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III

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ADSORPTION OF ORGANIC SUBSTANCES AT THE METAL/ELECTROLYTE SOLUTION INTERFACE AND ITS INFLUENCE ON ELECTROCHEMICAL PROCESSES

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To investigate the mechanism of adsorption of organic substances at the metal-electrolyte solution interface it is convenient to proceed by considering the adsorption conditions at the free surface of electrolyte solutions, taking into account the complications arising from the neighbourhood of the metallic phase, as for instance the interaction of the π*-electrons of the organic molecule with the positively charged metal surface, the influence of the electric field of the double layer on the adsorption energy, etc.*

The manifestation of the influence of adsorbed layers on the kinetics of electrode processes reduces in some cases to a rise of the constant a *in Tafel's equation, but in other cases a new rate-determining 'penetration' step appears. The effects observed in the presence of adsorbed organic cations can partly be explained by considering the change of the* ψ_1*-potential in the double layer caused by adsorption.*

By comparing electrocapillary data with results of measurements of surface tension and Volta potentials at the solution/air interface, it can be shown that the behaviour of saturated aliphatic compounds with an oxygen containing polar group at an uncharged mercury/solution interface is in many respects similar to their behaviour at the solution/air interface, the polar group being orientated towards the solution. The surface activities at both interfaces are not very different either[1]*. In the case of compounds with a larger number of polar groups of this kind and especially in the case of compounds with polar groups containing nitrogen, bromine, iodine or sulphur there appear differences connected with the interaction between the polar groups and the metal surface. Thus, thiourea, which is practically inactive at the air/water interface, in a molar solution lowers the mercury/water interfacial tension by *ca.* 40 units. As has been shown by Gerovich[3], an increased surface activity at the mercury/solution interface, especially pronounced when the mercury is positively charged, is observed in the case of aromatic hydrocarbons or aliphatic hydrocarbons with conjugated double bonds. This increased surface activity is probably caused by an interaction between the positive charges of the metal surface and the π-electrons of the organic molecule. The surface activity of hydrocarbons with a similar structure increases *ca.* 21·5 times with the addition of each benzene ring, as shown by *Figure 1*. Considering the adsorption process of aromatic compounds containing polar groups, for instance, phenols, we

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* On adsorption from solutions nearly saturated with capillary active substances polymolecular layers at the mercury/solution interface are built up, which are not observed at the air/water interface[2].

must have in mind, that the benzene ring lying flat at the metal/solution interface, the possibility of interaction between the metal surface and the polar groups is increased compared with the case of the adsorption of long chain aliphatic alcohols, when the polar group is separated from the metal surface by orientated hydrocarbon chains.

As far as it can be judged from electrocapillary data, which are rather scarce, the conditions of adsorption of organic compounds at the interfaces between aqueous solutions and liquid gallium or concentrated Tl-amalgams are not very different from those at the mercury/water interface[4,5].

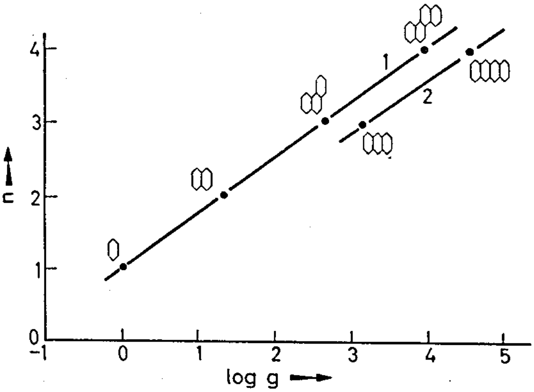

Figure 1. Dependence of the surface activity g of aromatic hydrocarbons in ethyl alcoholic solution on the number of benzene rings in the molecule n. The surface activity g is defined as the reciprocal of the concentration corresponding to a lowering of the mercury/solution interfacial tension by 6·2 *units* (*Gerovich*)

