Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ON THE ROLE OF POLARITY OF ADSORBATE AND SOLVENT MOLECULES IN ADSORPTION OF ORGANIC SUBSTANCES ON ELECTRODES

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(Received 24th March 1971; in revised form 18th June 1971)

Adsorption of organic substances on electrodes involves interaction of solvent and adsorbate dipoles with surface charges. However, in our treatment of adsorption of organic compounds[1–5] attention was primarily focussed on the influence of the adsorption of organic molecules on the double layer capacity, and relatively less attention was given to the role of the polarity of molecules. According to the theory of Bockris *et al.*[6,7] it is the interaction of water dipoles with the double layer field and the mercury surface which determines the dependence of the adsorption of aliphatic compounds on the electrode charge. It is of interest to consider this problem in more detail on the basis of recent experimental data on adsorption of various aliphatic compounds with different effective dipole moments at the interface of a mercury electrode with aqueous solutions.

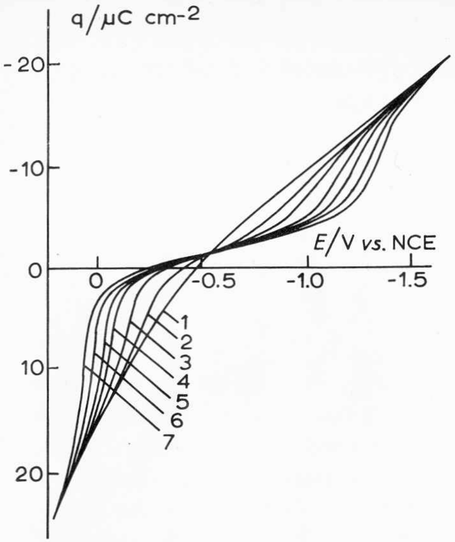
As follows from experimental data, the dependence of the electrode charge q on its potential E in aqueous solutions containing different concentrations of an aliphatic organic compound has the characteristic shape shown in Fig. 1. On the basis of such dependences it is easy to conclude that the q, E-curves for different concentrations of the organic substance are confined between two limiting curves: (i) $q_0 - E$ and (ii) $q_1 - E$, which characterize the dependence of the electrode charge on its potential for the pure supporting electrolyte solution and at the surface coverage with organic substance $\theta = 1$ (see Fig. 2). If no account is taken of the potential drop localized completely in the metal phase, the shift of the potential of zero charge upon transition from $\theta = 0$ to $\theta = 1$, designated by us E_N (Fig. 2), will be equal to the difference

$$E_N = \chi_1^{q=0} - \chi_0^{q=0} \tag{1}$$

where $\chi_1^{q=0}$ and $\chi_0^{q=0}$ are the potential drops due to oriented adsorption of organic substance dipoles (subscript 1) and water (subscript 0) respectively* on the uncharged mercury surface.

Of a more complex nature is the potential shift ΔE, characterizing the transition from $\theta = 0$ to $\theta = 1$ at $q = \text{const.} \neq 0$. Let us denote by C_0 and C_1 the differential

* According to the B.D.M. theory[6] $\chi_1^{q=0} = 0$ and hence the value of E_N, in this case determined by displaced water dipoles, should be the same for all aliphatic compounds. In the later paper of Bockris *et al.*[7] an eqn. (21) is given which contains a term taking account of the dipole effect of adsorbed organic molecules. This should influence the position of the point of intersection of curves 1 and 2 on Fig. 2(see below). However, at the end of this contribution the authors state "that solvent–field and solvent–solvent interactions are the most important contributions to the changes in the free energy of adsorption when the interfacial charge density is varied" that is, the solute–field interaction is considered as of secondary importance.



