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The Present State and Problems of the Theory of the Kinetics of Electrode Reactions Accompanied by the Adsorption of Inactive Substances and Reagents

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Problems in the theoretical description of the influence of the adsorption of dissolved species on the rates of electrode processes have been discussed. Present-day theories of the mechanism of the interaction between adsorbed species and ionic reagents have been used to develop a general statistical-mechanical approach to the quantitative examination of the macrokinetics of heterogeneous transformations complicated by the adsorption of ionic or dipolar components of the solution, including the adsorption of the reagents themselves.
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I. INTRODUCTION

The adsorption of both electrochemically inactive substances and reagents has a significant influence on the kinetics of electrode processes. Extensive experimental material has now been accumulated on the influence of the adsorption of electrochemically inactive substances on the kinetics of electrode reactions. A number of papers also discuss the problem of the existence of a stage involving the adsorption of the reacting species themselves (the ions or dipolar molecules of an organic depolariser) in the resulting electrode process.

An extensive literature has been devoted to various theoretical approaches to the description of the influence of surface-active substances (SAS) on the rates of electrochemical reactions. As yet, however, there is no unique method of interpreting experimental data in terms of current theories of the nature of the elementary stage in electrochemical processes and the mechanism of reactions between reagents and adsorbed species. At the same time, the problem of the mechanism of the influence of SAS and the kinetics of the adsorption of reagents on the rates of electrochemical reactions is of fundamental importance. The problem of the influence of SAS is closely related to the development of a scientific basis for improving many processes in electrochemical technology. The mechanism of this influence must be known in order to investigate the factors determining the anti-corrosion, flotation, extraction, and other properties of SAS of practical importance. These factors characterise the efficiency of the application of surface-active substances in chemical engineering, technology, and other fields. Most existing approaches to the above theoretical problems are based on the so-called transition state method, in which the original problem is formulated in a general phenomenological basis. A specific method for examining the kinetics of reactions in an adsorption layer has also been developed, based on the thermodynamic theory of "partial charge transfer".

The importance of allowance for the electrical double layer in the description of the kinetics of electrode processes was first pointed out in 1933 by Frumkin. He introduced into the equation for retarded discharge (the Tafel equation) two, now familiar, corrections corresponding to the physical "renormalisation" of two quantities: the electrode potential ϕ_0 in the exponent in the Tafel equation and the bulk concentration of the reagent c_{0X}. The quantity ϕ_0 was renormalised to $\phi_0 - \psi_1$, and c_{0X} to $c_{0X} \exp[-z_{0X}F\psi_1/RT]$, where ψ_1 is the potential in the plane in which the reacting species is situated, z_{0X} its charge, F the Faraday number, R the gas constant, and T the absolute temperature.

The equation for retarded discharge with Frumkin corrections provides a qualitative explanation of the observed regular features of the kinetics of charge transfer, and in some cases it makes possible a quantitative interpretation of the experimental data (the ψ_1-potential is usually identified with the potential of the outer Helmholtz plane). When there is adsorption of ions or surface-active organic substances (SAOS), however, it is difficult to explain the experimental data on the basis of the classical theory of retarded discharge. The influence of the specific adsorption of inorganic ions (chloride, bromide, and iodide) on electrochemical kinetics was first observed by Iofa and co-workers.[1] They detected an appreciable decrease in the overpotential of hydrogen liberation on mercury in the presence of these ions. The simple theory of retarded discharge could not explain these facts.

In 1952, Frumkin[2] proposed the following equation for the magnitude of the current in the presence of SAS

$$i = \text{const} \cdot f(\theta) \cdot \exp\left\{-\frac{\alpha n F(\varphi_0 - \psi_1) + z_{0x}F\psi_1}{RT}\right\} \qquad (1)$$

where $f(\theta)$ is a function of the degree of coverage θ of the electrode surface by the inhibitor, n the number of electrons transferred in an individual step, and α the electron transfer coefficient. If an equation of the type $k = k_0(1 - \theta) + k_1\theta$ [3,4] is taken for the standard reaction rate constant, then when

the condition $k_0 \gg k_1$ is fulfilled, the dependence of the function f on θ will have the form $f(\theta) = 1 - \theta$.[5] The existence of this relationship means that, other conditions being equal, the probability of the penetration of the reacting species into an adsorption layer containing SAOS is equal to the fraction $1 - \theta$ of the probability of their penetration into the same layer not containing the organic substance. In the electrochemical literature, this factor corresponding to the inhibition of electrode processes by added SAOS has been called, not very systematically, the "blocking effect" (it is assumed that the adsorbed molecules of the SAOS are segregated on the electrode and that they block a fraction of the surface θ, and that the electrochemical reaction takes place only on the free area of the surface, corresponding to the fraction $1 - \theta$).

The expression $f = (1 - \theta)^b$ has been proposed for the function $f(\theta)$,[6] but the parameter b was not given a clearly defined physical significance. In Ref.7 the function $f(\theta)$ was approximated by an expression of the form $f = \exp(-\Delta U/RT)$, where the quantity ΔU is related to the additional activation energy in the presence of the SAS (the potential barrier due to the hindered penetration of the reagent species into the compact layer).

Since surface-active halide ions have an extremely marked influence on the liberation of hydrogen, it was suggested[8] that the influence of adsorbed anions is not due to a change in the ψ_1-potential (in other words, to the ψ_1-effect), but is due to a decrease in the activity coefficient of the activated complex.

It was subsequently shown,[9,10] however, that if this suggestion is correct, hydrogen ions will be adsorbed and accumulate on the electrode surface. This is not observed experimentally, however. To eliminate this contradiction, it was suggested[9] that the coefficient $l (l \ll 1)$ be introduced into the equation for retarded discharge:

$$i = \text{const} \cdot \frac{f_{\text{Ox}} c_{\text{Ox}}}{f_{\neq}} l \cdot \exp\left\{-\frac{(\alpha n - z_0) F\psi_1 + \alpha n F\varphi_0}{RT}\right\}. \qquad (2)$$

This coefficient characterises the degree of inhibition of the transfer of an ion from the bulk of the solution into a surface layer with a much lower dielectric constant. In Eqn.(2), the quantities f_{0X} and $f_{\neq}$ represent the activity coefficients of the discharging species in the initial state in the bulk of the solution and in the intermediate complex, and c_{0X} is the bulk concentration of the reagent.

The introduction of the coefficient $l \ll 1$ means that only a small proportion of hydrogen ions penetrates into the compact layer from which discharge takes place, and that the potential of the outer Helmholtz layer changes little, so that no appreciable adsorption of these ions takes place. The coefficient l has been interpreted quantatively.[11,12] Thus according to Ref.12, it is possible to write for the coefficient l the expression $l = l_0 \cdot \exp(-k_D\theta - 2a\tilde{\gamma}\theta)$, where k_D is a coefficient characterising the decrease in the dielectric constant in the compact layer when a SAS is introduced into the solution, and $\tilde{\gamma}$ a coefficient which corrects for the mutual attraction of the reagent species in the compact layer. The problem of the influence of ions undergoing specific adsorption on the kinetics of electron transfer has been discussed repeatedly in the literature. In a study[13] of the influence of electrochemically inactive anions undergoing specific adsorption on the kinetics of electrode processes, it was assumed that it is possible to use Frumkin's equation, in which the ψ_1-potential can be identified with the potential in the plane within the compact part of the double layer in which the activated complex is situated. The charge of the specifically adsorbed ions was assumed[13] to be continuously distributed throughout the inner Helmholtz plane. In Ref.14, account was taken of the discrete nature of the specifically adsorbed charge, and the ψ_1-potential was identified with the micro-potential at the point where the centre of the activated complex was localised.

The effects of the discrete character of the charge in the kinetics of electrode processes were dealt with in a paper[15] which derived the dependence of $\lg(k_{q_1}/k_0)$ on q_1 (here, k_{q_1} is the charge transfer rate constant for a density of specifically adsorbed ions q_1, and k_0 the rate constant for $q_1 = 0$). The derivation is analogous to that of the equation for retarded discharge with a correction for the double layer. It was assumed[15] that the plane in which the centres of the reagent ions are situated coincides with the inner Helmholtz plane, and the effect of the discrete character of the charge is taken into account both in the calculation of the activity coefficient of the reagent ion and in the calculation of the free energy of activation. In all the works cited, the dependence of $\lg(k_{q_1}/k_0)$ on q_1 is linear, whereas the experimental data, at least for the discharge of the hydrogen ion in the presence of iodide ions, give relationships which deviate considerably from linearity, particularly at high values of q_1.

For a more detailed explanation of the experimentally observed effect of a marked decrease in the hydrogen overvoltage in the presence of specifically adsorbed halide ions in terms of statistical thermodynamics, a theory was developed[16-18] on the assumption that associates or ion pairs are formed, including the reagent ions and adsorbed inactive species. The effect of an increase in the rate of electrode processes as a result of the association of the reagents with inert ions, predicted in the works cited, shows qualitative agreement with available experimental data.[19-23]

The study of the effects related to the change in the rate of an electrochemical reaction when an organic substance capable of being adsorbed on an electrode surface is introduced into the solution is of considerable practical and theoretical interest. Many studies, mainly experimental, have been carried out in this field, and the results have been discussed in many monographs and reviews.[24-32] Theoretical aspects of the influence of SAOS on electrochemical kinetics have been dealt with.[33-36] An equation has been obtained[37] for the current density i

$$i = \text{const} \cdot \bar{\Phi}(\Gamma) \cdot \exp\left\{-\frac{\alpha n F\varphi_0}{RT} + \bar{\gamma}(\varphi_0 - \varphi_m)^2\right\} \qquad (3)$$

which takes account of the stage involving the adsorption of the organic depolariser. The quantities $\bar{\gamma}$ and θ_m in Eqn.(3) are empirical constants, and $\bar{\Phi}(\Gamma)$ the familiar Gibbs adsorption (Γ) function of the surface-active substance. The influence of the nature and degree of coverage of an electrochemically inactive organic adsorbate on the kinetics of an electrode process has been studied.[38]

The state of the theory in 1977 and the mechanisms proposed in the literature at that time for the influence of SAOS on the kinetics of electrode processes have been fairly fully reviewed.[35] Here, therefore, only the most widely encountered recent theories will be briefly discussed.