The existence of an intensive electric field at the metal/solution interface hinders the adsorption of organic molecules. If the potential drop in the ionic double layer, whether positive or negative, reaches a sufficiently large value, neutral organic molecules are desorbed[6]. Large organic cations, like $N(C_4H_9)_4^+$, behave in a similar manner, although the desorption of cations on the negative branch of the electrocapillary curve occurs at more negative potentials than the desorption of neutral molecules (for instance, at —1·56 V vs. N.C.E. in the case of 5×10^{-4} N $N(C_4H_9)_4Cl$ + 1 N HCl[7] as compared with *ca.*—1·02 in the case of 0·01 M $C_5H_{11}OH$ + 1 N NaCl). The desorption of organic molecules with the increase of the potential drop, especially if the carbon chain is sufficiently long and the solution not too dilute, occurs within a narrow interval of potentials*. As the charge of the electrode surface is strongly influenced by the presence of adsorbed organic molecules, sharp maxima of the differential capacity, measured for instance by the a.c. method, are observed in the neighbourhood of these desorption potentials[8] (*Figure 2*). The position of these maxima indicate the limits of the potentials which cannot be exceeded without the disappearance of the adsorbed layer. Similar maxima appear on the differential capacity/voltage curves in the presence of capillary active substances also in the case of solid metals[9], indicating that these relationships are not restricted to the case of mercury†.

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* Actually in the case of higher members of homologous series, a two phase transition in the adsorbed layer must occur at a definite potential value.

† According to Kheifetz and Krasikov[10], the desorption of the organic substances from a solid surface on stronger cathodic polarizations is not complete, as in the case of mercury, a part of the adsorbed molecules remaining unaffected.

As the adsorption depends upon the potential drop in the electric double layer, it is necessary in order to determine whether organic molecules can be adsorbed at a definite potential to know the position of this potential relative to the point of zero charge of the given metal. At a potential of —1·4 vs. N.C.E. *iso*amylalcohol (0·1 M $C_5H_{11}OH$ + 1 N KCl) is practically completely desorbed from the mercury/solution interface, whereas there is a considerable adsorption under the same conditions at the surface of liquid Ga, as shown by a lowering of surface tension by *ca.* 25 units[5].

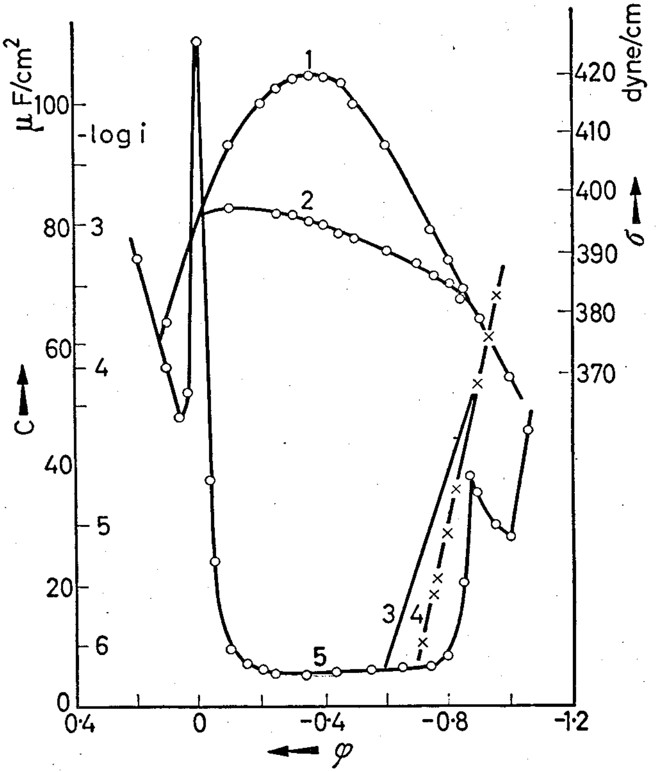

Figure 2. Determination of the desorption potential from measurements of interfacial tension, overvoltage and differential capacity. 1: electrocapillary curve of 2 N HCl; *2: same,* 2 N HCl + 0·01 M n-$C_6H_{13}OH$; *3: current density/voltage curve for* H_2 *evolution from* 2 N HCl; *4: same,* 2 N HCl + 0·01 M n-$C_6H_{13}OH$; *5: differential capacity of* Hg *in* 2 N HCl + 0·01 M n-$C_6H_{13}OH$. *Potentials referred to hydrogen electrode in* 2 N HCl

