ADSORPTION OF MOLECULES ON ELECTRODES

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Adsorption of organic substances at the electrode/solution interface is one of the important factors determining the kinetics and mechanism of electrode processes. First of all we should mention electroorganic synthesis reactions, the role of organic additions in the processes of electrodeposition of metals and alloys and the inhibition of metallic corrosion by organic inhibitors. In some cases it is necessary to have data on adsorption of organic substances on the surface of the dropping mercury electrode for successful use of polarography. Moreover, the investigation of adsorption phenomena at the electrode/solution interface is of interest by itself in connection with further development of the theory of the electric double layer structure. These circumstances are responsible for the interest shown lately in the investigation of adsorption of organic substances on electrodes.

Most of the theoretical and experimental investigations of adsorption have been carried out on the mercury electrode, using mainly the methods of surface tension and differential capacity measurements. The investigation of adsorption of organic substances on solid electrodes involves a number of experimental difficulties. Thus there are no methods available at present which would permit us to determine the absolute surface tensions of solid electrodes, whereas the interfacial impedance measurements, giving quantitative data on the state of the surface of a liquid electrode, for a number of reasons are of limited applicability in the case of many solid electrodes (e.g. platinum metals). Quantitative investigations of adsorption of organic compounds on solid metals have become possible only in the past 10–15 years, following the development of the radioactive tracer technique, the pulse-potentiostatic, galvanostatic and some other methods. Even now, adsorption measurements on solid metals are performed with less accuracy than on the mercury electrode. This is due both to limitations of the methods and to specific properties of solid surfaces.

Since adsorption of organic compounds at the electrode/solution interface changes the wetting of the metal by the solution, affects its mechanical properties (e.g. hardness, creep, etc.), and in most cases leads to an appreciable change in the rate of electrochemical reactions, all these phenomena can be used for a qualitative description of adsorption processes. A detailed review of various methods for the investigation of adsorption of organic substances on the surface of liquid and solid electrodes is to be found in Reference 1.

In this review we shall consider the main regularities in adsorption of organic molecules on the mercury electrode surface and in the last section also the problem of the influence of the nature of the metal on adsorption of organic compounds.

I. THERMODYNAMIC METHODS OF ESTIMATION OF ORGANIC SUBSTANCE ADSORPTION FROM THE SURFACE TENSION AND DOUBLE LAYER CAPACITY MEASUREMENTS

As has been shown independently by a number of authors,[2–4] it is possible to apply to the electrode/solution interface the thermodynamic equations relating the surface tension σ to the electrode potential E, as well as to the adsorptions and activities of ions and molecules of the solution (Γ_i and a_i, respectively). At constant pressure and temperature the basic equation of electrocapillarity can be written as

$$d\sigma = -q\,dE - \sum_i \Gamma_i\,d\mu_i = -q\,dE - RT\sum_i \Gamma_i\,d\log a_i \qquad (1)$$

where μ_i is the chemical potential of the i-th component, R is the gas constant and T is the absolute temperature. In the general case, the quantity q in eqn (1) is the Gibbs adsorption of the potential-determining ions expressed in electric units. In the case of the mercury electrode, however, which can be considered with sufficient accuracy as being ideally polarizable, q coincides with the surface charge of the metal.

Equation (1) can be used for a quantitative determination of adsorption of the solution components on the mercury surface. It should be borne in mind however that the physical significance of Γ_i varies depending on the conditions of the choice of the Gibbs plane.[5] Let us consider this question for the case of a two-component system: an alcohol solution (2) in water (1). At E = constant it follows from eqn (1) that

$$\mathrm{d}\sigma = -\Gamma_1\,\mathrm{d}\mu_1 - \Gamma_2\,\mathrm{d}\mu_2 \tag{2*}$$

If the Gibbs plane is chosen in such a way that $\Gamma_1 = 0$, the experimental value of $\Gamma_2^0 = -\mathrm{d}\sigma/\mathrm{d}\mu_2$ determined by this condition is the excess of alcohol moles in a solution fraction containing unit interface over the solution fraction from homogeneous bulk containing an equal amount of water moles.

