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INFLUENCE OF ADSORPTION OF NEUTRAL MOLECULES AND ORGANIC CATIONS ON THE KINETICS OF ELECTRODE PROCESSES*

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Abstract—The dependence of the kinetics of electrode processes on the adsorption of the reacting particles at small coverages is treated on the assumption that the process rate is proportional to the amount adsorbed Taking into account the dependence of adsorption on the potential, it is possible to explain by means of this assumption the appearance of descending branches on the I/E curves in the case of some electroreduction and catalytic hydrogen-evolution reactions

Of special interest is the question of the orientation of reacting molecules in the case of reactions at very negative potentials, when the usual forms of adsorption are not favoured owing to the salting-out of the electric field of the double layer

At coverages approaching unity, increase in the coverage may lead to a reduction in the reaction rate

When considering the influence of adsorption of organic substances on the course of electrode processes on different metals it should be borne in mind that upon the transition from one metal to another, the orientations of adsorbed molecules and their adsorption energies may change appreciably

Résumé—La relation entre la cinétique des processus électrochimiques et l'adsorption des particules réagissantes est traitée en admettant que pour le cas de faibles recouvrements la vitesse de la réaction est proportionelle à la quantité adsorbée En se basant sur cette supposition et en tenant compte de l'influence exercée sur l'adsorption par le champ electrique de la couche double on peut expliquer l'apparition des branches descendantes des courbes de polarisation de certains processus de réduction et de l'évolution catalytique de l'hydrogène La question de l'orientation des molécules réagissantes aux potentiels négatifs prononcés présente un interêt spécial, vu que l'action exercée par le champ électrique de la couche double rend improbable les orientations observees dans le voisinage du point de la charge nulle

Aux recouvrements de la surface de l'électrode qui s'approchent de l'unité une augmentation du recouvrement peut causer un décroissement de la vitesse de la reaction

Quand on compare l'influence des molecules organiques adsorbées sur les réactions qui se déroulent à la surface de differents metaux, il faut tenir compte du fait que le changement de la nature de l'électrode peut changer considerablement les énergies d'adsorption et l'orientation des molécules adsorbées

Zusammenfassung—Die Abhangigkeit der Kinetik der Elektrodenprozesse von der Adsorption der reagierenden Teilchen wird unter der Annahme behandelt, dass die Reaktionsgeschwindigkeit der adsorbierten Stoffmenge bei kleinen Besetzungsdichten proportional ist Auf Grund dieser Annahme kann man, die Abhangigkeit der Adsorption vom Potential in Betracht ziehend, das Auftreten von absteigenden Asten auf den Stromspannungskurven im Falle einiger Reduktionsvorgange und der katalytischen Wasserstoffentwicklung erklaren Besonderer Beachtung verdient die Frage uber die Orientierung der reagierenden Molekule im Falle von Reaktionen, welche bei sehr negativen Potentialen verlaufen, bei denen die gewohnlichen Formen der Adsorption durch die aussalzende Wirkung des elektrischen Feldes der Doppelschicht behindert werden

Bei nahezu vollstandiger Besetzung der Oberflache mit reagierenden Molekulen kann eine weitere Vergrosserung der Besetzungsdichte zu einer Verminderung der Reaktionsgeschwindigkeit fuhren

Beim Vergleich des Einflusses der Adsorption organischer Verbindungen auf den Verlauf von Elektrodenprozessen an verschiedenen Metallen muss in Betracht gezogen werden, dass beim Übergange von einem Metall zu einem anderen die Orientierung von adsorbierten Molekulen sowie deren Adsorptionsenergien sich merklich andern konnen

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INTRODUCTION

IN ORDER to understand the mechanism of electrochemical processes it is of importance to elucidate the dependence of the process rate on the adsorption of the reacting particle. 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 This problem was first considered in respect to the hydrogen-evolution reaction.[1] Antropov pointed out the necessity to take in account this dependence in the case of reactions occurring with the participation of organic compounds [2] Of special importance for the demonstration of the rôle of this dependence in electrochemical kinetics was the investigation of the electroreduction of inorganic anions [3–5]