The shape of the adsorption isotherms of organic substances at the mercury/solution interface at the potential of the electrocapillary maximum is not very different from that of the adsorption isotherms at the air/water interface, but with increasing charging of the surface the adsorption isotherms assume an S-shaped form even in the case of substances like *tert*amylalcohol, which would give approximately Langmuir type isotherms on an uncharged interface[11]. That means, that the electric field of the double layer hinders the adsorption of the organic molecule in a greater measure at small coverages than at higher ones, which can be explained by a gradual decrease of the surface occupied by each molecule with increasing coverage.

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The height of the maxima on the differential capacity/voltage curves determined by the a.c. method decreases with frequency increase, as there is not enough time for the adsorption equilibrium to establish itself at higher frequencies. From the dependence of the height of maxima on the frequency conclusions concerning the rate determining step of the adsorption process can be drawn[12]. Using this method Melik-Gaikasjan[11] found that the rate of adsorption of aliphatic alcohols at the mercury/solution interface is diffusion controlled, the adsorption process itself being too fast to be measured. According to Lorenz[13], who used a similar method, the rate of exchange between the solution and the adsorbed layer, although very large, in some cases still can be determined. Thus, in the case of a 0·2 M solution of phenol, the rate of exchange was found equal to $1{\cdot}6 \times 10^{-4}$ M cm^{-2} sec^{-1}, which means that adsorption equilibrium is reached within *ca.* 2×10^{-6} sec, the concentration in the vicinity of the adsorbing surface being kept constant.

Adsorption equilibrium is apparently reached much more slowly in the case of solid metals. Vahramjan[14] observed a rise of the polarization during the deposition of zinc from a 2 N $ZnSO_4$ solution containing octyl alcohol after an interruption of electrolysis for a certain period of time. The effect became more pronounced with increase of the duration of the interruption and reached its maximum value only if the interruption lasted for *ca.* 30 sec. This delay in reaching adsorption equilibrium might be explained by supposing that a slow chemical process is necessary for the fixation of the alcohol molecules on the electrode surface; it is probable that the inhomogeneity of the solid surface plays a role too.

INFLUENCE OF THE ADSORPTION OF ORGANIC SUBSTANCES ON ELECTROCHEMICAL PROCESSES

Various electrochemical and corrosion processes are greatly influenced by the adsorption of organic substances. It would be certainly impossible to give here a general review of the problem. The author confines himself to some of its particular aspects which have been discussed recently in the Russian literature.

The influence of adsorbed layers on electrochemical processes is sometimes limited, as in the case of hydrogen evolution on mercury from HCl solutions in the presence of saturated fatty acids[15], to an increase of the constant a in Tafel's equation, which means that the mechanism of the process remains essentially the same as in the absence of the organic substance. With hexyl alcohol, although Tafel's relationship still holds in the presence of the adsorbed layer, both constants a and b are affected. The hydrogen overvoltage increase vanishes, as it should be expected, at the desorption potential (*Figure 2.*)

Another reaction, the rate of which is decreased by surface active substances without apparent change in the mechanism, is the exchange of Zn between Zn-amalgam and $ZnSO_4$ solution. In the absence of an inhibitor this exchange is a fast reaction; it has been investigated by Ershler[16], Randles[17] and Gerischer[18] using an a.c. method. Gerischer found the exchange current equal to 0·1 A/cm^2 ($[ZnSO_4] = 0{\cdot}05$ M; $[Zn] = 0{\cdot}6$ M). From the dependence of the exchange current on the concentration of the Zn-amalgam and of the Zn^{2+} ions Ershler and Gerischer calculated the transfer coefficients α and β*. According to

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* The significance of the symbols α and β as used here follows from the statement that the rate of the discharge of Zn^{2+} ions is proportional to $\exp(-\alpha n\varphi F/RT)$ and the rate of ionization of Zn to $\exp(\beta n\varphi F/RT)$, φ being the metal/solution p.d. and $n = 2$ the number of electrons involved.