Another method for the choice of the Gibbs plane conforms to the condition

$$\mathrm{v}_1\Gamma_1^{\mathrm{v}} + \mathrm{v}_2\Gamma_2^{\mathrm{v}} = 0 \tag{3}$$

where v_1 and v_2 are partial molar volumes of water and alcohol, respectively. The quantity Γ_2^{v} determined by this condition is the excess of alcohol moles in the solution fraction containing unit interface over the same volume fraction of homogeneous solution. This corresponds to the closest approach of the Gibbs plane to the physical boundary between the electrode and the solution.

Equations (2) and (3) in combination with the Gibbs-Duhem equation

$$N_1\,\mathrm{d}\mu_1 + N_2\,\mathrm{d}\mu_2 = 0 \tag{4}$$

where N_1 and N_2 are molar fractions of water and alcohol in the bulk of the solution, permit to relate Γ_2^{v} to Γ_2^0. In fact, eliminating from these equations Γ_1^{v} and $\mathrm{d}\mu_1$, we obtain

$$-\frac{\mathrm{d}\sigma}{\mathrm{d}\mu_2} = \Gamma_2^0 = \Gamma_2^{\mathrm{v}}\left(1 + \frac{\mathrm{v}_2 N_2}{\mathrm{v}_1 N_1}\right) \tag{5}$$

It follows from eqn (5) that in sufficiently diluted solutions, when the quantity $\mathrm{v}_2N_2/\mathrm{v}_1N_1$ can be neglected compared to unity, $\Gamma_2^0 \approx \Gamma_2^{\mathrm{v}}$.

It follows from the above that the physical significance of Γ_2^0 and Γ_2^{v} does not conform to the concept of adsorption as the surface concentration of the substance being adsorbed. For the quantities Γ_1 and Γ_2 contained in eqn (2) to have the physical significance of surface concentrations it is necessary to assume that the heterogeneous region near the electrode surface is confined

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* Equation (2) remains valid if in addition there is an indifferent electrolyte with constant activity present in the solution.

within the monolayer of the substance being adsorbed and that the Gibbs plane separates this monolayer from the homogeneous solution.[5] Let us designate the surface concentrations of water and alcohol thus determined by Γ_1^1 and Γ_2^1. Then from eqns (2) and (4) we obtain

$$-\frac{\mathrm{d}\sigma}{\mathrm{d}\mu_2} = \Gamma_2^0 = \Gamma_2^1 - \Gamma_1^1 \frac{N_2}{N_1} \tag{6}$$

Formula (6) is an equation in two unknowns: Γ_1^1 and Γ_2^1, which therefore cannot be determined by a strictly thermodynamic method.

In order to determine Γ_2^1 (or Γ_1^1), it is necessary to make some model assumptions regarding the structure of the interface from which it will be possible to estimate the areas per 1 mole of organic substance and 1 mole of water in the surface layer (S_2 and S_1, respectively). Then Γ_1^1 and Γ_2^1 can be found by solving the set of equations:

$$\left.\begin{aligned} \Gamma_2^0 &= \Gamma_2^1 - \Gamma_1^1 \frac{N_2}{N_1} \\ \Gamma_1^1 S_1 + \Gamma_2^1 S_2 &= 1 \end{aligned}\right\} \tag{7}$$

A rough calculation based on the assumption that an organic substance molecule occupies on the surface an area 22 Å^2 and a water molecule—10 Å^2 leads to the conclusion that at the organic compound concentration in aqueous solutions $c_2 \leqslant 0{\cdot}5$ M with an accuracy not less than 3 per cent, $\Gamma_2^1 \approx \Gamma_2^0$. Thus under these conditions the experimental values of Γ_2^0 can be considered as surface concentrations of organic substances. For simplicity, hence we shall write the experimental value of Γ_2^0 as Γ_2, bearing in mind however that the values thus obtained refer to the plane where $\Gamma_1 = 0$.

From electrocapillary measurements the values of Γ at a given potential can be readily determined by means of eqn (1), which gives:

$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \log a_i}\right)_E \approx -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \log c_i}\right)_E \tag{8}$$

where c_i is the concentration of the ith component.

