recorded for desorption of thioglycol from a Hg/Au ultramicroelectrode (5 μm in radius) in 1 M KOH. Sweep rate was 100000 V/s. Initial electrode coverage with thioglycol varied from 0.1 to 0.7. $\alpha$ and $g^\#$ parameters were determined by the multiple linear regression.
Table 4.3. Kinetic parameters for the electrosorption of thioglycol from 1 M KOH and 1 M H$_2$SO$_4$ solution calculated according to eqn. (4.38). Experimental conditions the same as in Table 4.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard rate constant / s$^{-1}$</th>
<th>Charge transfer coefficient</th>
<th>Activated complex interaction parameter / J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M KOH</td>
<td>(3.77±0.1)×10$^6$</td>
<td>0.71±0.05</td>
<td>5460±80</td>
</tr>
<tr>
<td>1 M H$_2$SO$_4$</td>
<td>(3.47±0.1)×10$^6$</td>
<td>0.65±0.03</td>
<td>-476±33</td>
</tr>
</tbody>
</table>
Fig. 4.21. Dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant for the adsorption of thioglycol from acidic and basic solution at 5 μm in radius hemispherical Hg ultramicroelectrode. Thioglycol concentration varied from $8 \times 10^{-6}$ to $6.4 \times 10^{-5}$ M.
the adsorption rate constant on the logarithm of the equilibrium constant for both systems. The adsorption rate constant has higher values in the case of basic solution, indicating that the process is faster in this case, under otherwise identical conditions. Analysis of these curves allows a comparison of kinetics of adsorption for these two solutions, which would be otherwise difficult, as adsorption process takes place at different potentials in the acidic and basic solution.

Results obtained for the adsorption of thioglycol from the basic solution show larger random errors than those obtained from the acidic solution. This may be explained by experimental difficulties. As was mentioned before, contamination of the electrode and consequent inhibition of the process occurs much faster in 1 M KOH than in 1 M H₂SO₄. Also some systematic errors are possible due to an inadequacy of the theoretical model. As it was stated earlier, a prepeak appears at voltammograms recorded for high initial coverages. This prepeak overlaps with the main peak at low sweep rates but at high sweep rates it is clearly visible. The process associated with this peak seems to be very fast, and it may involve a reorientation of adsorbate molecules on the electrode surface. The present theoretical model cannot properly account for such a change.

4.1.3.1.2 Adsorption of cysteine from acidic solution

The adsorption kinetics of cysteine at mercury electrodes also was examined. Cysteine, like thioglycol, contains an —SH group through which chemical adsorption on a mercury surface is possible. The cysteine system was studied at the same concentrations as thioglycol (8×10⁻⁶ to 6.4×10⁻⁵ M, as at higher concentrations a formation of mercury complexes with cysteine is expected) in 1 M H₂SO₄. The same procedures were involved in data acquisition and analysis, as both systems are characterised by similar properties. As in the case of thioglycol, the thermodynamics of cysteine
adsorption were determined from cyclic voltammograms recorded at 1000 V/s.

As the simplest description of the system was sought, the analysis based on the Langmuir adsorption isotherm was first attempted. As in the case of thioglycol, the analysis of cysteine adsorption from acidic solution showed that thermodynamic parameters depend on the electrode coverage. The electrosorption valency calculated with the aid of the Langmuir isotherm analysis depends on the electrode coverage in a similar way to the thioglycol adsorption from acidic solution (compare Figs. 4.18 and 4.22). This indicates that also in this case there are also attractive interactions between cysteine molecules adsorbed at the electrode surface.

The analysis based on the Frumkin adsorption isotherm gave results confirming the conclusion that cysteine molecules adsorbed at the electrode surface from acidic solution attract each other. The electrosorption valency obtained is close to -1 (-0.91). This indicates the existence of an almost covalent bond between cysteine molecules and the mercury electrode, with electrons being transferred from the adsorbate to the electrode. The formal potential obtained from the analysis is -729.5 mV with respect to the Ag|Ag₂SO₄ | 1 M H₂SO₄ reference electrode. This value is similar to that observed in the case of thioglycol adsorption from acidic solution. The interaction parameter is negative (-3.27 kJ/mol), indicating attractive interactions between the adsorbed molecules, and its value is close to that for thioglycol adsorption from acidic solution (-2.3 kJ/mol). The method of multiple regression used in case of the analysis based on the Frumkin adsorption isotherm is expected to be imperfect, due to the difficulty of separating the effect of different, interdependent parameters on the examined parameter. Nevertheless, the analysis of the dependence of the equilibrium constant, after the subtraction of its dependence on potential, on the electrode coverage (Fig. 4.23) indicates that the determined values describe the system relatively well. The same conclusion may be drawn
Fig. 4.22. Dependence of the electrosorption valency determined with the assumption that the Langmuir adsorption isotherm is obeyed for the adsorption of cysteine from 1 M H₂SO₄ at 5 μm in radius Hg hemispherical ultramicroelectrode. Cysteine concentration varied from 8×10⁻⁶ to 6.4×10⁻⁵ M.
Fig. 4.23. Adsorption equilibrium constant corrected for the effect of potential as a function of the electrode coverage. Experimental conditions as in Fig. 4.22.
when the curve representing the dependence of the equilibrium constant, after the elimination of the effect of the electrode coverage, on potential is considered (Fig. 4.24).

The kinetic parameters determined with the analysis based on the Frumkin isotherm also seem to describe the dependence of the desorption rate constant on potential and electrode coverage relatively well. The standard rate constant obtained from the analysis of data at 100000 V/s, with the use of thermodynamic parameters described above, is $7.6 \times 10^6$ s$^{-1}$. The rate of the process is comparable with the rate of thioglycol adsorption ($3.47 \times 10^6$ s$^{-1}$) from acidic solution. The charge transfer coefficient is 0.74, and the value is slightly higher than that obtained for the thioglycol adsorption in identical conditions (0.65). The interaction parameter of the activated complex is also similar to the value obtained for thioglycol (-476 J/mol) and is equal to -290 J/mol. This means that the interactions between the activated complex and the adsorbed molecules are less attractive than between adsorbed molecules. The analysis of the dependence of the desorption rate constant corrected for the effect of the electrode coverage on potential (Fig. 4.25) indicates that the effect of the interactions between the activated complex and the adsorbed cysteine molecules is well accounted for with the activated complex interaction parameter, $g^*$, as the analysed points form an almost perfect straight line. The dependence of the desorption rate constant, corrected for the effect of potential, on the electrode coverage is also linear. As it is almost independent of potential, this indicates that the interactions between the activated complex and adsorbed molecules are weak. This is also reflected in the value of the activated complex interaction parameter being close to zero.

Fig. 4.26 shows the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant. As both values are functions of the electrode coverage and the potential, the analysis of this dependence may provide some useful information. The slope of this curve,
Fig. 4.24. Adsorption equilibrium constant corrected for the effect of the electrode coverage as a function of potential. Experimental conditions as in Fig. 4.22.
Fig. 4.25. Desorption rate constant corrected for the effect of the electrode coverage as a function of potential. Experimental conditions as in Fig. 4.22.
Fig. 4.26. Comparison of the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant for the adsorption of cysteine and thioglycol from 1 M H₂SO₄ solution at 5 µm in radius hemispherical Hg ultramicroelectrode. The concentrations of adsorbates varied from 8×10⁻⁶ to 6.4×10⁻⁶ M for both solutions.
called the symmetry factor, $\xi$, reflects the effect of interactions between adsorbed molecules and the symmetry of the energy barrier (see eqn. (4.45)). In this case the symmetry factor was determined to be 0.57. The value of this parameter determined for the adsorption of thioglycol at the mercury electrode from 1 M $\text{H}_2\text{SO}_4$ solution was 0.53. As it can be seen from Fig. 4.26, the process is slightly faster in the case of cysteine, which agrees with the conclusions drawn from the analysis of standard adsorption rate constants, as all the thermodynamic parameters are similar in both cases. In the case of a discrepancy between thermodynamic parameters of two systems (as in the case of thioglycol adsorption from acidic and basic solution) a comparison of standard adsorption rate constants wouldn't provide any useful information, as it would be a value obtained at different conditions.

Generally, at the mercury electrode the adsorption of cysteine from acidic solution is similar to the adsorption of thioglycol from acidic solution. The differences in thermodynamic and kinetic parameters are not significant and may result from imperfections in the method of multiple regression. Similar kinds of interactions are expected to exist between the adsorbed thioglycol and cysteine molecules, as the dependence of the parameters determined from the Langmuir isotherm method of data analysis on the electrode coverage is similar. The same sign and similar values of the interaction parameters for these systems calculated by using the Frumkin isotherm confirms this conclusion.

4.1.3.1.3 Determination of kinetics of chemisorption of other systems at mercury electrodes

In the previous sections two different methods for the determination of kinetics of adsorption were presented. In the case of the adsorption of cysteine and thioglycol from aqueous acidic and basic solutions a method based on the Frumkin adsorption isotherm was used. This is a method of choice as it takes into account the effect of both the potential and the
electrode coverage on the examined process. However, as was already stated before, this method presents some risks. Experimental data should be free of the effect of any other parameters than those taken into account, which is often difficult to accomplish. Any deviation of the examined data from ideality would lead to serious errors in the determination of the kinetics of the adsorption process. The adsorption process of thioglycol and cysteine from acidic and basic solutions at mercury electrodes proved to be ideal for such an analysis. However, during the analysis of data for other systems problems associated with the limitations of the method were encountered. It was observed that a whole series of different thermodynamic parameters successfully describes the dependence of the equilibrium constant on potential and the electrode coverage. This makes drawing any conclusions regarding the nature of the process difficult. This fact led to the application of the Langmuir adsorption isotherm to the determination of both thermodynamic and kinetic parameters of the process, with the equilibrium constant used in the determination of kinetic parameters being a function of both potential and the electrode coverage. Several systems were examined this way, with a subsequent analysis of the dependence of the data on the electrode coverage. These results will be presented below.

*L-cysteine ethyl ester*

The adsorption of L-cysteine ethyl ester from 1 M H₂SO₄ at mercury ultramicroelectrodes was examined for ester concentrations 1×10⁻⁵ to 4×10⁻⁵ M. The data obtained were scattered. The Langmuir analysis was performed and the data was later analysed as a function of the electrode coverage. The results are similar as for the adsorption of thioglycol from acidic solution.

The electrosorption valency becomes more negative as the electrode coverage increases indicating the existence of attractive interactions
between adsorbed molecules ($g=0$). Fig. 4.27 presents this dependence. Notice that the electrosorption valency for L-cysteine ethyl ester depends on the electrode coverage in a way that is similar to the adsorption of thioglycol and cysteine from acidic solutions.

The formal potential is almost independent of the electrode coverage (Fig. 4.28) becoming slightly more positive with an increase in the electrode coverage.

The kinetic parameters determined for the adsorption of L-cysteine ethyl ester from acidic solution at mercury electrodes also indicate an electrode coverage dependence. The standard adsorption rate constant decreases with increasing electrode coverage (Fig. 4.29), while the charge transfer coefficient (Fig. 4.30) is almost independent of the electrode coverage.

The results presented above indicate that this system cannot be successfully described with the Langmuir adsorption isotherm. This means that a further analysis of the data is required to determine the real thermodynamic and kinetic parameters of the adsorption process. However, the data is scattered, making such an analysis difficult.

*Mercaptopropionic acid*

Adsorption of mercaptopropionic acid ($8 \times 10^{-6}$ to $6.4 \times 10^{-5}$ M) from 1 M KOH solution at mercury electrodes was examined. The thermodynamics of the process were determined from the 50 V/s cyclic voltammograms, whereas the kinetics were obtained from the 100000 V/s cyclic voltammetric curves. The analysis of equation (4.30) which is used to calculate the adsorbate concentration in the iHp leads to the conclusion that it can be successfully used only if the maximum concentration of the adsorbate at the electrode produced during the desorption process is at least 100 times higher than its
Electrode coverage

Fig. 4.27. Electrosorption valency determined on the basis of the Langmuir isotherm as a function of initial coverage for L-cysteine ethyl ester desorption in 1 M H₂SO₄.
Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
Fig. 4.28. Formal potential determined on the basis of the Langmuir isotherm as a function of initial coverage for L-cysteine ethyl ester desorption in 1 M H₂SO₄. Experimental conditions as in Fig. 4.27.
Fig. 4.29. Standard adsorption rate constant determined on the basis of the Langmuir isotherm as a function of initial coverage for L-cysteine ethyl ester desorption in 1 M H₂SO₄.

Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
Initial electrode coverage

Fig. 4.30. Charge transfer coefficient determined on the basis of the Langmuir isotherm as a function of initial coverage for L-cysteine ethyl ester desorption in 1 M \( \text{H}_2\text{SO}_4 \).

Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Hg/Au ultramicroelectrode (5 \( \mu \text{m} \) in radius).
bulk concentration. This assumption is not fulfilled at the low sweep rates used during the determination of thermodynamic parameters, possibly resulting in some errors. Nevertheless, the analysis of data was carried out and the results are presented below.

Several sets of data characterised by similar initial electrode coverages for low and high potential sweep rate experiments were selected and analysed with the method based on the Langmuir adsorption isotherm. The results obtained are scattered and do not permit drawing any definite conclusions. Any further analysis of the data also seems difficult if not impossible.

The electrosorption valency (Fig. 4.31) becomes slightly more positive as the electrode coverage increases. This is a similar trend to that observed for the adsorption of thioglycol from basic solutions and indicates the existence of repulsive interactions between the molecules on the electrode surface. The values are close to -0.9 indicating a significant charge transfer from the ester molecule to the electrode (almost a covalent bond).

The formal potential becomes more negative as the electrode coverage increases (Fig. 4.32). These two facts indicate that the thermodynamics of the system are not perfectly described with the Langmuir adsorption isotherm. However, as the changes with the electrode coverage are not significant the error resulting from the application of this isotherm is not large.

The charge transfer coefficient (Fig. 4.33) decreases slightly with an increasing electrode coverage. The data are very scattered and do not allow any definite conclusion to be reached regarding the change of this parameter with the electrode coverage. At higher electrode coverages the charge transfer coefficient is close to 0.25. The rate of the process seems to be high (the standard adsorption rate constant ca. $1.5\times10^7 \text{ s}^{-1}$) and almost independent of the electrode coverage (Fig. 4.34). Large random errors make a more advanced analysis of the data impossible.
Fig. 4.31. Electrosorption valency determined on the basis of the Langmuir isotherm as a function of initial coverage for mercaptopropionic acid desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Hg/Au ultramicroelectrode (5 µm in radius).
Fig. 4.32. Standard potential determined on the basis of the Langmuir isotherm as a function of initial coverage for mercaptopropionic acid desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
Fig. 4.33. Charge transfer coefficient determined on the basis of the Langmuir isotherm as a function of initial coverage for mercaptobenetic acid desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
Fig. 4.34. Standard adsorption rate constant determined on the basis of the Langmuir isotherm as a function of initial coverage for mercaptopyruvic acid desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Hg/Au ultramicroelectrode (5 µm in radius).
Thioglycol adsorption from heavy water solutions

The adsorption of thioglycol from 1 M D$_2$SO$_4$ in D$_2$O at mercury ultramicroelectrodes was examined. A method based on the Langmuir adsorption isotherm was employed to analyse data for both D$_2$O and H$_2$O solution. The results obtained will be discussed below.

For the case of the adsorption of thioglycol from H$_2$O and from D$_2$O solutions the electrosorption valency changes with the increasing electrode coverage in the same way. Values range from -0.82 at low coverages to -1.6 at high coverages (Fig. 4.35) for both systems. In both cases the formal potential determined with the method based on the Langmuir adsorption isotherm is independent of the electrode coverage (Fig. 4.36) and is the same for both systems (ca. -745 mV). This indicates that the thermodynamic parameters for both systems are identical and that the substitution of D$_2$O for H$_2$O doesn't change the nature of the process.

