Influence of Adsorption of Neutral Molecules and Organic Cations on the Kinetics of Electrode Processes.

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1.

Let us first consider the case when the adsorbed particle itself does not participate in the reaction. The principal effect in the case of adsorption of foreign neutral molecules is the decrease in the process rate. The relevant data of a qualitative character from the field of polarography, the effect of inhibitors and of the electrodeposition of metals are too numerous to be covered in the present communication. Therefore, only some particular questions will be considered here.

1. Dependence of the reaction rate in the presence of adsorbed layers upon the surface coverage and the particle charge. Practically all quantitative experimental data are concerned with the mercury electrode, the surface coverage with adsorbed molecules having been determined from the decrease in the double layer capacity and from electrocapillary measurements, or calculated by means of Ilkovic's equation from the time elapsed since the beginning of the growth of the drop, assuming the adsorption process to be irreversible. The latter procedure forms the basis of the method of confronting the strength of the current on the growing drop in the presence and in the absence of the adsorbed substance, which was experimentally and theoreti-

cally developed by Czech scientists[1]. The results of the investigations carried out so far for the case of neutral adsorbed molecules are in fair agreement with the assumption according to which the inhibitive action is proportional to the coverage of the surface θ which in its turn is considered to be proportional to the adsorbed amount[2,3]. The latter conclusion is, undoubtedly, approximate, since generally speaking the area per molecule may decrease somewhat with the coverage[4]. The experimental data available in the field of kinetics, however, are not accurate enough for the verification of these conclusions. The concept of the proportionality of the reaction rate to the uncovered part of the surface cannot be however used at adsorption values close to the limiting one. Probably, in this case it is meaningless to speak of the uncovered part of the surface. Considering that there is a possibility of a certain change in the orientation of the hydrocarbon chains, it should be assumed that at the values of Γ close to the limiting one Γ_∞ the surface is completely covered and that it is not the coverage which changes with a change in Γ, but the mean thickness of the adsorbed layer. Under these conditions, the process rate is probably proportional not to $1-\theta$, but to the quantity $\exp(-N\omega_d/RT)$, where ω_d is the work to be expended to form a pore in the adsorbed layer by introducing into it the reacting particle in the transition state of reaction[5]. Unlike the case considered above, under these conditions, the degree of inhibition should essentially depend on the nature of the reacting particle. This

circumstance can account for the substantial decrease in the inhibition of reduction reactions of inorganic cations by neutral or positively charged organic substances in the presence of halogen ions[6]. The complex formation reduces hydration and increases the "solubility" of the reacting particle in the surface layer. As can be seen from Loshkarev's paper, in the case of surface-active additions of anionic character the result is different, which is also quite understandable from the point of view given above if the electrostatic interaction between the reacting particles and those of the inhibitor is taken into consideration. If the electrochemical act proper of the reaction proceeds at a fast enough rate and the penetration work is large enough, the penetration step may become the slowest step of the process. In this case, at potentials close to that of the maximum adsorption of the surface-active substance, at which the work of pore formation should depend but little on the potential, the i, E curves show a limiting kinetic current of penetration, which within a certain potential range practically does not depend on the potential (the Loshkarev effect).

Along with the inhibiting effects dependent on the surface coverage, the adsorption of organic ions affects the kinetics of electrode processes also through the changes in the distribution of the charges in the electric double layer. The instances of such effects are given in Kuta's paper. In the general case, one should take into consideration the direct action of the charges of the adsorbed ions upon the reacting particles, the displacement by the adsorbed ions

4158

of the ions, which formed part of the double layer undisturbed by the adsorption process, and the coverage of a part of the surface with the adsorbed ions. The combination of these factors may result in a rather complicated picture and in transitions from inhibition of the reaction to its acceleration occurring with a change in the potential or in the concentration of the adsorbed substance, as shown, e.g. in Fig.1 (according to Nikolaeva-Fedorovich[7]), which, however, will not be discussed at length in the present paper. As it should be expected, in the case of reactions occurring with the participation of charged particles, the maximum inhibition results when the signs of the reacting particle charge and of that of the particles responsible for the inhibition of the reaction coincide.

The rates of reactions occurring in the presence of a given surface-active substance may be quite different. Thus, it is well known that the electroreduction of singly charged silver or thallium ions is much less inhibited than that of copper or cadmium ions, As shown in the works of Holleck[8], similar differences can be observed in the case of the products of subsequent steps of the same reaction as well. The relationship of the rates of inhibited reactions must be determined by the increase in the activation energy caused by the presence of the adsorbed layer, which, as pointed out above, in the case of dense adsorbed layers depends on the nature of the transition state of the reaction, and on the relationship of the rates of the same reactions in the absence of inhibitors. The latter factor is often neglected, as under

polarographic conditions the rate of the uninhibited reaction is usually limited by diffusion. A systematic comparison of the rates of inhibited reactions with those of the uninhibited ones unaffected by concentration polarization would be of considerable interest.

A hypothesis has been advanced that processes the rates of which are determined by the electron transfer step are not inhibited by adsorbed organic compounds at all. This is, however, incorrect, as it is e.g. evident from the reduction reaction of the $Fe(CN)_6^{3-}$ ion in $Fe(CN)_6^{4-}$, which is readily inhibited, as shown in Fig.2 (according to Nikolaeva-Fedorovich and Rybalko). As shown by numerous experiments carried out with the aid of the mercury dropping electrode, the effect of adsorbed substances decreases as their desorption potential is approached and completely disappears at this potential[9].