In order to obtain the values for the extent of adsorption at a given electrode charge, it is necessary to introduce a new function $\xi = \sigma + qE$,[6] the total differential of which is

$$\mathrm{d}\xi = \mathrm{d}\sigma + q\,\mathrm{d}E + E\,\mathrm{d}q \tag{9}$$

It follows from eqns (1) and (9) that

$$\mathrm{d}\xi = E\,\mathrm{d}q - RT\sum_i \Gamma_i\,\mathrm{d}\log a_i \tag{10}$$

whence

$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial \xi}{\partial \log a_i}\right)_q \approx -\frac{1}{RT}\left(\frac{\partial \xi}{\partial \log c_i}\right)_q \tag{11}$$

The adsorption isotherms obtained from the experimental data by means of eqns (8) and (11) are self-consistent in the sense that by calculating by means of eqn (8) the Γ,c-curve at E = constant and knowing the dependence of q on E at various concentrations of the substance being adsorbed, it is possible to plot the Γ,c-curve at q = constant, coinciding exactly with the adsorption isotherm calculated by means of eqn (11). Thus with a strictly thermodynamic approach to the investigation of the adsorption isotherms, the choice of the electric variable is of no fundamental significance and is determined by considerations of convenience.

Apart from electrocapillary measurements, the data on adsorption of organic compounds at the electrode/solution interface can be obtained also from differential capacity (C) measurements. The thermodynamic method of the application of the capacity measurements is based on double integration of the C,E-curve, which in accordance with the Lippmann equation gives the dependence of the surface tension on the electrode potential

$$q = \int_{E_{q=0}}^{E} C\,\mathrm{d}E \tag{12}$$

$$\sigma = \sigma_{q=0} - \int_{E_{q=0}}^{E} q\,\mathrm{d}E \tag{13}$$

Then the σ,E-curves (or the ξ,q-curves) thus obtained are used to estimate adsorption of the components, as is described above.

This method requires two integration constants to be known. In eqn (12) such a constant is the potential of zero charge $E_{q=0}$, and in eqn (13) $-\sigma_{q=0}$, i.e. the value of σ at the electrocapillary curve maximum.

A review of various methods for the determination of the zero charge potentials as well as the most reliable values of $E_{q=0}$ are to be found.[7] As regards the second integration constant, its determination involves electrocapillary measurements near $E_{q=0}$.

The capacity method is much simplified when it is used to study adsorption of an organic substance which is added in small concentrations to an indifferent electrolyte solution (the supporting electrolyte) and desorbed at sufficiently negative electrode potentials, so that the differential capacity curves measured in the presence of organic substance additions coincide with the C,E-curve of the supporting electrolyte. The double layer structure being determined under such conditions only by the indifferent electrolyte composition, it is quite natural to assume that at such negative potential (say, E_1) not only the differential capacity values should coincide in a pure electrolyte solution and in solutions with organic substance additions but also those of q and σ. Thus in this case the integration constant in eqn (12) is the electrode charge in the supporting electrolyte solution at $E = E_1$, and the integration constant in eqn (13) the value of σ in the supporting electrolyte solution at $E = E_1$. Under these conditions integration is performed from negative (beginning with E_1) to positive potentials (the 'backward integration' method).[8] Since in further calculations of adsorption by means of eqn (8) it is necessary to know only the change in the surface tension with increasing organic substance concentration rather than the absolute values of σ, in calculating the electrocapillary curve of the supporting electrolyte it is possible to put the constant $\sigma_{q=0}$ equal to zero. Thus in calculating adsorption from differential capacity measurements, the only necessary constant under given conditions is the value of $E_{q=0}$ in the supporting electrolyte solution.

The drawback of this method is that at small organic substance concentrations there is not enough time for the equilibrium in the double layer to be established within the half-period of the alternating current used to perform the differential capacity measurements and it becomes necessary to extrapolate the non-equilibrium capacity values measured to zero frequency.[9–12] This method was used for the investigation of thiourea adsorption on mercury[13] and, along with others for the adsorption of aniline, phenol and pentafluorophenol.[14–16]

II. BASIC QUALITATIVE REGULARITIES IN ADSORPTION OF ORGANIC SUBSTANCES ON THE MERCURY ELECTRODE

Beginning with the works of Gouy,[17] the method of electrocapillary curve measurements has been widely used for the investigation of adsorption of a great variety of organic compounds.[14–16,18–60] As is clear from Fig. 1, adsorption of an organic substance (in this case n-butanol) markedly lowers the surface tension of mercury, the decrease of σ being maximal near $E_{q=0}$ of the supporting electrolyte and becoming less pronounced with increasing negative or positive surface charge. In the case of aliphatic compounds, at large enough $|q|$, the electrocapillary curve measured in the presence of organic substance additions coincides with the σ,E-curve of the supporting electrolyte (Fig. 1). According to eqn (8), this means that at large charges organic molecules are desorbed from the electrode surface.