ADSORPTION OF ORGANIC MOLECULES PARTICIPATING IN THE REACTION

Small coverages

This case was treated by Ershler *et al*[6] in the assumption that the electron transfer is the rate-determining step of the electroreduction process. In the case of small coverages, it may be supposed that the process rate is proportional to the adsorbed amount and 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 $\exp(-\alpha nFE/RT)$, where α is the transfer coefficient, and n the number of electrons participating in the rate-determining step These assumptions must be considered as a first approximation since the electric field of the double layer can also influence the rate of processes for other reasons, *eg* of processes which are associated 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 [7]

With these approximate assumptions and taking into account the dependence of the standard free energy of adsorption upon the electrode potential,[8] we find that the rate of the one-electron transfer must be proportional to the quantity

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

where Γ_∞ is the limiting value of Γ, the amount adsorbed, C and C' the double layer capacitances at $\Gamma = 0$ and $\Gamma = \Gamma_\infty$, and $E - E_M$ the potential referred to the point of maximum adsorption.*

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

$$E_e = E_M - \frac{\alpha F\Gamma_\infty}{C-C'}. \tag{2}$$

If it is assumed that $\alpha = 0\,5$, $C - C' = 13\ \mu F/cm^2$, $\Gamma_\infty = 5 \times 10^{-10}$ mole/cm^2 and $E_M = -0{\cdot}6$ V (NCE), which is in keeping with the conditions frequently observed in the case of adsorption of aliphatic compounds, $E_e = -1{\cdot}85$ V Thus,

* This theory has been worked out for the case of an electrode of the mercury type When considering the behaviour of an organic substance adsorbed at the platinum electrode it must be kept in mind that in this case changes of electrode potential involve changes of the hydrogen and oxygen coverage, which also influence the adsorption of the organic substance

the electroreduction rate should pass through a maximum at sufficiently negative potentials and then decrease. Curves with a maximum are actually 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. In Fig. 1, plotted for the reduction of benzyl

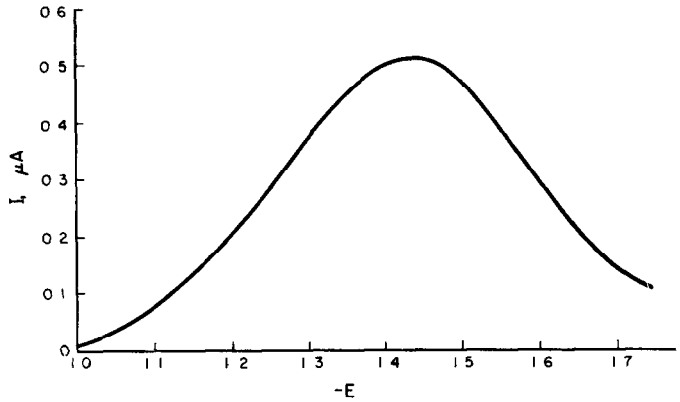

FIG 1 Polarogram of benzyl chloride electroreduction in the presence of Na^+ cations
Solution composition 60% C_2H_5OH + 0 0009 M $C_6H_5CH_2Cl$ + 0 5 N $NaC_2H_3O_2$