2. Effect of the metal nature. Since it is most convenient to investigate the inhibiting effects on a mercury electrode, in particular on a dropping one, a number of attempts have been made to use the data thus obtained for comparison with those on the inhibiting action of the same substances in the case of their adsorption on solid electrodes, e.g. when they are used as inhibitors of acid corrosion. Sometimes the data obtained from the suppression of polarographic maxima have also been made use of which is not substantiated theoretically, as the suppressing action is determined by the value of $\frac{\Gamma^2}{c}$, rather than

by the value of Γ (C - concentration of the surface active substance). Even in those cases however when the adsorbed substance inhibits not the tangential motions of the surface, but the reaction itself, one should be very cautious in extending the data obtained for mercury upon other metals. First of all it should be noted that the comparison of adsorption effects should be made at potentials equidistant from the points of zero charge of respective metals, as it was pointed out by Antropov[10]. But even under these conditions the adsorption of organic substances may depend on the metal nature and, as shown by experiment, this dependence is highly pronounced. This can be seen, e.g. in Fig.3, where electrocapillary curves for some organic compounds on mercury and liquid gallium are compared (according to Polyanovskaya). The decrease in the surface tension caused by adsorption proved to be much less for gallium than for mercury. Especially noteworthy is the fact that, as it is evident from the shape of the electrocapillary curves, the effect of the π-electronic interaction is not very apparent in the case of adsorption of aromatic compounds on gallium, unlike that on mercury. The behaviour of hexyl alcohol may be taken as another example. In the case of silver, gallium and lead electrodes, the desorption potentials of hexyl alcohol lie at approximately the same distance from the potentials of zero charge, which points to the proximity of the adsorption energy values (Leikis and Sevastyanov). In the case of mercury, however, the distance from the potential of zero charge to the desorption potential is by 0.25 v greater, whereas,

as shown by Jofa and Batrakov, judging from the effect upon the capacity and hydrogen overvoltage values in H_2SO_4, no adsorption of hexyl alcohol at all occurs on iron. There is a certain difference in this respect between iron and cobalt, since according to the above authors, an addition of hexyl alcohol to the solution results in a certain increase, although a small one, in hydrogen overvoltage and in a decrease in the capacity of the cobalt electrode. To use the classic terms of colloid chemistry. we may say that iron is much more hydrophilic than other metals mentioned above, and mercury is the most hydrophobic one.

The analogy between the adsorption of organic compounds at the mercury-solution interface and their activity as inhibitors of acid corrosion of iron has been many times emphasized in the literature[11,12]. As it follows from the work of Jofa et al., however, the adsorption of inhibitors on iron at the stationary open-circuit potential in acids is closely bound with the presence of surface-active anions (Cl^-, Br^-, J^-, SH^-). A particularly sharp difference between the behaviour of iron and that of mercury is observed when zone refined high-purity iron is used and the effect of the H_2S traces, which appear in the case of dissolution of commercial iron in acids and increase the inhibiting action, particularly in the case of basic inhibitors, is eliminated[13]. These problems are considered in more detail in Jofa's paper.

Since in the case of adsorption of organic compounds from aqueous solutions we always have to deal with the competition

4158

between the molecules of water and those of organic substance (the significance of this fact was emphasized in Rome in the paper of Bockris, Devanathan and Miller), in order to understand the different behaviour of various metals it would be of importance to know the free energy of wetting of the uncharged metal surface by water W_{Me-H_2O}. Unfortunately, apart from mercury, this value can be calculated only for liquid gallium. Since the surface tension of gallium at 30° is equal to ~ 720 (mean value from the data obtained in [14] and [15]), the interfacial tension at the maximum of the electrocapillary curve 606 erg/cm^2, W_{Me-H_2O} per cm^2 is equal to 720+72-606=186, which appreciably exceeds the value for mercury: 480 + 72 - 427 = 125 erg/cm^2.

3. Inhibition by reaction products. The inhibition by reaction products is a frequent case of inhibition. It is especially effective if the reaction product has a higher molecular weight than the initial substance. A typical case of inhibition as a result of dimerization is the reduction of the tropylium ion on a dropping mercury electrode. As shown by Zhdanov[16] and later by Zuman[17], the reaction product ditropylium blocks the surface and limits the process rate, which attains normal values only at more negative potentials. Surface-active anions and some neutral molecules bring about the desorption of reaction products and eliminate the inhibition (Fig.4). In this case, the polarograms

observed are somewhat similar in their appearance to those obtained in the case of Brdička's adsorption pre-wave, although the mechanism of the process is different. The occurrence of the adsorption pre-waves is due to the adsorption of the product of an reversible reaction, resulting in a shift in the reduction potential in the direction of more positive values, whereas the adsorption of ditropylium formed as a result of an irreversible reduction process leads to a decrease in the reaction rate. In this case, the dependence of i on E is complicated by the possibility of different orientations of ditropylium in the surface layer[17].