Ershler $\alpha = 0{\cdot}41$; Gerischer found $\alpha = 0{\cdot}28$, $\beta = 0{\cdot}72$. This reaction as shown by Pleskov[19] is strongly inhibited by $N(C_4H_9)_4^+$. If tetrabutylammonium-sulphate is added in a 5×10^{-5} M concentration to the solution, the exchange current for the same concentrations of $ZnSO_4$ and Zn^{2+} is lowered to a value of 4×10^{-5} A/cm². Under these conditions Losev[20] could determine α and β by direct measurements using traced Zn; he found $\alpha = 0{\cdot}37$ and $\beta = 0{\cdot}58$ in reasonable agreement with the results quoted above.

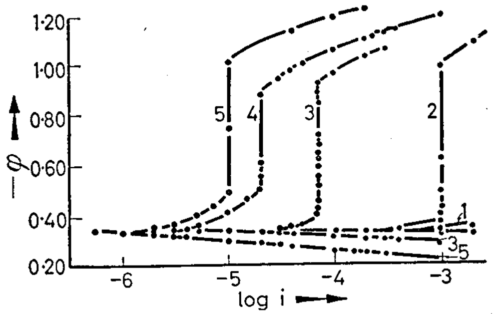

Figure 3. Current density/voltage curves for the deposition and dissolution of cadmium. Cd-*amalgam in* 0·1 N $CdSO_4$ + 4 N $MgSO_4$ + 0·01 N H_2SO_4 + x M $[N(C_4H_9)_4]_2SO_4$. *1:* $x = 0$; *2:* $x = 10^{-5}$; *3:* $x = 5 \times 10^{-5}$; *4:* $x = 2 \times 10^{-4}$; *5:* $x = 1 \times 10^{-3}$ (*Losev*)

Adsorbed layers can cause more pronounced changes in the kinetics of electrochemical processes, too. In some cases in the presence of adsorbed layers a limiting current nearly independent of the potential is observed, indicating that the rate determining step consists now in the penetration of the dissolved reacting particles in the adsorbed layer. Examples of systems of this kind have been given by Loshkarev[21]. In the case of the reduction of Cd^{2+} ions on the surface of a Cd-amalgam in the presence of $N(C_4H_9)_4^+$ in a certain interval of potentials a limiting 'penetration' current is observed, whereas at other potentials, although the reaction is still strongly inhibited, the dependence of the current on the potential is normal[21,22] (*Figure 3*).

The inhibiting effect of organic substances is observed only in the interval of potentials within which the organic molecules are adsorbed, as it was for the first time stated by Kolthoff and Barnum, who investigated the reduction of cystine on a D.M.E. in the presence of camphor and other capillary active substances[23]. Often on increasing the cathodic polarization a limiting diffusion current is observed before the desorption potential is reached, but this does not necessarily mean that the inhibition has disappeared. The correct explanation is that although the inhibition still persists, the reaction rate with increasing polarization has become sufficiently large to make the process as a whole diffusion controlled.

The shape of the current/voltage curves observed in the presence of capillary active substances can be explained using the relationship[24]

$$i = kf(\Gamma)c \exp\left[-\frac{\alpha F}{RT}\left(\varphi + \frac{n-\alpha}{\alpha}\,\psi_1\right)\right] \qquad \ldots(1)$$

which can be applied as long as the whole process is controlled by the discharge step (i: current density; c: bulk concentration of the reacting substance; Γ: amount adsorbed; ψ_1: potential at the distance of closest approach of the reacting particle to the electrode surface; n: number of charges on the reacting particle; $f(\Gamma)$ decreasing function of Γ).