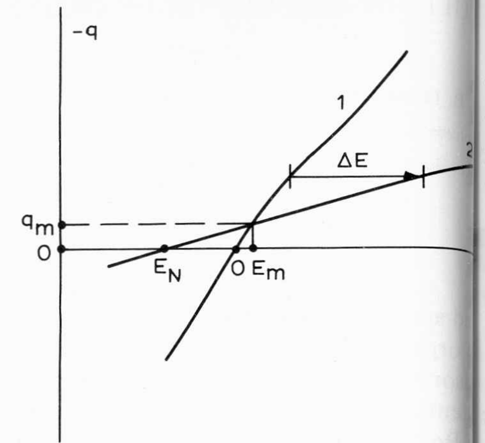


Fig. 1. Dependence of the mercury electrode charge on potential in 0.05 M Na_2SO_4 solns. with differe additions of n-butyl alcohol: (1) 0, (2) 0.05, (3) 0.1, (4) 0.2, (5) 0.4, (6) 0.6, (7) 0.8 M.

Fig. 2. Limiting dependences of the electrode charge on its potential, corresponding to: (1) absence organic substance on the electrode surface, (2) complete coverage of the electrode surface with orga substance.

capacities of the double layer in a pure supporting electrolyte solution and at comple surface coverage with organic substance, respectively. Then for electrode charges $\theta=0$ and $\theta=1$ we shall have the expressions

$$q_0 = \int_0^E C_0 \mathrm{d}E = \bar{C}_0 E$$

and

$$q_1 = \int_{E_N}^E C_1 \mathrm{d}E = \bar{C}_1 (E - E_N)$$

where the potential E is read from the point of zero charge at $\theta=0$, and $\bar{C}_0$ and $\bar{C}_1$ a the double layer integral capacities at $\theta=0$ and $\theta=1$, respectively. If $q_0=q_1=q$, th $E_0=q/\bar{C}_0$; $E_1=E_N+q/\bar{C}_1$ and

$$\Delta E = E_1 - E_0 = E_N + q(1/\bar{C}_1 - 1/\bar{C}_0) = E_N + q\left(\frac{4\pi\delta_1}{\varepsilon_1} - \frac{4\pi\delta_0}{\varepsilon_0}\right)$$

where δ_i is the surface layer thickness and ε_i its dielectric constant, which is a functi of the electrode charge and accounts both for the reorientation effects of organic water dipoles and the polarizability of adsorbed molecules.

Although an unambiguous splitting of the Galvani potential into its comp nents determined by the orientation of the dipoles and the double layer charg respectively, is impossible and depends on the choice of a particular model (se for example, refs. 8–10), for convenience in further treatment we shall carry out th division and, as before, will ignore the change in the electron density distributio

within the metal upon transition from $\theta=0$ to $\theta=1$*. Thus, in accordance with eqns. (1) and (4), we can write:

$$\Delta E = \chi_1^{q=0} - \chi_0^{q=0} + \Delta\chi_1 - \Delta\chi_0 + q\left(\frac{4\pi\delta_1}{\varepsilon_1^0} - \frac{4\pi\delta_0}{\varepsilon_0^0}\right) \tag{5}$$

where $\Delta\chi_i$ are the changes in the surface potential drops determined by the oriented adsorption of dipoles of organic substance (subscript 1) and water (subscript 0) which are caused by the electrode charge and ε_i^0 is the dielectric constant of the surface layer depending only on the polarizability of adsorbed molecules.

According to the B.D.M. theory, the point of intersection of curves 1 and 2 in Fig. 2 determining, as follows from the thermodynamic electrocapillarity equation, the charge q_m (corresponding to the maximum adsorption) should not depend on the adsorbate nature.

The theory based on the two parallel capacitors model makes use of the value of E_N found by extrapolation and the experimental curve of the q_0-E dependence, obtained by integration of the experimental C_0-E curve. Thus, account is taken in eqn. (5) of the terms:

$$\chi_1^{q=0} - \chi_0^{q=0} \ (=E_N) \quad \text{and} \quad -\Delta\chi_0 - \frac{4\pi\delta_0}{\varepsilon_0^0} \ (= -q/\bar{C}_0)$$