To construct a theory of the influence of SAOS on the kinetics of electrode processes, it has been assumed[32,38] that as a result of the different reaction conditions on regions of the electrode surface occupied by an adsorbate and on unoccupied regions, the surface becomes non-uniform with respect to the electrochemical process. Assuming that the rate of the electrode process on the surface occupied by the adsorbate is independent of θ, the expression

for the rate constant is written in the form $k = k_0(1 - \hat{c}) + k_1\theta$, where k_0 and k_1 are the rate constants of the process on the regions formally unoccupied and occupied by the adsorbate respectively. On the basis of the theory of absolute reaction rates, the authors cited[32,38] essentially postulated that the quantities k_0 and k_1 depend on θ in different ways. In particular, in the range $\theta < 0.9$ with the condition that the composition of the solution, the positions of the centres of the activated complexes, and the mechanism of retarded discharge remain unchanged, the following expression was proposed for k:

$$k = k_0(1-\theta)\cdot\exp(-s_1\theta-s_2\theta^\sigma) \quad (4)$$

where the parameters s_1 and s_2 characterise the electrostatic, orientational, and dispersion interactions in the adsorption layer, and the parameter σ takes account of the dependence of the energy of interaction on the distance between the adsorbed species.

A slightly different approach to the problem of the influence of SAOS on the kinetics of electrochemical processes was proposed in Refs.5 and 35. The authors cited also started from the theory of absolute reaction rates, but made a number of additional assumptions. In particular, in accordance with Refs.9 and 10, they introduced into the expression for the rate constant a coefficient $l \ll 1$, which takes account of the inhibition of the stage of ion transfer from the bulk of the solution into the structured surface layer consisting of molecules of the solvent and the SAOS. They also introduced an additional parameter r, equal to the number of solvent molecules displaced from the electrode surface by the activated complex. Assuming that the ψ_1-potential and the free energy associated with the change in the dielectric constant in the surface layer are linearly dependent on θ, they obtained the following equation:

$$k = k_0(1-\theta)^r\exp(-s\theta) \quad (5)$$

The coefficient s characterises the properties of the surface layer, and takes account of the possibility of specific interaction between the activated complex and the molecules of the adsorbate, and can take both positive and negative values. A similar equation was obtained in Ref.39. The problem of the influence of SAOS on the kinetics of electrode processes has also been examined in terms of the thermodynamics of surface phases;[40] equations of type (5) were again obtained, and various particular cases analysed.

A common unsatisfactory feature of most published work on the problem being discussed is that no sufficiently convincing theoretical basis has been given for the original relationships used to calculate the rates of electrode reactions in the presence of SAS. The semi-empirical or purely phenomenological equations used for specific calculations are often questionable, and in a number of aspects simply unsatisfactory.

In the present review, particular attention has been paid to the analysis of theoretical studies in which attempts have been made to develop a more correct approach to the quantitative examination of electrochemical processes complicated by adsorption phenomena at the metal–electrolyte solution interface. The estimation of the significance of these studies and the extent to which they correspond to real electrochemical systems starts from the fundamental fact that any adequate theory must be based on a correct statistical analysis of the process of going from the elementary act of charge transfer through the metal–solution interface to the resulting rate of the electrochemical process. Thus from the physical viewpoint, a feature of fundamental importance is that, in accordance with the Franck–Condon principle, electron transfer takes place at fixed values of the coordinates of the "heavy" species (ions, molecules) in the system. In the absence of specific adsorption, this transfer takes place at fixed positions of the ions or dipoles in the electrical double layer and in the solution. When specifically adsorbed ions or dipoles are present, however, this transfer takes place at fixed positions of all other heavy species. At the same time it is obvious that the rate of the overall heterogeneous process is averaged over the different configurations of all the heavy species in the system, that is the local probability of electron transfer must be averaged in accordance with the corresponding distribution function of all the "heavy" species in the system.

Another problem, directly related to the previous one, is associated with taking account of the effects of the discrete character of the ion or dipole charges in the system, including species undergoing specific adsorption at the metal–solution interface. Thus the local electric field acting on the discrete particles (ions, dipoles) close to the interphase boundary, as a result of the polarisation of the boundary by these particles, differs from the average field described by the Maxwell equations for a continuous distribution of dipole moments or free charges. The characteristic relaxation times of the forces of the "intrinsic electrostatic image", that is the redistribution times of the bound charges of the solvent on the interfacial surface (as a result of the polarisation of this surface by species present in the solution) are about 10^{-14}–10^{-15} s. The characteristic times of many types of electrochemical reaction, however, have orders of magnitude comparable with those of the fluctuational reorientation times of dipolar solvent molecules in the solvation layers of reactant ions ($\sim 10^{-11}$ s), that is they are greater by several powers of ten than the relaxation times of the forces of the "intrinsic electrostatic image". Thus the discrete character of the charged species and dipolar molecules adsorbed at the interface should influence the probability of the elementary act of electrochemical processes. Moreover, since the magnitude of the electric field created by the forces of the "intrinsic electrostatic image" depends to a significant extent on the state of the polarisation of the solvent close to the electrode, it follows that in a quantitative examination of the influence of the electric double layer and the effects of the discrete nature of the charge on the rate of electrode processes, an important role should also be played by a physically adequate description of the spatial non-uniformity and dispersion of the dielectric characteristics of the solvent in the layer next to the electrode.

II. PHENOMENOLOGICAL APPROACH TO THE DESCRIPTION OF THE INFLUENCE OF ORGANIC SURFACE-ACTANTS ON THE RATE OF THE DISCHARGE STAGE

1. The Physical Premises of the Theory

As noted above, the adsorption of organic substances has a significant influence on the rate of charge transfer. This influence is due to a number of factors which in the presence of organic substances lead to changes in the concentration of the reactant species in the layer next to the surface and in the activation energy of the electrode process. Thus for example if the adsorbed molecules of an organic substance are uniformly distributed over the electrode surface and the degree of coverage of the surface by these molecules is θ, then the probability of the introduction of the reactant species into the adsorption layer without allowance for all

other factors will be a fraction 1 − θ of the probability of their introduction into the adsorption layer in the solution in the absence of the added organic substance. Under these conditions, the factor 1 − θ can be related to the change in the configurational entropy of activation $\Delta\Delta s^{\neq}$:

$$1-\theta=\exp(\Delta\Delta S^{\neq}/R)$$

The interactions of the reacting species with the molecules of the SAOS and the solvent are generally different. The difference between the energies of these interactions is an additional (energetic) reason for the change in the surface concentration of reactant species in the presence of SAOS. The replacement of some solvent molecules by SAOS molecules close to the reactant species also leads to a change in the energy of reorganisation of the medium, and this in turn brings about a change in the activation energy of the elementary act of discharge. Finally, the adsorption of an organic substance on an electrode leads to a change in the distribution of the electric field of the double layer. In other words, in the presence of SAOS there is a change in the ψ_1-potential at the point where the activated complex is localised. It follows from the theory of retarded discharge that a change in the ψ_1-potential influences the rate of an electrode process both as a result of a change in the surface concentration of the reactant species (if they are charged) and as a result of a change in the activation energy (in all cases).

In many published studies, the theoretical examination of the problems of the inhibition of electrode reactions by added SAOS has taken account of the individual factors indicated, or some combination of them, with the introduction of appropriate corrections into the final equation of the theory of retarded discharge.

Thus the following equations have been obtained, reflecting the dependence on θ of the ratio $i_\theta/i_{\theta=0}$ where i_θ and $i_{\theta=0}$ are the current densities of the discharge stage at degrees of coverage of the surface by the SAOS of θ and θ = 0 respectively:

$$i_\theta/i_{\theta=0}=1-\theta \qquad [3—4]$$

$$i_\theta/i_{\theta=0}=(1-\theta)\exp(-s\theta) \qquad [5]$$

$$i_\theta/i_{\theta=0}=(1-\theta)\exp(-s_1\theta-s_2\theta^\sigma) \qquad [38]$$

$$i_\theta/i_{\theta=0}=(1-\theta)^r \qquad [6]$$

$$i_\theta/i_{\theta=0}=(1-\theta)^r\exp(-s\theta) \qquad [35]$$

The inhibition parameters s, s_1, s_2, σ, and r appearing in these equations in papers by different authors often have a different physical significance, depending on the model used and the assumptions made in the derivation of the equation. To avoid this ambiguity, a different more correct method is used in the present work to derive the fundamental inhibition equation, which does not require the introduction of corrections into the final equation of the theory of retarded discharge and which takes account of the combined adsorption of the reactant substances and the SAOS molecules.

2. Derivation of the Fundamental Inhibition Equation

It is assumed that the electrode reaction is the reduction of Ox to Red

$$Ox+ne\rightarrow Red \qquad (6)$$

the rate of which is limited by the discharge stage. Since the current density i is determined by the rate v of reaction (6), it follows from Faraday's law that

$$i=nvF \qquad (7)$$

From the theory of absolute reaction rates, the quantity v can be represented as:

$$v=(kT/h)\varkappa c_{\neq} \qquad (8)$$

Here, k is the Boltzmann constant, h Planck's constant, $\varkappa$ the transmission coefficient, and $c_{\neq}$ the concentration of the activated complex. To use Eqn.(8) for a real electrochemical system in which reaction (6) is taking place, the numerator and denominator are multiplied by the activity coefficient of the activated complex, $\gamma_{\neq}$, and by the activity of the substance Ox in the adsorbed state, $a_{Ox}^{(ads)}$.