The adsorption of an organic substance on the electrode surface increases with increase of its bulk concentration (Fig. 1) and of the indifferent electrolyte concentration (the salting out effect), as well as with increasing length of the hydrocarbon chain in molecules of organic substances of a homologous series. A detailed study of the last-mentioned effect for the case of adsorption of normal acids, alcohols and amines of the fatty series[50-51] showed the Traube rule to be valid under such conditions.

The electrocapillary curves measured in the presence of organic compounds often exhibit a shift of the electrocapillary maximum $\Delta E_{q=0}$.

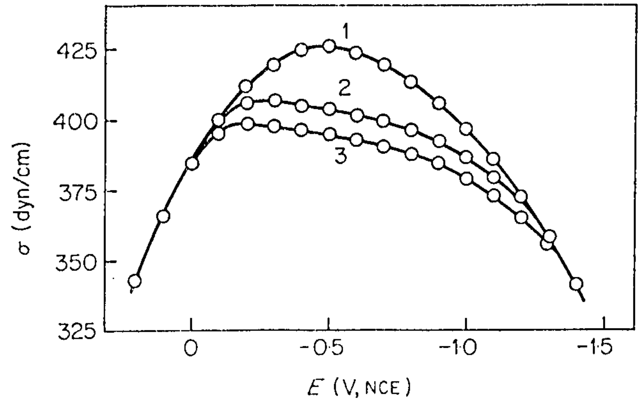

Fig. 1. Electrocapillary curves of a mercury electrode in 1 N Na_2SO_4 solution (1) and with additions of *n*-butyl alcohol in concentrations: 2 — 0·1 M, 3 — 0·2 M.

The comparison of the values of $\Delta E_{q=0}$ and the adsorption shifts of the potential ΔE at the solution/gas interface in the same solutions shows that the adsorption of molecules of aliphatic oxygen compounds at both interfaces involves identical in sign and nearly equal potential drops.[19-22] This result can be explained as being due to the substitution of the water dipoles oriented with their negative end towards air or mercury by the organic substance molecules oriented with their hydrocarbon chain towards the interface, so that the C—O bond sets up a positive potential difference between the outer phase and the bulk of the solution. However, Devanathan,[61] as well as Bockris, Devanathan and Müller,[62] associated the shift of $E_{q=0}$ in the presence of aliphatic compound only with the expulsion of water dipoles from the double layer, the polar group of the organic molecule located outside the double layer having, in their opinion, no effect on the value of $\Delta E_{q=0}$ being measured. These concepts are difficult to accept.[64,65] It should be noted that a similar concept for the case of the solution/air interface advanced by Kamiensky[63] leads to impossible values of chemical hydration energies of cations and anions.[66]

The comparison of the adsorption potential drops at the two interfaces in the case of aromatic compounds shows considerable discrepancies between $\Delta E_{q=0}$ and ΔE to the extent of their having different signs in some cases.[20,21] Another anomaly is that the electrocapillary curves measured in the presence of some aromatic compounds do not coincide with the σ,E-curve of the supporting electrolyte even when the most positive values of q are reached. The σ,E-curves measured in the presence of aniline, which are shown in Fig. 2 are an example of this case. The reasons for these anomalies were first established by Gerovich and collaborators.[28-31] The investigation of adsorption on mercury of benzene, naphthalene, anthracene, phenanthrene and chrysene as well as the comparison of the electrocapillary behaviours of aromatic and of the corresponding hydroaromatic hydrocarbons showed that the shift of the point of zero charge in the negative direction (or a decrease in the positive value of $E_{q=0}$) and the adsorption of aromatic compounds at larger positive q are associated with the effect of the interaction between π-electrons of the aromatic ring and the charges of the mercury surface. Later these conclusions were experimentally confirmed in the case of adsorption of other aromatic and heterocyclic compounds.[35-46] The substitution of fluorine for hydrogen atoms in aromatic compounds leads to the depletion of the aromatic ring π-electron density owing to the strong electron affinity of fluorine atoms. As a result, the π-electron interaction hardly affects the adsorption on mercury of the molecules of pentafluoroaniline, pentafluorobenzoic acid and pentafluorophenol.[16,52]