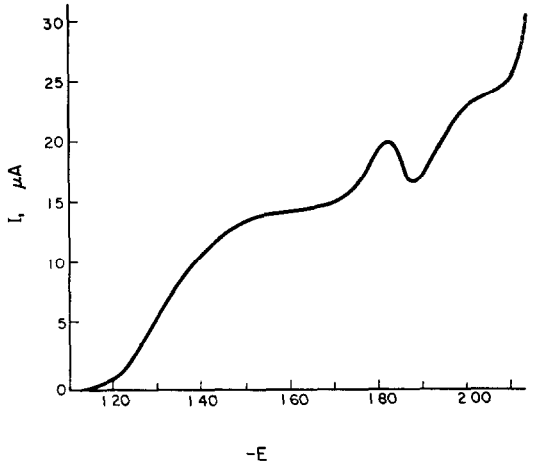

FIG 2 Polarogram of benzyl chloride electroreduction in the presence of Cs^+ cations
Solution composition 40% CH_3OH + 0 003 M $C_6H_5CH_2Cl$ + 0 0015 N sodium tetraborate + 0 05 N CsCl

chloride with a 0 5 N $NaC_2H_3O_2$ + 60% CH_3OH supporting electrolyte (according to Ershler, Tedoradze and Mairanovskii[6]), the second rise of the polarization curve is hidden by the wave of the supporting electrolyte and has been omitted It becomes apparent in the presence of CsCl (Fig 2) 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 sufficiently negative potentials the absolute value of the first term within the brackets in expression (1) is 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_∞, *ie* 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 would be expected from the data obtained on the basis of differential capacitance in the neighbourhood of E_M 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 the occurrence of the reaction is due to a tunnelling of electrons at distances greater than the double-layer thickness In fact, this conclusion about the possibility of the reaction occurring without previous adsorption has been drawn more than once in the present-day literature. However, it should be pointed out that the conclusion is at variance with the strong dependence of the reduction rate in the range of negative potentials upon the electric-double-layer structure 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 (data of Feoktistov[9]) In the case of LiCl the value of $-E_{1/2}$ for the detachment of bromine is equal to 2·03 V, in the case of KCl to $-1{\cdot}92$ V and CsCl $-1{\cdot}80$ V. In the case of iodobenzene reduction (data of Ershler, Preis and Tedoradze[10]) in 85% ethanol with 0 1 N $NaC_2H_3O_2$ as supporting electrolyte $E_{1/2} = -1{\cdot}74$ V, with 0·1 N $KC_2H_3O_2$ $E = -1{\cdot}67$ V and with 0 1 N CsCl $E = -1{\cdot}53$ V(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 [5] It may 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 general

The effect that the dependence of adsorption on the double-layer field at small coverages 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 [10] 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, the discharge of this particle being accompanied by the evolution of hydrogen according to the scheme

$$BH^+ + e^- \rightleftarrows BH,$$

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

When the proton donor is a neutral molecule, such as water or boric acid, with a concentration in the surface layer taken as constant within the potential range in question, the dependence of the reaction rate on the potential is adequately expressed if it is assumed that the adsorbed amount is proportional to

$$\exp\left[-(C - C')(E - E_M)^2/2RT\Gamma_\infty\right],*$$

the values of the constants lying within the usual limits, *eg* $C - C' = 10\ \mu F/cm^2$

* No allowance is made here for the specificities of the operation of a dropping electrode, such as the incomplete establishment of the adsorption equilibrium, which were however taken into account in the original work of Mairanovskii [11]

and $\Gamma_\infty = 3\,2 \times 10^{-10}$ mole/cm^2 in the case of the catalytic wave of anabasine In Fig 3 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 [12] The change in Na^+ concentrations gives rise to a shift in the ψ_1 -potential and therefore affects the protolytic equilibrium in the surface layer between the buffer components of the solution, as well as the desorption effects

In contrast to halogen electroreduction, in the case of the surface catalytic currents the substitution of Cs^+ for Li^+ in the supporting electrolyte results in a decrease in reaction rate in accordance with the increase in the desorbing action