The charge transfer coefficient is independent of the electrode coverage and for both systems is equal to 0.6 (Fig. 4.37). The standard adsorption rate constant is higher for the adsorption of thioglycol from aqueous solution, but the change of its value with the electrode coverage is the same in both solvents. As the electrode coverage increases the rate of the process decreases exponentially (Fig. 4.38). This indicates that the kinetics of adsorption of thioglycol from both solvent systems are similar and that there are similar interactions between the activated complex and the adsorbed molecules. The only difference is the slower rate of the process in D$_2$O. As well, a comparison of the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant (see Fig. 4.39) was made for both systems. In both cases the resulting symmetry factor has the same value (0.53) indicating similar adsorption processes in both systems. In the case of thioglycol adsorption from a heavy water solution the process
Fig. 4.35. Comparison of electrosorption valency determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M H₂SO₄/H₂O (□) and in 1 M D₂SO₄/D₂O (♦). Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
Fig. 4.36. Comparison of standard potential determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M H₂SO₄/H₂O (□) and in 1 M D₂SO₄/D₂O (◇). Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
Fig. 4.37. Comparison of the charge transfer coefficient determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M H₂SO₄/H₂O (□) and in 1 M D₂SO₄/D₂O (♦). Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
Fig. 4.38. Comparison of the standard adsorption rate constant determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M H₂SO₄/H₂O (□) and in 1 M D₂SO₄/D₂O (◆). Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Hg/Au ultramicroelectrode (5 μm in radius).
\[ y = 0.5343x + 14.698 \]
\[ R^2 = 0.925 \]

\[ y = 0.5269x + 14.266 \]
\[ R^2 = 0.962 \]

Fig. 4.39. Comparison of the dependence of the logarithm of the standard adsorption rate constant on the logarithm of the equilibrium constant for thioglycol desorption in 1 M H₂SO₄/H₂O and in 1 M D₂SO₄/D₂O. Cyclic voltammograms used in the analysis were recorded at Hg/Au ultramicroelectrode (5 μm in radius). Lines determined with the least square method (equations given on graph).
is slightly slower than in case of the adsorption from aqueous solution, which agrees with the previous observation, based on the comparison of the standard adsorption rate constants.

An attempt to determine the kinetics of the process using data analysis based on the Frumkin adsorption isotherm (as used in the case of adsorption of thioglycol from H₂SO₄/H₂O solution) gave results different from those for the aqueous solution. However, when the same set of thermodynamic parameters obtained for aqueous solution was used, the system was equally well described by these parameters. This proves that use of the multiple regression method fails in this case.

4.1.3.2 Thallium amalgam ultramicroelectrodes

It was already stressed in the theoretical part of the thesis that liquid electrodes (mercury and mercury amalgams) are characterised by a uniform, well defined surface. Such a property is desirable in any initial studies, where unnecessary complications should be avoided. This influenced the choice of other metal electrodes to be used for studies of adsorption kinetics. One of the metals that has high solubility in mercury is thallium. The thallium amalgam has a relatively positive standard potential (-0.3338 V [20]) which allows an investigation of adsorption processes of thiocompounds without any interference from thallium oxidation processes.

Thallium amalgam ultramicroelectrodes were prepared in a manner similar to the mercury ultramicroelectrodes. The first step involved an electrochemical deposition of a mercury hemisphere on a 5 μm radius Au electrode (see experimental part). After the electrode was washed in concentrated H₂SO₄ and rinsed with destilled water it was transferred into a solution containing 1×10⁻² M Tl₂SO₄ and 1×10⁻⁴ M thioglycol in 1 M KOH supporting electrolyte. This solution allowed the deposition of thallium and provided a fresh thallium amalgam surface before each experiment. The electrode was used to obtain high and low potential sweep rate
voltammograms. Following this the concentration of thallium amalgam was determined through thallium stripping. This procedure eliminated the possibility of the loss of thallium deposited from a separate solution due to its oxidation during the process of transferring the electrode to the solution to be studied. The concentration of thallium amalgam was controlled by changing the thallium deposition time. Experiments were performed at thallium amalgam electrodes of concentration ranging from 1.4 to 41.6 %.

Between experiments the electrode was kept at -500 mV with respect to Ag\|Ag_2SO_4 \| 1 \text{M H}_2\text{SO}_4. At this potential no thallium reduction takes place. Before the experiment the potential was changed to -1600 mV and kept at this value for 0.5 to 10 s. At this potential thallium is reduced to thallium amalgam. At the same time thioglycol accumulated at the electrode surface (at the rest potential) is desorbed. This allows a thallium amalgam electrode of a desired concentration and free of thioglycol adsorbed at its surface to be obtained. The subsequent change of potential to the initial value of -1200 mV allows deposition of thioglycol. No oxidation of thallium takes place at this potential. The most positive potential at which no oxidation of thallium was observed in any of the studied amalgams was determined experimentally through an analysis of cyclic voltammograms obtained at thallium amalgam ultramicroelectrodes of different concentrations. The amount of thioglycol adsorbed at the electrode surface was controlled by the time an electrode was kept at the initial potential (0.1 to 1 s). The electrode coverage was determined from the charge corresponding to the desorption peak.

Analysis of data obtained at thallium amalgam electrodes of different concentrations and with different initial electrode coverage with thioglycol allowed for the determination of the dependence of thermodynamic and kinetic properties of the system on these parameters. The thermodynamic and kinetic properties of the examined system were determined following
the method described in the previous chapter from curves obtained for potential sweep rates equal to 1000 V/s and 100000 V/s.

AC voltammetric experiments performed in $10^{-3}\text{ M }\text{Na}_2\text{SO}_4$ solution at different thallium amalgam electrodes (hanging thallium amalgam electrode, 0.015 cm$^2$ area) were used in an attempt to determine the zero charge potential from the minimum in the double layer capacitance. The value obtained from these curves for different thallium amalgam concentrations changed significantly from a pure Hg electrode to the thallium amalgam electrode of the lowest concentration studied in this work. Subsequent changes corresponding to an increase in thallium concentration are very small (Fig. 4.40).

Another method used for the evaluation of the potential of zero charge can be based on the fact that in the case of physical adsorption the energy of adsorption is a quadratic function of potential with a zero value at the potential of zero charge. The two sets of adsorption and desorption peaks are symmetrical with respect to the potential of zero charge. The adsorption process of 1-hexanol from its saturated solution in 0.5 M Na$_2$SO$_4$ at hanging thallium amalgam electrodes was examined (see Fig. 4.41). It was observed that the electroosorption valency determined from a desorption peak at potentials more positive than the potential of zero charge is independent of the thallium amalgam concentration. Analysis of thermodynamic data presented for the adsorption of different aliphatic alcohols by Moncelli et al. [141] indicates that there is a linear dependence of the electroosorption valency on potential. The fact that the electroosorption valency is independent of the amalgam concentration indicates that for all thallium amalgams studied the desorption takes place at potentials for which the difference between the desorption potential and the zero charge
Fig. 4.40. Potential of minimum capacitance determined for different hanging Tl(Hg) drop electrodes (0.0151 cm² in area) in 1×10⁻³ M Na₂SO₄.
Fig. 4.41. CV curves obtained for adsorption of sat. n-hexanol from 0.5 M Na₂SO₄ at different hanging Tl(Hg) drop electrodes (0.0151 cm² in area).
potential is the same. As the hexanol desorption potential changes linearly with the change of the thallium amalgam concentration it indicates that the potential of zero charge corresponding to different thallium amalgam electrodes also depends linearly on the thallium amalgam concentration. It is also the case that the potential of zero charge obtained from the minimum in the capacitance vs. potential curve (Fig. 4.40) depends exponentially on the activity of the thallium amalgam. This discrepancy can be explained only if one considers the possibility that the minimum observed in the double layer capacitance curve is caused by the oxidation of thallium from the thallium amalgam electrode, resulting in the value of the potential corresponding to this minimum being more negative than the actual potential of zero charge. This means that the latter method cannot be used in this case. Similarly, the method based on measurement of the equilibrium potential of the streaming amalgam electrode cannot be used, as the results of this method would also be affected by the thallium oxidation. As a result, it appears that the zero charge potential can only be successfully estimated from the analysis of the dependence of the desorption potential of aliphatic alcohols from thallium amalgam electrodes.

Thus for thallium amalgam electrodes the analysis method used in the case of adsorption of thioglycol at mercury electrode becomes difficult to perform due to an increased number of parameters affecting the results. The method of obtaining thallium amalgam electrodes through direct deposition of thallium from the solution presents many advantages with respect to methods based on the preparation of the electrode outside of the solution. The main advantages include i) a better control of thallium concentration, as there is no loss of thallium during the process of the electrode transfer to the examined solution, ii) the possibility of preparing a new electrode surface before each experiment and iii) verification of the thallium amalgam concentration through thallium oxidation. But even with this method it is almost impossible to obtain a series of experiments for different electrode
coverages of the adsorbing substance for exactly the same thallium amalgam concentration.

Analysis based on an attempt to describe the experimental data with as small a number of parameters as possible was employed in this case. Analysis of results was based on a one-parameter regression of the equilibrium constant and the adsorption rate constant on potential. This corresponds to use of the Langmuir adsorption isotherm, with the exception that the equilibrium constant used in the calculation of the adsorption rate constant is described as a function of both potential and the electrode coverage. This method can be used only if no interactions between the adsorbate molecules and between the adsorbate and the activated complex are observed. As there is no data corresponding to different electrode coverages and identical thallium amalgam concentrations, four series of experiments for similar thallium amalgam concentration within a series (maximum range of 1.3%) and different coverages were selected. It is expected that such a small difference in the concentration of thallium shouldn't significantly affect the dependence of the examined parameters on the electrode coverage. Fig. 4.42 presents the dependence of the electrosorption valency on the initial electrode coverage for four different thallium amalgams. The reported thallium concentrations correspond to an average value for four thallium amalgam electrodes from one series. It can be seen that the electrosorption valency is independent of the electrode coverage. This indicates that the thermodynamic parameters determined from the one-parameter regression have a physical meaning and they adequately describe adsorption of thioglycol at the thallium amalgam electrode. The investigation of the dependence of the charge transfer coefficient and the standard adsorption rate constant on the electrode coverage also indicates that the simple one-parameter regression with respect to potential provides a good description of the kinetics of the process.
Fig. 4.42. Electrosorption valency determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M KOH.
Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Tl(lg) ultramicroelectrode (5 μm in radius). Thallium concentrations given as average values for 4 amalgams; errors reported as standard deviations.
It can be seen (Fig. 4.43) that the charge transfer coefficient is almost independent of the electrode coverage, increasing only very slightly. The standard adsorption rate constant (Fig. 4.44) is also independent of the electrode coverage, with the exception of very low coverages where an increase in the rate constant is observed. This probably results from the difficulty of accurate accounting for the background and an increased noise level at smaller coverages, as the desorption peak in such cases is very small. The average value of the standard adsorption rate constant for all the examined thallium amalgams is $1.8 \times 10^6$ s$^{-1}$. The above results indicate that the adsorption of thioglycol from basic solutions at thallium amalgam electrodes is adequately described by the Langmuir adsorption isotherm.

In the case of the Langmuir adsorption isotherm no interactions take place between the adsorbed substances. The equilibrium constant is described with the same equation as in the case of the Frumkin adsorption isotherm, with the assumption that the interaction parameter, $g$, is equal to zero. A similar situation takes place in the case of the kinetics of the process. The Frumkin isotherm equation can be used, with the interaction parameter of the activated complex, $g^*$, equal to zero. Analysis based on the Langmuir adsorption isotherm is much simpler than that based on the Frumkin isotherm, as the thermodynamic and kinetic properties of the system depend only on one parameter, namely on potential. In this case there is no difficulty with the deconvolution of the dependence of the examined properties on the electrode coverage and on potential, and all the required parameters can be obtained from the analysis of a single curve. This approach is very advantageous in the case of thallium amalgam electrodes, as was already stressed above. Results obtained from the analysis of thirty nine experimental CV curves obtained for different thallium and thioglycol deposition times are presented below.
Fig. 4.43. Charge transfer coefficient determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Tl(Hg) ultramicroelectrode (5 μm in radius). Thallium concentrations given as average values for 4 amalgams. Error values as in Fig. 4.42.
Fig. 4.44. Standard adsorption rate constant determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M KOH.
Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Tl(Hg) ultramicroelectrode (5 μm in radius). Thallium concentrations given as average values for 4 amalgams. Error values as in Fig. 4.42.
The formal potential (Figs. 4.45 and 4.46) is independent of the electrode coverage and decreases exponentially with increasing amalgam concentration, in a similar way to the potential corresponding to a minimum in the double layer capacitance curve, observed in a diluted Na₂SO₄ solution (see discussion above). Again, the largest change in the formal potential is observed between the pure mercury electrode and an electrode containing the smallest studied concentration of thallium.

An increase in the thallium amalgam concentration leads to a more positive electrosorption valency, indicating a reduced transfer of electrons from thioglycol to the electrode as the thallium content of the electrode increases (Fig. 4.47). However, it is difficult to separate the effect of increasing thallium concentration and the effect of an increasingly more negative potential at which the process takes place as the thallium concentration increases. A more negative electrode potential may reduce the transfer of electrons from thioglycol to the electrode, causing the electrosorption valency to become more positive. Another factor that should be taken into account is the smaller electronegativity of thallium compared to mercury. This also would lead to a smaller transfer of electrons from the adsorbate to the electrode.

The charge transfer coefficient obtained for the adsorption of thioglycol at thallium amalgam electrodes increases slightly with increasing thallium amalgam concentration, but the change in its value is very small (Fig. 4.48).

Analysis of the dependence of the standard adsorption rate constant on the thallium amalgam concentration (Fig. 4.49) indicates that even a small content of thallium in mercury significantly reduces the standard rate constant of the adsorption process. The standard potential for which the standard rate constant is determined is much more positive for mercury than for thallium amalgam electrodes. The dependence of rate constants on potential for both kinds of electrodes (Fig. 4.50) allows a more accurate evaluation of the trend in the change of the rate of the process with the
Fig. 4.45. Formal potential determined on the basis of the Langmuir isotherm as a function of thallium amalgam concentration for thioglycol desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Tl(Hg) ultramicroelectrode (5 μm in radius). Thioglycol initial coverage varied from 0.2 to 0.95.
Fig. 4.46: Formal potential determined on the basis of the Langmuir isotherm as a function of initial coverage for thioglycol desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a TI (FG) ultramicroelectrode (5 μm in radius). Thallium concentration varied from 1.4 to 41%. 
Fig. 4.47. Electrosorption valency determined on the basis of the Langmuir isotherm as a function of thallium amalgam concentration for thioglycol desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 1000 V/s with a Tl(Hg) ultramicroelectrode (5 µm in radius). Electrode initial coverage varied from 0.2 to 0.95.
Fig. 4.48. Charge transfer coefficient determined on the basis of the Langmuir isotherm as a function of thallium amalgam concentration for thioglycol desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Tl(Hg) ultramicroelectrode (5 μm in radius). Electrode initial coverage varied from 0.2 to 0.95.
Fig. 4.49. Standard adsorption rate constant determined on the basis of the Langmuir isotherm as a function of thallium amalgam concentration for thioglycol desorption in 1 M KOH.

Cyclic voltammograms used in the analysis were recorded at 100000 V/s with a Tl(Hg) ultramicroelectrode (5 µm in radius). Electrode initial coverage varied from 0.2 to 0.95.
Fig. 4.50. Dependence of the adsorption and desorption rate constant on potential for adsorption of thioglycol from 1 M KOH at Hg and different Tl(Hg) electrodes (5 μm in radius). Thallium amalgam concentration varied from 4.3 to 41.6%.
change of the properties of the electrode. The comparison of adsorption rate constants for electrodes of different thallium amalgam concentration with that for the mercury electrode obtained at the same electrode potential leads to the conclusion that the adsorption process is most rapid for the most concentrated amalgam and is the slowest for a pure mercury electrode. The opposite is true for the desorption process.