Substituting the result in Eqn.(7) and taking account of the fact that $c_{\neq}\gamma_{\neq} = a_{\neq}$ gives

$$i=nF\varkappa\frac{kT}{h}\cdot\frac{a_{Ox}^{(ads)}}{\gamma_{\neq}}\cdot\frac{a_{\neq}}{a_{Ox}^{(ads)}} \qquad (9)$$

The theory of absolute reaction rates assumes that equilibrium is established between the original state of the system (the substance Ox in the adsorbed state and n electrons in the metal) and the activated complex. The condition for this equilibrium is given by the expression

$$\bar{\mu}_0^{(ads)}+n\bar{\mu}_e^{(m)}=\bar{\mu}_{\neq}^{(ads)} \qquad (10)$$

relating the electrochemical potentials of the participants. Since the activity of the electrons in the given metal is constant, that is

$$\bar{\mu}_e^{(m)}=\bar{\mu}_e^{0(m)}$$

$$\bar{\mu}_{Ox}^{(ads)}=\bar{\mu}_{Ox}^{0(ads)}+RT\ln a_{Ox}^{(ads)}$$

$$\bar{\mu}_{\neq}^{(ads)}=\bar{\mu}_{\neq}^{0(ads)}+RT\ln a_{\neq}$$

the condition for equilibrium (10) can be rewritten as:

$$-\Delta\bar{G}_{\neq}^0=\bar{\mu}_{Ox}^{0(ads)}+\bar{\mu}_e^{0(m)}-\bar{\mu}_{\neq}^{0(ads)}=RT\ln[a_{\neq}/a_{Ox}^{(ads)}] \qquad (11)$$

where $\bar{\mu}_j^0$ represents the standard electrochemical potentials different components j, and $\Delta\bar{G}_{\neq}^0$ the standard electrochemical free energy of activation of process (6). Substituting the ratio $a_{\neq}/a_{Ox}^{(ads)}$ from Eqn.(11) in Eqn.(9) gives

$$i=nF\varkappa\frac{kT}{h}\frac{a_{Ox}^{(ads)}}{\gamma_{\neq}}\exp\left(-\frac{\Delta\bar{G}_{\neq}^0}{RT}\right) \qquad (12)$$

Eqn.(12) is usually the starting point for the derivation of the basic relationships of the theory of retarded discharge. There is lack of agreement among different authors, however, on whether the activation energy $\Delta\bar{G}_{\neq}^0$ contains an electrical component or is determined only by the chemical activation energy. As shown above, the quantity $\Delta\bar{G}_{\neq}^0$ contains both chemical and electrical components.

To use Eqn.(12) it is necessary to obtain explicit expressions for the quantities $\Delta\bar{G}_{\neq}^0$, $a_{Ox}^{(ads)}$, and $\gamma_{\neq}$. The quantity $\Delta\bar{G}_{\neq}^0$ can be calculated using a schematic diagram representing the change in the standard electrochemical free energy of the system along the reaction path (Fig.1). This path, which corresponds to movement along the abscissa, represents provisionally the sequence of states through which the reaction system passes in the course of the reaction described by Eqn.(12).

The initial state *I* corresponds to the component Ox in the volume of the solution and n electrons in the metal; state *II* to the component Ox in the adsorption layer and n electrons in the metal; the state ≠ represents the activated complex (in the adsorption layer); state *III* corresponds to the component Red adsorbed on the electrode; and the final

state *IV* to the same component in the bulk of the solution. It is assumed that the transfer of all n electrons takes place in one elementary act.

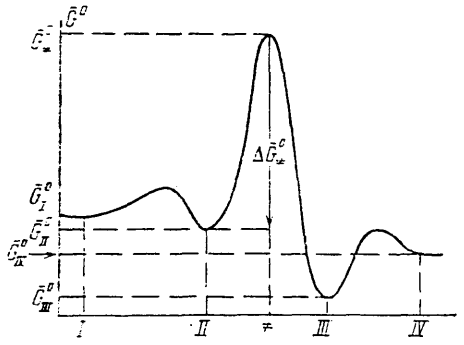


Figure 1. Diagram representing the change in the standard electrochemical free energy of a system $\bar{G}^0$ along the reaction path.

Fig.1 shows that $\Delta\bar{G}^0_{\neq} = \bar{G}^0_{\neq} - \bar{G}^0_{II}$. On the other hand, in accordance with Bronsted's principle, several different interpretations of which are possible at present, the standard electrochemical free energy of activation is given by

$$\Delta\bar{G}^0_{\neq} = \Delta\bar{G}^0_{0\neq} + \alpha(\bar{G}^0_{III} - \bar{G}^0_{II}) \qquad (13)$$

where α is the transfer coefficient ($0 \leq \alpha \leq 1$), and the constant $\Delta\bar{G}^0_{0\neq}$ corresponds to the standard free energy of activation with the condition $\bar{G}^0_{II} = \bar{G}^0_{III}$ (see Fig.1).

Analysis of the quantities appearing on the right-hand side of Eqn.(13) shows that the final expression for $\Delta\bar{G}^0_{\neq}$ can be recast in the form

$$\Delta\bar{G}^0_{\neq} = \Delta\bar{G}^0_{0\neq} + \alpha[g_{Ox} - g_{Red} - nF\psi_1 + nF(\varphi_0 - \varphi^0_0)] \qquad (14)$$

where g_{Ox} and g_{Red} are the standard energies of specific adsorption of the species Ox and Red (for positive adsorption, $g_{Ox} > 0$ and $g_{Red} > 0$), and ϕ^0_0 the standard electrode potential corresponding to reaction (6). Since the standard values of $\Delta\bar{G}^0_{0\neq}$, g_{Ox}, g_{Red}, and ϕ^0_0 are independent of the presence of SAOS in the system, it follows that at a given electrode potential (ϕ_0 = const), the dependence of $\Delta\bar{G}^0_{\neq}$ on θ is due entirely to the change in the distribution of the electric field in the double layer and is revealed by the corresponding change in the ψ_1-potential.

To find the quantities $a_0^{(ads)}$ and $\gamma_{\neq}$ appearing in Eqn.(12), it is assumed that the adsorption of each component of the solution j (except the solvent molecules) is described by isotherms of the form

$$B_j a_j = \frac{\theta_j}{r_j\left(1 - \sum_k \theta_k\right)^{r_j}} \exp\left\{-r_j \sum_k A_{jk}\theta_k + \frac{z_j F\psi_1}{RT}\right\} \qquad (15)$$

Here, B_j is the adsorption equilibrium constant, which depends on the potential; r_j the coefficient of the displacement of the solvent (water) by the component j; A_{jk} the constant of the intermolecular interaction between the components j and k; and z_j the charge number of the component j (with allowance for the sign).

Eqn.(15) represents a generalised isotherm describing the combined adsorption of both charged and neutral species within one common adsorption layer.

As shown recently,[76] it follows from Eqn.(15) that

$$a_{Ox}^{(ads)} = a_{Ox}\exp\left(\frac{g_{Ox} - z_{Ox}F\psi_1}{RT}\right) \qquad (16)$$

and under conditions in which Ox represents a weakly adsorbed inorganic ion and the solution contains no other surface-active components apart from the SAOS,

$$\gamma_{\neq} = [(1-\theta)^r \exp(rA\theta)]^{-1} \qquad (17)$$

Here, a_{Ox} is the bulk activity of the substance Ox; $r = r_{\neq}$ the coefficient of the displacement of the solvent by the activated complex; θ the degree of coverage of the surface by the SAOS; and A the constant of the intermolecular interaction between the activated complex and the SAOS molecules.

Substituting Eqns.(14), (16), and (17) in Eqn.(12) gives an expression for the discharge current of reaction (6) in the presence of SAOS:

$$i_\theta = nFk^0_s \cdot \exp\left\{\frac{(1-\alpha)g_{Ox} + \alpha g_{Red} + (\alpha n - z_{Ox})F\psi_{1(\theta)}}{RT}\right\} \times$$
$$\times a_{Ox} \cdot \exp\left[-\frac{\alpha nF(\varphi_0 - \varphi^0_0)}{RT}\right] \cdot (1-\theta)^r \exp(rA\theta) \qquad (18)$$

where $k^0_S = (\varkappa kT/h).\exp(-\Delta\bar{G}^0_{0\neq}/RT)$ is the absolute heterogeneous rate constant of the electrochemical reaction.

If the addition of the SAOS does not change the bulk activity of the reaction substance (a_{Ox} = const) and does not change the mechanism of the electrode process (k^0_S = const and α = const), it follows from Eqn.(18) that

$$i_{\theta=0} = nFk^0_s a_{Ox} \cdot \exp\left\{\frac{(1-\alpha)g_{Ox} + \alpha g_{Red} + (\alpha n - z_{Ox})F\psi_{1(\theta=0)} - \alpha nF(\varphi_0 - \varphi^0_0)}{RT}\right\} \qquad (19)$$

Thus for a given ϕ_0 = const, the following expression is obtained:

$$\frac{i_\theta}{i_{\theta=0}} = (1-\theta)^r \exp\left\{\frac{(\alpha n - z_{Ox})F[\psi_{1(\theta)} - \psi_{1(\theta=0)}]}{RT} + rA\theta\right\} \qquad (20)$$

It is convenient to break down the ψ_1-potential into two terms:

$$\psi_1 = \psi_0 + \psi_a \qquad (21)$$

where ψ_0 is the potential of the outer Helmholtz plane, which can be calculated from the Gouy–Chapman equation using the experimentally established dependence of the charge on the electrode q on θ. For the quantity ψ_a, in a first approximation, a linear dependence on θ is postulated:

$$\psi_{a(\theta)} = \psi_{a(\theta=0)} - k'\theta \qquad (22)$$

where k' is a constant determined by the position of the activated complex in the compact layer and by the dielectric properties of the latter.

With allowance for Eqns.(21) and (22), Eqn.(20) can be transferred to

$$\frac{i_\theta \cdot \exp[-(\alpha n - z_{Ox})F\psi_{0(\theta)}/RT]}{i_{\theta=0} \cdot \exp[-(\alpha n - z_{Ox})F\psi_{0(\theta=0)}/RT]} = (1-\theta)^r \exp(-s\theta) \qquad (23)$$

where s is the inhibition parameter, equal to

$$s = k'(\alpha n - z_{Ox})F/RT - rA$$

The parameter s reflects both the electrostatic and the "chemical" interaction of the activated complex with the adsorption layer. The other inhibition parameter, r, is related to the change in the configurational entropy of

activation $\Delta s^{\neq}$:

$$r \ln(1-\theta) = \Delta(\Delta S^{\neq}/R)$$

Thus examination of the derivation of the fundamental equation of the theory of retarded discharge under the conditions of SAOS adsorption gives Eqn.(23), the right-hand side of which has the form proposed in Ref.35. As shown by the present authors, however, the left-hand side should contain not the usual values of the discharge currents i_θ and $i_{\theta=0}$ but the corresponding quantities with a correction for the change in the potential of the outer Helmholtz plane in the presence of SAOS. This correction is easily introduced by means of the Gouy–Chapman equation using the experimentally determined dependence of q on θ. Thus for example in the case of a solution containing an excess of a surface-inactive 1,1-valent electrolyte with a concentration c_{el},

$$\psi_0 = (2RT/F)\,\mathrm{arcsh}[q/(8\varepsilon_0\varepsilon RT c_{el})^{1/2}]$$

where ε_0 is the dielectric constant of a vacuum, and ε the dielectric constant of the solvent.