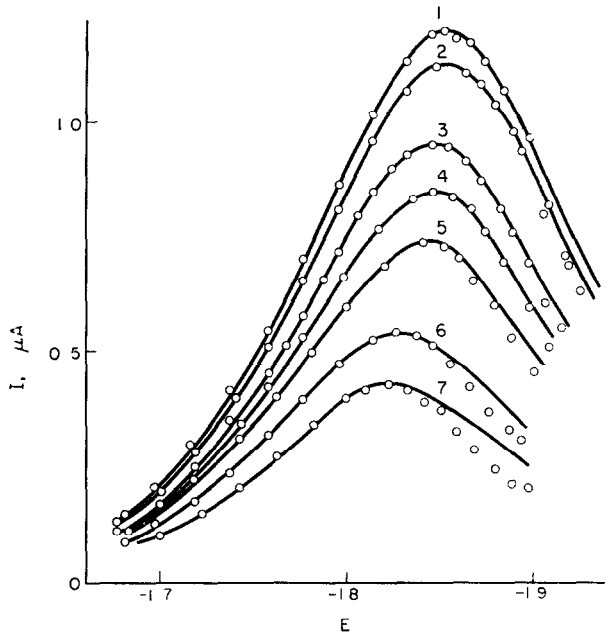

FIG 3 Catalytic waves of quinine in borate buffer (pH = 9 5) Quinine conc 3×10^{-6} M, Na^+ conc 1, 0 040, 2, 0 045, 3, 0 050, 4, 0 055, 5, 0 060, 6, 0 070, 7, 0 080 M

Mairanovskii has developed a quantitative theory of the electroreduction reactions on a dropping electrode, with the protonization of the adsorbed molecule as one of the steps [11] At sufficiently negative potentials, on account of the acceleration of the electron transfer, the protonization step becomes rate-determining and the current density diminishes with increasing polarization in accordance with the decreasing coverage In Fig 4, curve 3 gives the calculated and experimental values of the current for the first wave of 5-brom-2-acetylthiophene reduction (with 0 1 N KCl + 0 1 N KOH as supporting electrolyte), curve 2 gives the shape of the curve which would be observed if adsorption were independent of potential, curve 1 gives 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 calculation the value $(C - C')/2RT\Gamma_\infty$ was assumed to be equal to 11 3 V^{-2}, which would correspond to $\Gamma_\infty = 1\,85 \times 10^{-10}$ mole/cm^2 at $C - C' = 10\ \mu$F/cm^2 *ie* to a relatively larger area per adsorbed molecule than 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. It follows from the comparison of the kinetics of the process in the presence of various cations, that in the present case the desorption phenomenon is superimposed by the interaction of the bromine atom with the cations of the double layer [13]

Medium coverages

At medium coverages, interaction forces between the adsorbed particles come into play, they may assume the form of attraction or repulsion If there is a sufficiently