regardless of what the components of E_N and $q/\bar{C}_0$ actually are. Further, it is assumed in this theory that $C_1=\bar{C}_1=$const. and, hence $4\pi\delta_1/\varepsilon_1 = 4\pi\delta_1/\varepsilon_1^0$, *i.e.* in eqn. (5) $\Delta\chi_1=0$. Thus, the theory assumes that the possible change of the limiting orientation (at $\theta=1$) of organic dipoles with the change of electrode charge makes an insignificant contribution to the total value of ΔE. This assumption could be avoided if the dependence of C_1 on E were known. Unfortunately, however, it is impossible to obtain by experimental means the C_1-E curve since water molecules cannot be completely eliminated from the surface layer (see also ref. 11). The assumption $\Delta\chi_1=0$ introduces certain errors into the theory. Owing to these errors, in comparing theory with experiment the value of E_N calculated from the drop in adsorption potential at $q=0$ ($E_{q=0}$) proves to be somewhat different from that of E_N found from the position of the maximum adsorption potential E_m, *i.e.* at $q=q_m$.

According to the theory based on the two parallel capacitors model, the q_1-E curve and hence the maximum adsorption charge q_m, depend on the nature of the organic substance, the dipole moment value, the kind of orientation of these dipoles on the electrode surface and on the size of the organic molecule, *i.e.* on all the factors determining the values of $\chi_1^{q=0}$, δ_1 and ε_1^0 contained in eqn. (5).

To verify these conclusions let us consider two relations obtained[2] from the two parallel capacitors model at $C_1=$const.

$$E_{q=0} = E_N C_1 \theta / [\bar{C}_0(1-\theta) + C_1\theta] \tag{6}$$

and

$$E_m = -E_N C_1/(\bar{C}_0 - C_1) = q_m/\bar{C}_0 \tag{7}$$

* This approximation, which might be an important source of error, cannot be avoided as we know practically nothing about this potential drop.

It was pointed out[3,5,11] that for many organic substances the dependence $E_{q=0}-$ follows eqn. (6). For solution of the problem under consideration in the present pape of particular interest is the verification of the relation between E_m and E_N expresse by eqn. (7). However, since E_N cannot be determined directly from experimental dat with sufficient accuracy, it is expedient to use a somewhat different approach. I follows from eqn. (6) that $(\partial E_{q=0}/\partial\theta)_{\theta\to 0}=E_N C_1/\bar{C}_0$. Finding thus an expression fo E_N and substituting it into eqn. (7), we obtain

$$q_m = -\left(\frac{\partial E_{q=0}}{\partial\theta}\right)_{\theta\to 0}\left(\frac{\bar{C}_0^2}{\bar{C}_0-C_1}\right) \quad (8$$

Thus, according to the two parallel capacitors model, the dependence of the quantit $(\partial E_{q=0}/\partial\theta)_{\theta\to 0}(\bar{C}_0^2/(\bar{C}_0-C_1))$ on $-q_m$ should be a straight line with unit slope. Figur 3 shows such a dependence plotted by us from experimental data obtained in ref 12–22 for various aliphatic compounds. In this case the value of $(\partial E_{q=0}/\partial\theta)_{\theta\to 0}$ wa determined on the basis of electrocapillary measurements in solutions containin different concentrations of the organic substance. The values of q_m and C_1 were foun from the position and depth of the minimum on the C–E curves and the value of (to the first approximation was taken to be 20 μF cm^{-2} for all systems.

It follows from Fig. 3 first of all that the maximum adsorption charge does n remain constant and depends on the nature of the aliphatic compound*. Second, as clear from Fig. 3, at $q_m \leqslant 5$ μC cm^{-2} the experimental date are in good agreement wi the theoretical dependence shown in the Figure by the solid line**. Hence, under the conditions the assumption of the constant limiting orientation of organic dipol $(\Delta\chi_1=0)$ is valid. Finally, Fig. 3 shows that the assumption $\Delta\chi_1=0$ is invalid for com pounds with large q_m values. In this case, as would be expected, the value of E_N ca culated by means of eqn. (6) at $q=0$ proves to be less than that found from eqn. (at $q=q_m$: the appearance of a negative charge on the electrode increases the orient tion of organic dipoles with their positive end to the electrode surface. This effe seems to be the more pronounced the greater the potential drop caused by adsorptio of organic substance on the uncharged mercury surface. This assumption correspon to the dashed line in Fig. 3, which expresses the experimental results better.