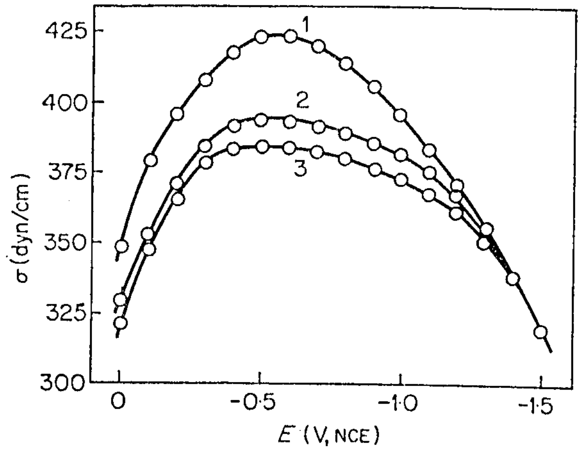

Fig. 2. Electrocapillary curves of a mercury electrode in 1 N KCl solution (1) and with additions of aniline in concentrations: 2 — 0·05 M, 3 — 0·1 M.

According to Blomgren, Bockris, and Jesch,[37] in the case of adsorption on mercury of molecules both of aliphatic and aromatic compounds the role of the functional group is determined mainly by its influence on the solubility. The comparison of the adsorption behaviour of organic molecules at the solution/mercury and solution/gas interfaces shows these relations to be somewhat more complicated.[54] In fact, it follows[50–51] that the adsorption behaviour of aliphatic alcohols, acids and amines does not differ much at the solution/mercury and solution/gas interfaces. However, in the case of acids and especially of alcohols, the surface activity at the interface with mercury is somewhat lower than at the interface with air, whereas the opposite is true for amylamine and partly for butylamine. Therefore the nature of the polar group, in spite of its being turned towards the solution and thus removed from the mercury surface, affects somewhat the change in the adsorption energy when passing from the free surface of the solution to the interface with mercury.

The slight difference in the adsorptivities of normal aliphatic compounds of the fatty series at the interfaces with mercury and with air indicates that the gain in free energy upon contact of mercury with hydrocarbon tails of organic molecules is approximately compensated by its consumption in the removal of adsorbed water molecules. Such compensation however cannot be general, as is evident from the consideration of adsorption of organic compounds with horizontal orientation at the interface. The horizontal orientation is to be expected in the case of hydrocarbons without polar groups, at any rate at small surface coverages. Under these conditions the adsorptivity of *n*-hexane decreases greatly when passing to the interface with mercury.[53] In this case the decrease in the free energy gain when a hydrocarbon molecule is transferred from the bulk of the solution to the surface is due to the fact that with horizontal orientation of hydrocarbon molecules water is displaced from the mercury surface mainly by $>CH_2$ rather than by $—CH_3$ groups. This phenomenon is also observed in the case of adsorption of perfluorinated compounds where it is even more pronounced.[49] Hence the gain in free energy upon wetting of mercury by the $—CF_3$ and $>CF_2$ groups is much less than upon its wetting by water.

In addition to hydrocarbons, the horizontal orientation is also characteristic of aliphatic compounds with two or more functional groups, e.g. glycols, glycerine, or ethylenediamine. Under these conditions, the interaction of the polar group with the mercury surface results in the adsorptivity of the organic compound being appreciably higher at the solution/mercury than at the solution/gas interface.[21]

A sharp increase in the surface activity when passing to the solution/mercury interface is observed in the case of tetrabutyl- and tetrapropylammonium cations.[67] This effect can be accounted for by electrostatic interaction of the charge of R_4N^+ cation with the induced charge in the metal phase. However in the case of propyl-, butyl-, and amylammonium cations, the mirror image effect is much weaker due to strong hydration of the functional group in compounds of the RNH_3^+ type.[67]

As has been already pointed out above, the main difference in the adsorption behaviours of aromatic and heterocyclic compounds at the interface with mercury and at the solution/gas interface is due to the π-electronic interaction. However of essential importance for the increase of adsorptivity of these compounds when passing to the interface with mercury is the interaction of mercury with the polar group as well. The π-electronic interaction favours a more horizontal orientation of the molecules of aromatic substances at the solution/mercury interface and this, in its turn, facilitates the interaction of the polar group with the metal. Thus the introduction of the polar group into the aromatic compound molecule along with decreasing the surface activity at the solution/gas interface (due to increasing solubility) can lead to an increase in the surface activity at the interface with mercury. Such an effect is observed in the case of a transition from benzene to aniline.[54]