III. LOCALISED ADSORPTION OF IONS AND DIPOLAR MOLECULES

In this section, the statistical-mechanical theory of irreversible electrochemical processes complicated by the localised adsorption of inactive ions and molecules is discussed. A central problem in the development of a statistical-mechanical theory describing the influence of SAS on the kinetics of electrochemical processes is the development of an adequate approach to the statistical averaging of the probability of the elementary act of electron transfer over the entire ensemble of "heavy" species in the system. The principles of this approach were described in papers[41,42] dealing with allowance for the influence of the local electric field of the double layer in the equations for the statistical averaging of the probability of the elementary act. In particular, it was shown that the problem of finding the statistically averaged density of the current generated in the elementary act of an electrochemical process can be solved satisfactorily only in two cases: 1) when the electrochemical process does not break down the statistical equilibrium either with respect to the reactants or with respect to the ions of the inactive electrolyte, and 2) when there is no equilibrium with respect to the reacting species, but the reaction takes place in an excess of an electrochemically indifferent electrolyte. The latter should be distributed in space in a quasi-equilibrium fashion, in the sense that its local concentration at each fixed moment of time should be described by the Boltzmann equation, and the magnitude of the field is determined by the instantaneous (not necessarily equilibrium) value of the electrode potential.

The extension of these methods to systems with specific adsorption of ionic and dipolar components of the solution, including the adsorption of reactant species, pointed the way to the development of a quantitative theory of electrochemical kinetics in the presence of SAS.[43–57,60,63,71] This theory takes unified account of inter-particle interaction in an adsorption layer, the influence of the fine structure of the electrical double layer and the influence of the discrete nature of adsorbed ionic or dipolar charges, etc. on the averaged kinetic characteristics of the process.

To illustrate the essential features of the present theory, the irreversible electrochemical reaction of one-electron transfer (6) for $n = 1$, that is the reaction $Ox_z + e \to Red_{z-1}$, where the indices z and $z-1$ of Ox and Red denote the charges of the corresponding ions†, can be considered. It is assumed below that this reaction takes place under conditions in which the centres of specifically adsorbed electrochemically inactive ions are situated within the Helmholtz layer or, more accurately, the reaction layer ($-\beta \leqslant x \leqslant \gamma$ and $\delta = \beta + \gamma$, where δ is the thickness of this layer).

It will be assumed that the positions of the centres of the adsorbed ions are characterised by the coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_M$ (in the general case, $\mathbf{r}_k$ also denotes all other degrees of freedom of the particles, so that, for example, for dipolar molecules, it includes the orientational and other degrees of freedom of the given particles). The positions of all other species of the solution, including the reactant ions, will be denoted $\mathbf{R}_1, \ldots, \mathbf{R}_N$.

According to the general principles of the theory of the kinetics of heterogeneous processes, the probability W of the elementary act of interphase electron transfer is an exponential function of the activation energy of the process E_a:

$$W(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M) = \bar{O}x(\mathbf{R}_1)\cdot\exp(-E_a/kT) \qquad (24)$$

where $\bar{O}x(\mathbf{R}_1)$ is a function which includes the transmission coefficient for the given process. The factor $\bar{O}x = \bar{O}x_z$ is specially distinguished here, since the probability being considered is that of electron transfer to the ion $Ox = Ox_z$ situated at the point $\mathbf{R}_1$, and this factor contains the strongest dependence of W on $\mathbf{R}_1$. The dependence of E_a on the heat of reaction ΔI, however, can be described either strictly quantum-mechanically[58,59] or using the Bronsted relationship. In the general case, the Bronsted relationship is non-linear $E_a = E_a(\Delta I)$, but there is often a linear relationship between E_a and ΔI, that is $E_a = E_a^0 + \alpha\cdot\Delta I$, where α is the transfer coefficient.

From ΔI it is appropriate to separate the quantity ΔI_0, which is defined by the relationship

$$\Delta I_0(\varphi_0, \mathbf{R}_1) = E_{Ox} - E_m + E_{Red}^{(solv)} - E_{Ox}^{(solv)} + e\varphi_0 + U_{Red}^{(im)}(\mathbf{R}_1) - U_{Ox}^{(im)}(\mathbf{R}_1) \qquad (25)$$

and which takes specific account of the stage of electron transfer from the energy level E_m in the metal to the level E_{Ox} in the ion $Ox = Ox_z$. Thus the total heat of the reaction is written as:

$$\begin{aligned}\Delta I(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M) &= \Delta I_0(\varphi_0, \mathbf{R}_1) + \\ &+ [V_{Red}(\mathbf{R}_1, \ldots, \mathbf{R}_N) - V_{Ox}(\mathbf{R}_1, \ldots, \mathbf{R}_N)] + \\ &+ [\Omega_{Red}(\mathbf{R}_1, \mathbf{r}_1, \ldots, \mathbf{r}_M) - \Omega_{Ox}(\mathbf{R}_1, \mathbf{r}_1, \ldots, \mathbf{r}_M)]\end{aligned} \qquad (26)$$

In Eqns.(25) and (26), the quantities $E_{Red}^{(solv)}$ and $E_{Ox}^{(solv)}$ are the solvation energies of the ions Red and Ox, ϕ_0 the electrode potential (relative to the bulk of the solution it can be taken as zero), $U_{Red}^{(im)}$ and $U_{Ox}^{(im)}$ the energies of the interactions of the ions Red and Ox with the "electrostatic images" of these ions in the metal and in the electrolyte solution, and V_{Red} and V_{Ox} the energies of the interactions of the ions Red and Ox with the adsorbed ions and the "electrostatic images" of the latter in the metal and solution.

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†Here and subsequently, for uniformity of indexing, this method will be used to represent the reaction which in Refs.43–57 and subsequent papers is represented as $A^z + e \to B^{z-1}$, that is, subsequently, $Ox = Ox_z$ will be written throughout instead of A^z, and $Red = Red_{z-1}$ instead of B^{z-1}.

The probability of the elementary act W is related to the current density i passing through the system by the expression

$$i = e[\mathrm{Ox}]f\langle W\rangle \qquad (27)$$

where [Ox] is the total number of reactant ions in the solution, and $f = f(\theta)$ a factor which allows for the "effective area" of the electrode surface on which the reaction can take place. The angle brackets denote the operation of statistical averaging of the quantity W over the entire system of "heavy" species present in the solution, including specifically adsorbed species. For the general case of an arbitrary non-linear dependence of E_a on ΔI, the quantity $\langle W\rangle$ is conveniently represented[50] as a contour integral in the complex plane, which in a number of cases is effectively calculated by the method of steepest descent.

It should be emphasised that the averaging of the quantity W depends to a significant extent on the form of the distribution function D_{N+M} of all $N + M$ "heavy" species in the system. At a low concentration of reactant ions, the function D_{N+M} can be written as $D_{N+M} = \Phi_Z(\mathbf{R}_1).D_{N-1,M}$, where $\Phi_Z(\mathbf{R}_1)$ is the one-particle distribution function of the ions Ox_Z, and $D_{N-1,M}$ the distribution function of all other species, with the condition that the reactant ion Ox is situated at the point $\mathbf{R}_1$. The form of the function $D_{N-1,M}$ in turn depends on the nature of the adsorption. The following three physical situations are possible in principle:[50] a) during the characteristic time of the electrochemical reaction, the adsorbed ions remain at the points where they are localised on the electrode surface, that is they act as sources of an additional external field; (b) adsorption is reversible, and in the characteristic time of the electrochemical reaction, equilibrium can be established between the adsorbed ions and the ions in the bulk of the solution; c) in the characteristic time of the electrochemical process, the adsorbed ions are unable to exchange with the ions in the bulk of the solution.

The results for case (a) are given below. In this case

$$\langle W\rangle = \int W(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M)\, D_{N+M}(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M) \times \times d\mathbf{R}_1 \ldots d\mathbf{R}_N \qquad (28)$$

and the final result can be represented as

$$i = i_{z-\alpha}(\varphi_0, \theta)\cdot f(\theta)\cdot \exp\{-\Omega_{z-\alpha}(\theta)/kT\} \qquad (29)$$

$$_{-\alpha}(\varphi_0, \theta) = \mathrm{const}\cdot \exp\left\{-\frac{E_a^{(0)} + \alpha e\varphi_0}{kT}\right\}\cdot \exp\left(\frac{\Delta U^{(*)} + F_z - F_{z-\alpha}}{kT}\right)\Phi_{z-\alpha}(x_0) \qquad (30)$$

$$\Omega_{z-\alpha}(\theta) = \frac{e^2 z_0 (z-\alpha)}{\epsilon_{\mathrm{pl}}}\sum_{(m,n)}\int_0^\infty \chi(\lambda)\cdot \exp(-\lambda x_0)\cdot J_0(\lambda R_{mn})\, d\lambda \qquad (31)$$

here z_0 is the charge of the adsorbed ion, ϵ_{pl} the effective dielectric constant of the reaction region, $J_0(x)$ the Bessel function of the first kind of zeroth order, R_{mn} the distance from the centre of the ion Ox (in the adsorption plane) to an arbitrary ion having coordinates (ξ_{mn}, η_{mn}) in this plane, $\chi(\lambda)$ a definite function of the integration variable , and the summation is carried out over the entire system adsorbed ions. The plane $x = x_0$ corresponds to the stance of the most probable point for the discharge of the ns from the electrode, and the quantity $\Delta U^{(*)}$ is a mbination of the quantities $U^{(\mathrm{im})}_{\mathrm{Ox}}$ and $U^{(\mathrm{im})}_{\mathrm{Red}}$ at the point . The quantities F_Z and $F_{Z-\alpha}$ are the partial free ergies of the system of ions present in the solution, nus the energy of the interaction of an ion having a harge ez or $e(z - \alpha)$ respectively with the "intrinsic ectrostatic image" in the metal and the solution, $\Phi_{Z-\alpha}(x_0)$ the paired distribution function of the ions; and $\Omega_{Z-\alpha}(\theta)$ e energy of the interaction of the discharging ion with all the adsorbed ions (and their "electrostatic images" in the metal and the solution), which is calculated for the transition state of the discharging ion, characterised by the "effective charge" $e(z - \alpha)$. Under the conditions of the localised adsorption of ions it is necessary to examine in principle both the regular distribution of their adsorption centres (for example the ionic lattice model) and random distribution of the adsorption centres. In a number of cases, the calculations of $\Omega_{z-\alpha}$ are simplified by using the so-called "cut-out disc model"[77] and replacing the summation, for example in Eqn.(31), by integration according to the scheme:

$$\sum_{m,n} J_0(\lambda R_{mn}) \to 2\pi\Gamma_\infty\theta\int_{r_0}^\infty \rho J_0(\lambda\rho)\, d\rho \qquad (32)$$

where r_0 is the radius of the cut-out disc, which depends on the degree of coverage θ, and Γ_∞ is the limiting coverage of the adsorption layer. This model is naturally an approximation to the real situation.