II

In order to understand the mechanism of electrochemical processes it is of especial importance to elucidate the dependence of the process rate on the adsorption of the reacting particle. At the present time, however, less is known about this problem than about that of the effect of foreign adsorbed particles. I shall dwell in the first instance on the influence upon the reaction rate of the changes in adsorption associated with the dependence of the adsorption energy on the electric field of the double layer. Antropov was the first to note the importance of this dependence for the kinetics of electrochemical reactions occurring with the participation of organic compounds.[10] It is expedient to consider the cases of small, medium and large coverages separately.

4I58

a) Small coverages. This case was treated by Ershler, Tedoradze and Mairanovskii[18] in the assumption that the electron transfer is the rate determining step of the process. In the case of small coverages, it may be supposed that the process rate is proportional to the adsorbed amount and that the dependence of the reaction rate on the potential is determined both by the change in the reaction activation energy, which is usually taken into consideration, and by that in the surface concentration. It is further assumed that the change in the probability of every single adsorbed molecule reacting under the influence of the electric field can be expressed by the quantity $\exp\left(-\frac{\alpha n F E}{RT}\right)$. Generally speaking, this supposition is incorrect, since the electric field of the double layer can influence the rate of processes which are not accompanied by changes in the charge, but which are associated, e.g., with an increase in the dipole moment of the adsorbed molecule in the transition state. An instance of such process is given in the paper of Vincenz-Chodkowska and Grabowski.

It is impossible, however, to make general allowance for the influence of the electric field on the reactivity of molecules. Moreover, such an allowance, probably, would not affect materially the conclusions given below. Since the dependence of the standard free energy of adsorption upon the electrode potential E is determined by the value $-\frac{1}{2}\frac{(C - C')(E - E_M)^2}{\Gamma_\infty}$, where C and C' represent the double layer capacities at $\Gamma = 0$ and $\Gamma = \Gamma_\infty$ and $E - E_M$ is the potential referred to the point of maximum adsorption, the

rate of the one - electron transfer must be proportional to the quantity

$$\exp\left[-\frac{1}{2}\frac{(C-C')(E-E_M)^2}{RT\Gamma_\infty} - \frac{\alpha EF}{RT}\right] \quad \ldots (1)$$

When the potential shifts in the direction of more negative values this quantity passes through a maximum at

$$E_e = E_M - \frac{\alpha F \Gamma_\infty}{C-C'} \quad \ldots (2)$$

If it is assumed that $\alpha = 0.5$, $C - C' = 13\,\mu f/cm^2$, $\Gamma_\infty = 5\times10^{-10}$ and $E_M = -0.6$ (NCE), which is in keeping with the conditions frequently observed in the case of adsorption of aliphatic compounds, $E_e = -1.85$. Thus, the electroreduction rate should pass through a maximum at sufficiently negative potentials and then decrease. Curves with a maximum are really observed in the case of some reduction reactions, but it seems, as a rule, that the decrease in the process rate is followed by a new rise, the second ascending branch of the curve being characterized by the usual values of In Fig.5, plotted for the reduction of benzyl chloride with a 0.5N $C_2H_3O_2$ + 60% CH_3OH supporting electrolyte, the second rise of the polarization curve is hidden by the wave of the supporting electrolyte, but becomes apparent in the presence of CsCl (Fig.6, according to Ershler, Tedoradze and Mairanovskii). Moreover, many polarization curves for electroreduction reactions in the range of very negative potentials are known to show no anomalies in the slope. We have to admit therefore that at suffieiently negative potentials the first term in the expression within the brackets in eq (1) is

4158

less than we supposed. This diminution of the term in question may be due both to the smallness of the value of C - C' and to a higher value of Γ_∞, i.e. to a smaller area per molecule adsorbed. In other words, we are to suppose that the adsorption of molecules in the transition state of the reaction at negative potentials results in a lesser disturbance in the double layer structure than it should be expected from the data obtained on the basis of differential capacity measurements. Hence we might conclude that at potentials more negative than the cathodic desorption peak, the reacting particles are not in an adsorbed state at all and that, e.g., the occurrence of the reaction is due to a tunnelling of electrons at distances greater than the double layer thickness. In fact, the conclusion about the possibility of the reaction occurring without previous adsorption has been drawn more than once in the present day literature (Grabowski, Delahay, Breiter). Although the experimental data available are not adequate for the solution of this fundamental problem, it should be pointed out that the above conclusion is at variance with the strong dependence of the reduction rate in the range of negative potentials upon the electric double layer structure observed. Let us take as an example the half-wave potential of the reduction of β-brompropionitryl with 0.1 M solutions of chlorides of different cations as supporting electrolyte (the data of Feoktistov). In the case of LiCl the value of $-E_{1/2}$ for the detachment of bromine is equal to 2.03, in the case of KCl to 1.92 and

CsCl - 1.80 . In the case of iodbenzene reduction (the data of Ershler, Preis and Tedoradze) in 85% ethanol with 0.1N $NaC_2H_3O_2$ as supporting electrolyte $E_{1/2}$ = -1.74, with 0.1N $KC_2H_3O_2$ E = -1.67 and with 0.1N CsCl E= -1.53 (SCE). These data point to an appreciable interaction between the negatively charged part of the reacting particle and the cations of the double layer, similar to that which to a still greater degree is observed in the case of the electroreduction of anions, Relationships of this kind are observed in the case of other reactions of electroreduction of halogen derivatives as well. Thus, it should be supposed that at least in these cases, the reacting particle in the transition state of the reaction is oriented with its polar group not in the direction of the solution, but towards the electrode, probably with the formation of a cationic bridge as in the case of anion electroreduction. However, it is impossible to establish as yet how far this conclusion can be considered to be of a general character.