The influence of adsorbed layers on electrochemical processes is certainly a complex phenomenon. A few relevant points should be mentioned here. The retarding action of KCl or $BaCl_2$ on the hydrogen evolution on a Hg-electrode from a dilute solution of hydrochloric acid, as it is known from the theory of hydrogen overvoltage, is quantitatively explained if we take into account the change in the distribution of the potential within the double layer at the metal/solution interface, particularly the shift of the ψ_1-potential towards less negative values[25]. The question arises, whether this electrostatic picture can be applied to organic inhibitors. It appears that this is at least partly possible in the case of organic cations. In fact, as it was already mentioned, organic cations like $N(C_4H_9)_4^+$, which shift the ψ_1-potential towards positive values, strongly inhibit the discharge of Zn^{2+} or Cd^{2+}, as well as the discharge of hydrogen ions on mercury and lead[26], whereas they accelerate the discharge of persulphate anions[27]. In a dilute solution of $K_2S_2O_8$ at potentials which are more negative than the electrocapillary maximum of Hg, the reduction of $S_2O_8^{2-}$ on a mercury electrode is a slow process, the approach of the $S_2O_8^{2-}$ anions to the electrode surface being hindered by electrostatic repulsion[28]. In the presence of capillary active cations even at small concentrations the sign of the ψ_1-potential is reversed, the surface concentration of $S_2O_8^{2-}$ increases and the whole process, as shown by *Figure 4*, becomes diffusion controlled. Such 'ψ_1-effects' become noticeable even at small coverages of the surface by adsorbed ions, as they are dependent on coulombic forces. The accelerating influence

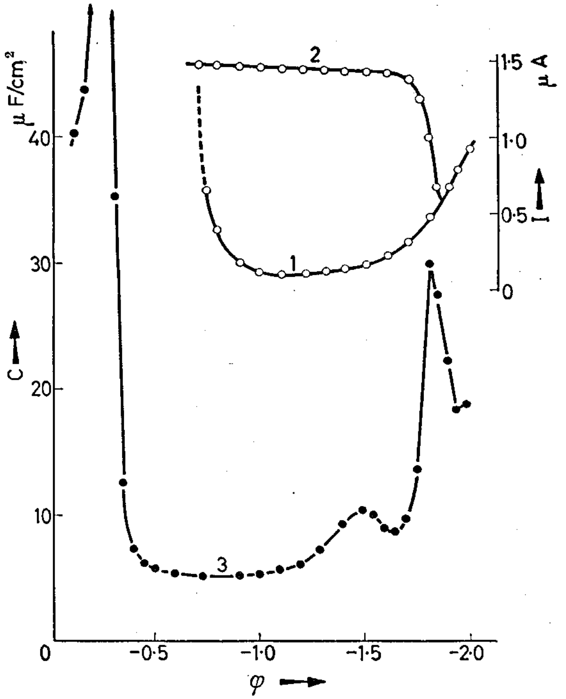

Figure 4. Current/voltage curves for the reduction of $S_2O_8^{2-}$. *1:* 0·001 M $K_2S_2O_8$; *2:* 0·001 M $K_2S_2O_8 + 10^{-5}$ N $[N(C_4H_9)_4]_2SO_4$; *3: differential capacity of* Hg *in* 0·01 N $Na_2SO_4 + 10^{-5}$ N $[N(C_4H_9)_4]_2SO_4$ (*Nikolajeva*)

of the $N(C_4H_9)_4^+$ ions disappears at sufficiently negative potentials, the large organic cations being displaced from the metal/solution interface by inorganic cations and water molecules.

Although, as it follows from this example, the electrostatic factor plays an important role in the case of capillary active organic cations, other factors must be certainly taken into account, too. It follows from equation 1 that in the case of a neutral molecule, that is with $n = 0$, we should expect an acceleration of the electrochemical reaction with increase of ψ_1, if the whole effect of adsorbed cations would be determined by the change of the ψ_1-potential. This conclusion was checked by Loshkarev and A. Kryukova[29]. They found that the rate of electroreduction of cystine is decreased by an addition of capillary active cations, such as for instance tribenzylammoniumsulphate, which shows that the inhibiting action in this case cannot be interpreted as a simple electrostatic effect.