A specific calculation based on the above procedure, carried out in Refs.46 and 47, with the condition that there is a linear relationship between E_a and ΔI, gives the following expression for the rate of the electrochemical process:

$$i = \mathrm{const}\cdot f(\theta)\cdot \exp\left\{-\frac{\alpha e[\varphi_0 - \varphi(x_0, \theta)] + \Omega_{z-\alpha}(\theta)}{kT}\right\} \qquad (33)$$

It was assumed that the discharge takes place from the compact part of the electrical double layer, and that the solution contains an excess of a background electrolyte, so that the diffuse character of the double layer can be neglected (the last assumption is more justified, the smaller the ratio $\epsilon_{\mathrm{pl}}/\epsilon_0$, where ϵ_0 is the dielectric constant of the diffuse region of the double layer). In Eqn.(33), k is the Boltzmann constant, and $\phi(x_0, \theta)$ is the potential of the plane in which the ion Ox is situated, and depends on the degree of coverage of the layer θ by adsorbed ions. The latter are situated in the adsorption plane $x = 0$; (ξ_{mn}, η_{mn}) are the coordinates of the adsorbed ions in this plane.

The physical significance of the quantity $\Omega_{z-\alpha}$ in Eqn.(33) was explained above, and the next task is the specific calculation of this quantity. In Ref.56 it was calculated with allowance for the effect of the penetration of the electric field into the metal (that is the double layer in the metal itself, or in other words the "electron condenser" factor together with the "molecular dipole condenser" in the solution phase of this interphase boundary):

$$\Omega_{z-\alpha}(\theta) = \frac{e^2 z_0 (z-\alpha)}{\epsilon_{\mathrm{pl}}}\cdot\sum_{m,n}\left\{(R_{mn}^2 + x_0^2)^{-1/2} - \right.$$
$$\left. - [R_{mn}^2 + (x_0 - 2\gamma)^2]^{-1/2} - \int_0^\infty \Lambda(x_0, \lambda)\cdot J_0(\lambda, R_{mn})\, d\lambda\right\} \qquad (34)$$

Here, $R_{mn} = (\xi_{mn}^2 + \eta_{mn}^2)^{1/2}$, and the function $\Lambda(x_0, \lambda)$ under the integral sign has the form

$$\Lambda(x_0, \lambda) = \frac{[\exp(2\lambda\gamma) - 1]\cdot\{\exp[\lambda(x_0 - 2\gamma)] - \exp(-\lambda x_0)\}}{\left[1 + \left(\frac{2}{\nu} - 1\right)\cdot\exp(2\lambda\delta)\right]} \qquad (35)$$

and

$$\nu = \nu(\lambda) = 1 - (\epsilon_{\mathrm{pl}}\lambda)^{-1}\epsilon_s(\lambda^2 + \kappa_m^2)^{1/2} \qquad (36)$$

$$\Delta\varphi_s - \kappa_m^2\varphi_s = 0 \qquad (37)$$

In the derivation of Eqns.(34)–(36), the electron density distribution in the region of the metal next to the surface was described in the Thomas–Fermi linear approximation (37); ϵ_S is the short-wave ("optical") dielectric constant of the metal, characterising the polarisability of the valence electrons of the ionic core of the metal; κ_m^{-1} the Thomas–Fermi length for the electrons of the metal (for

a number of metals, the value of ε_s is close to 1, and the value of κ_m^{-1} is ~1 Å). The Thomas–Fermi distribution of electrons in the metal is the simplest model of the double layer in the metal, but it makes it possible to reveal the principal physical aspects of the phenomenon. A more rigorous but mathematically much more complex approach to this problem involves taking account of collective effects in the shielding, allowance for the discrete nature of the ion charge in the metal itself, and other factors.

In Refs. 46 and 47, the following equation was obtained for calculating the quantity $\Omega_{z-\alpha}$ in Eqn. (33) for the inactive ion adsorption conditions being considered:

$$\Omega_{z-\alpha}(\theta) = \frac{e^2 z_0 (z-\alpha)}{\varepsilon_{pl} x_0} - \frac{e^2 z_0 (z-\alpha)}{\varepsilon_{pl}\delta}\left[\Psi\left(\frac{2\delta - x_0}{2\delta}\right) + \Psi\left(\frac{2\delta + x_0}{2\delta}\right) - \Psi\left(\frac{2\gamma - x_0}{2\delta}\right) - \Psi\left(\frac{2\beta + x_0}{2\delta}\right)\right] + \frac{4e^2 z_0 (z-\alpha)}{\varepsilon_{pl}\delta} \sum_{m,n} \sum_{p=1}^{\infty} \sin\left(\frac{\pi p \beta}{\delta}\right) \cdot \sin\left[\frac{\pi p (x_0 + \beta)}{\delta}\right] \cdot K_0\left(\frac{\pi p}{\delta} R_{mn}\right) \quad (38)$$

Here, Ψ is the Euler psi-function, and $K_0(x)$ the zeroth-order McDonald function, which, as in higher orders, has an exponential asymptote at large values of the argument.

The statistical-mechanical theory developed in Refs. 41 to 47 reveals the mechanism of the influence of the electric field, created by specifically adsorbed ions, on the rate of electrode processes. In Eqn. (38) the local electric field appearing in the statistically averaged probability of electron transfer corresponds to the effective configuration of the ionic components of the solution close to the given reactant ion which would be in equilibrium with the reactant if the charge on the latter were $e(z - \alpha)$. The ion with charge $e(z - \alpha)$ is in a certain sense the analogue of the activated complex appearing in the theory of absolute reaction rates. Contrary to the conclusions of this theory, however, the resulting rate of the electrode process is determined by the local electric potential, and not by the average potential corresponding to continuously distributed ionic charges.

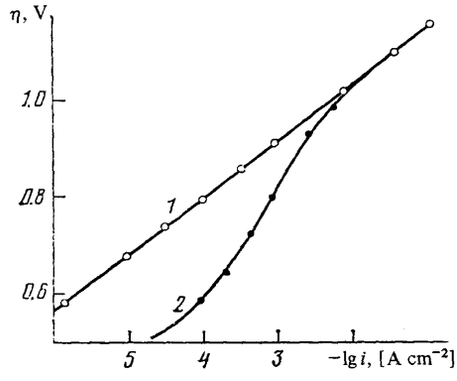


Figure 2. Polarisation curves for the discharge of hydrogen ions on mercury from aqueous solutions of 1 M HCl + 2 M KCl (*1*) and 1 M HCl + 2 M KI (*2*); continuous lines—result of the theoretical calculation.[46,47]

In Refs. 46 and 47, the results of calculations based on Eqns. (33) and (38) were used to describe the experimental data from Refs. 1 and 64 on the kinetics of the discharge of hydrogen ions on mercury from mixed aqueous HCl + KCl and HCl + KI solutions. The pre-exponential constant appearing in Eqn. (33) was determined by combining the experimental and theoretical curves in the range of the desorption of the iodide ions. The quantity x_0 was used as the fitting parameter of the theory. Quantitative agreement between theory and the experimental data was achieved for the following values of the remaining parameters: $\alpha = 0.5$, $\beta = \gamma = 2.3$ Å, $\Gamma_\infty = 6 \times 10^{14}$ cm^{-2}, $\varepsilon_{pl} = 8$, $x_0 = 1.5$ Å (see Fig. 2).

A more detailed analysis of the applicability of Eqns. (33) and (38) for interpreting published data on the influence of the adsorption of ions on the rates of electrochemical reactions were carried out in Refs. 65 and 66. In particular, it was shown that Eqn. (38) gives good agreement between theory and experimental data when the charges on the inactive adsorbed ions and the reactant ions have the same sign. It should be noted, however, that the agreement between theory and experimental data obtained in Refs. 65 and 66 was achieved using additional model representations not present initially in the theoretical equations (33) and (38).

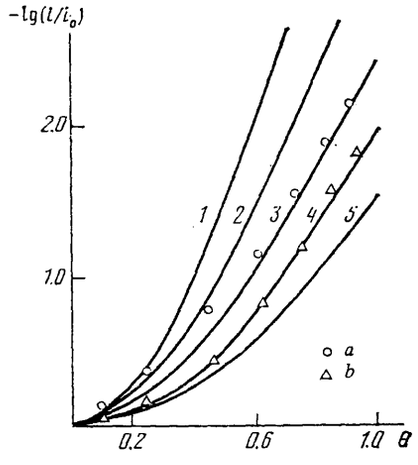


Figure 3. Inhibition of the electroreduction of cadmium cations in the presence of t-butylamine (*a*) and t-butyl alcohol (*b*); the continuous lines give the results of the calculation with the following fixed values of the parameters: $\alpha = 0.5$, $\delta = 3$ Å, $\Gamma_\infty = 1.5 \times 10^{14}$ cm^{-2}, $x^0 = 1.5$ Å, $z = 2$, $z_0 = 1$, $\varepsilon_{pl} = 8$ and different $x_a = 0.5$, 1.0, 1.5, 2.0, and 2.5 Å (curves *1*–*5* respectively).

Fig. 3 gives the experimental data obtained[67] by measuring the currents for the electrochemical reduction of cadmium cations at a mercury electrode from concentrated aqueous $HClO_4$ solution in the presence of added t-butylamine and t-butyl alcohol. Since these surface-active substances can be adsorbed on mercury from an acidic medium in two forms, neutral and cationic, the rates of the electroreduction were calculated using Eqns. (33) and (38), which take account of the ionic nature of the adsorbed species. Since the theoretical equations contain several parameters for which no reliable experimental values exist (these parameters are, for example ε_{pl}, δ, α, x_0, x_a), the calculations are qualitative. The main aim was to establish the general trend in the influence of cationic SAS in relation to their

position relative to the electrode surface. This problem was solved by constructing a series of curves corresponding to a fixed distance x_0 (for constant values of all other parameters of the theory) for varying distances x_a. The results of the calculations (see curves *1–5* in Fig.3) indicate that the inhibition effect increases with decrease in x_a. A qualitatively different dependence of the rate of electrolytic reduction on the degree of coverage is observed when the charges on the ions of the adsorbate and the depolariser have different signs.[66,68] This case is examined theoretically in the next section.