The effect which the dependence of adsorption on the double layer field has upon the reaction kinetics has been shown by Mairanovskii to be very pronounced in the case of the "surface" waves of catalytic hydrogen evolution on a mercury electrode[19]. A decrease in the catalytic current is observed with rising negative potential within the potential range where the rate determining step of the process is the formation of the BH^+ particle from the

adsorbed base B owing to its interaction with proton donors[x], the discharge of this particle being accompanied by the evolution of hydrogen. The dependence of the reaction rate on the potential is adequately expressed if it is assumed that the adsorbed amount is proportional to $\exp\left(-\frac{1}{2}\frac{(C - C')(E - E_M)^2}{RT\Gamma_\infty}\right)$, the values of the constants lying within the usual limits, e.g. $C - C' = 10\ \mu f/cm^2$ and $\Gamma_\infty = 3.2 \times 10^{-10}$ in the case of the catalytic wave of anabasine In Fig.7 the calculated and experimental catalytic waves of hydrogen evolution produced by quinine in a borate buffer at pH = 9.5 with varying concentrations of Na^+ ions are compared[20]. The change in Na^+ concentration gives rise to a shift in the ψ_1 - potential and affects the protolytic equilibrium in the surface layer between the buffer components of the solution, as well as the desorption effects.

In contrast to the halogen electroreduction in the case

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x) Further the reaction proceeds according to the scheme

$$BH^+ + e^- \rightarrow BH$$

$$BH \rightarrow B + \tfrac{1}{2} H_2$$

The quantitative theory was worked out on the assumption that the proton donor is a neutral molecule, such as of water or of boric acid with a concentration in the surface layer to be considered constant within the potential range in question.

No allowance has been made in this paper for the specificities of the operation of a dropping electrode, such as the incomplete establishment of the adsorption equilibrium, which have been however taken into account in the original work of Mairanovskii.

of the surface catalytic currents the substitution of Cs^+ for Li^+ in the supporting electrolyte results in a decrease in the reaction rate in accordance with the increase in the desorbing action.

Mairanovskii has developed a complete quantitative theory of the electroreduction reactions on a dropping electrode, with the protonization of the adsorbed molecule as one of their steps[19]. At sufficiently negative potentials, on account of the acceleration of the electron transfer, the protonization step becomes rate determining and the current strength diminisches with increasing polarization in accordance with the decreasing coverage. In Fig.8, curve 3 gives the calculated and experimental values of the current for the first wave of 5-brom-2-acetylthiophene reduction (with 0.1N KCl + 0.1N KOH as supporting electrolyte), curve 2 gives the shape of the curve which would be observed if adsorption were independent of the potential, curve 1 - the shape which would be observed if the kinetics of the process depended on the protonization and diffusion steps only (curve 4 represents the limiting diffusion current). In the calculations the value $\frac{1}{2}\frac{(C-C')}{RT\Gamma_\infty}$ was assumed to be equal to $11.3\ v^{-2}$, which would correspond to $\Gamma_\infty = 1.85 \times 10^{-10}$ at $C - C' = 10\ \mu f/cm^2$ i.e., to a relatively larger area per adsorbed molecule as should be expected. It is possible that the rather fast decrease in adsorption with the potential is due to the repulsion by the negatively charged surface of the Br atom, which was not taken into account in the calculations. As it follows

from the comparison of the kinetics of the process in the presence of various cations, in the case under consideration the desorption phenomenon is superimposed by the interaction of the bromine atom with the cations of the double layer[21]. This problem is considered in more detail in Mairanovskii's paper.

b) Medium coverages. At medium coverages, the interaction forces between the adsorbed particles come into play, which may assume the form of attraction or repulsion. If there is a sufficiently pronounced attractive interaction, upon cathodic polarization a sharp decrease in the surface coverage occurs over a narrow potential range, which is represented by the appearance of well known peaks on the C - E curves (at high enough values of the attraction constant, the maximum on the capacity curve corresponds to the coverage $\theta = 1/2$). At the peak potential an appreciable change in the reaction rate and in the slope of the polarization curve might be expected, with the values and even the sign of the effects being dependent of the character of the interaction of the molecule in the transition state of the reaction with the adsorbed molecules in their initial state. If this interaction does not differ too much from that between the adsorbed molecules in their initial state, a decrease in the process rate should be expected upon desorption. We have been trying for some time to find instances of this effect, but so far have not obtained any convincing results. It is