To examine the molecularity of the rate of thioglycol adsorption on thallium amalgam electrodes with respect to thallium in the electrode, the difference between the formal thallium concentration and its activity in the amalgam has to be taken into account. The dependence of the activity of thallium on its formal concentration in thallium amalgam electrodes was taken from [142]. According to the data presented there, thallium activity in the thallium amalgam, \( a_T \), may be represented as a function of its mole fraction in the amalgam, \( x_T \), by the following equation:

\[
a_T = -2.125x_T^3 + 2.409x_T^2 + 9.9 \times 10^{-3}x_T + 1.3 \times 10^{-3}
\]

(4.48)

A linear regression of results obtained for ten different thallium amalgam electrodes gave a molecularity for the adsorption with respect to thallium of 1.014 with a coefficient of determination, \( r^2 = 0.99 \). This indicates that one thallium atom interacts with one thioglycol molecule during the process of adsorption. Analysis of the dependence of the adsorption and desorption rate constant on potential (see Fig. 4.50) indicates that both of them change with the changing thallium concentration. This indicates that thallium participates in the formation of the activated complex.

The dependence of both the formal potential and the adsorption and desorption rate constant on thallium amalgam concentration indicates a preferential adsorption of thioglycol at thallium. This preferential interaction of thioglycol with thallium leads to an increased concentration of thallium at the electrode surface compared to its mean concentration in the
electrode. This effect leads to similar properties of thallium amalgam electrodes of different concentrations and causes a significant difference between the properties of a pure mercury electrode and thallium amalgam electrodes. In the case of a mercury electrode, adsorption of thioglycol takes place through its interactions with mercury, while in the case of even very diluted thallium amalgam electrodes the interactions are almost exclusively with thallium (Fig. 4.51).

A comparison of kinetic results obtained for the adsorption of thioglycol from basic solutions at thallium amalgam and mercury electrodes can be carried out if a dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant is considered. Fig. 4.52 presents such a comparison. It can be seen that the rate of the adsorption process is slower in the case of thallium amalgam electrodes. Such a comparison is more reliable than the comparison of the rate of adsorption and desorption processes at the same potential. As in case of thioglycol adsorption at a mercury electrode, the rate of the process depends also on the electrode coverage. The symmetry factor determined for thallium amalgam electrodes (0.63) is higher than in the case of thioglycol adsorption at the mercury electrode (0.52).

4.1.4 Kinetics of physical adsorption

An attempt was made to determine the kinetics of adsorption of different alcohols at mercury ultramicroelectrodes by means of using the above method of analysis of cyclic voltammetric curves. Three systems were examined: 0.2 M n-butanol, 0.18 M n-pentanol and 0.19 M cyclohexanol, all from 1 M H₂SO₄ at a 5 μm radius mercury hemispherical electrode. The electrosorption valency at potentials corresponding to adsorption/desorption peaks (at potentials more positive than \( E_{pc} \)) was calculated from the experimentally determined maximum charge and from the maximum
Fig. 4.51. Diagram illustrating a preferential adsorption of thioglycol at Tl. Note that the thallium concentration in the bulk of the electrode is much smaller than at its surface.
Fig. 4.52. Comparison of the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant for the adsorption of thiolecular from 1 M KOH at Hg and T1(Hg) electrodes (5 μm in radius). Thallium amalgam concentration varied from 4.3 to 41.6%.
surface concentration obtained from literature data (see Table 4.4). In the case of cyclohexanol no literature data was found and the maximum surface concentration was assumed to be the same as for a perpendicularly adsorbed phenol molecule (5.9×10^{-10} \text{ mol/cm}^2 [26]). The calculated values of the electrosorption valency were as follows: 0.20 for n-butanol, 0.17 for n-pentanol and 0.24 for cyclohexanol.

The thermodynamic parameters obtained from these analyses do not seem to be reliable, probably due to the difficulty in uncoupling the effect of potential and the electrode coverage on the equilibrium constant. However, the values obtained were successfully used to predict the equilibrium constant at conditions corresponding to the fast sweep rate cyclic voltammograms (recorded at 100000 V/s). The desorption rate constant was calculated, as in the case of chemisorption, from eqn. (4.28). The kinetic data obtained for these systems were compared with the data corresponding to thioglycol adsorption at mercury electrodes from acidic solution. Fig. 4.53 presents a set of plots showing the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant. It can be seen that the results obtained for alcohols are scattered. In the case of n-pentanol the rate of the process is comparable with the rate of the thioglycol adsorption. The two other systems give slightly higher values. This observation raises a question about possible systematic errors. The physical adsorption is expected to be faster than the chemisorption process, since in this case no charge transfer takes place between the adsorbate and the electrode. Lower than expected values of adsorption rate constants and the fact that the results are scattered indicate that cyclic voltammetry does not allow a precise determination of kinetics of physical adsorption. This is probably caused by the fact that the potential sweep rates used (100000 V/s)
Table 4.4. Thermodynamic parameters of adsorption of selected aliphatic compounds at mercury in 1 M Na₂SO₄

<table>
<thead>
<tr>
<th>Substance</th>
<th>$10^{10}c_{max}$ /molecm$^{-2}$</th>
<th>$\Delta G^0$ a/kJmol$^{-1}$</th>
<th>$g^b$ kJmol$^{-1}$</th>
<th>Regression coefficients of electrosorption valency*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M propan-1-ol</td>
<td>5.41d</td>
<td>-10.7</td>
<td>-3.00</td>
<td>$a_0$ = 0.22 $a_1$ = 0.9353 $a_2$ = 0.5722</td>
</tr>
<tr>
<td>0.5 M propan-2-ol</td>
<td>4.8e (-12.5, -12.1)</td>
<td>-8.94</td>
<td>-2.90</td>
<td>$a_0$ = 0.21 $a_1$ = -0.085 $a_2$ = 0.6472</td>
</tr>
<tr>
<td>0.2 M butan-1-ol</td>
<td>5.1f (-17.6, -15.1)</td>
<td>-12.1</td>
<td>-4.20</td>
<td>$a_0$ = 0.32 $a_1$ = -0.13 $a_2$ = 0.7352</td>
</tr>
<tr>
<td>0.2 M butyric acid</td>
<td>5.1h</td>
<td>-12.2</td>
<td>-3.79</td>
<td>$a_0$ = 0.24 $a_1$ = -0.12 $a_2$ = 0.6294</td>
</tr>
<tr>
<td>0.4 M methyl ethyl ketone</td>
<td>4.9i</td>
<td>-11.8</td>
<td>-3.78</td>
<td>$a_0$ = 0.26 $a_1$ = -0.14 $a_2$ = 0.6093</td>
</tr>
</tbody>
</table>

*The standard free energy of adsorption at the maximum adsorption potential extrapolated to the zero electrode coverage for a standard state defined by eqn. (4.73). Literature values are given in brackets, followed by our results recalculated to the same standard state.

b Interaction parameter determined from AC voltammetric measurements at ultramicroelectrodes; an average value for the positive and the negative adsorption peak. Literature values given in brackets.

c based on eqn.: $\gamma(E) = \eta_0 E^2 + \eta_1 E + \eta_0$; where $E$ is in volts vs. Hg|HgSO₄(s)|1 M K₂SO₄.

d values of mean electrosorption valency at the positive ($\gamma_+$) and negative ($\gamma_-$) adsorption peak are given in brackets

data from [143]

e data from [144]

f data from [145]

g data for sat. Na₂SO₄ from [146]
h assumed the same value as for butan-1-ol [145]
i assumed the same value as for butan-2-ol [28]
Fig. 4.53. Comparison of the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant for the adsorption of thioglycol, n-butanol, n-pentanol and cyclohexanol from 1 M H₂SO₄ at Hg hemispherical ultramicroelectrode (5 μm in radius).
are not high enough to allow a determination of kinetics of physical adsorption. As a result a different method, based on the analysis of AC curves for high potential excitation frequencies, was sought. It will be presented in section 4.2 of the thesis.

4.1.5 Comparison of simulated and experimental curves

The simulation program described in section 4.1.1 was designed to simulate cyclic voltammograms at ultramicroelectrodes in the case of adsorption processes. The program was created to assist and verify in the development of different methods for the determination of the kinetics and thermodynamics of adsorption. This application was previously described in the chapter presenting methods of analysis of experimental curves. There is always a risk that the experimentally observed curve is influenced by factors not taken into account in the analysis procedure. It is difficult to predict a priori all the possible complications encountered in real systems. In such cases application of the data analysis developed for a simplified system may lead to significant errors. A way of eliminating this problem is by simulating the experimental curve using the parameters determined from the analysis and all the experimental parameters (e.g. potential sweep rate, electrode size, etc.) characterising the system. Agreement between the simulated and the experimental curve would indicate that the assumed model describes the examined system well and that the results of analysis are correct. This procedure was used as a means of verifying the analysis of experimental curves obtained for the adsorption of thiocompounds at mercury ultramicroelectrode. It was observed that the simulated cyclic voltammetric curves agree well with the experimental curves. As an example a comparison between the experimental curves and simulated curves for the adsorption of thioglycol from acidic and basic solutions is shown in Fig. 4.54. This agreement indicates that despite problems encountered during the analysis of cyclic voltammograms obtained for the
adsorption of thioglycol from basic solution (a prepeak altering the background) the results obtained describe the system reasonably well.

4.1.6 Discussion of results

The results presented in section 4.1.3.1.1 for the adsorption of thioglycol at mercury ultramicroelectrodes from acidic and basic solutions show that the standard energy of adsorption determined at the potential of zero charge (-426 mV vs. SSCE) is much more negative in 1 M KOH (-46.6 kJ/mol) than in 1M H$_2$SO$_4$ solution (2.93 kJ/mol). This difference arises from the energy needed to remove the proton from the -SH group in acidic solution. Assuming that the pH in 1 M H$_2$SO$_4$ solution is about 0, this energy should be equal to $RT \ln K_a$ (where $K_a$ is the dissociation constant of the thiogroup). By taking $pK_a = 9.4$ [139] one can estimate the expected energy difference as 53.6 kJ/mol, which is in good agreement with the observed value.

Another fact confirming the above conclusion is a decrease of the rate of thioglycol adsorption at mercury electrodes from heavy water, compared to aqueous solutions. The process of thioglycol adsorption from H$_2$SO$_4$/H$_2$O and from D$_2$SO$_4$/D$_2$O solutions is similar (section 4.1.3.1.3), except for the fact that the rate of the process is about 1.5 to 2 times smaller in the case of adsorption from heavy water. This means that in this case a primary isotopic effect is observed. The primary isotopic effect is characterised by the reduction of the rate of the process resulting from a substitution of H in the molecule for D. It is well known [140] that such an effect is caused by a slower rate of breaking R—D than R—H bond. The change in the rate of the process is observed only if the breaking of the bond takes place in the rate limiting step. The above fact indicates that in the case of thioglycol
Fig. 4.54. Comparison of experimental (markers) and simulated (solid lines) voltamograms for the desorption/adsorption process of thioglycol from 1M KOH (curve a) and 1M H₂SO₄ (curve b) on Hg/Au ultramicroelectrode (5 μm in radius) at 100000 V/s. Initial coverage was 0.47 (a) and 0.83 (b). Parameters used in simulations: (a) \( k_s = 3.77 \times 10^6 \text{ s}^{-1} \), \( \alpha = 0.7 \), \( E^o = -901 \text{ mV} \), \( \gamma = -1.02 \), \( g = 2430 \text{ J/mol} \), \( g^# = 5500 \text{ J/mol} \), \( R_s = 1200 \Omega \); (b) \( k_s = 3.47 \times 10^6 \text{ s}^{-1} \), \( \alpha = 0.61 \), \( E^o = -393 \text{ mV} \), \( \gamma = -0.94 \), \( g = 3676 \text{ J/mol} \), \( g^# = -476 \text{ J/mol} \), \( R_s = 900 \Omega \). In both simulations the double layer capacitance was 25 μF/cm² and initial coverages were as for experimental curves.
adsorption from acidic solution at a mercury electrode the rate of the adsorption process is limited by the breaking of the S—H bond prior to thioglycol adsorption. Another factor affecting the rate of the adsorption process may be the rate of the solvent desorption from the electrode surface. As the change from H₂O to D₂O would result in slightly different solvent-solvent interactions inside the double layer, the energy of the solvent adsorption, and hence the rate of its desorption, could be affected. However, the data does not allow one to draw any conclusion about the extent of this effect on the reduction of the observed rate constant.

It was observed that the standard rate constants in acidic and basic solutions are similar, despite the fact that additional energy is needed to remove the proton from the —SH group in acid solution. Comparison of standard rate constants in this case is misleading, because they describe the rate of the process at different potentials. It is more appropriate to compare rates of adsorption and desorption processes extrapolated to the potential of zero charge. For 1 M H₂SO₄ the adsorption and desorption rate constants determined at the potential of zero charge are as follows $k^a = (4.7 \pm 0.1) \times 10^5$ s⁻¹ and $k^d = (9.8 \pm 0.2) \times 10^6$ s⁻¹, and for the basic solution corresponding values are $k^b = (1.7 \pm 0.2) \times 10^{12}$ s⁻¹ and $k^b = (2.1 \pm 0.2) \times 10^4$ s⁻¹. It is interesting that both rates of adsorption and desorption are affected by the pH. This may be explained assuming that the activated state in the acidic solution is protonated. As it was stated earlier, the adsorbed molecules are not protonated, and since thioglycol in 1 M KOH solution is dissociated, it is reasonable to assume that the activated complex in this solution is also without a proton. Hence, one can estimate the acid dissociation constant of the activated complex:

$$K_a^* = \exp\left(\frac{\Delta G_{d,pH=14}^* - \Delta G_{d,pH=0}^*}{RT}\right) = \frac{k^a_{d,pH=14}}{k^a_{d,pH=0}} \approx 2.16 \times 10^{-3}$$ (4.49)
The interaction parameter values obtained for the adsorption of thioglycol from acidic (-3680 J/mol) and basic solution (2450 J/mol) at mercury electrodes indicate a different kind of interaction at the electrode surface in both solutions. The difference should not be attributed to a different activity of H⁺ ions, since the R-OH group does not exhibit acidic nor basic properties in this pH range, and, as it was discussed before, the proton is removed from the -SH group during adsorption. The difference in the interaction parameter may arise from a different desorption potential in both solutions (about +250 mV in the acid and about -300 mV in the base, both versus the zero charge potential). Attractive interactions observed at a positively charged mercury electrode may arise from hydrogen bonding between -OH groups in the adsorbate. It is probable that in basic solution, due to a negative charge on the electrode, the O-H bond becomes oriented with the hydrogen atom pointing towards the metal, making hydrogen bonding between OH groups impossible. Instead, repulsions between non-bonding electron pairs on sulphur and oxygen atoms would lead to a positive interaction parameter.

A slightly different situation is encountered in the case of thioglycol adsorption at thallium amalgam electrodes from basic solutions. In this case the system is described by a Langmuir adsorption isotherm, indicating that the interaction parameter is close to 0. As the interactions between adsorbed thioglycol molecules shouldn't be affected by the electrode material, another explanation has to be sought. It was shown in section 4.1.3.2 that thioglycol adsorption is favoured at thallium compared to mercury. This indicates that in this case the adsorption of thioglycol is accompanied by a simultaneous adsorption of thallium on the metal side of the interface. The latter adsorption process can also be described by one of the isotherms. As the observed response corresponds to a superposition of these two effects, it is
probable that the zero value of the interaction parameter is caused by the fact the interactions on both sides of the interface are opposite (probably repulsive for thioglycol and attractive for thallium) but of similar magnitude.