In the case of a very strong dependence of the orientation of adsorbed dipol on the electrode charge it is impossible to restrict oneself to introducing correctio into the two parallel capacitors model, since in regions of different charge two limiti adsorbate states can be realized, characterized not only by different dipole orient

* The maximum adsorption of many aliphatic alcohols and acids is observed at $q_m \approx 2$ μC cm^{-2}. Acco ing to the B.D.M. theory, this q_m value corresponds to $\chi_0^q=0$ (equal number of water molecules in the s face layer oriented in opposite directions). However, this q_m value can be obtained from eqn. (7) and experimental value of E_N without any assumptions concerning the orientation of water molecules. In fa as follows from eqn. (7)

$$q_m = -E_N C_1 \bar{C}_0/(\bar{C}_0-C_1)$$

Substituting in eqn. (9) $E_N=0.3$ V, $\bar{C}_0=20$ μF cm^{-2} and $C_1=5$ μF cm^{-2} (values characteristic of this ca we find $q_m=2$ μC cm^{-2}.

** The results obtained recently for ethylene glycol[23] are close to our results for propylene glycol (poi on Fig. 3).

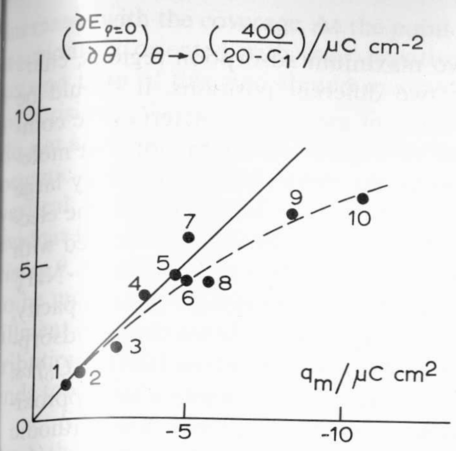
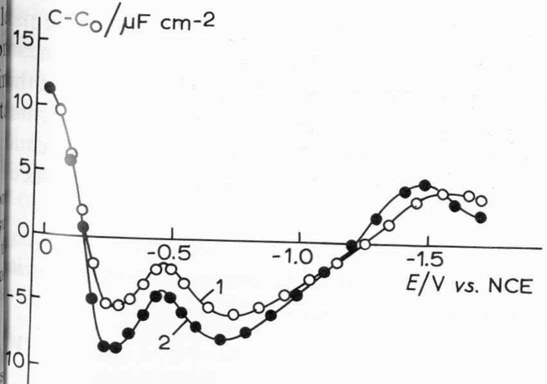


Fig. 3. Dependence of the quantity $400/(20-C_1)\,(\partial E_{q=0}/\partial\theta)_{\theta\to 0}$ on the charge corresponding to maximum adsorption. Solid line corresponds to eqn. (9); points are exptl. data obtained for the following substances: (1) glycerol, (2) different aliphatic alcohols and acids, (3) n-amylamine, (4) 1,2-propyleneglycol, (5) dipropyleneglycol, (6) diethylketone, (7) triethylphosphate, (8) diethyl ether, (9) diethyleneglycol, (10) dimethylformamide.

tion, but also by different free adsorption energy as well as by different interaction between adsorbed dipoles. Such behavior is realized in the case of adsorption on mercury of various aromatic and heterocyclic compounds. A sharp change in orientation of organic molecules with changing electrode potential was recorded for the first time by one of the authors[24] for aromatic amines and some sulfur-containing compounds. Later similar effects were reported by many other investigators (see for example refs. 25–30). For a qualitative description of the behavior of such systems the three parallel capacitors model can be used[4,11], which assumes the existence of two limiting (at $\theta=1$) dependences of the charge on potential, each of which corresponds to one of the possible orientations of organic dipoles. A quantitative correlation of this model with experimental data requires, however, very cumbersome calculations and has not yet



ig. 4. Change of differential capacity of a mercury electrode in 0.05 M Na_2SO_4 soln. upon addition to the ln. of: (1) 0.5 M ω-aminocaproic acid, (2) 0.1 M ω-aminoenanthic acid.

been achieved.