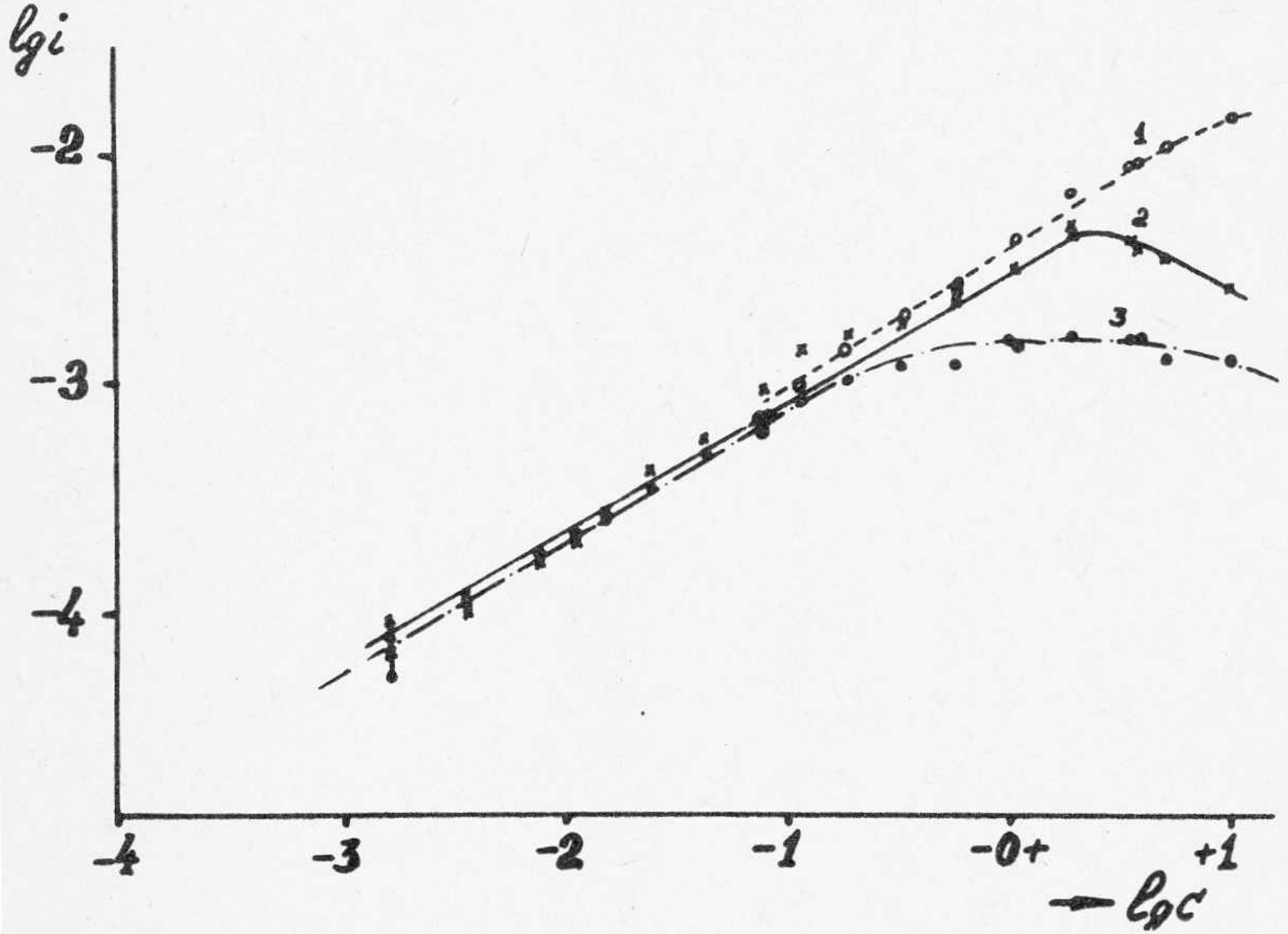

Fig. 11.

possible that the i, E curve observed in the case of 1-2-di-[pyridyl 2] - ethylene reduction may serve as an example. This reaction first studied by Laviron[22/] and recently in more detail by Zolotarizkiy, Ershler and Tedoradze is, however, rather complicated and necessitates further investigation.

The problem of the adsorption kinetics and of the slow discharge reaction of adsorbed particles was treated recently in an elaborate way by Delahay and Mohilner[23/], especially for the case of particles obeying Temkin's adsorption isotherm. Temkin's isotherm, which in the case of adsorption on the homogenous mercury surface points to a repulsive interaction between the adsorbed molecules is applicable to small molecules with a pronounced dipole moment and to aromatic compounds with a flat orientation of the ring on a positively charged metal. The author is not aware of the existence of experimental data on the kinetics of reactions on a mercury electrode to suit the above conditions. Temkin's isotherm was initially deduced and applied for the interpretation of reaction kinetics for the case of adsorption on a uniformly inhomogeneus platinum surface in the assumption that the change in the activation energy constitutes a certain definite portion of that in the adsorption energy[24/]. Under this assumption, over the range of medium coverages the rate of the reaction occurring with the participation of adsorbed molecules should depend exponentially on the coverage[25/]. This conclusion is valid for any kind of inhomogeneity, if it is pronounced enough

and if the relationship between the activation and the reaction energies is of the type of Polanyi-Brönsted's relation.