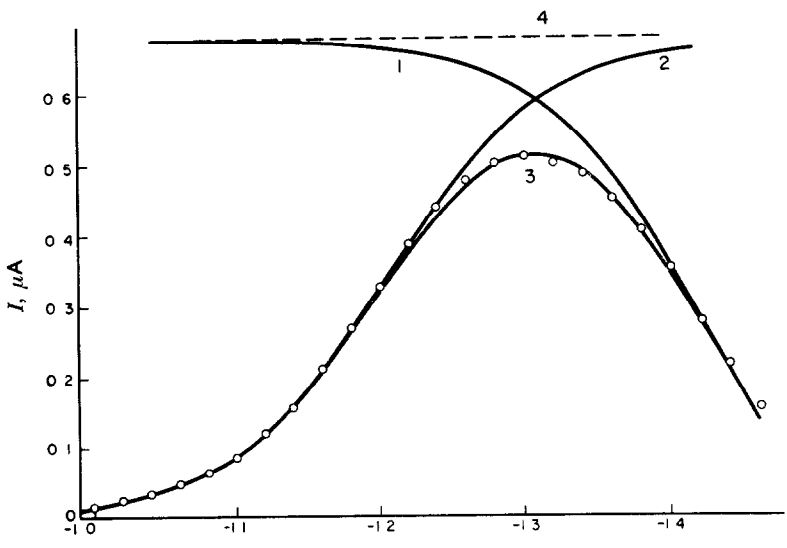

FIG 4 The first reduction wave of 5-brom-2-acetylthiophene with a 0 1 N KCl + 0 1 N KOH supporting electrolyte Curve 1, expected I/E dependence if the kinetics were determined by the protonization and diffusion steps only, curve 2, expected I/E dependence at constant adsorbed amount, curve 3, theoretical I/E dependence according to Mairanovskii, curve 4, diffusion limiting current, open circles—experimental data

pronounced attractive interaction, upon cathodic polarization a sharp decrease in the surface coverage occurs over a narrow potential range, which results in the appearance of well known peaks on the C/E curves At the peak potential an appreciable change in the reaction rate and in the slope of the polarization curve might be expected, the character of the effects being dependent on 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

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,[14] 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 the positively charged metal Experimental data on the kinetics of reactions which would suit the above conditions to the author's knowledge are yet lacking Temkin's isotherm was initially deduced and applied for the interpretation of reaction kinetics for the case of adsorption on a uniformly inhomogenous platinum surface on the assumption that the change in the activation energy constitutes a certain definite portion of that in the adsorption energy [15] On 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 [16] 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 the Polanyi–Bronsted relation

The reaction behaviour of the molecules adsorbed on an inhomogenous surface is distinguished by some rather unexpected features Thus, the rate-determining step of the oxidation of aliphatic alcohols at not too positive potentials is apparently the detachment of the hydrogen atom from the adsorbed molecule

$$RH_{2ads} \rightarrow RH_{ads} + H_{ads}, \tag{3}$$

ie 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 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 hydrogen ion 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 [17] This example shows how much risk there is in drawing conclusions about the nature of the rate-determining step from the dependence of the potential on log I

Large coverages

In all cases so far considered the reaction rate increases with the coverage At coverages approaching unity, however, an opposite effect may be expected, resulting from the autoblocking of the surface with the initial substance, for example if the particle in the transition state of the reaction occupies a larger area than in the normal adsorbed state Such effects are especially liable to occur if the realization of the transition state requires the adsorption not only of the organic molecule but of some other component of the solution as well Figure 5 shows the dependence of the rate of the catalytic hydrogen evolution from $(C_6H_5)_2NH$ + 0 2 N HCl solutions, which is determined by the discharge rate of the adsorbed ions of diphenylammonium (unpublished 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 θ were determined from the decrease in the differential capacitance of the double layer As can be seen from the figure, as the value $\theta = 1$ is approached, a distinct, though not very large, decrease in the current density 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 [18] Figure 6 shows the dependence of the oxidation rate of methanol on

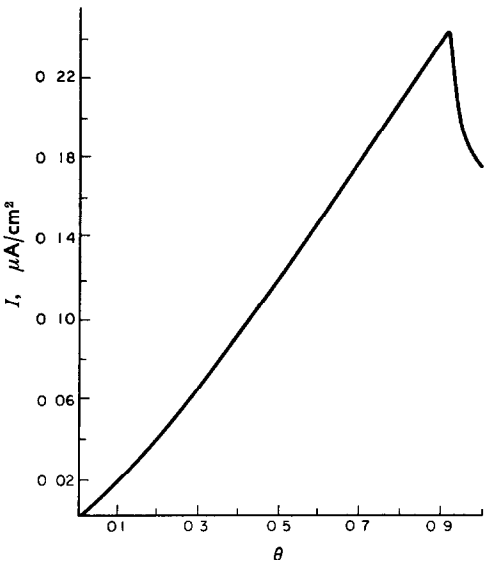

FIG 5 Dependence of catalytic current of hydrogen evolution in 0 2 N HCl + $(C_6H_5)_2NH$ solution at $E = -0\ 8$ V (NCE) on coverage