Kinetic equations used to analyse experimental data presented in this work can formally describe a process in which the oxidation reaction:

\[ \text{Hg}_\text{(l)} + \text{RS}^-\text{(aq)} \rightarrow \text{RSHg}^+\text{(aq)} + 2e^- \quad (4.50) \]

is followed by a strong adsorption of the product on the electrode:

\[ \text{RSHg}^+\text{(aq)} \rightarrow \text{RSHg}^+\text{(ads)} \quad (4.51) \]

However, in such a case the physical meaning of the determined kinetic parameters would be different. A consideration of the adsorption of the product of reaction (4.50) is presented below. In the case of thioglycol one can not expect a strong adsorption with the \(-R\) group pointing toward the electrode and \(-SHg\) towards the solution, simply because \(-R\) (in case of thioglycol it is \(-C_2H_4OH\)) is not hydrophobic enough to justify such an assumption. Indeed, ethanol at concentrations \(10^{-4}\) to \(10^{-5}\) mol/L does not adsorb on mercury electrode from aqueous solutions. Therefore in the adsorbed state the Hg atom of the product must be in direct contact with the electrode. However in such a case, electrons from the electrode would interact with the mercury atom. Since atoms in liquid metals are very mobile, mercury atom from the product would very quickly reach an equilibrium position with respect to other atoms in the electrode and, in consequence, would become a part of the electrode. The above considerations imply that there is no difference between final states attained during adsorption of RSHg\(^+\) and RS\(^-\) on liquid mercury. Some differences may only be expected in the case of a solid mercury electrode, where mobility of atoms is restricted.
It can also be shown that RSHg\(^+\) cannot be an intermediate in the adsorption process. Note that under cyclic voltammetric conditions in KOH solution, for example, the adsorption (oxidation) peak is observed at -800 mV vs. SSCE and the process is quasi reversible at 10000 V/s sweep rate. Oxidation processes under such conditions can not involve a formation of hydrated mercury ion at any stage, because the standard Gibbs energy of such a process would be \(-2F(E - E^{\circ}_{\text{Hg}^{2+/\text{Hg}}}) = 251 \text{ kJ/mol}\), resulting in a very large activation energy and a very slow electrode process. Therefore, reaction (4.50) may only occur via preceding adsorption of \(-\text{RS}\) on the electrode. If adsorption is an intermediate state in the complex formation then the complex formation cannot be an intermediate state in the adsorption process. Under conditions described in here the formation of RSHg\(^+\) is not observed, and as was pointed out above there is no reason for including such a possibility in the mechanistic considerations.

It was shown above that the kinetics of chemisorption can be successfully determined from the analysis of FCV curves. In all adsorption processes of thiocompounds studied the adsorption rate constant was in the range of \(10^6 \text{ s}^{-1}\). The values of kinetic parameters obtained from the analysis of CV curves in the case of physical adsorption were only slightly higher or comparable to those for chemisorption. This is evidently a false result as the rate of a physical adsorption process is expected to be much faster. During physical adsorption no charge transfer between the electrode and the adsorbate takes place. This reduces the energy barrier of the adsorption process and leads to a higher rate of the process. The above discrepancy may result from the application of potential sweep rates that are too small. Higher values are not accessible with the electronic set-up used. Also, the effect of the ohmic drop and the double layer capacitance is more pronounced, and hence difficult to eliminate, at higher potential sweep
rates. The above factors led to the development of a method for determination of kinetics of an adsorption process based on the analysis of high frequency AC experiments.
4.2 *AC methods*

The previous section showed the method for determination of adsorption kinetics based on the analysis of results for very fast CV experiments. It was shown that two experiments (one recorded at a low potential sweep rate and one at a very high potential sweep rate) are needed to determine kinetic parameters of an adsorption process. AC methods are superior to CV methods in this respect as both thermodynamic and kinetic data can be obtained from a single experiment. In AC experiments equilibrium conditions exist at the electrode due to a slow potential sweep while at the same time a small (few millivolts) high frequency potential excitation allows determination of the kinetics of the process at different potentials. This minimises errors introduced by a change of conditions between the two experiments.

In the AC experiments a lock-in amplifier may be used in order to determine an in-phase and out-of-phase component of the circuit current at a corresponding frequency. A determination of the frequency dependence of the analysed signal requires recording of several curves at different frequencies. As an alternative, FFT SWV may be used. In this case one experiment provides the signal corresponding to the whole spectrum of frequencies. It is analysed and separated into its component frequencies through the FFT technique. As FFT SWV is a method developed in our laboratory [145] and tested on several systems, the main principles of this method and the results of tests will be presented below.

4.2.1 *FFT Square Wave Voltammetry - foundations of the method*

The paper on *FFT Square Wave Voltammetry* [145] explains in detail the theory of the technique and the main differences between the technique and classical Square Wave Voltammetry, as well as AC Voltammetry. It also
presents the experimental results used for its testing, provides the evaluation of the usefulness of this technique for the determination of kinetic parameters and explains the influence of different parameters on the precision of the obtained data. It should be stressed that this technique is novel and very promising, due to the simplicity of the equipment used, the short time required to obtain impedance data for different frequencies and the low cost of the equipment compared to AC voltammetry. The theory of the FFT Square Wave Voltammetry is presented below, with some emphasis put on the differences between this technique and other AC techniques.

The excitation wave-form applied to the working electrode is shown in Fig. 4.55. A square-wave modulation of amplitude, $E_{sw}$, and frequency, $f_o$, is repeated $N_c$ times at a constant potential, $E_{dc}$. Then $E_{dc}$ is changed by a small value $\Delta E$ and the whole sequence is repeated again. The current is sampled in equal time intervals $N_s$ times during the square-wave period.

The discrete Fourier transformation is simple if the number of data points acquired per one square-wave cycle is equal to a number represented by $2^n$ (where $n$ is an integer greater than 2). The method was tested for 4, 32 and 64 data points per square-wave cycle. If the number of cycles at one potential step is greater than 1, then the current recorded in different cycles at the same dc potential is averaged (i.e., 1st data points in every cycle are added together and divided by the number of cycles, then 2nd, and subsequent data points are treated in the same way). If one square-wave cycle per potential step is applied, then the time domain response obtained under this technique is identical to that obtained under Osteryoung Square-wave Voltammetry [146]. For a larger number of cycles FFT SWV in time domain resembles to some extent the classical (Barker's) version of square-wave voltammetry [147].

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Fig. 4.55. Potential wave-form used in Fourier Transform Square-wave Voltammetry.
The admittance of the electrode is calculated at each potential step by the discrete Fourier Transformation method. If a time domain function is represented as a sequence of \( F(n) \) values (where \( n \) varies from 0 to \( N-1 \)), then the discrete Fourier transformation of this series produces a complex series [148] given by:

\[
f(k) = \sum_{n=0}^{N-1} F(n) \cos\left(\frac{2\pi nk}{N}\right) + j \sum_{n=0}^{N-1} F(n) \sin\left(\frac{2\pi nk}{N}\right)
\]

where \( k=1,2,...,N/2 \), and \( j = \sqrt{-1} \)

In the simplest case of 4 data points per cycle (FFT SW4) Fourier transformation is straight-forward. If the excitation potential and the electrode response can be represented by periodic functions as in Fig. 4.56 (curve b), the electrode admittance can be calculated as follows. The real components of the alternating current, \( I' \), and the square-wave potential, \( E' \), are given by:

\[
I' = i_2 - i_0
\]

\[
E' = e_2 - e_0 = -2E_{sw}
\]

The imaginary components of the current, \( I'' \), and potential, \( E'' \), are:

\[
I'' = i_1 - i_3
\]

\[
E'' = e_1 - e_3 = 2E_{sw}
\]

Consequently, the real, \( Y' \), and imaginary, \( Y'' \), components of the electrode admittance are given by:

\[
y' + jy'' = \frac{I' + jI''}{E' + jE''} = \frac{I'' - I' - j(I' + I'')}{4E_{sw}}
\]

\[
y' = \frac{i_2 + i_1 - i_2 - i_3}{4E_{sw}}
\]

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Fig. 4.56. Excitation potential (curve a) and electrode response (curves b-d) in FFT square-wave voltammetry; b - non-filtered response; c - curve (b) after passing through a 6th order Butterworth low pass filter with cut-off frequency 2 times greater than the square-wave frequency; d - curve (b) after passing through the same filter with cut-off frequency 8 times greater than the square-wave frequency.
\[ y'' = \frac{i_0 - i_1 - i_2 + i_3}{4E_{sw}} \quad (4.59) \]

As well, the average current at each potential step can be calculated as:

\[ I_{av} = \frac{i_0 + i_1 + i_2 + i_3}{4} \quad (4.60) \]

And the second harmonic response, \( Y_2 \), is given by:

\[ Y_2 = \frac{i_0 - i_1 + i_2 - i_3}{4E_{sw}} \quad (4.61) \]

A non-distorted square-wave function contains a combination of odd harmonics, therefore the electrode response is also composed of various odd and even harmonics. Even harmonics arise from a non-linearity of the system (current passing through the electrode is not directly proportional to the amplitude of the excitation signal). Suppose, that a non-filtered response of the electrode can be represented as a Fourier series:

\[ I(t) = \sum_{n=1}^{\infty} A_n \sin(2n\pi f_o t + \varphi_n) \quad (4.62) \]

where \( f_o \) is the square-wave frequency, \( n \) is the integer number indicating harmonics.

The sampling of current occurs in even time intervals: \( c, c + 1/(4f_o), c + 1/(2f_o) \) and \( c + 3/(4f_o) \). Consequently, values of the sampled current are:

\[ i_o = \sum_{n=1}^{\infty} A_n \sin(2n\pi f_o c + \varphi_n) \quad (4.63) \]
\[ i_1 = \sum_{n=1}^{\infty} A_n \sin(n\pi/2 + 2n\pi f_o c + \varphi_n) \quad (4.64) \]
\[ i_2 = \sum_{n=1}^{\infty} A_n \sin(n\pi + 2n\pi f_o c + \varphi_n) \quad (4.65) \]
\[ i_3 = \sum_{n=1}^{\infty} A_n \sin(3n\pi/2 + 2n\pi f_o c + \varphi_n) \quad (4.66) \]
Because of a phase shift equal to multiples of $\pi$, all even harmonic components of $i_0$ and $i_1$ (as well as $i_2$ and $i_3$) have the same absolute values, but opposite signs. The same is true for odd harmonic components of $i_0$ and $i_2$ (as well as $i_1$ and $i_3$). Therefore, according to eqns. (4.58) and (4.59), values of $Y'$ and $Y''$ are not affected by even-harmonic components, but they contain contribution from all odd harmonic components of the electrode response. Similarly, $Y_2$ (eqn. (4.61)) is affected only by even harmonic components of the electrode response. In order to avoid problems with the interpretation of the electrode admittance, it is necessary to remove all components of the electrode response at frequencies higher than 1/2 of the data acquisition frequency. This condition is known as the Nyquist sampling theorem [148]. The task of removing high frequency components is accomplished by placing an analog low pass filter between the current transducer and the analog-to-digital converter. Of course, such a filter will also distort, to a small extent, the magnitude and the phase of the fundamental and the 2nd harmonic frequency components. However, this distortion can be precisely determined by a calibration procedure and corrected during the data processing. Curve (c) in Fig. 4.56 represents the electrode response filtered by a 6th order Butterworth low-pass filter [149] with the cut-off frequency two times greater than the square-wave frequency. This filtered signal resembles somewhat a sinewave (it contains the fundamental and the 2nd harmonic, but a contribution from higher harmonics is less than 1%). FFT SW4 produces results similar to those obtained using a traditional AC voltammetric set-up with a phase sensitive lock-in amplifier. The cost of the equipment for the first technique is several times lower than for the second one, but the precision of admittance data obtained under FFT SW4 conditions may be lowered, because the
alternating current is measured only at four points per cycle. At lower frequencies the precision of the method can be improved by sampling the current several times and adding values together to obtain one data point. A more substantial improvement, however, can be achieved by increasing the number of points acquired per square-wave cycle. Theoretically, if, for example, 32 current values are measured per cycle (FFT SW32), the admittance of the electrode for 8 odd harmonics (1 to 15) can be calculated, together with 8 even harmonics generated by non-linear response of the electrode. Again, components with frequencies higher than 1/2 of the data acquisition frequency must be removed by an analog filter. In practice, to improve data accuracy, frequencies higher than about 1/4 of the data acquisition frequency are rejected, and only the first 4 odd harmonics are analysed. The filtered signal, appropriate for FFT SW32, is shown in Fig. 4.56 as curve (d).

The influence of different parameters (number of cycles, amplitude, harmonic order) on the accuracy and precision of the determination of kinetic parameters was tested on the reduction of Cd²⁺ from 1 M NH₄NO₃ + 1 M NH₃(aq) solution at SMDE [145]. It was observed that there are some benefits of selecting a large number of cycles. First, the staircase function used to advance the DC potential contains frequency components that overlap with square-wave frequencies; this interference diminishes with an increase in the number of cycles. The second advantage is a noise reduction due to averaging of data points. An obvious disadvantage of the large number of cycles is the increase of time needed to complete the potential scan. Numerical simulations indicate that determination of kinetic parameters should be accurate when the number of square-wave cycles per potential step is greater than 16. Both experimental results and numerical
simulations indicate that amplitude values higher than the height of the
potential step and lower than RT/nF provide accurate results. Larger
amplitudes cause positive systematic errors in the determination of the
standard rate constant and negative systematic error in the determination
of the charge transfer coefficient.

The FFT SW voltammetric method presented above was modified to
allow measurements at frequencies up to 10 MHz. The electronic set-up had
to be readjusted to make data acquisition at such frequencies possible. The
obvious advantage of this method is that a whole set of impedance curves for
different frequencies is obtained from a single experiment. This ensures that
there is no discrepancy between curves corresponding to different
frequencies that might arise from a change of conditions between
experiments (e.g. the change in the electrode area or a shift in the potential
of the reference electrode). However, it was observed that FFT SW
voltammetric curves recorded at high fundamental frequencies are noisy,
probably due to difficulty in designing the electronic set-up. As a
consequence only a few odd harmonics could be analysed (4 to 6), limiting
the possibility of the investigation of frequency dependence of the analysed
signal. Further work on the development of FFT SWV at high frequencies is
still required in order to improve the signal to noise ratio during the data
acquisition.

As the analysis of both AC and FFT SW voltammetric curves is
identical, the method of data analysis and the results of determination of
kinetics of adsorption will be presented for both methods.
4.2.2 Method of data analysis of AC curves

The method of the analysis of AC curves was developed based on the analysis of equations describing the dependence of the total admittance of the examined cell on different parameters. These equations are derived below (eqns. (4.80) to (4.93)) and their analysis leads to the conclusion that in the case of an adsorption process the cell can be represented by the equivalent circuit shown in Fig. 4.57. The determination of the kinetic parameters of an adsorption process is possible if the activation resistance can be estimated. The AC experiment allows the determination of the real and the imaginary part of the total impedance as a function of potential. In addition, if curves are recorded for several different frequencies, these values are also known as functions of frequency. The total impedance, \( Z_t \), composed of all components presented in Fig. 4.57, may be successfully used in the determination of the activation resistance, \( R_a \), and hence the kinetics of the adsorption process, only if other components present in the equivalent circuit can be eliminated.

The elements shown in Fig. 4.57 with dotted lines are negligible. The stray capacitance, \( C_s \), was practically eliminated by a special construction of the working electrode and a specially designed calibration procedure. Details of both are given in the experimental part of the thesis. The effect of the non-linear diffusion impedance, \( Z_N \), is practically negligible at the frequencies used. From eqns. (4.92) and (4.93), shown below, it can be seen that for ultramicroelectrodes used in this work this parameter is at least 100 times larger than the Warburg impedance, \( Z_W \), if the frequency exceeds 30 kHz. All the AC experiments in this work were performed at frequencies significantly higher than this value.