The physical principles on which the derivation of Eqn.(33) was based have been used[48,49] to describe the kinetics of electrochemical reactions in the presence of adsorbed inactive dipolar molecules. In the case of the localised adsorption of dipolar molecules, the rate of the electrochemical process is described by Eqn.(39), which is analogous to Eqn.(33):

$$i = i_0(1-\theta)\cdot\exp\left\{\frac{1}{kT}\left[\frac{4\pi e(z-\alpha)\mu x_0\Gamma_\infty\theta}{\epsilon_{p1}\delta} - \Omega_{z-\alpha}(\theta)\right]\right\} \qquad (39)$$

where

$$\Omega_{z-\alpha}(\theta) = \frac{4\pi e(z-\alpha)\mu}{\epsilon_{p1}\delta^2}\sum_{m,n}\cos\sigma_{mn}\sum_{p=1}^{\infty} p\sin\left(\frac{\pi p x_0}{\delta}\right)\times$$
$$\times\cos\left(\frac{\pi p x_a}{\delta}\right)K_0\left(\frac{\pi p}{\delta}\cdot R_{mn}\right) + \frac{4\pi e(z-\alpha)\mu}{\epsilon_{p1}\delta^2}\sum_{m,n}\sin\sigma_{mn}\times$$
$$\times\cos\gamma_{mn}\sum_{p=1}^{\infty} p\cdot\sin\left(\frac{\pi p x_0}{\delta}\right)\cdot\sin\left(\frac{\pi p x_a}{\delta}\right)\cdot K_1\left(\frac{\pi p}{\delta}R_{mn}\right) \qquad (40)$$

The current density i_0 corresponds to the absence of adsorbed dipoles. μ denotes the dipole moment of the adsorbed molecule, and $\mu > 0$ if the dipole is oriented with its negative pole towards the electrode surface; σ_{mn} and γ_{mn} are the angles characterising the orientation of the dipole with respect to the electrode surface and the reactant ion; and x_0 and x_a the positions of the planes in which the centres of the reactant ion and the adsorbed dipoles are localised.

As expected, in the theories adopted for the structure of the adsorption layer, the functional dependence $i(\theta)$ contains in explicit form the values of the angles of orientation of the adsorbed dipoles relative to the electrode surface.[48,49] To determine the influence of the spatial orientation of the adsorbed dipolar molecules on the rate of discharge of the cations, Eqns.(39) and (40) were used to construct two series of curves. The following parameters were unchanged in all the calculations: $\alpha = 0.5$, $\delta = 4$ Å, $x_a = 3$ Å, $x_0 = 2$ Å, $\varepsilon = 8$, $\mu = -1.6$ D, $\Gamma_\infty = 1.5\times10^{14}$ cm^{-2}, $z = 2$. Fig.4*a* gives three curves corresponding to the fixed angle $\sigma_{mn} = 45°$ and three different angles γ_{mn}: 120°, 90°, and 60° (curves *1*, *2*, and *3* respectively). The influence of the angle σ_{mn} (for a fixed angle $\gamma_{mn} = 90°$) is shown in Fig.4*b*, where curves *1–5* correspond to the angles $\sigma_{mn} = 15°$, 30°, 45°, 60°, and 90°. In the calculation it was assumed that the centres of the adsorbed molecules form a regular two-dimensional hexagonal lattice and that the reactant ion is situated at the centre of an equilateral triangle formed by three adjacent dipoles. Comparison of the two series of curves in Figs.4*a* and 4*b* shows that the influence of the orientation of the dipoles relative to the reactant ion is stronger than the influence of the angle of inclination to the plane of the electrode.

As in the case of adsorbed inactive ions examined above, the aim of the authors cited[48,49] was not a quantitative comparison of theory with available experimental data (a comparison of this kind has been carried out,[48,51] and gave positive results). It appears much more important and useful to demonstrate the fundamental predictive possibilities of the theory and to analyse the sensitivity of the analytical relationships obtained above to change in the model parameters. The qualitative analysis carried out shows that a satisfactory description of the experimental data can be obtained with completely realistic values of the parameters. In particular, data on the kinetics of the discharge of cadmium and zinc ions in the presence of n-butanol[6,69,70] agree well with the results of a calculation based on Eqns.(39) and (40) and using the values of δ, α, ε, x_0, and x_a most frequently encountered in the literature for systems of this kind (see Refs.48 and 51).

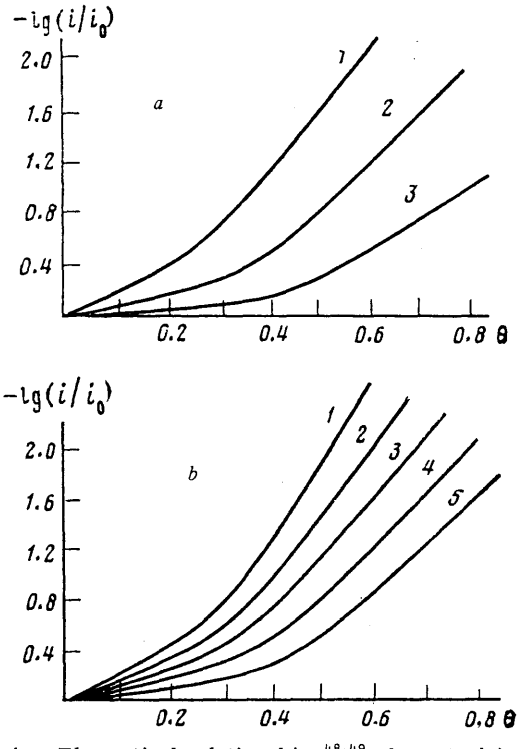


Figure 4. Theoretical relationships[48,49] characterising the effect of the inhibition of an electrode process by adsorbed dipolar molecules (the reduction of doubly-charged cations on mercury in the presence of molecules with $\mu = -1.6$ D, oriented mainly with the positive pole towards the electrode): *a*) influence of the orientation of the dipole relative to the reactant ion; *b*) influence of the orientation of the dipole relative to the electrode surface.

Analysis of Eqn.(39) shows that in those cases where the contribution of the interaction described by the term $\Omega_{z-\alpha}(\theta)$ predominates, an increase in the rate of the electrode process by adsorbed SAS is possible.[71] This effect should increase in systems in which the structure of the compact part of the double layer is such that the discharge plane of the ions is situated closer to the poles of the dipoles whose sign is the opposite of that of the charge on the discharging ions. A double-layer structure of this kind is apparently characteristic of the system studied in Ref.72, where a considerable increase in the rate of the discharge of europium ions on mercury from aqueous N,N-dimethylformamide solutions was observed. A number of other systems in which

the adsorption of organic molecules leads to an increase in the rate of electrochemical processes have been described.[33,73–75]

To explain the experimental data,[72] the authors cited obtained the following equation describing the kinetics of the discharge of the ions ez in this system:

$$i = i_0(1-\theta)\exp\left\{-\frac{e(z-\alpha)\Delta\varphi_{ads}+\Omega_{z-\alpha}(\theta_1,\theta_2)}{kT}\right\} \quad (41)$$

Here, $\theta = \theta_1 + \theta_2$ is the total degree of coverage, and $\Delta\phi_{ads}$ the adsorption potential jump, given by:

$$\Delta\varphi_{ads} = -\frac{4\pi}{\epsilon_{pl}\delta}[\mu_1\Gamma_{1,\infty}(\delta - x_0)\theta_1 - \mu_2\Gamma_{2,\infty}x_0\theta_2] \quad (42)$$

The energy of the electrostatic interaction of the reactant ion in the transition state, corresponding to the charge $e(z-\alpha)$, and the adsorbed species is given by the expression:

$$\Omega_{z-\alpha}(\theta_1,\theta_2) = \frac{4\pi e(z-\alpha)}{\epsilon_{pl}\delta^2}\sum_{p=1}^{\infty} p\cdot\sin\left(\frac{\pi p x_0}{\delta}\right)\left\{\mu_1\cdot\cos\left(\frac{\pi p x_1}{\delta}\right)\sum_{m_1,n_1}K_0\left(\frac{\pi p}{\delta}R_{m_1n_1}\right) + \right.$$
$$\left. + \mu_2\cdot\cos\left(\frac{\pi p x_2}{\delta}\right)\sum_{m_2,n_2}K_0\left(\frac{\pi p}{\delta}R_{m_2n_2}\right)\right\} \quad (43)$$

where the summation with respect to the indices m_K, n_K should be carried out in the corresponding adsorption plane ($x = x_1$ or $x = x_2$). With allowance for these results, Eqns.(41)–(43) were used to calculate the dependence of the ratio i/i_0 on the relative concentration of the organic phase in the water–organic solvent system.

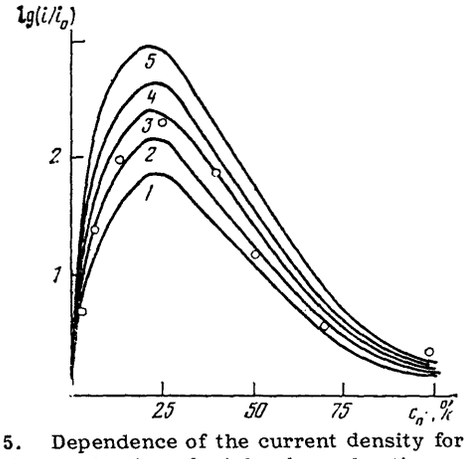


Figure 5. Dependence of the current density for the one-electron reduction of triply-charged cations on the relative composition of the mixed solvent, calculated from Eqns.(39) and (40) (c_0 is the concentration of the organic solvent); curves *1–3* correspond to values of the dipole moment μ equal to −2.5, −3.2, −3.9, −4.6, and −5.3 D; the experimental points were taken from Ref.72.