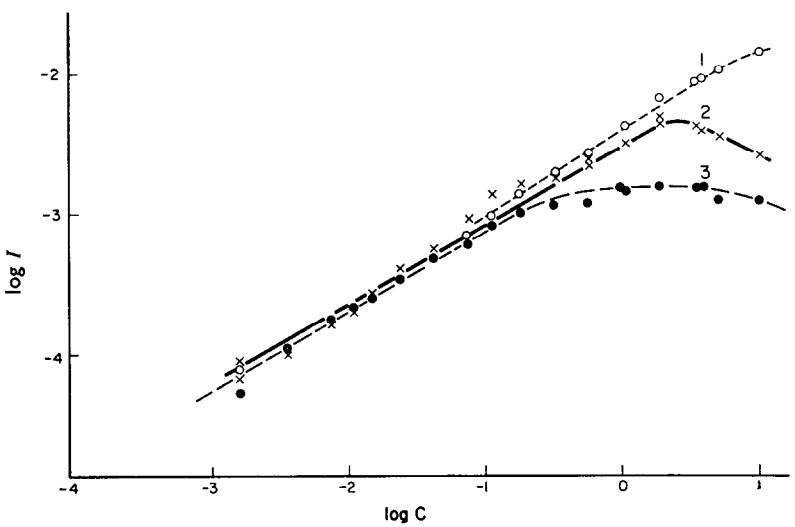

FIG 6 Dependence of oxidation rate of CH_3OH in N H_2SO_4 upon CH_3OH concentration. 1, $E = 1\ 35$ V, 2, $E = 0\ 85$ V, 3, $E = 0\ 65$ V (*vs* hydrogen electrode in same solution)

platinum on its bulk concentration at different potentials, plotted in a logarithmic scale (according to Khazova, Vasiliev and Bagotsky[19]) At not too positive potentials, the effect of large coverages considered above becomes apparent in this case as well

ADSORPTION OF ORGANIC MOLECULES NOT PARTICIPATING IN THE REACTION

At present there is much more information available on the influence of the adsorption of foreign molecules, than on that of the reacting molecules themselves Numerous data from the fields of polarography, metal electrodeposition and inhibiter action relate to this problem Here I shall confine myself to the consideration of two particular questions.

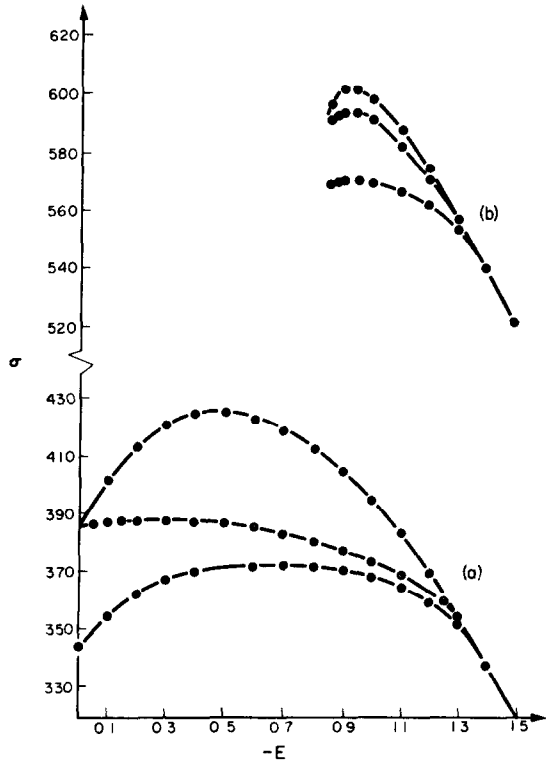

FIG 7 Electrocapillary curves of (a) mercury and (b) gallium in the presence of organic substances

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 (acidified), N KCl + 0 1 M isoamyl alcohol, N KCl + 0 5 M phenol