Figure 4 illustrates the existence of two maximum adsorption regions, cha acteristic of organic substances adsorbed in two different positions. It should b stressed that for illustration we have chosen here not aromatic or heterocyclic com pounds changing their orientation as the result of π-electronic interaction, but mol cules of ω-amino acids forming in aqueous solutions zwitter-ions with a very larg dipole moment, owing to which fact their orientation depends strongly on the ele trode charge[31,32]. On a positively charged surface these molecules are oriented wit the group $-COO^-$ towards the electrode, whereas at $q<0$ it is the group $-NH$ which faces the electrode. Since, as regards their effect on the double layer capacit both orientations of these molecules are practically equivalent, the maximum adsorp tion regions are characterized by minima of almost the same depth on the $(C-C_0)$ v E plots, as is clear from Fig. 4. The maximum separating these minima lies approx mately at $q=0$ and corresponds to the reorientation of zwitter-ions. The cathodi maximum and the anodic maximum are ordinary adsorption–desorption peak beyond which the solvent molecules displace organic molecules from the surfac The last conclusion is confirmed by corresponding electrocapillary measuremen carried out in refs. 31 and 32. The measurements of the anodic maximum at mo positive potentials are impeded by the commencing oxidation of the amino grou

Another example of the effect of the dipole moment of an organic substance o the position of the electrocapillary curve maximum is the behavior of halogenate aliphatic acids. While for unhalogenated acids $E_N = +0.24$ V[22], in 0.1 M β-chlor propionic acid solution $E_{q=0} = -0.02$ V, and in 0.2 M β-iodopropionic acid solutio $E_{q=0} = -0.32$ V[24].

The orientation of adsorbed organic and water dipoles determines not onl the limiting dependences of the charge on potential (at $\theta=0$ and at $\theta=1$), but also th relationship between the process of displacement of solvent molecules by those adsorbate and the electrode charge or potential. In fact, as follows from refs. 22 and 3 for the quantitative substantiation of the two parallel capacitors model, *i.e.* of th equation

$$q = \bar{C}_0 E(1-\theta) + C_1(E-E_N)\theta \qquad (1$$

it is necessary to assume that the change of the dipole moment component norm to the surface (μ) with increasing θ is compensated for by the increase of the mea thickness of the surface layer (δ), so that $\mu/\delta = $ const. It should be kept in mind that th value of μ is an effective value in the sense that it accounts not only for the norma component of the dipole moment of an organic molecule, but also for the norma component of those n water dipoles which are displaced by this adsorbate molecu le[6,7,34], *i.e.* $\mu = \mu_\perp^{(\mathrm{org})} - n\,\mu_\perp^{(\mathrm{water})}$.

The behavior of real systems deviates somewhat from the condition $\mu/\delta=$ const., but, as shown in ref. 22, in the case of various aliphatic compounds these devi tions are rather small, so that to the first approximation we can assume

$$[\mu_\perp^{(\mathrm{org})} - n\,\mu_\perp^{(\mathrm{water})}]/\delta \approx \mathrm{const.} \qquad (1$$

On account of the large size of organic molecules compared to those of water, th surface layer thickness δ always increases with increasing θ, therefore the validity o relation (11) means that the positive value of the algebraic sum $\mu_\perp^{(\mathrm{org})} - n\,\mu_\perp^{(\mathrm{water})}$ als

increases with the coverage. At the point of zero charge, where water dipoles are predominantly oriented with their negative ends towards the mercury surface[6,7], the second term of this sum should increase the positive value of effective μ. However, with rising θ, the value of $-n\mu_\perp^{(\mathrm{water})}$ will either remain constant (if organic molecules do not alter their orientation and, hence, $n=$const.), or will decrease (if orientation of organic molecules upon transition from $\theta\to 0$ to $\theta \to 1$ changes from horizontal to vertical, so that at larger θ an organic molecule displaces fewer water dipoles). It is evident that in the former case $\mu=$const. and the ratio μ/δ should drop sharply with rising θ, which is at variance with experimental data. In the latter case, which appears to be more realistic and also makes it possible to explain the Traube rule[35], the fulfillment of condition (11) can be substantiated only if it is assumed that the main contribution to the total value of μ is made by organic dipoles oriented with their positive ends towards the electrode surface.