In Fig. 4.57 \( R_s \) represents the solution resistance. Its value depends on the electrode size and the conductivity of the electrolyte. Under experimental conditions in this work (i.e. concentrated electrolyte solutions and frequencies lower than 10 MHz) the solution resistance is expected to be
Fig. 4.57. Diagram representing the components of the total cell impedance. Dotted lines correspond to elements that are negligible. Symbols used: $R_s$, solution resistance; $C_s$, stray capacitance; $C_{dl}$, double layer capacitance; $R_{dl}$, resistive element resulting from a finite dielectric relaxation in the double layer; $Z_c$, pseudocapacitive impedance; $R_a$, activation resistance; $Z_w$, Warburg impedance; and, $Z_N$, impedance resulting from a non-linear mass transport.
independent of frequency. However, it should be noted that at higher frequencies this assumption may be invalid due to the Debye-Falkenhagen effect. The real impedance of the electrode, as presented in Fig. 4.58, shows a significant frequency dispersion. This can be explained by the presence of a resistive element \( R_d \) resulting from a finite dielectric relaxation in the double layer [150, 151]. The double layer capacitance is represented in this diagram as \( C_{dl} \); the value of this element depends slightly on frequency. The remaining elements in Fig. 4.57 (\( Z_c, R_s \) and \( R_w \)) constitute the adsorption process impedance, \( Z_A \). The stray capacitance, \( C_s \), is taken into account through a specially designed calibration procedure and a specially modified electrode, described in the experimental part of the thesis.

The elimination of the effect of the solution resistance, \( R_s \), and the double layer capacitance, \( C_{dl} \), on the recorded AC curves is much easier than in the case of cyclic voltammograms. In the case of AC curves a simple subtraction of the solution resistance value, determined from high frequency experiments, from the total impedance leads to the elimination of the ohmic drop. As the double layer capacitance changes with potential its elimination is more complex than the elimination of the solution resistance, but it is still straightforward.

In the first step of data processing \( R_s \) was subtracted from the total cell impedance:

\[
Z_l = Z_t - R_s
\]  \hspace{1cm} (4.67)

The impedance obtained after this subtraction is composed of 3 major elements connected in parallel: the double layer capacitance, the dielectric relaxation resistance and the adsorption impedance. In order to calculate the adsorption impedance \( Z_l \) should be converted into an admittance:

\[
Y_l = 1/Z_l
\]  \hspace{1cm} (4.68)
Fig. 4.58. Dependence of the real impedance on potential for 1M Na$_2$SO$_4$ containing 0.4 M methyl ethyl ketone obtained at Hg hemispherical electrode, 5 µm in radius at 23°C. Frequencies used in measurements: 0.22 (top curve), 0.39, 0.78, 1.56, 3.13, 6.25 MHz (bottom curve).
This allows a subtraction of the admittances associated with $C_{dl}$ and $R_{dl}$
elements. The subtraction is possible because the potential dependence of
$C_{dl}$ and $R_{dl}$ is small compared to the potential dependence of the adsorption
admittance (see Fig. 4.59). At potentials far from the peak the admittance is
determined only by $C_{dl}$ and $R_{dl}$. To take advantage of this behaviour, the
curves before and after the peak were fitted to a 5th or 6th order polynomial
expression by the least-squares method. The regression coefficients obtained
were used to estimate the admittance due to the double layer capacitance
and dielectric relaxation resistance in the potential region where the
adsorption/desorption process takes place, and consequently, these
estimated values were subtracted from $Y_i$. The procedure is graphically
illustrated in Fig. 4.59. Two separate operations were performed on the real
and the imaginary components of $Y_i$ and, as a result, the real, $Y_{A, re}$, and
imaginary, $Y_{A, im}$, components of the adsorption admittance were obtained.
Subsequently the admittance was converted into the impedance:

$$Z_{A, re} = \frac{Y_{A, re}}{y^2 + Y_{A, im}^2}, \quad Z_{A, im} = -\frac{Y_{A, im}}{y^2 + Y_{A, re}^2} \quad (4.69)$$

with

$$Z_A = Z_{A, re} + jZ_{A, im} = R_a + Z_e + Z_w \quad (4.70)$$

where $j = \sqrt{-1}$.

The description of the adsorption process can be simplified by
introducing surface coverages: $\theta$ and $\theta_0$, a normalised current, $\tilde{i}$, and a
normalised potential, $\tilde{E}$:

$$\theta_0 = \frac{c_s}{c_{max}}, \quad \tilde{i} = \frac{i_s}{FAc_{max}}, \quad \tilde{E} = \frac{EF}{RT} \quad (4.71)$$

Now eqn. (4.22) can be written as:

$$\tilde{i} = -\gamma [k_\alpha \theta_0 (1 - \theta) - k_f \theta] \quad (4.72)$$

If the adsorption current approaches zero, the system approaches
equilibrium and then:

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Fig. 4.59. Subtraction of the admittance corresponding to $C_d$ and $R_d$ from the real and imaginary parts of the total cell admittance corrected for solution resistance.

Dashed line represents an estimation of the background admittance by a 6th order polynomial curve fitting. Experimental points (markers) obtained for 0.5 M propan-2-ol in 1 M Na$_2$SO$_4$ with 5 µm Hg hemispherical electrode at 6.25 MHz frequency.
\[ K_{ads}(\tilde{E}, \theta) = \frac{k_a}{k_d} = \frac{\theta}{\theta_0^e (1 - \theta^e)} \exp \left[ -\frac{\Delta G_{ads}^o(\tilde{E}, \theta)}{RT} \right] \] (4.73)

where \( K_{ads} \) is the apparent equilibrium constant of the process. This constant is a function of electrode potential and it usually retains some dependence on the surface coverage, \( \theta \), arising from the non-ideal behaviour of an adsorbate at the electrode surface. It should be noted that because the surface coverage in the outer Helmholtz layer is usually very small, \( K_{ads} \) is expected to be independent of \( \theta \).

Now eqn. (4.72) can be formulated as:

\[ \tilde{i} = -\gamma k_d \theta \left( \frac{K_{ads}}{Q_{ads}} - 1 \right) \] (4.74)

where \( Q_{ads} = \frac{\theta}{\theta_0^e (1 - \theta)} \) represents the reaction quotient. The term in brackets describes the departure of the system from an equilibrium.

The rate of the adsorption process can be written as:

\[ k_a(\tilde{E}, \theta) = Z \exp \left[ -\frac{\Delta G_{ads}^o(\tilde{E}, \theta)}{RT} \right] \] (4.75)

where \( Z \) is the frequency factor and \( \Delta G_{ads}^o(\tilde{E}, \theta) \) is the activation energy of the process.

Four important partial derivatives can be defined:

the electroosorption valency, \( \gamma \):

\[ \gamma = \frac{1}{RT} \left( \frac{\partial \Delta G_{ads}^o(\tilde{E}, \theta)}{\partial \tilde{E}} \right)_\theta = \frac{1}{K_{ads}} \left( \frac{\partial K_{ads}}{\partial \tilde{E}} \right)_\theta \] (4.76)

the normalised lateral interaction parameter, \( \bar{g} \):

\[ \bar{g} = \frac{2g}{RT} = \frac{1}{RT} \left( \frac{\partial \Delta G_{ads}^o(\tilde{E}, \theta)}{\partial \theta} \right)_{\tilde{E}} = \frac{1}{K_{ads}} \left( \frac{\partial K_{ads}}{\partial \theta} \right)_{\tilde{E}} \] (4.77)

the constant coverage symmetry factor, \( \alpha \):
\[
\alpha = \left( \frac{\partial \Delta G_{\text{ads}}^e (\tilde{E}, \theta)}{\partial \Delta G_{\text{ads}}^0 (\tilde{E}, \theta)} \right) = \frac{K_{\text{ads}}}{k_a} \frac{\partial k_a}{\partial K_{\text{ads}}} \tag{4.78}
\]

and the constant potential symmetry factor, \(\chi\):

\[
\chi = \left( \frac{\partial \Delta G_{\text{ads}}^e (\tilde{E}, \theta)}{\partial \Delta G_{\text{ads}}^0 (\tilde{E}, \theta)} \right) = \frac{K_{\text{ads}}}{k_a} \frac{\partial k_a}{\partial K_{\text{ads}}} \tag{4.79}
\]

\(\gamma\) defined by eqn. (4.76) is identical with the one defined by eqn. (2.7).

In general, parameters \(\gamma, \tilde{\theta}, \alpha\) and \(\chi\) are expected to vary only slightly with potential and the electrode coverage; as a consequence, they can be treated as constants in a narrow range of potentials and coverages.

*Description of the electrode impedance.* The electrode impedance due to an adsorption process can be derived by using a standard mathematical procedure [152]. According to eqn. (4.72) the adsorption current is a function of three variables: \(\theta\), \(\theta_\alpha\) and \(\tilde{E}\).

A change in \(\tilde{i}\) caused by small periodic changes of these variables can be easily calculated:

\[
\Delta \tilde{i} = \left( \frac{\partial \tilde{i}}{\partial \tilde{E}} \right)_{\theta, \theta_\alpha} \Delta \tilde{E} + \left( \frac{\partial \tilde{i}}{\partial \theta} \right)_{\theta_\alpha, \tilde{E}} \Delta \theta + \left( \frac{\partial \tilde{i}}{\partial \theta_\alpha} \right)_{\tilde{E}, \theta} \Delta \theta_\alpha \tag{4.80}
\]

\(\Delta \tilde{i}\), \(\Delta \theta\), \(\Delta \theta_\alpha\) and \(\Delta \tilde{E}\) are functions of time and they are interrelated. A change in \(\theta\) occurring in a certain time interval, \(\tau\), can be obtained by an integration of changes in current, in a manner similar to the case for CV curves:

\[
\Delta \theta = -\frac{1}{\gamma} \int_0^\tau \Delta \tilde{i} \, dt \tag{4.81}
\]

A change in \(\theta_\alpha\) is related to a change in adsorbate concentration near the electrode surface. The latter quantity can be obtained from the convolution of current with an appropriate mass transport function (see eqn. (4.30)).

By applying Laplace transformation eqns. (4.80), (4.81) and (4.30) can be converted from the time domain into the frequency domain.
\[ \Delta \tilde{E}(s) = \begin{bmatrix} \frac{\partial \tilde{\theta}}{\partial \Delta E} \\ \frac{\partial \tilde{\theta}}{\partial \theta} \end{bmatrix} + \begin{bmatrix} \frac{\partial \tilde{\theta}}{\partial \Delta \tilde{\theta}} \\ \frac{\partial \tilde{\theta}}{\partial \theta} \end{bmatrix} \Delta \theta(s) + \begin{bmatrix} \frac{\partial \tilde{\theta}}{\partial \Delta \tilde{\theta}} \\ \frac{\partial \tilde{\theta}}{\partial \theta} \end{bmatrix} \Delta \theta_\circ(s) \] (4.82)

\[ \Delta \theta(s) = -\frac{\Delta \tilde{\theta}(s)}{s \gamma} \] (4.83)

\[ \Delta \theta_\circ(s) = \frac{\rho_{\text{sol}} \Delta \tilde{\theta}(s)}{\gamma(\sqrt{D_s + D / r})} \] (4.84)

The normalised adsorption process impedance is given by

\[ \tilde{Z}_A = \frac{\Delta \tilde{E}(s)}{\Delta \tilde{\theta}(s)} \]

and it can be calculated from eqns. (4.82) to (4.84):

\[ \tilde{Z}_A = \left[ 1 + \frac{1}{\gamma s} \left( \frac{\partial \tilde{\theta}}{\partial \theta} \right)_{\theta, \tilde{E}} - \frac{\rho_{\text{sol}}}{\gamma(\sqrt{D_s + D / r})} \left( \frac{\partial \tilde{\theta}}{\partial \theta} \right)_{\tilde{E}, \theta} \right] \times \left( \frac{\partial \tilde{\theta}}{\partial \theta} \right)_{\tilde{E}, \theta} \] (4.85)

From eqns. (4.74), (4.76) and (4.77) we can obtain:

\[ \left( \frac{\partial \tilde{\theta}}{\partial \tilde{E}} \right)_{\theta, \tilde{E}} = \gamma \theta k_d \frac{K_{\text{ad}}}{{Q_{\text{ad}}} - \theta \left( \frac{K_{\text{ad}}}{{Q_{\text{ad}}} - 1} \right)} \times \left[ \gamma \left( \frac{\partial k_d}{\partial \tilde{E}} \right)_{\theta} + k_d \left( \frac{\partial \gamma}{\partial \tilde{E}} \right)_{\theta} \right] \] (4.86)

\[ \left( \frac{\partial \tilde{\theta}}{\partial \theta} \right)_{\theta, \tilde{E}} = \gamma k_d \frac{K_{\text{ad}}}{Q_{\text{ad}}} \frac{1 + \alpha \theta (1 - \theta)}{(1 - \theta)} - \left( \frac{K_{\text{ad}}}{{Q_{\text{ad}}} - 1} \right) \times \] \[ \left[ \gamma \left( \frac{\partial k_d}{\partial \theta} \right)_{\tilde{E}} + k_d \theta \left( \frac{\partial \gamma}{\partial \theta} \right)_{\tilde{E}} + \gamma k_d \right] \] (4.87)

\[ \left( \frac{\partial \tilde{\theta}}{\partial \theta} \right)_{\theta, \tilde{E}} = -\gamma k_d \theta \frac{K_{\text{ad}}}{Q_{\text{ad}}} \] (4.88)

Since the perturbation applied to the system is very small, the system is always near equilibrium and \( Q_{\text{ad}} \approx K_{\text{ad}} \); by taking this into account eqns. (4.86) to (4.88) can be greatly simplified and an explicit description of the normalised adsorption impedance can be obtained:

\[ \tilde{Z}_A = \frac{1}{\gamma^2 \theta k_d} \left[ 1 + \frac{1 + \theta (1 - \theta)}{\gamma^2 \theta (1 - \theta)} + \frac{\rho_{\text{sol}}}{\gamma^2 \theta_\circ(\sqrt{D_s + D / r})} \right] \] (4.89)

Since we are only interested in sustained periodic changes we can set the real part of the complex variable \( s \) to 0. As a result, \( s = j \omega \) (where \( \omega \) is
the angular frequency and \( j = \sqrt{-1} \). We can also convert the normalised adsorption impedance into experimentally measured quantities by using eqns. (4.1) and (4.71):

\[
Z_A = \frac{RT}{\gamma^2 F^2 A \theta k_d} - j \left[ 1 + \frac{\bar{E} \theta (1 - \theta)}{\gamma^2 F^2 A \omega \theta (1 - \theta)} \right] \frac{RT}{\gamma^2 F^2 A (\sqrt{j \omega D} + D/r)}
\]

(4.90)

The 1st term in this equation represents the activation resistance, \( R_a \), the 2nd term describes the reactance associated with the adsorption pseudocapacitance, \( Z_c \), and the 3rd term describes the mass transport impedance, \( Z_m \).

\( Z_m \) can be conveniently represented as the Warburg impedance, \( Z_w \), connected in parallel with a resistive element, \( Z_N \), which describes the contribution to mass transport from a non-linear diffusion.

\[
Z_m = \left( \frac{1}{Z_w} + \frac{1}{Z_N} \right)^{-1}
\]

(4.91)

where:

\[
Z_w = \frac{RT(1-j)}{\gamma^2 F^2 A \sqrt{2D \omega}}
\]

(4.92)

and

\[
Z_N = \frac{rRT}{\gamma^2 F^2 A D}
\]

(4.93)

It was shown previously that the non-linear mass transport impedance, \( Z_N \), is negligible at the frequencies used in this work. This simplifies the expression for the mass transport impedance and, as a consequence, for the adsorption process impedance.