The rôle of the nature of the metal

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, *eg* when they are used as inhibiters 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 Γ^2/c, rather than by the value of $\Gamma(c$, concentration of the surface active substance) [20] Even in those cases however when the adsorbed substance inhibits, not tangential

motions of the surface but the reaction itself, one should be very cautious in extending the data obtained for mercury to other metals First 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 pointed out by Antropov [21] But even under these conditions the adsorption of organic substances depends on the nature of metal, experiment shows a pronounced dependence This can be seen, *eg* in Fig 7, where electrocapillary curves for isoamyl alcohol and phenol solutions on mercury and liquid gallium are compared (according to Polyanovskaya) [22] The decrease in the surface tension caused by adsorption proves to be much less for gallium than for mercury Especially noteworthy is the fact that, as 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, in contrast to the marked effect 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 a closeness of the adsorption energy values [23] 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 Iofa and Batrakov,[24] judging from the effect upon the capacitance 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 capacitance of the cobalt electrode [24] To use the classic terms of colloid chemistry, we may say that iron is much the most hydrophilic of the 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 inhibiters of acid corrosion of iron has been many times emphasized in the literature It follows from the work of Iofa *et al*,[25] however, that the adsorption of inhibiters on iron at the stationary open-circuit potential in acids is closely bound up with the presence of surface-active anions (Cl^-, Br^-, I^-, SH^-) A 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 inhibiters, is eliminated These problems are considered in more detail by Iofa [26]

Since in the case of adsorption of organic compounds from aqueous solutions we always have to deal with the competition between the molecules of water and those of organic substance (the significance of this point was emphasized recently by Bockris, Devanathan and Muller),[27] in order to understand the different behaviour of various metals it is important to know the free energy of wetting of the uncharged metal surface by water, which can be determined from the surface tensions of the metal and of water and the interfacial tension at the metal/water interface at the maximum of the electrocapillary curve Unfortunately, apart from mercury, these data are available only for liquid gallium The free energy of wetting amounts in that case to *ca* 180–190 erg/cm^2, which appreciably exceeds the value for mercury, 125 erg/cm ^{2}

Inhibition of electron-transfer reactions

It has been stated in the literature that only those reactions that involve a rate-determining chemical step are inhibited by adsorbed organic substances, and that reactions 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 evident, for example, from the reduction reaction of the $Fe(CN)_6^{3-}$ ion to $Fe(CN)_6^{4-}$, which is readily inhibited as shown in Fig 8 (according to Nikolaeva-Fedorovich and Rybalko) [28]

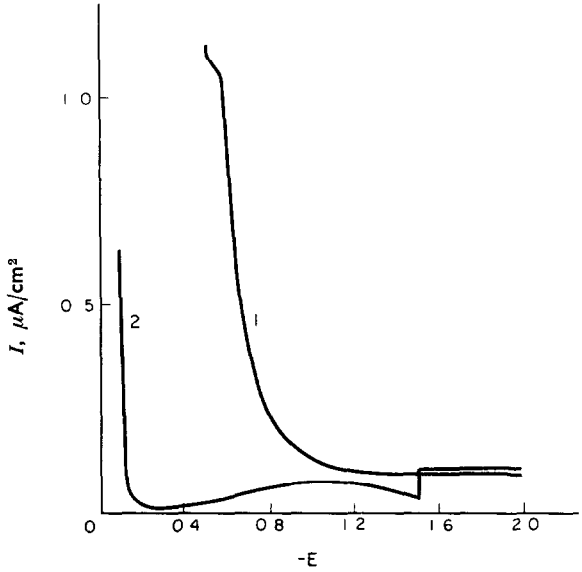

FIG 8 Effect of camphor upon the electroreduction of $Fe(CN)_6^{3-}$ 1, 10^{-3} N $K_3Fe(CN)_6$, 2, 10^{-3} N $K_3Fe(CN)_6$ saturated with camphor

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