Lately, numerous experimental data on the oxidation kinetics of organic compounds on platinum have been obtained, which confirm the conclusions from the theory of reactions on inhomogenous surfaces. These problems are treated at length in Bagozky's paper. I shall consider here only Fig.9, plotted from the data of Chazova, Vasiliev and Bagozky, which shows the dependence of the oxidation rate of methyl alcohol in a N H_2SO_4 solution at the potential 0.92 v (N.H.E. in the same solution) on the coverage. The coverages are taken from Breiter work[26]. Unfortunately, the coverages at the reaction potential are too small to be reliably determined; the values plotted on the abcissa refer to open circuit measurements, i.e. to conditions under which the reaction has not yet started. Therefore, the results of this comparison should be considered with caution. The reaction behaviour of the molecules adsorbed on an inhomogenous surface is distinguished by some unexpected features. Thus, the rate determining step of the oxidation of alcohols at not too positive potentials is the detachment of the hydrogen atom from the adsorbed molecule

$$RH_{2ads} \longrightarrow RH_{ads} + H_{ads} \qquad \ldots (3)$$

i.e. a purely chemical process, in which charged particles do not participate. The dependence of this reaction rate on the potential, however, at a constant adsorbed amount of RH_2 is expressed by the Tafel equation. This can be explained if it is taken into consideration that the rate of reaction 3 is determined by the energy of adsorption of the reaction

product, that is hydrogen, the latter changing with the coverage of the inhomogenous surface with adsorbed hydrogen, which is in equilibrium with the hydrogen ions in the solution. By taking into consideration the dependence of this equilibrium on the electrode potential, we obtain the expression for the reaction rate sought for[27]. This example shows how much risk there is in drawing conclusions about the nature of the step determining the process rate from the dependence of the potential on lg i.

c) Large coverages. In all cases so far considered the reaction rate increased monotonously with the coverage, although in accordance with different laws, depending on the shape of the adsorption isotherm. At coverages approaching unity, however, an opposite effect may be expected resulting from the autoblocking of the surface with the initial substance if the particle in the transition state of the reaction occupies a larger area than in the normal adsorbed state. Fig.9 shows the dependence of the rate of the catalytic hydrogen evolution from $(C_6H_5)_2NH$ + 0.2N HCl solutions, which is determined by the discharge rate of the adsorbed ions of diphenylammonium (data of Dzhaparidze and Tedoradze). In the case of HCl of the given concentration mostly the molecules of the base $(C_6H_5)_2NH$ are present in the surface layer. The coverages were determined from the decrease in the differential capacity of the double layer. As can be seen from the figure, as the value $\theta = 1$ is approached, a pronounced, though not very large, decrease in the current strength is observed, in other words, the reaction

rate decreases with a rising concentration of the reactant. A similar phenomenon is observed in the case of a normal concentration of HCl, although the dependence of i on E is here of a more complicated character.[28] Fig.11 shows the dependence of the oxidation rate of methanol on Pt on its bulk concentration at different potentials, plotted in a logarithmic scale (according to Chazova, Vasiliev and Bagozky). At not too positive potentials the effect of large coverages considered above becomes apparent in this case as well.

This paper does not give an exhaustive treatment of the problem of the influence of adsorption on the kinetics of electrode processes and I have not set myself this task. My object was only to point out the questions which in my opinion deserve particular attention at present.

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SUBSCRIPTS TO FIGURES

Fig.1. Effect of N $(C_4H_9)_4^+$ upon the electroreduction of $PtCl_4^{2-}$
—o—o— 10^{-3} N K_2PtCl_4 + 0.1 N Na_2SO_4
—•—•— 10^{-3} N K_2PtCl_4 + 0.1 N Na_2SO_4 + 10^{-3}N $N(C_4H_9)_4$.

Fig.2. Effect of camphor upon the electroreduction of $Fe(CN)_6^{3-}$
1 - 10^{-3} N $K_3Fe(CN)_6$; 2 - 10^{-3}N $K_3Fe(CN)_6$ sat.with camphor.

Fig.3. Electrocapillary curves of mercury (α) and gallium (β) in the presence of organic substances.
Hg. Downwards: N Na_2SO_4, N Na_2SO_4 + 0.1 M isoamyl alcohol, N Na_2SO_4 + 0.4 M phenol.
Ga. Downwards: N KCl, N KCl + 0.1 M isoamyl alcohol, N KCl + 0.5 M phenol.

Fig.4. Effect of KJ upon polarization curves of the tropylium electroreduction. Solution composition: 0.1 M LiCl + 10^{-3} M $C_7H_7ClO_4$ + KJ [KJ]: 1 - 0;2 - $5x10^{-5}$; 3 - $5x10^{-4}$M; 4 - 0.1 M KJ + 10^{-3}M $C_7H_7ClO_4$ + $5x10^{-3}$% gelatine.

Fig.5. Polarogram of benzyl chloride electroreduction in the presence of Na^+ cations.
Solution composition: 60% C_2H_5OH + 0.0009 M $C_6H_5CH_2Cl$ + 0.5 N Na $C_2H_3O_2$.

Fig.6. Polarogram of benzyl chloride electroreduction in the presence of Cs^+ cations.
Solution composition: 40% CH_3OH + 0.003 M $C_6H_5CH_2$ + 0.0015 n sodium tetraborate + 0.05 N CsCl.

Fig.7. Catalytic waves of quinine in borate buffer (pH = 9.5) Quinine conc. 3×10^{-6} M , Na^+ conc.: 1 - 0.040; 2 - 0.045; 3 - 0.050; 4 - 0.055; 5 - 0.060; 6 - 0.070; 7 - 0.080.

Fig.8. Curve 3 - the first reduction wave of 5-brom-2-acetylthiophene with a 0.1N KCl + 0.1 N KOH supporting electrolyte; curve 2 - expected i - E dependence at constant adsorbed amount; curve 1 - expected dependence if the kinetics depended on the protonization and diffusion step only; curve 4 - diffusion limiting current.