4.2.2.1 Analysis of curves obtained for multiple frequencies

The adsorption process impedance, \( Z_A \), is composed of a real and an imaginary part as shown in eqn. (4.70). If we consider the dependence of the
components of the process impedance on frequency and their other properties, then a method for the determination of the activation resistance, and hence the kinetics of the adsorption process, may be obtained. The components of the adsorption impedance can be represented by the following equations:

\[
R_a = \frac{RT}{k_a(E, \theta)A(\gamma F)^2c_s(1-\theta)} \tag{4.94}
\]

\[
Z_c = \frac{RT + 2g(1-\theta)}{\theta(1-\theta)c_mA\omega(\gamma F)^2}j \tag{4.95}
\]

\[
Z_w = \frac{\sqrt{2}}{2} \frac{\rho_mRT}{c_sA(\gamma F)^2\sqrt{D\omega}}(1-j) \tag{4.96}
\]

Note that both the real and imaginary parts of the Warburg impedance are equal in value, but opposite in sign, that the pseudocapacitive term is purely imaginary and depends on frequency and that the activation resistance is independent of frequency and is purely real. When these facts are taken into account it leads to the conclusion that, if the values of the real and the imaginary adsorption impedance are added, then the resulting value is free of the effect of the Warburg impedance, as shown below:

\[
Z_{A, real} + Z_{A, im} = |Z_c| + |R_a| = \beta \frac{1}{\omega} + R_a = \beta \tau + R_a \tag{4.97}
\]

where \(\beta\) represents the slope of the dependence of the sum of the real and imaginary part of the process impedance on time parameter, \(\tau\), (equal to the reciprocal frequency). If several AC curves are available for different frequencies, then the determination of the activation resistance from the intercept of this dependence is possible. Fig. 4.60 shows a 3D plot of \(Z_{A, real} + Z_{A, im}\) versus the time parameter and the potential; the plot was obtained from the experimental data recorded in 0.4 M methyl ethyl ketone solution in 1 M Na2SO4 supporting electrolyte. \(R_a\) and \(\beta\) were obtained by a least-squares linear regression of \(Z_{A, real} + Z_{A, im}\) versus the time parameter.
Fig. 4.60. Sum of real and imaginary components of the adsorption impedance plotted as a function of potential and time parameter. Based on data presented in Fig. 4.68 and 4.67.
The dependence of these parameters on potential is given in Fig. 4.61. \( R_s \) contains information about the kinetics and \( \beta \) about the thermodynamics of the process.

The adsorption rate constant can be determined from the activation resistance for different potential values:

\[
\ln k_r(E, \theta) = \ln \left( \frac{1}{R_s} \right) + \ln \left( \frac{RT}{A(YF)^2 c_s(1-\theta)} \right) = \ln k_r - \frac{\alpha Y F}{RT} (E - E^*) - \frac{2g^* \theta}{RT} \tag{4.98}
\]

This equation indicates that the adsorption rate constant can be determined from the activation resistance if the values of the concentrations in the \( iH_p \) and the \( oH_p \) are known.

The electrode coverage can be calculated from the slope, \( \beta \), after taking into account the following dependencies. Since the normalised \( \beta \) parameter can be calculated as a function of potential

\[
\bar{\beta}(E) = -\frac{\left[ \frac{Y}{(E^*)} F \right]^2 A_{c_{\text{max}}}^c \beta}{RT} \tag{4.99}
\]

then according to eqn. (4.95):

\[
\bar{\beta}(E) = \frac{1}{\theta(E)(1 - \theta(E))} + \frac{2g}{RT} \tag{4.100}
\]

If the change of \( g \) with potential is negligible then this function reaches a minimum, \( \bar{\beta}_{\text{min}} \), at \( E = E_u \), where \( \theta(E_u) = 0.5 \); therefore the electrode coverage can be calculated as:

\[
\theta(E) = 0.5 \pm 0.5 \sqrt{\frac{\bar{\beta} - \bar{\beta}_{\text{min}}}{\bar{\beta} - \bar{\beta}_{\text{min}} + 4}} \tag{4.101}
\]

The second term in this equation describes a difference in coverage due to the change of potential from \( E_u \) to \( E \). The nature of the process requires that \( \theta(E) \) decreases monotonically when the potential moves away from the potential of zero charge \( (E_{pz}) \). Therefore, the second term in eqn. (4.101) must have a positive sign when \( E < E_{pz} \) and \( E > E_u \) or when \( E > E_{pz} \) and \( E < E_u \); a negative sign must be used when \( E < E_{pz} \) and \( E < E_u \) or when \( E > E_{pz} \).
Fig. 4.61. Dependence of the activation resistance and the slope, $\beta$ of the sum of the real and imaginary components of the adsorption impedance vs. $\tau$ on potential. Values determined for a frequency range of 0.22 to 6.25 MHz. Conditions as in Fig. 4.58.
and $E > E_\nu$. Values of $c_{max}$ used in these calculations were taken from the literature and they are listed in Table 4.4.

This method for determination of the electrode coverage requires a knowledge of the electrosorption valency at the potentials where the adsorption process is examined. As the literature data in this area is scarce, a method for the evaluation of the electrosorption valency was developed.

The electrosorption valency was calculated from the differential capacity data obtained at relatively low frequencies (750 Hz) to ensure that the results are not affected by the activation resistance and the Warburg impedance. AC measurements at such low frequencies are difficult to carry out at ultramicroelectrodes because of inherently low currents and a strong edge effect, likely caused by an imperfect sealing of the electrode [153, 154]. To avoid potential problems these measurements were performed at a static mercury drop electrode (SMDE) 0.0106 cm$^2$ in surface area. A change in the charge density at the electrode, $\Delta \sigma_{ads}$, caused by the adsorption process can be calculated in the following way:

$$\Delta \sigma_{ads} = \int_{E_0}^{E} [C_{q^\infty}(E) - C_{q}(E)] dE$$

(4.102)

where $C_{q^\infty}(E)$ is the differential capacitance of the electrode in equilibrium with a solution containing adsorbate and $C_{q}(E)$ is the capacitance of the electrode in the same supporting electrolyte in the absence of adsorbate.

The integration must start at potential, $E_0$, where no change in the charge density takes place. This can be any potential at which adsorption is thermodynamically impossible or the zero charge potential. The electrosorption valency is given as the ratio of the number of electrons leaving the interface to the number of adsorbate molecules entering the interface; consequently in the potential region where $\theta^q$ approaches 1 this parameter can be calculated as follows:
\[
\gamma = \frac{\Delta \sigma_{ad}}{F c_{max}}
\] (4.103)

Since the change in an electrical charge is also equal to the derivative of the free energy of the interface with respect to potential, this calculation is in agreement with the definition of this parameter provided by eqn. (2.7). To ensure a small effect of mass transport (expressed through the Warburg impedance) on the data obtained, a large concentration of an adsorbate was used in all experiments. This, together with a high concentration of supporting electrolyte used to ensure a highly conducting media, allows the assumption that the concentration of the adsorbate in the oHp is equal to its bulk value. As the concentration needed in the analysis should be expressed in mol/cm², the bulk concentration is multiplied by a water (solvent) diameter. This comes from the assumption that the thickness of the oHp corresponds to the thickness of a solvent layer (eqn. (4.1)).

As the activation resistance and concentrations of the adsorbate in the iHp and the oHp are known for different potentials, the adsorption rate constant can be determined as a function of potential (see eqn. (4.98)).

In the analysis of all AC curves the adsorption rate constant as well as the equilibrium constant were considered to be functions of both the potential and the electrode coverage, as the separation of the effect of these two parameters is difficult to accomplish.

The standard free energy of adsorption, \( \Delta G_{ad}^\circ = -RT \ln K_{ad} \), can be represented as a sum of the electrical, \( \Delta G_{el}^\circ \), and non-electrical, \( \Delta G_{mol}^\circ \), components.

The electrical component of the standard free energy can be obtained by the integration of the electrosorption valency from the potential of maximum adsorption, \( E_m \) (i.e. the potential at which the electrosorption valency is equal to zero):
\[ \Delta G_{el}^0(E) = \int_{E_m}^{E} \gamma(E)dE \]  

Consequently, the non-electrical component is given by:

\[ \Delta G_{net}^0(\theta) = -RT \ln[K_{ad}(E,\theta)] - \Delta G_{el}^0(E) \]  

The dependence of \( \Delta G_{net}^0 \) on \( \theta \) can be approximated by a linear function:

\[ \Delta G_{net}^0 = \Delta G_m^0 + 2g\theta \]  

where \( \Delta G_m^0 \) is the standard free energy of adsorption at the potential of maximum adsorption for \( \theta \to 0 \). Parameters \( \Delta G_m^0 \) and \( g \) can be obtained by a least squares regression of \( \Delta G_{net}^0 \) versus \( \theta \).

### 4.2.2.2 Analysis of curves obtained for a single frequency

If necessary, the kinetic parameters of the adsorption process can be obtained from the analysis of results obtained at only one frequency. In such a case a different approach has to be taken.

As before, the Warburg impedance has to be eliminated. It was observed that the maximum value of the imaginary part of the adsorption impedance contains \( Z_\infty \) for \( \theta = 0.5 \) and \( Z_m \). If this maximum value is subtracted from the values of the imaginary part of the adsorption impedance at different potentials then the resulting impedance is free of the Warburg impedance and can be used to calculate the electrode coverage.

The interaction parameter may be obtained as before from the maximum value of the imaginary adsorption impedance after the value of the Warburg impedance is subtracted. The latter is calculated from eqn. (4.92). As the concentration of the adsorbate is high, the value of the Warburg impedance is small and a small error in its determination is insignificant.

Further analysis is performed in a way similar to that described for the analysis of curves obtained for several frequencies.
4.2.3 AC experiments at high frequencies

Studies of the double layer at ultramicroelectrodes in aqueous solutions are very challenging. The small dimensions of the ultramicroelectrodes cause an increase of the mass transport to the electrode. As a result, a rapid contamination of the surface takes place even in the presence of trace impurities in solution. For each series of experiments only a few curves were recorded (for different frequencies) in order to avoid this contamination. The last curve of the series of experiments was recorded for the same conditions as the first one. If these two curves were significantly different, the whole series was rejected. The frequency dependence of the serial capacitance (negative reciprocal product of the imaginary part of the cell impedance and the angular frequency) and the solution resistance was studied in 3.74 M H$_2$SO$_4$ under AC voltammetric conditions at frequencies ranging from 300 kHz to 50 MHz. Similar experiments were also performed in 4.45 M H$_2$SO$_4$ using the FFT SWV technique at frequencies 0.625 to 6.88 MHz. The serial capacitance curves obtained under these conditions from the imaginary part of the cell impedance are shown in Fig. 4.62 (AC voltammetry) and in Fig. 4.63 (FFT SWV). In both cases the shape of the serial capacitance curves is similar. However, the FFT SW voltammograms are noisier than the AC curves. A well defined peak observed near the zero charge potential is most likely related to the reorientation of water molecules in the double layer. There is a good correlation between curves in the frequency range of 0.3 to 11.1 MHz, however capacitance values determined at 23.4 MHz are larger than those observed at lower frequencies and capacitance calculated for 50 MHz (not shown in Fig. 4.62) is negative. It is possible that these unusual results are caused by the deteriorating accuracy of measurements. However, observed differences are larger than the expected errors. Another possible explanation is that a dispersion of the solution resistance at very high frequencies contributes to the imaginary
Fig. 4.62. Dependence of the serial capacitance on potential (AC voltammetry) for 3.74 M H₂SO₄ obtained at Hg hemispherical electrode, 6.25 μm in radius at 23°C.
The frequencies of measurements for the curves from the top to the bottom of the figure: 23.4, 0.30, 0.59, 1.1, 2.0, 3.3, 11.1 MHz.
Fig. 4.63. Dependence of the serial capacitance on potential (FFT SWV) for 4.45 M H₂SO₄ obtained at Hg hemispherical electrode, 6.25 μm in radius at 23°C. The frequencies of measurements for the curves from the top to the bottom of the figure are: 0.625, 1.88, 3.13, 4.38, 5.63, 6.88 MHz.
part of the cell impedance. The real component of the cell impedance is shown in Figs. 4.64 (AC voltammograms) and 4.65 (FFT SWV). As in the case of serial capacitance, the results are similar for both methods; curves obtained for FFT SWV experiments are more noisy than those for AC voltammetry. In this case the frequency dispersion is even more pronounced than in the case of serial capacitance curves. The very low impedance observed at 50 MHz cannot be explained by experimental errors. The direction of the change is consistent with the Debye-Falkenhagen effect, but the magnitude seems to be too large. Changes in the real impedance at lower frequencies can be explained in terms of dielectric relaxation of the double layer. Due to this relaxation the dielectric permittivity in the Helmholtz layer acquires an imaginary component, which leads to the development of a resistive conductance in parallel with the double layer capacitance. A detailed description of this phenomenon is given by Bockris et al. [155]. A relative change in the serial capacitance caused by the frequency change from 0.59 MHz to 3.32 MHz and relative changes in the real impedance for the same frequency range are shown in Fig. 4.66. Each of the curves shows a minimum near the potential of zero charge. The asymmetric character of the second curve can be explained by taking into account that the real impedance dispersion is inversely proportional to the series capacitance. The magnitude of the observed frequency dispersion can be explained if the assumption is made that the relaxation time of water molecules in the double layer, \( \tau \), is in the range of \( 10^{-7} \) s at potentials far from the potential of zero charge and 3-5 times smaller near to the potential of zero charge. Bulk water at 25°C has the relaxation time of about 8.2 ps [156], but a monolayer of water adsorbed at porous solids such as silica or jarosite shows a relaxation time in the range of 50 μs [157]. Therefore, the dielectric relaxation time suggested for the Hg/H₂O interface seems to be reasonable. The double layer relaxation can also involve other phenomena
Fig. 4.64. Dependence of the real impedance on potential (AC voltammetry) for 3.74 M H₂SO₄ obtained at Hg hemispherical electrode, 6.25 µm in radius at 23°C. Frequencies used in measurements: 0.30 (top curve), 0.59, 1.1, 2.0, 3.3, 11.1, 23.4, 50.0 MHz (bottom curve).
Fig. 4.65. Dependence of the real impedance on potential (FFT SWV) for 4.45 M H₂SO₄ obtained at Hg hemispherical electrode, 6.25 μm in radius at 23°C. The frequencies of measurements for curves from the top to the bottom of the figure are: 0.625, 1.88, 3.13, 4.38, 5.63, 6.88 MHz.
Fig. 4.66. The potential dependence of the relative change of the serial capacitance (solid line) and solution resistance (dashed line), both caused by frequency change from 0.59 MHz to 3.32 MHz, based on data presented in Figs. 4.62 and 4.64.
such as the relaxation of the diffuse-layer charges [158] and the mass transport of adsorbed ions [159]. The first phenomenon leads to a maximum dispersion near the zero charge potential but it should play an insignificant role under experimental conditions described in this work because the contribution of the diffuse layer to the interfacial capacitance in 3.74 M solution is negligible. The potential dependence of the dispersion caused by the second phenomenon is in agreement with experimental data; however, according to the theoretical model [159], the expected frequency dispersion should be at least one order of magnitude smaller than observed. Suggested values of water relaxation in the double layer seem to be too slow in comparison with the rate of some interfacial processes. However, since the adsorption of surfactant distorts the structure of solvent at the interface it isn’t apparent to what extent these two quantities are related. Clearly more studies are needed before a complete discussion of these phenomena can be provided.

4.2.3.1 Determination of kinetics of physical adsorption

AC voltammograms at mercury ultramicroelectrodes in the frequency range of 0.22 to 6.25 MHz were obtained for aqueous 1 M Na₂SO₄ containing one of the following adsorbates: 0.25 M iso-propanol, 0.5 M iso-propanol, 0.5 M n-propanol, 0.5 M n-butanol, 0.4 M methyl-ethyl ketone or 0.2 M n-butyric acid. As the curves obtained for all the solutions examined were characterised by similar properties, they will be discussed using the methyl ethyl ketone solution as an example. Similar conclusions to those drawn below are also true for the other systems.