In the calculations it was assumed that in the adsorbed state the dipole moments of the molecules of both solvents are oriented at right angles to the electrode surface (the water molecules with their negative poles towards the electrode, and the organic molecules with their positive poles) and are fixed at the points of a rigid hexagonal lattice. In addition, it was assumed that $\alpha = 0.5$, $x_1 = 1$ Å, $x_0 = 2$ Å, $x_2 = 3$ Å, $\delta = 5$ Å, $\Gamma_{1,\infty} = 5.5 \times 10^{14}$ cm^{-2}, $\Gamma_{2,\infty} = 1.2 \times 10^{14}$ cm^{-2}, $\mu_2 = 1.8$ D; the value of μ_1 (the dipole moment of the molecule of the organic solvent) was varied from −2.5 D to −5.3 D. The results of the calculations[48,49] are given in Fig.5, which also gives the experimental points obtained for the water–N,N-dimethylformamide system in Ref.72. The simplified character of the picture of the structure of the electrical double layer assumed in the calculations, and the extremely approximate nature of the parameters used, do not provide a basis for a quantitative comparison of the results of the calculation with experimental data. Qualitative agreement can be seen, however, between the theoretical curves in Fig.5 and the experimental data.[72]

The general statistical-mechanical approach described above can be used to calculate the rates of electrochemical processes with allowance for the combined adsorption of several different SAS. Effects of this kind are reflected in the form of the curves giving the dependence of the current density on the degree of coverage.[78] With an adequate quantitative theory, the form of these curves can be used to obtain information on the composition of the adsorption layers next to the electrode.

A method has been proposed[57] for including the effects of the combined adsorption of two surface-active substances in the description of the kinetics of an electrode reaction. A model of the structure of the adsorption layer with two planes ($x = x_1$ and $x = x_2$) in which the centres of the adsorbed species (ions or dipolar molecules) are localised, and a discharge plane $x = x_0$ was examined. This model was used to derive a kinetic equation analogous to Eqn.(41). Cases of the combined adsorption of two different ions or two different dipoles, and also of individual ions with charge ez_1, and dipoles (for which the projection of the dipole moment on the perpendicular to the plane of the electrode was $\mu = \mu_1$) were examined. For the last case, in particular, the energy $\Omega_{z-\alpha}(\theta_1, \theta_2)$ is given by the expression:

$$\Omega_{z-\alpha}(\theta_1,\theta_2) = \frac{4\pi e(z-\alpha)\mu}{\epsilon_{pl}\delta^2}\sum_{m_1,n_1}\sum_{p=1}^{\infty} p\cdot\sin\left(\frac{\pi p x_0}{\delta}\right)\cdot\cos\left(\frac{\pi p x_1}{\delta}\right)\cdot K_0\left(\frac{\pi p}{\delta}R_{m_1n_1}\right) +$$
$$+ \frac{4\pi e^2 z_1(z-\alpha)}{\epsilon_{pl}\delta}\sum_{m_2,n_2}\sum_{p=1}^{\infty}\sin\left(\frac{\pi p x_0}{\delta}\right)\cdot\sin\left(\frac{\pi p x_2}{\delta}\right)K_0\left(\frac{\pi p}{\delta}R_{m_2n_2}\right) \quad (44)$$

In the case of the adsorption of two different dipolar molecules with dipole moments μ_1 and μ_2, the corresponding expression for $\Omega_{z-\alpha}(\theta_1, \theta_2)$ has the form (43). To determine the nature of the kinetic curves corresponding to an electrochemical process complicated by the influence of the adsorption of different combinations of SAS, numerical calculations were carried out[57] to determine the dependence of the ratio i/i_0 on θ for the discharge of doubly-charged cations in the presence of two dipolar electrochemically inert SAS, oriented in different ways. The following values were selected for the parameters: $\delta = 5$ Å, $x_0 = 1$ Å, $x_1 = 2$ Å, $x_2 = 3$ Å, $\alpha = 0.5$, $\Gamma_{1,\infty} = \Gamma_{2,\infty} = 1.5 \times 10^{14}$ cm^{-2}; the dipole moments μ_1 and μ_2 were assumed to be 1 CGSE unit. The energy $\Omega_{z-\alpha}(\theta_1, \theta_2)$ was calculated from Eqn.(43), but in contrast to the analysis represented by the graphs in Fig.6, the relationship $\theta_1 = f(\theta_2)$ was not determined; it was assumed that $\theta_2 = 1$, and θ_1 was varied. The results of the calculation are given in Fig.6. Qualitative agreement is observed between the calculated graphs for the degree of inhibition and the experimental curves obtained in Ref.78.

IV. NON-LOCALISED ADSORPTION OF INACTIVE IONS AND MOLECULES AT AN ELECTRODE/SOLUTION INTERFACE

In the examination of the case of the non-localised adsorption of ions and molecules at an electrode/solution interface it is also necessary to carry out statistical averaging of the

probability of the elementary act over the entire ensemble of adsorbed species. A procedure for this averaging has been developed,[52,53] and on the basis of the previously described general approach the authors cited obtained the following expression for the rate of a one-electron reduction:

$$i = \text{const} \cdot (1 - \theta) \cdot \exp\left\{-\frac{\alpha e [\varphi_0 - \varphi(x_0, \theta)] - \Delta F}{kT}\right\} \qquad (45)$$

where $\phi(x_0, \theta)$ is the potential at the point $\xi_0 = \eta_0 = 0$ of the plane $x = x_0$ from which the discharge of the reactant ion takes place, and the quantity $\Delta F = F_z(T, \theta) - F_{z-\alpha}(T, \theta)$ is the difference in the free energies of the system for a charge ez on the ion Ox and an "effective charge" $e(z - \alpha)$ on this ion.

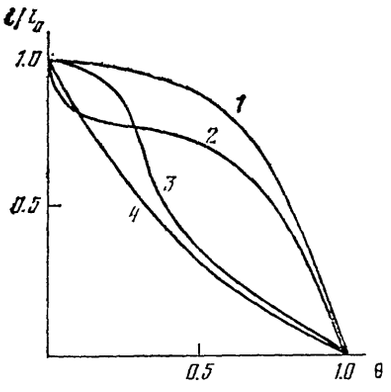


Figure 6. Dependence of the current for the electroreduction of doubly-charged cations on the degree of coverage θ under the conditions of the combined adsorption of dipolar molecules of two kinds[57] with the following values of the dipole moments: *1*) $\mu_1 = \mu_2 = 1$; *2*) $\mu_1 = 1$, $\mu_2 = -1$; *3*) $\mu_1 = -1$, $\mu_2 = 1$; *4*) $\mu_1 = \mu_2 = -1$ CGSE unit.

Since F_z and $F_{z-\alpha}$ are related to the corresponding mean-statistical values of $\bar{E}_z$ and $\bar{E}_{z-\alpha}$ of the energies of the system by the Gibbs–Helmholtz thermodynamic relationship, these last quantities are first found by the method of correlative functions (or distribution functions):[79]

$$\frac{\partial \Phi_1(\varrho_1)}{\partial \xi_1} + \frac{1}{kT}\frac{\partial U_1(x_0, \varrho_1)}{\partial \xi_1}\Phi_1(\rho_1) + \frac{1}{v_s kT}\int \frac{\partial U_2(\varrho_1, \varrho_2)}{\partial \xi_1}\Phi_2(\rho_1, \rho_2)\,d\rho_2 = 0 \qquad (46)$$

etc., where Φ_1, Φ_2, ... are the unary, binary, etc. distribution functions, U_1 and U_2 represent respectively the unary and binary (paired) species interaction potentials; and $v_S = \Gamma^{-1} = (\Gamma_\infty \theta)^{-1}$. Relationships (46) represent an infinite system of coupled equations[79] or "chain of equations", and an analogous system of equations is written for the component η_1 of the two-dimensional vector $\rho_1 = (\xi_1, \eta_1)$ in the adsorption plane $x_a = \text{const}$. The main task is to find an effective method for "terminating" the chain of interrelated equations (46).

Specific results have been obtained[52,53] by introducing "two-dimensional expansions" (with the condition that $\theta < 1$ and that the corresponding integrals converge), that is by expansion of all the distribution functions and thermodynamic quantities being sought in power series with respect to θ; in particular, for $\Delta F(T, \theta)$:

$$\Delta F(T, \theta) = \theta \Delta F_1(T) + \theta^2 \Delta F_2(T) + \ldots \qquad (47)$$

In Eqn.(47), ΔF_p represents the expansion coefficients which do not depend on θ. For ΔF_1, for example, this method gave the expression

$$\Delta F_1(T) = 2\pi kT\Gamma_\infty \int_0^\infty \{\exp[-U_1^{(z-\alpha)}(x_0, \rho_1)/kT] - \exp[-U_1^{(z)}(x_0, \rho_1)/kT]\}\,\rho_1 d\rho_1 \qquad (48)$$

where U_1 is the potential of the interaction of the reactant ion with an arbitrary adsorbed species (with allowance for the interactions of the species with their "electrostatic images" in the metal and the solution). The superscripts on U_1 indicate that the reactant ion has the corresponding charge ez or $e(z - \alpha)$.

It follows from Eqns.(47) and (48) that for the non-localised adsorption of the species, the exponent in the expression for the current (45) (with the condition that integral (48) converges) contains a term linear with respect to θ. This is predicted by the theory of the relationship and is apparently reflected in the nature of the behaviour of the experimental i, θ curves for systems with adsorption of organic ions.