Fig.9. Dependence of logarithm of the current of CH_3OH oxidation on a pt electrode in N H_2SO_4 at E = 0.92 upon surface coverage of the electrode with CH_3OH at open circuit.

Fig.10. Dependence of catalytic current of hydrogen evolution in 0.2 N HCl + $(C_6H_5)_2NH$ solution at E= -0.8 (NCE).

Fig.11. Dependence of oxidation rate of CH_3OH in N H_2SO_4 upon CH_3OH concentration: 1 - E = 1.35v ; 2 - E = 0.85 v; 3 - E = 0.65 v.

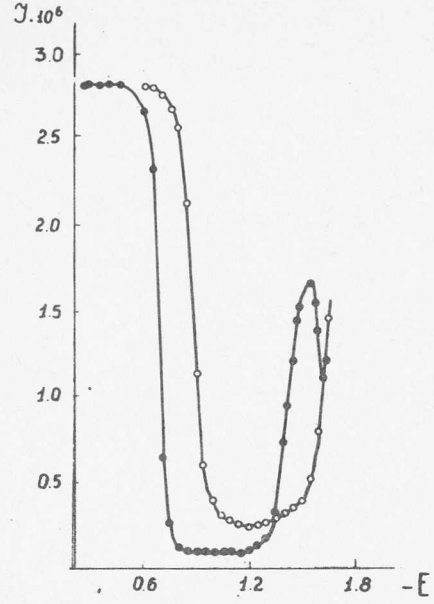

Fig. 1.

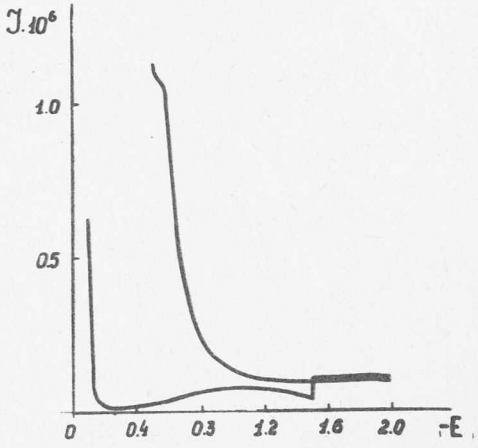

Fig. 2.

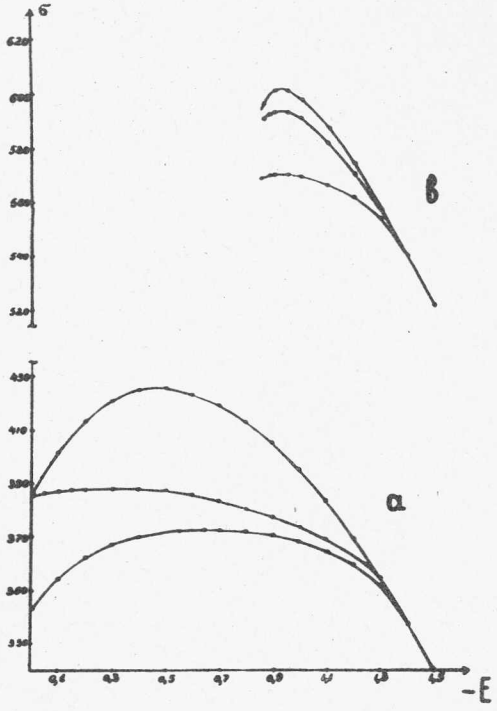

Fig. 3.

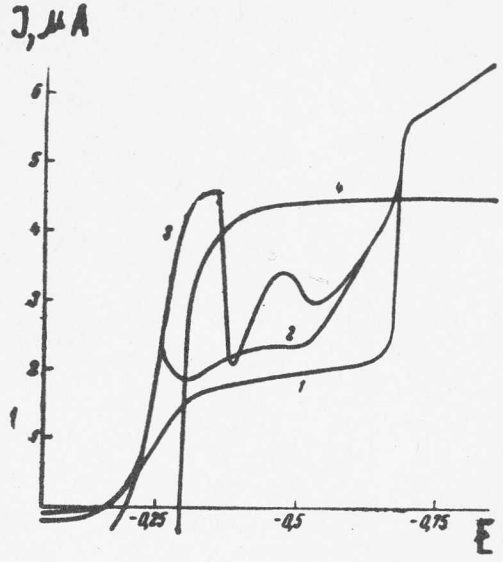

Fig. 4.

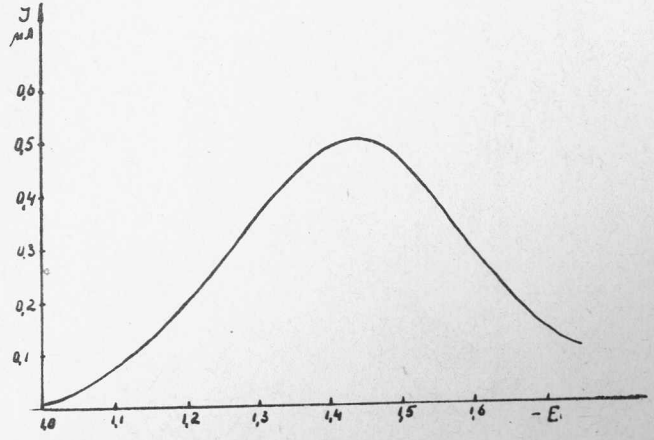

Fig. 5.