Since $E_N = 4\pi\mu\nu_\infty/\varepsilon_1$, where ν_∞ is the number of organic dipoles per 1 cm^2 at $\theta=1$, the above reasoning leads us to the conclusion that the major part of the adsorption potential E_N is due to the orientation of organic dipoles and to a lesser degree to the displaced water dipoles, *i.e.* $|\chi_1^{q=0}| > |\chi_0^{q=0}|$. This conclusion is supported by the fact that the electron work function is practically independent of the water vapour adsorption on mercury up to monolayer formation[36]*. Thus, the change in the orientation of water dipoles under the action of the double layer field affects the shape of the q_0 *vs.* E curve only insignificantly (see Fig. 2)**. It is this fact which makes it possible to interpret qualitatively all the characteristic regularities of adsorption of organic substances on electrodes on the basis of linear dependences of q_0 on E and q_1 on E (see ref. 2).

The importance attached to the role of the interaction of water dipoles with the electric double layer field[6,7] leads to the conclusion that those molecules which have the largest dipole moment per unit surface should be preferentially adsorbed at a large electrode charge. In accordance with this conclusion, it would be expected that adsorption of molecules of ω-aminocaproic and ω-aminoenanthic acids (whose dipole moment[43] in aqueous solutions is about 29 D) on a mercury electrode should increase with increasing electrode charge (both positive and negative). However, Fig. 4 shows that in accordance with the two or three parallel capacitors model, any substance whose adsorption decreases the capacity at low charges, at high charges is displaced from the surface by the solvent molecules regardless of the ratio between the dipole moments of organic substance and water.

Gileadi *et al.*[44,45] suggest that in the case of phenol adsorption on platinum and hydrazine adsorption on gold, in the anodic potential range these substances compete with a completely oriented layer of water dipoles. As shown by calculation, the existence of such a layer of adsorbed water dipoles should cause a potential drop

* Our conclusion concerning the value of $|\chi_0^{q=0}|$ contradicts that of Oel and Strehlow[37]. In order to explain the supposed difference between the Lippmann and the Billiter potentials of zero charge, Oel and Strehlow had to assume that $|\chi_0^{q=0}|$ amounts to as much as 0.7 V. However, the whole Billiter potential concept apparently has to be abandoned now[38,39].

It has also to be kept in mind that the adsorption isotherm of water vapour on mercury has an S-shaped form[40,41], which points to an attractive interaction between water dipoles adsorbed on an uncharged mercury surface, incompatible with their parallel orientation.

** These conclusions agree with the model of the mercury/water interface presented in ref. 42.

of ~1.2 V. Since these dipoles are oriented with their negative ends towards the e trode surface, at a given distance from the point of zero charge this should lead sharp increase of the positive electrode charge. In actual fact, however, in the an range on platinum metals, in the absence of pronounced specific anion adsorpt a marked decrease of positive q is observed[46]. This phenomenon is explained by sorption of oxygen atoms which, together with surface metal atoms, form dip oriented with their positive ends towards the electrode. The appearance on the e trode surface of O_{ads}, rather than that of oriented water dipoles, is the main rea of desorption of adsorbed molecules in the systems considered by Gileadi. The of adsorbed hydrogen and oxygen atoms in adsorption of organic substances electrodes was discussed earlier[5].

SUMMARY

The role of the orientation of adsorbed dipoles of water and organic substa at the electrode/solution interface is discussed. It is shown that the charge correspo ing to maximum adsorption on mercury of different aliphatic compounds does remain constant but varies within rather wide limits depending on the polarit adsorbate molecules. This proves the importance of the interaction of adsor organic dipoles with the double layer field in the adsorption of organic substances electrodes.

The displacement of adsorbed organic molecules by water molecules at su cient large electrode charges is determined by the ratio of the capacities in the abse of adsorbate and at complete coverage of the electrode surface with it, rather than the ratio of the effective dipole moments of these molecules per unit surface.

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