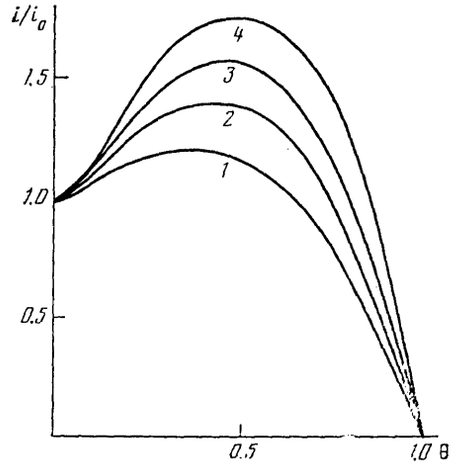


Figure 7. Dependence of the current for the electroreduction of doubly-charged cations on the degree of coverage of the electrode surface by inactive singly-charged organic anions.[52,53]

Thus the dependence of the current density on the degree of coverage has been studied[68] under the conditions of the electroreduction of cadmium ions at a mercury electrode in the presence of decyl, nonyl, and octyl sulphate anions. For all the systems studied, the i, θ curves show two regions: a region of initial increase and a region of subsequent decrease in the rate of the electrochemical process. According to the theory developed in the present section, these regular features are explained by the different arrangements of the planes in which the centres of the adsorbed ions are localised relative to the plane of the electrode: the closer the localisation of the adsorbed organic anions to the electrode, the more clearly defined the initial region of increase in the current. This effect is illustrated in Fig.7 by four

curves constructed using Eqns.(45)–(48). The common parameters for all four curves were: $z = 2$, $z_0 = -1$, $\alpha = 0.5$, $\varepsilon_{pl} = 8$, $x_0 = 1.5$ Å. The parameters Γ_∞ and x_a were varied; curves *1*–*4* in Fig.7 correspond to the following pairs of values of Γ_∞ and x_a (in units of $10^{-10}\Gamma_\infty$ and $10^8 x_a$): 4.0 and 2.0 (*1*), 3.0 and 2.5 (*2*), 2.0 and 3.0 (*3*), and 1.0 and 3.5 (*4*). The same trend in the behaviour of the i, θ-curves when one organic anion is replaced by another was observed experimentally.[68]

V. THE INFLUENCE OF THE ADSORPTION OF IONIC REAGENTS ON THE KINETICS OF ELECTROCHEMICAL PROCESSES

A large number of experiments (see for example Refs.9, 10, 29, 32, 33, 80, 81) have established that many electrochemical reactions take place with the reactants in the adsorbed state. The most typical example of reactions of this kind is the discharge of hydrogen ions at a mercury electrode.[1,64] Systems in which even slight adsorption of the reactants can completely change the mechanism of an electrode process have been described. At the same time there have been insufficient quantitative studies of kinetics complicated by adsorption of the reactants. The reason for this is the additional experimental difficulties associated with the need to measure simultaneously, at a given electrode potential, the reaction rate and the concentration of the reacting substance next to the electrode. The first attempts to carry out a theoretical analysis of the influence of adsorption on kinetics were made[33,37] for the reduction of organic substances at a mercury electrode. The analysis was based on the activated-complex method.

A statistical-mechanical approach to the description of the kinetics of electron transfer reactions accompanied by adsorption of the reactants was recently proposed.[53–56] Because of the complexity of the problem, in the initial approximation of the equation for the current i it was assumed that the rate of the process is proportional to the activity g^*_{ads} of the reactant ions in the adsorbed state and the statistically averaged probability $\langle W \rangle$ of the elementary act of electron transfer:

$$i = \text{const} \cdot g^*_{ads} \langle W \rangle \qquad (49)$$

It should be emphasised that completely rigorous and systematic averaging on the right-hand side of Eqn.(49) under the conditions being considered should include the simultaneous determination of both the probability of the given configuration of the system and the probability of the elementary act of the electrode process. This formulation of the problem is extremely complex from both the quantum-mechanical and statistical viewpoints, and its general "analytical" solution (at least without the introduction of any numerically miscalculable model systems) is not yet possible. Eqn.(49) has a factorised (multiplicative) structure, and this is only a definite approximation, whose accuracy cannot be estimated beforehand within a completely rigorous theory.

At the same time, the multiplicative form of the approximation of the equation for the current from Eqn.(49) makes it possible, at least in a whole series of particular cases, to take the solution of this problem to a conclusion.[56] The quantity g^*_{ads} is found from the adsorption isotherms of the species.[53–56] In the works cited, this gave the following equation for the current with adsorption of the ionic depolariser:

$$i = \text{const} \cdot \frac{\theta}{(1-\theta)} \exp\left\{\frac{\mu^{(e)}(\theta) - e[\phi_0 + (z-\alpha)Q(x_1)] - \Omega_{z-\alpha}(\theta)}{kT}\right\} \qquad (50)$$

where the following notation has been introduced:

$$Q(x_1) = \begin{cases} \varphi_0\left(1 - \frac{x_1}{\delta}\right) + \frac{4\pi e z \Gamma_\infty \theta}{\epsilon_{pl}\theta} x_1(\delta - x_0), & \text{for } 0 \leqslant x_1 < x_0 \\ \varphi_0\left(1 - \frac{x_1}{\delta}\right) + \frac{4\pi e z \Gamma_\infty \theta}{\epsilon_{pl}\theta} x_0(\delta - x_1), & \text{for } x_0 \leqslant x_1 \leqslant \delta \end{cases} \qquad (51)$$

Here, x_0 is the position of the plane of the adsorption of the reactants in the "inactive adsorbed" state, and x_1 the position of the plane from which the discharge of the adsorbed ion takes place; the quantity $\mu^{(e)}(\theta)$ is the electrostatic component of the electrochemical potential of the adsorbed ions. The calculation equations for $\Omega_{z-\alpha}$ are given in the works cited. With allowance for the effect of the penetration of the field into the metal (that is the influence of the "electronic condenser"), it is necessary to modify the quantity $\Omega_{z-\alpha}$ in Eqn.(50) in accordance with Eqns.(34)–(37). Ref.56 also gives an equation for $U_{z,\mu}$, that is the energy of the reaction of the ion with a dipolar molecule with allowance for the penetration of the field into the metal. This quantity is necessary for calculations for conditions in which an organic depolariser is adsorbed.

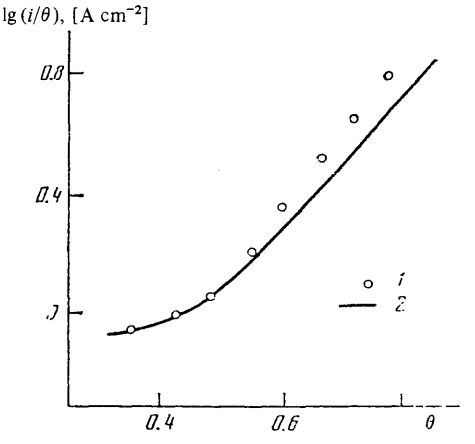


Figure 8. Dependence of the current for the electroreduction of the cationic complex *cis*-Cr(en)(NCS)$^+$ on the degree of coverage of the mercury electrode surface: *1*) experimental points, *2*) results of the calculation using Eqns.(50) and (51).

Eqns.(50) and (51) have been used[55] to calculate the dependence of the current density on the degree of coverage at a constant potential. The numerical values of the parameters were selected for the specific system formed by mercury with the isothiocyanato-complex of chromium *cis*-Cr(en)$_2$(NCS)$_2^+$, where en = ethylenediamine. The kinetics of the discharge of complexes in this system have been studied experimentally.[82] The values of Γ_∞ and α measured in this study were 1.5×10^{14} cm^{-2} and 0.8 respectively. The following values were taken for the other parameters in the calculations: $\delta = 5$ Å, $x_0 = 3$ Å, $x_1 = 2$ Å, $\varepsilon_{pl} = 6$, $z = 1$. The results of the calculations are compared with the experimental data in Fig.8. It can be seen that at sufficiently low degrees of coverage, the agreement between theory and experiment is satisfactory. The appreciable discrepancy at high degrees of coverage

is apparently related to the fact that at high values of θ it is not physically justified to regard the discharging complex as a point charge. It would be more adequate to examine the discrete structure of the charges within the actual complex. Another reason for the lack of agreement between the results of the calculation and the experimental data may be the neglect of the contribution from the effects of the penetration of the electric field into the metal, although, as noted above, it is possible in principle to take account of these effects on the basis of the equations given in the present review.

VI. SUMMARY

Studies directly in the field of the theory of the electrical double layer and the theory of the adsorption of SAS and SAOS on electrodes and also in the field of the theory of the kinetics of electrode processes are now being intensively developed to solve a number of problems in theoretical and applied electrochemistry. These fields of present-day theoretical electrochemistry are organically related and interact naturally with one another, and this interaction process is gradually becoming more interpenetrating and requiring the development of theoretical correlations and self-consistency. An example is provided by the aspects, examined in the present review, of the theory of electrochemical processes complicated by adsorption phenomena at the interface between the electrode and the electrolyte solution.

It should be emphasised that progress in the first two fields naturally provides a basis for the further development of the theory of the kinetics of electrode reactions. In this connection, there is no doubt that recent developments in the theory of the equilibrium double layer, such as the "three state" model or the "cluster" model, the concept of condensed adsorption layers on electrodes with the interpretation of the reorientation of adsorbed molecules as a two-dimensional phase transformation, the representation of two electronic "parts" of the total charge of an electrode (the part of the charge "spread" uniformly over the metal surface and the other part which is the sum of the electronic counter-charges localised close to specifically adsorbed ions) may be reflected in the theory of the kinetics of electrochemical reactions (a bibliography) of relevant work can be found, for example, in a published review).[62]

The present review has dealt partly with the kinetic aspects of the penetration of the electric field into a metal. As has been pointed out,[52] however, it is also necessary to take account of the effect of the shielding of the field of the metal by the "outer" electrons, that is the electrons of the metal penetrating into the effective range of the "compact" layer adjoining the metal (the so-called "electron tails"). These electrons interact with the solvent molecules and adsorbed species, and in this connection it has been emphasised[52] that under these conditions the actual concept of "compact layer" (or "reaction region" in the kinetic aspect) requires physically more correct and electrochemically constructice definitions (concepts), and also definition of the concept of the phase interface (thus for example the theory of the "capacity of the double layer" should include a factor associated with the "electron condenser", etc.).

In addition to these factors, other characteristic features such as the specific structure of the region of the solvent next to the surface (in particular, the influence on its structure of the "outer" electrons of the metal[52] and the possibility in principle of hydrogen bond formation between water molecules in the solvent monolayer [83,84]), the effects of the spatial dispersion of the dielectric constant of the two phases in contact, the questions of "partial charge transfer" in the adsorption of species on electrodes, and a number of other questions will undoubtedly be reflected in the theory of electrode kinetics.

The problem of the statistical averaging of the probability of the elementary act of an electrochemical process accompanied by the adsorption of electrochemically inert species or the reactants themselves was analysed in detail above, and it was shown, in particular, that the interaction between the reactants and adsorbed species is determined by the fine structure of the electrical double layer at the electrode/solution interface. A unique type of electrochemical system is provided by systems in which electrode reactions take place with the reactants in the adsorbed state. In this case, in the averaging of the probability of the elementary act, it is necessary to take into account both the contribution made to the free energy of adsorption of the reactants by the electric field created by these reactants, and the entropy factor, which influences the production of the ionic adsorption isotherm. In the theory of the kinetics of reactions complicated by adsorption, it is also necessary to take account of the structure and parameters of the electronic spectrum of the metals. Thus it is obvious that from the physical viewpoint also, the further development of the theory of the kinetics of electrode reactions complicated by adsorption phenomena at the metal/solution interface is an extremely urgent task.

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