The Bode plot for 0.4 M methyl ethyl ketone in 1 M Na₂SO₄ solution at mercury ultramicroelectrode is presented in Fig. 4.67. The double layer capacitance of a mercury ultramicroelectrode in the same solution is presented in Fig. 4.68 as a function of potential at different frequencies. It can be seen that at the most positive potentials the capacitance values
Fig. 4.67 Modulus and the phase angle of the cell impedance as a function of the angular frequency (the Bode plot). Markers represent experimental data obtained with Hg hemispherical electrode, 5 μm in radius for 1M Na₂SO₄ containing 0.4 M methyl ethyl keton at 23°C. The electrode potential was -1.861 V vs. Hg|Hg₂SO₄(0)|1 M K₂SO₄. The solid line represents the cell impedance calculated according to kinetic, thermodynamic, and equivalent circuit parameters determined in this work ($k_a = 3\times10^6$ s⁻¹, $k_d = 7.6\times10^5$ s⁻¹), $A = 1.6\times10^{-6}$ cm², $\gamma = -0.14$, $\Gamma_m = 4.9\times10^{-10}$ mol/cm², $\delta = 0.5$, $g = -3.05$, $C_h = 0.4$ M, $D = 10^{-5}$ cm²/s, $C_{dl} = 15.5$ μF/cm², $R_a = 4500\Omega$). The dashed line represents the cell impedance expected for the same process controlled only by the rate of diffusion.
Fig. 4.68. Dependence of the serial capacitance on potential for 1M Na₂SO₄ containing 0.4 M methyl ethyl ketone obtained at Hg hemispherical electrode, 5 μm in radius at 23°C. Frequencies used in measurements: 0.22 (top curve), 0.39, 0.78, 1.56, 3.13, 6.25 MHz (bottom curve).
correspond to a surface free of any adsorbed substances. The electrode at this potential range is covered by a layer of water molecules. As the potential becomes more negative and approaches the zero charge potential, the adsorption of water is no longer favoured (smaller electrostatic interactions) and the electrode becomes covered with a layer of neutral organic molecules, repelled from the bulk of the solution due to a hydrophobic effect. A resulting pseudocapacitance peak due a change in the electrode coverage is observed. After that the capacitance value decreases due to an increase in the Helmholtz layer thickness. As the potential is further changed in the negative direction, beyond the zero charge potential, the charge on the electrode causes the attraction of water dipoles and a desorption of organic molecules is observed. Once again, due to changes in the electrode coverage, the pseudocapacitance peak is observed at negative potentials. At even more negative potentials the capacitance returns to the value characteristic for an adsorbate free surface.

The potential dependence of the real impedance at different frequencies is shown in Fig. 4.58 for the same system as above. The observed peaks reflect changes of the real component of the Warburg impedance and of the activation resistance due to the adsorption process. Frequency dispersion observed outside these peaks can be explained, as mentioned earlier, by the dielectric relaxation in the double layer. As the frequency increases the values of the real impedance approach a constant value, which provides a good approximation of the solution resistance. The value of the real impedance measured at 6.25 MHz at the potential ca. -250 mV was treated as the solution resistance, $R_s$. It can be seen that the curves obtained at lower frequencies are very noisy. This results from the fact that at these frequencies the phase angle approaches 90° making an accurate determination of the real impedance impossible.
It was said before that the electrosorption valency value needed for the
determination of the kinetics of adsorption from AC curves was calculated
from the change in charge at the electrode surface resulting from the
adsorption of surfactant (eqn. (4.103)). Fig. 4.69 presents $\Delta \sigma_{ad}$ and $\gamma$
calculated from experimental data obtained for 0.2 M 1-butanol in 1 M
Na$_2$SO$_4$. The relationship of $\gamma$ versus $E$, numerically defined in the potential
region where $\theta^* \approx 1$, was fitted to a 3rd order polynomial and the resulting
regression coefficients were used to extrapolate this relationship to smaller
electrode coverages. The result of this operation is shown in Fig. 4.69 by a
dotted line. This figure also shows the electrosorption valency calculated
from the data given by Koppitz et al. [28] for the same surfactant. The
authors reported only two parameters: the value of $\gamma$ and $d\gamma/dE$ at the zero
charge potential. As shown in Fig. 4.69, these parameters are in accord with
the values calculated according to eqn. (4.103).

Parameters describing the adsorption equilibrium for all systems
studied are given in Table 4.4. Parameters $\Delta G^0_m$ and $g$ were obtained by a
least squares regression of $\Delta G^0_m$ versus $\theta$. In order to compare the values of
$\Delta G^0_m$ obtained with the literature data a correction for a different definition
of the standard state must be made. In the literature the equilibrium
constant expression (eqn. (4.73)) is usually written with the concentration of
surfactant at the initial state expressed in terms of the mole fraction and at
the final state in terms of the surface coverage. In adsorption kinetics such
formulation is unacceptable (definition of the standard state changes as a
molecule passes through the activation barrier). Therefore, we have to
choose one way of expressing the concentration of the adsorbate before and
after the adsorption event. The surface concentrations were selected to be
used in this work. The surface concentration in the oHp, $c_o$, and the mole
fraction, $x_o$, are proportional to each other for $x_o<<1$ ($x_o = c_o A_w N_A$, where $A_w$
is the area occupied by 1 water molecule and $N_A$ is the Avogadro constant).
Fig. 4.69. Change of charge at the electrode surface caused by the adsorption process (markers) and the electrosorption valency as functions of potential. Dotted line represents the electrosorption valency calculated from experimental data according to eqn. (4.103). The equation gives the regression parameters allowing determination of $\gamma$ as a function of potential. Dashed line shows values reported by Koppitz et al. [28] for n-butanol. Experimental data obtained in 0.2 M n-butanol solution in 1 M Na$_2$SO$_4$ supporting electrolyte with SMDE 0.0106 cm$^2$ in surface area at frequency 750 Hz.
This allows a simple recalculation of equilibrium constants and standard free energies defined in different systems. The adjusted values are given in the 3rd column of Table 4.4 in brackets and they are followed by the literature values. A discrepancy in the case of n-butanol is probably due to the fact that in our case $\Delta G_m^0$ was obtained by a linear extrapolation (i.e. assuming that $g$ is independent of potential). However, Moncelli et al. [41] have shown that in the case of n-butanol $g$ decreases significantly when the electrode potential approaches the zero charge potential.

The kinetic parameters of physical adsorption were determined with the method based on curves recorded for many frequencies. In general the quality of the results was satisfactory. The kinetic data obtained around $\theta = 0.5$ were the most accurate. The results obtained for negative adsorption peaks were usually more scattered but showed a more regular behaviour than the results obtained at positive potentials. The major source of errors is probably associated with the subtraction of $C_{di}$ and $R_{di}$ components (see Fig. 4.59). Some problems were also observed for systems for which $g<-2.42 \text{ kJ/mol (} g^-<-3)$ (e.g. n-butanol). These problems may be associated with a too simplistic treatment of the interaction parameter in this work. Two general trends were noted: i) adsorption on the negative side of the zero charge potential is usually faster than at the positive side, and ii) surfactants adsorbing farther from the zero charge potential show lower rate constants.

A comparison of results obtained from the analysis of AC and CV curves was performed in case of 1-butanol adsorption from 1 M H$_2$SO$_4$ (CV) and 1 M Na$_2$SO$_4$ (AC). Fig. 4.70 shows the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant for both kinds of experiments. It can be seen that the values are similar in both cases but the data obtained from the analysis of CV curves is more scattered.

It was found for all systems studied that the rate of the adsorption
Fig. 4.70. Comparison of the dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant determined from AC and CV experiments for the adsorption of 1-butanol at mercury electrode 5 μm in radius. Solutions used: 0.2 M 1-butanol in 1 M H₂SO₄ (CV) and 0.5 M 1-butanol in 1 M Na₂SO₄ (AC).
process determined from the analysis of AC voltammograms shows a good correlation with the electrical component of the standard free energy of adsorption. In order to evaluate more exactly the relative contribution of \( \Delta G^0_{el} \) and \( \Delta G^0_{ad} \) to the activation energy a multiple linear regression method was used (ln\( k_a \) against \( \Delta G^0_{el} \) and \( \Delta G^0_{ad} \)). On this basis the following empirical relation was found:

\[
k_a = k_0 \exp \left( -\frac{\alpha \Delta G^0_{el} + \chi (\Delta G^0_{ad} - \Delta G^0_{el})}{RT} \right)
\]

(4.107)

where \( k_0 = (4.6 \pm 0.3) \times 10^9 \text{ s}^{-1} \), \( \alpha = 1.09 \pm 0.02 \) and \( \chi = 0.36 \pm 0.02 \). Errors are reported as standard deviations obtained from the least-squares method. The kinetic data for all studied systems were included in the analysis. The agreement between the experimental data and eqn. (4.107) is graphically shown in Fig. 4.71.

A large value of \( \alpha \) indicates that in the adsorption processes studied \( \Delta G^0_{el} \) rises before \( \Delta G^0_{ad} \) drops; in other words, before excess energy (due to the change in the hydrophobic hydration) is released work must be performed against the electrical field. The mechanism suggested in Fig. 4.72 is in agreement with this conclusion. A surfactant most likely approaches the electrode with a random orientation of the hydrophobic group with respect to the metal. When this approach takes place ions from the double layer are pushed away. Since centres of charges at the surface site and in solution are farther apart, the local double layer capacitance decreases. In order to explain \( \alpha \) close to one (or higher) we have to assume that the double layer capacitance at the transition state is almost the same (or lower) as the final state. After reaching the maximum energy state the reaction proceeds by translation through the last layer of water molecules and rotation (from a random to a fixed orientation with the hydrophobic group pointing towards the surface, an average change of the angle by \( \pi/2 \)). When this process occurs a part of the hydrophobic group is removed from solution and the
Fig. 4.71. Dependence of the adsorption rate constant on the linear combination of electrical and non-electrical components of the standard free energy of adsorption ($\alpha = 1.09$ and $\chi = 0.36$, details in text). Data points were obtained in 1 M Na$_2$SO$_4$ containing: 0.4 M methyl ethyl ketone (○), 0.5 M butan-1-ol (△), 0.25 M propan-2-ol (■), 0.5 M propan-2-ol (◇), 0.5 M propan-1-ol (○), 0.2 M butyric acid (●). Results for both negative and positive (with respect to $E_{p\infty}$) adsorption peaks are included.
Fig. 4.72. Simplified diagram of the proposed mechanism of the physical adsorption process (see details in text). Circles with a negative sign indicate centres of the counter charge for given surface sites, rather than of specific ions in solution. Orientation of the surfactant molecule is random in the initial and fixed in the final state. Lines represent changes in the electrical ($\Delta G_{elc}^\circ$) and non-electrical ($\Delta G_{nel}^\circ$) components of the standard free energy of adsorption as well as overall changes in the standard free energy of the reacting system ($\Delta G_{elc}^\circ + \Delta G_{nel}^\circ$).
excess energy is dispersed in the system. It should be noted that at larger
coverages the transition state is stabilised by attractive lateral interactions
with adsorbed surfactant molecules. This explains a 36% contribution of
\((\Delta G_{md}^{2} - \Delta G_{m}^{2})\) to the activation energy (since \(\Delta G_{md}^{2} - \Delta G_{m}^{2} < 0\), this contribution
lowers the activation barrier). Parameter \(k_0\) represents the rate constant of
the adsorption process at the zero charge potential and for \(\theta \to 0\). This
parameter must account for the translation and rotation of surfactant in the
double layer. It can be expressed in terms of bulk values of rotational \((D_r)\)
and translational \((D_t)\) diffusion coefficients. The extra friction associated
with molecular motions in the double layer, as compared with the bulk
solution, can be taken into account with a new activation energy term (the
interfacial friction, \(\Delta G_{d}^{0}\)). Based on Einstein's equation [160] the average
time of the translational step is:

\[
\tau_t = \frac{\langle d \rangle^2}{2D_t} = \frac{d_w^2}{2D_t}, \tag{4.108}
\]

where \(\langle d \rangle\) is the root mean square (r.m.s.) displacement of surfactant
molecules in time \(\tau\) and \(d_w\) is the diameter of the water molecule. By taking
\(d_w = 3.1 \times 10^{-8}\) cm and \(D_t = 10^{-5}\) cm²/s [161] we obtain \(\tau = 4.8 \times 10^{-11}\) s.

The average time of the rotational motion is:

\[
\tau_r = \frac{\langle \Theta \rangle^2}{4D_r} = \frac{\pi^2}{16D_r}, \tag{4.109}
\]

where \(\langle \Theta \rangle\) is the r.m.s. displacement angle in radians.

The rotational diffusion coefficient of water molecules in liquid water is
7×10¹⁰ s⁻¹ at 25°C ([41] p. 5.44). The value of \(D_r\) is inversely proportional to
the molecular volume ([41] Chapter 6.5g) (a fivefold decrease with respect to
water is expected on this basis for the systems studied). In addition, the
rotational diffusion coefficient is smaller if rotation of a nonspherical
molecule about the axis perpendicular to its larger dimension is considered.
Consequently, \(D_r = 5 \times 10^9\) s⁻¹ can be expected for the compounds studied in
bulk solution. If this value is entered into eqn. (4.109) \( \tau = 1.24 \times 10^{-10} \) s is obtained.

Based on the experimental results the mean reaction time for the process, \( \tau \), at the zero charge potential is:

\[
\tau = \frac{1}{k_0} = 2.17 \times 10^{-10} \text{s}
\] (4.110)

Therefore we can evaluate the interfacial friction term as:

\[
\Delta G_{\text{if}}^0 = RT \ln \left( \frac{\tau}{\tau_i + \tau_r} \right)
\] (4.111)

For the studied systems this term is very small (about 0.23 \( RT \)). This result is interesting because it indicates that at mercury electrodes the viscosity of interfacial water near the zero charge potential is only slightly larger (say, 1.3 times) than the viscosity of bulk water. Recently, adsorption kinetics of pentanoic acid at the solution/air interface was studied by ripplon spectroscopy [162]. The authors concluded that the rate of the process is controlled by diffusion and that the diffusion process in close vicinity to the surface (1000 - 10 nm) is the same as in the bulk phase. This is in accord with our results, although it should be noted that in the case of our research the diffusion process in the double layer region, i.e. less than 1 nm from the surface, is examined.

The results presented in Fig. 4.71 indicate that adsorption rate constants in the range of \( 10^9 \) s\(^{-1} \) can be measured with high frequency AC voltammetry at ultramicroelectrodes. It should be stressed that these results are within the limits of the applied method. Analysis of eqn. (4.22) indicates that the rate at which the system relaxes is determined by \( k_d + k_a \theta_a \). In measurements carried out in this work this expression was lower than \( 10^8 \) s\(^{-1} \) and it was comparable with (or smaller than) the maximum angular frequency of the excitation waveform \( (4 \times 10^7 \text{Hz}) \). The rate of \( 5 \times 10^9 \) s\(^{-1} \) is equivalent to the heterogeneous rate constant of 150 cm/s (conversion factor is the thickness of a monolayer of water molecules). AC voltammetry at
standard size electrodes was successfully used in studies of electrode processes with standard rate constants up to about 1.5 cm/s [163]. In such studies frequencies up to 5 kHz and electrodes about 0.025 cm in radius were usually employed. Here, kinetic processes faster by two orders of magnitude were measured by using frequencies three orders of magnitude higher and electrodes 50 times smaller. Furthermore, measurements of physical adsorption kinetics are easier than measurements of redox kinetics. Since the typical value of $\gamma$ for the physical adsorption is less than 0.3, the activation resistance is at least 10 times higher than it would be for a redox process with the same rate constant (see eqn. (4.94)). Consequently, errors due to an inaccurate evaluation of the solution resistance are greatly reduced.

4.2.3.2 Comparison of single and multiple frequency method

The kinetic parameters for physical adsorption discussed in the previous section were obtained from the analysis of curves recorded for several frequencies. This method seems to be preferable in respect to the one based on the analysis of curves recorded for one frequency since it is based on a larger set of data. As a result the systematic errors are expected to be largely reduced in this case.