The inhibiting action of adsorbed neutral molecules and, as it follows from what has been already said, to some extent the inhibiting action of large organic cations, too, is connected with the coverage of the surface by adsorbed particles. The adsorbed layer can act either by hindering the approach of the reacting particle to the electrode surface or by creating at the interface conditions unfavourable for the process of discharge (for instance by increasing the distance between the opposite charges in the double layer and thus weakening the electric field at the interface). According to Heyrovsky[30] one-electron transfer processes are not inhibited by adsorbed layers, the inhibiting action being always connected with some intermediate chemical stage of the process. However, Loshkarev and Kryukova were able by a suitable choice of organic substances (camphor, tribenzylammoniumsulphate) to inhibit one-electron processes, like the electroreduction of Tl^+ or Ag^+[29].

As the inhibiting effects are caused by adsorbed molecules, it is obvious that the inhibiting action must increase with increasing adsorbability, if we compare solutions of equal bulk concentration. It would be more correct, however, to compare inhibiting actions at equal surface concentrations, for instance for a complete coverage of the surface by adsorbed molecules. The data available are too scarce to draw definite conclusions. It could be supposed that the substance which has a larger adsorption energy will have a greater influence on the reaction rate, but it follows from the work of Sagaynova and Stromberg[31] that this is not the case. Adsorbed camphor strongly inhibits the exchange of ions between a cadmium amalgam and Cd^{2+} ions. The camphor molecules, as it can be shown by electrocapillary measurements, are at least partly displaced from the mercury/solution interface by gelatine, but the exchange current is thereby raised. It has been shown by Loshkarev that exceptionally great inhibiting effects can be sometimes achieved by a simultaneous adsorption of two (or even three) capillary active substances, for instance β-naphtol + diphenylamine.

Interesting relationships are observed on simultaneous adsorption of surface active anions and organic cations. Only one example will be given here. As it follows from electrocapillary data of Frumkin, the activity of surface active anions like J^- in the presence of $N(C_3H_7)_4^+$ manifests itself even when the mercury surface has a large negative charge. Analogous relations are observed when the kinetics of electrochemical processes are investigated.

The rate of the reduction of $S_2O_8^{2-}$ on a negatively charged mercury surface is not markedly influenced by surface active anions, but in the presence of

$N(C_4H_9)_4^+$ cations on addition of KBr there appears a dip on the current-voltage curve extending to a potential equal to 0·9 vs. N.C.E.[27] (*Figure 5*).

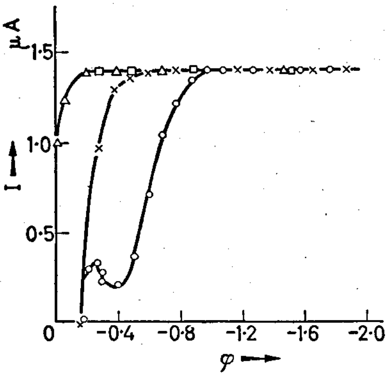

Figure 5. Current/voltage curves for the reduction of $S_2O_8^{2-}$ (*Nikolajeva*)

△: 10^{-3} N $K_2S_2O_8$ + 1 N Na_2SO_4
□: 10^{-3} N $K_2S_2O_8$ + 1 N Na_2SO_4 + 10^{-3} N $[(C_4H_9)_4N]_2SO_4$
×: 10^{-3} N $K_2S_2O_8$ + 1 N KBr
⊙: 10^{-3} N $K_2S_2O_8$ + 1 N KBr + 10^{-3} N $[(C_4H_9)_4N]_2SO_4$

Some other cases of a simultaneous action of surface active organic substances and inorganic ions were discussed by Martirosyan and Kryukova[32]*.

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* A series of papers on the action of surface active substances on the electrodeposition of metals, to be published in a separate issue at the beginning of 1957, were presented at a conference held in Vilnus in June, 1956.

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