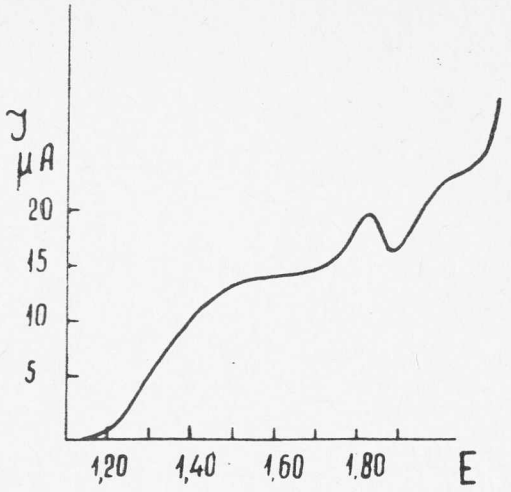

Fig. 6

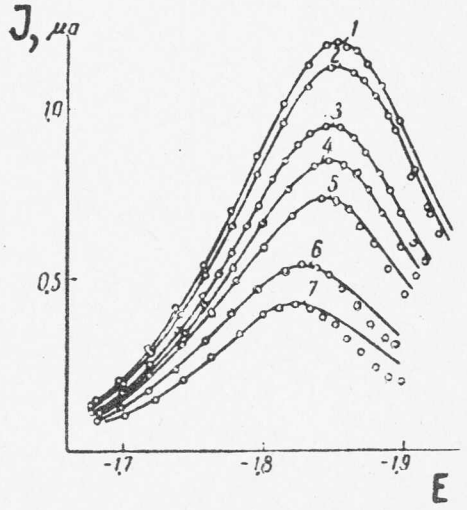

Fig. 7.

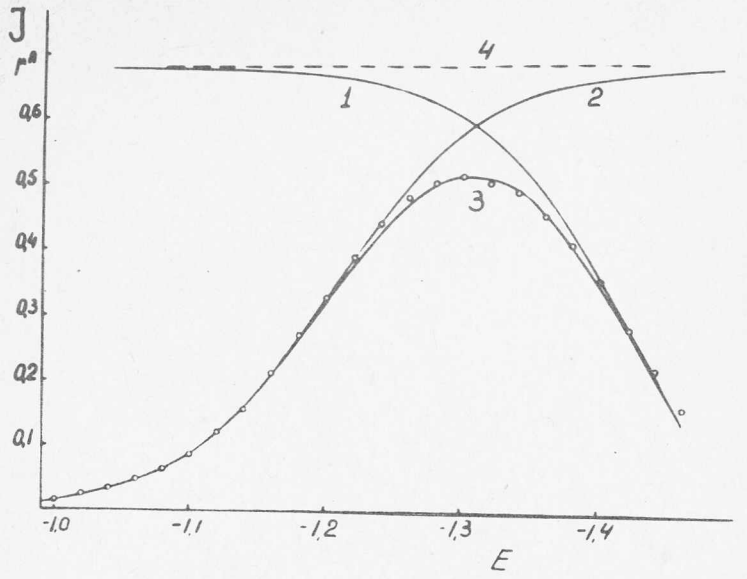

Fig. 8.

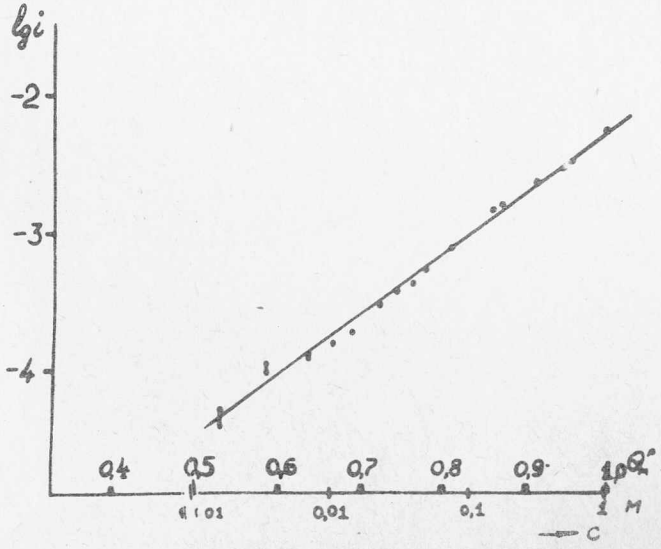

Fig 9.

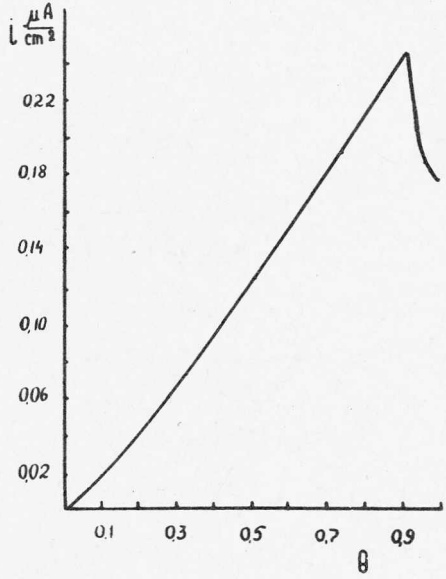

Fig. 10.