It will be shown below (section 4.2.3.3) that in some cases the analysis of results obtained at only one frequency is desirable. This section aims at a verification of the usefulness of this method by a comparison of results obtained with the two methods for the case of propan-2-ol adsorption from 1 M Na$_2$SO$_4$.

The set of AC voltammetric curves recorded at frequencies 0.22 to 3.13 MHz was analysed with the multiple frequency method (section 4.2.2.1). In addition, curves obtained at frequencies 0.22 to 6.25 MHz were analysed with the single frequency method (section 4.2.2.2). Fig. 4.73 shows a comparison of these results. It can be seen that the results obtained at all
Fig. 4.73. Comparison of the dependence of the adsorption rate constant on the logarithm of the equilibrium constant determined with the single (SF) and multiple (MF) frequency method of data analysis for the adsorption of propan-2-ol from Na$_2$SO$_4$ at Hg ultramicroelectrode 5 µm in radius.
frequencies are similar. The dependence of the logarithm of the adsorption rate constant on the logarithm of the equilibrium constant is more scattered at lower frequencies, approaching the results of the multiple frequency analysis as the frequency value increases. Such behaviour may be explained if we take into account the properties of the systems studied. The simulation program developed by Baranski [164] allows a determination of optimal conditions for the calculation of adsorption kinetics. It examines the dependence of the total cell impedance on the activation resistance at different experimental conditions. In the case of propan-2-ol adsorption from 1 M Na$_2$SO$_4$ at a 5 $\mu$m Hg electrode the optimal conditions were determined to be 316 kHz (minimum frequency at which the error in the activation resistance determination is smaller than 5%) to 3.16 MHz (above this frequency the error in the pseudocapacitance is larger than 5%). This result indicates that the curves recorded at higher frequencies are expected to give more accurate results. This is in agreement with the results presented in Fig. 4.73.

The data presented in Fig. 4.73 indicates that the single frequency method of data analysis gives results that are less accurate than the results of multiple frequency analysis but close to the expected values if the appropriate frequencies are used.

4.2.3.3 Determination of kinetics of chemisorption

AC voltammetry was also used for the determination of chemisorption kinetics, but the technique was not optimised for this task. Chemical adsorption is slower than physical adsorption and as a result lower frequencies are required for the determination of kinetic parameters. The simulation program briefly described in section 4.2.3.2 was also used for the determination of optimal conditions at which kinetics of cysteine adsorption from 1 M H$_2$SO$_4$ should be obtained. For optimal results (Fig. 4.74 A) an AC modulation frequency between 10 kHz (below this frequency the error in the
Fig. 4.74. A. Simulation of the dependence of the ratio of the total impedance change to the change in the activation resistance on frequency and electrode coverage. Conditions as for cysteine adsorption from 1 M H₂SO₄: γ = -0.91, g = -3.27 kJ/mol, kₚ = 7.6×10⁸ s⁻¹, gₚ = -290 J/mol, α = 0.74, Rₛ = 1000 Ω, Cₐ = 23 μF/cm², r = 5 μm, D = 1×10⁻⁶ cm²/s, C₀ = 0.19 M.
activation resistance is larger than 5%.) and 500 kHz (above this frequency
the error in the adsorption pseudocapacitance is larger than 5%, Fig. 4.74 B)
should be used. Unfortunately, the available equipment only allows
measurements at frequencies above 200 kHz or below 10 kHz. This
limitation dramatically decreased the possibilities of conducting accurate
studies of chemisorption kinetics. An additional limitation arises from the
fact that the method of data analysis is based on the assumption that the
concentration of an adsorbate in the oHp is constant during the experiment.
This condition is fulfilled if the bulk concentration of an adsorbate is high
(0.1 to 0.5 M). In case of thiocompounds the usage of such high
concentrations results in oxidation of mercury and the formation of soluble
complexes R—S—Hg⁺ in addition to the adsorption process. This problem is
especially severe in the case of thioglycol. As a consequence the kinetics of
its adsorption were not investigated using the AC method. However, in the
case of cysteine this complex formation is less pronounced. It was possible to
obtain some meaningful kinetic results for cysteine adsorption from 1 M
H₂SO₄ with the single frequency analysis method of AC voltammograms
recorded at 220 kHz. The single frequency method of data analysis was
selected in this case as the available electronic equipment doesn't allow
recording curves for several frequencies in the optimal frequency range
(10 kHz to 500 kHz) for cysteine adsorption.

The complications resulting from complex formation could be reduced if
the concentration of thiocompound in solution was the same as in the CV
experiments (10⁻⁶ to 10⁻⁵ M). However, in such a case the concentration of
the adsorbate in the oHp would have to be determined from the convolution
of a DC current (see section 4.1.2) recorded simultaneously with an AC
signal. It should be noted that the magnitude of a DC current is about
1000000 times smaller than of high frequency AC currents. Such small
currents cannot be recorded without a complete redesign of the current
monitoring system. If appropriate changes in the electronic set-up are made
Fig. 4.74. B. Simulation of the dependence of the ratio of the total impedance change to the change in the pseudocapacitive impedance on frequency and electrode coverage. Conditions as in Fig. 4.74.A.
AC voltammetry may be superior to cyclic voltammetry in measurements of chemisorption kinetics. However, at the present stage the set-up was optimised for the studies of physical adsorption. It was shown in section 4.2.3.2 that the optimum frequency range for measuring kinetics of 0.5 M propan-2-ol adsorption from 1 M Na₂SO₄ is between 3.16 kHz to 3.16 MHz. In the case of physical adsorption there is no adverse effect when high concentrations of surfactants are used.

The double layer capacitance curve obtained with the FFT SWV technique for the adsorption of cysteine from its 0.18 M solution in 1 M H₂SO₄ supporting electrolyte at Hg ultramicroelectrode (5 μm in radius) is presented in Fig. 4.75. It can be seen that at higher frequencies the pseudocapacitive peak becomes smaller, making an accurate background subtraction difficult. This agrees with the conclusions drawn from the simulation (see Fig. 4.74). Fig. 4.76 presents a comparison of kinetics of cysteine adsorption from 1 M H₂SO₄ at a mercury electrode obtained with the single frequency AC method (0.18 M cysteine, 220 kHz for AC and 156 kHz for FFT SW voltammetry) and from the analysis of CV curves. The results obtained are similar in all cases indicating that both techniques may be used in the determination of chemisorption kinetics despite the difficulties mentioned above. It should be remembered that precautions have to be taken to reduce the possibility of complex formation. In all AC experiments the potential scan was started from more negative potentials to reduce the time an electrode was kept at potentials at which mercury oxidation is possible.

Adsorption of cysteine was also examined from different supporting electrolytes. In the case of AC voltammetric experiments the use of supporting electrolytes characterised by a low conductivity is much easier than in the case of high potential sweep rate CV curves, as the solution resistance can be easily eliminated through the simple subtraction procedure described above. Three different buffer solutions were used as
Fig. 4.75. Capacitance curves obtained with the FFT SWV technique for the adsorption of 0.18 M cysteine from 1 M H₂SO₄ at 11g ultramicroelectrode 5 μm in radius. Frequencies as indicated on graph.
Fig. 4.76. Comparison of kinetic results obtained for the adsorption of cysteine from 1 M H₂SO₄ solution at 5 μm Hg ultramicroelectrode from the analysis of CV and AC voltammograms.

AC experiments performed for 0.18 M cysteine (220 kHz (SF, AC), 156 kHz (SF, FFT)), CV experiments for 8×10⁻⁶ to 6.4×10⁻⁵ M cysteine. SF-single frequency analysis. Details in text.
supporting electrolytes in experiments examining the kinetics of cysteine adsorption: 2 M (NH₄)₂SO₄ + 2 M H₂SO₄, 0.5 M + 0.5 M acetic buffer and 2 M (NH₄)₂SO₄ + 0.5 M NH₃. The cysteine concentration was 0.18 M in all solutions. In all cases the kinetic parameters were obtained from AC voltammograms recorded at 220 kHz. The results of these analyses are presented in Fig. 4.77. It can be seen that no definite conclusion about the effect of the solution pH on the kinetic parameters can be drawn from these results. The values of the adsorption rate constants are similar for all the studied systems and close to those for the adsorption of cysteine from acidic solution. The differences in the obtained parameters may result from experimental errors making impossible the evaluation of the effect of supporting electrolyte.

In case of the determination of kinetics of chemisorption the advantages of the AC method are diminished by the fact that the activation resistance is high and hence difficult to determine and also by the possibility of the formation of a complex between the adsorbate and the electrode material. This method requires further modification to allow more accurate determination of kinetics of chemisorption.
Fig. 4.77. Comparison of kinetic results obtained for the adsorption of cysteine from different supporting electrolyte solutions at 5 μm Hg ultramicroelectrode.

AC experiments performed for 0.18 M cysteine, CV experiments for 8×10^-6 to 6.4×10^-8 M cysteine. Analysis of AC curves performed for a single frequency (220 kHz). Details in text.
5. Conclusions and future work

The aim of this work was to develop methodologies for studying kinetics of adsorption processes at metal electrodes. Two different experimental methods, namely, FCV and high frequency AC voltammetry, were developed and tested for this purpose. Data processing in these methods was based on a uniform theoretical description of the process created in the course of this work. In addition, a computer program was devised for numerical simulation of adsorption processes under FCV conditions. This program was used to verify the data processing method as well as to examine relations between observed and calculated quantities.

The simulation program describes equally well both chemisorption and physical adsorption. The two processes are characterised by different interactions of an adsorbate with the electrode material, which consequently leads to a different dependence of the free energy of adsorption on potential. However, the electric current caused by an adsorption process can be described with the same equation. Different characteristics of cyclic voltammograms in case of physical and chemical adsorption can be accounted for by a different functional dependence of the electrosorption valency on potential. In the case of chemisorption, this parameter is independent of potential and close to 1 or -1 (for a covalent bond). The free energy of chemical adsorption is a linear function of potential, consequently a single adsorption peak is observed at the potential where the free adsorption energy of the process passes through zero. The physical adsorption is characterised by an almost linear dependence of the electrosorption valency on potential. Its value is a fractional number which decreases with potential and crosses zero near the zero charge potential.
This leads to a quadratic dependence of the standard free energy of adsorption on potential as well as to two adsorption peaks more or less symmetrically positioned around the zero charge potential. The simulation program allowed the derivations of the relationships between the shape of the adsorption peak and various thermodynamic and kinetic parameters of the process.

The determination of the kinetics of adsorption based on the analysis of FCV curves (namely of a desorption peak) gave satisfactory results in the case of chemical adsorption. The potential sweep rate used for the determination of kinetic parameters was 100000 V/s. The elimination of the effect of both solution resistance as well as the double layer capacitance, which is usually significant at the potential sweep rates used, is difficult in the case of cyclic voltammetric curves. In addition the determination of kinetic parameters of adsorption requires prior knowledge of the thermodynamics of the process. As a result, two sets of curves are needed: i) a low potential sweep rate curve (1000 V/s, used for the determination of the equilibrium constant) and ii) a high potential sweep rate curve (100000 V/s, for the determination of kinetic parameters). In both cases, the adsorption process takes place at slightly different potentials; this makes an extrapolation of the thermodynamic parameters to the conditions characterising the high potential sweep rate experiment necessary. The two problems mentioned above may be a potential source of error in determining the kinetics of adsorption.

The kinetics of adsorption were examined for different thiocompounds (chemisorption) as well as for aliphatic alcohols (physical adsorption) at mercury ultramicroelectrodes. It was observed that the chemisorption process is much slower (in the range of $10^6 \text{s}^{-1}$) than the process of physical adsorption. In the case of thioglycol adsorption, two factors indicate that the proton from the -S-H group dissociates prior to adsorption in the rate determining step; these factors are i) the dependence of the adsorption rate
constant on the solution pH, and ii) the decrease of the adsorption rate constant in a heavy water solution. A preferential adsorption of thioglycol at thallium was observed when thallium amalgam electrodes were used.

In the case of physical adsorption, the method of determining the adsorption kinetic parameters based on the analysis of FCV curves gave unreliable results. The most probable reason for this problem is a potential sweep rate that was too low to allow for accurate determination of the kinetics of physical adsorption.

The difficulties in applying the FCV technique to determine the kinetics of physical adsorption led to the development of a different method, and the latter was based on the analysis of AC curves. High frequency AC voltammetry was used for determining the kinetics of adsorption. The kinetic parameters were extracted from experimental curves obtained for a frequency range from 220 kHz to 10 MHz. The method of determining the adsorption kinetics from these curves is based on an analysis of the properties of elements of the equivalent circuit (Fig. 4.57). A specially designed electrode made possible the elimination of stray capacitance. The frequency dependence of the response of the electronic system used in data acquisition was taken into account and corrected by a calibration procedure. In the case of AC curves, an easy subtraction procedure was used to eliminate the effect of solution resistance and that of double layer capacitance. In all AC experiments, high concentrations of the adsorbate were used to reduce the value of mass transport impedance as well as to ensure that the adsorbate concentration in the oHp remained constant during the adsorption process. With regard to the adsorption of thiocompounds at mercury electrodes, the above method has to be used with caution because of the possibility of complexes forming when high concentrations are used. Nevertheless, the results obtained for the adsorption of cysteine are comparable with those determined from the
analysis of FCV curves. The technique needs further optimisation to allow an accurate determination of chemisorption kinetics.

In the case of AC experiments, both thermodynamic and kinetic parameters of the adsorption process can be determined from one curve. This is because the slowly changing potential ensures equilibrium conditions at the electrode surface and at the same time the high frequency potential excitation allows the determination of kinetic parameters. It is much easier to obtain curves characterised by a low time parameter and at the same time corrected for the effect of the ohmic drop in the case of AC techniques than in the case of CV experiments. This allows the determination of higher rate constants and reduces the risk of errors; these errors could result from i) an imperfect evaluation, and ii) subtraction of the ohmic drop as well as the double layer capacitance. AC voltammetry and FFT SWV were successfully used for determining the kinetics of physical adsorption for several aliphatic alcohols, methyl ethyl ketone and butyric acid. In all cases, the kinetics of the process are comparable and correlate with a linear combination of the electrical component of the standard free energy of adsorption (a major contribution) and the energy of lateral interactions (a minor contribution). The results suggest that, during the adsorption process, work against an electrical field must be performed before excess energy (due to the change in the hydrophobic interactions) is released. The final state is reached by a rotational and translational motion of the surfactant molecule. At the zero charge potential, the rate constant reaches the maximum value of $(4.6\pm0.3)\times10^9$ s$^{-1}$. This value indicates that the viscosity of interfacial water at mercury near the zero charge potential is approximately 1.3 times higher than the bulk viscosity.

Future research in this area could involve further testing of the methods presented for determining the kinetic parameters. The kinetics of adsorption of other substances at mercury as well as at other metal (preferably single
crystal or liquid) electrodes could be tested. Further research in systems containing several adsorbates or at modified electrodes could help in better understanding the properties of the double layer. The effect of solvent properties on the kinetics of an adsorption process is also of interest since it is known to affect the kinetics of charge transfer processes taking place at the electrode surface. As the high frequencies used allow the evaluation of solvent viscosity inside the double layer, this could be used to determine the changes of solvent properties when it transfers from the bulk of the solution to the electrode surface.

The application of high frequency FFT SWV for determining the kinetics of adsorption has been initiated in this work. However, the electronic set-up needs further modification in order to reduce the noise as well as to improve the quality of data. A distinct advantage of this technique is that one experiment can provide a set of curves for several frequencies. This is thus expected to reduce systematic errors that may possibly result from difficulties in maintaining reproducible conditions between several experiments. Further research in this area is expected to be beneficial.

The importance of evaluating the kinetics of adsorption was presented in the introductory section of this thesis. The foregoing work provides a means for determining the kinetics of adsorption, and hence a more thorough understanding and a better choice of experimental conditions is made possible for many industrial systems.
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