When two surface-active substances are simultaneously present in the solution their adsorption is largely determined by the interaction of the molecules of these substances within the adsorption layer.[24,60] It is of interest to note that the regularities of the simultaneous adsorption of *n*-butyl alcohol and aniline are essentially different for positive and negative charges of the mercury electrode.[60] Thus at $q < 0$ the simultaneous presence of these two substances in the solution can increase the adsorption and the electrocapillary curve of the solution of the aniline-butanol mixture lies below the σ,E-curves for the solutions of individual substances. At positive electrode charges with increasing q, the σ,E-curve in the presence of two additions approaches the electrocapillary curve for the aniline solution. Butanol is desorbed from the electrode surface covered by aniline molecules, as it would be desorbed in the absence of aniline. Evidently, the difference in the behaviour of the aniline—*n*-butanol mixture on different branches of the electrocapillary curve is accounted for by different orientations of adsorbed aniline molecules at $q > 0$ and at $q < 0$.[14]

The differential capacity being the second derivative of the surface tension with respect to the potential, the shape of the C,E-curve is much more sensitive to any changes in the double layer structure than that of the electrocapillary curve. High sensitivity of the double layer capacity to traces of organic impurities in the solution was the reason why many investigators failed to verify by this method the Lippmann equation. After Proskurnin and Frumkin's work[68] the method of differential capacity measurements come into general use for investigations of the electric double layer structure and adsorption of various organic substances.

However, the differential capacity of the double layer is a much more complex function of adsorption of organic molecules than surface tension, so that a strictly thermodynamic approach to the estimation of adsorption from the *C,E*-curves measurements is not very extensively used. In quantitative investigations the *C,E*-curves measurements are as a rule supplemented by electrocapillary measurements or some model representations of the systems being investigated.[10–16,46,56–61,69–82]

In most cases the region of organic substance adsorption on the *C,E*-curves corresponds to a region of low capacity values limited on both sides by the adsorption—desorption peaks (Fig. 3). At large enough positive and negative electrode charges, when organic molecules are practically completely desorbed from the surface, the *C,E*-curves measured in solutions with organic substance additions coincide with the *C,E*-curve of the supporting electrolyte. As is clear from Fig. 3, with increasing organic substance concentration, the

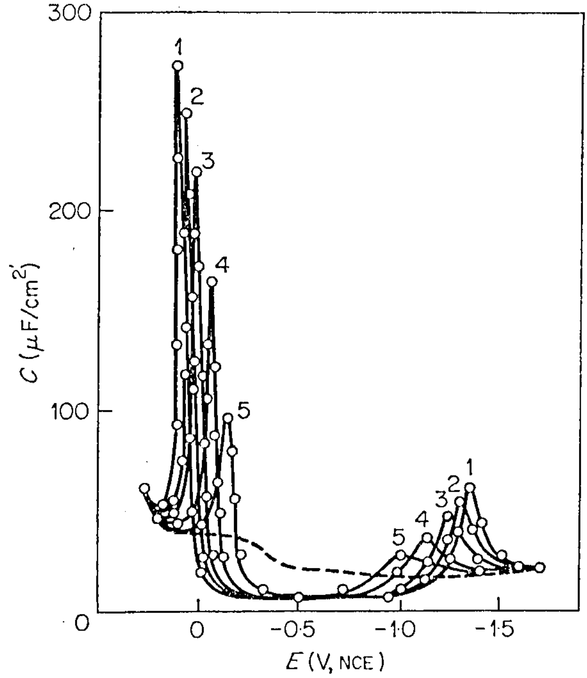

Fig. 3. Differential capacity curves of a mercury electrode in 0·1 N Na_2SO_4 solution (dashed line) and with additions of *n*-butyl alcohol in concentrations: 1 — 0·8, 2 — 0·6, 3 — 0·4, 4 — 0·2, and 5 — 0·1 M. Frequency 400 cps.

adsorption region widens, the adsorption peaks become higher and the capacity at the minimum of the *C*,*E*-curve tends to approach a limiting value of the order of 4–5 μF/cm^2. These regularities make it possible to use the method of differential capacity curves measurements for a qualitative determination of adsorptivity of various organic substances at the electrode/solution interface. Quite a number of studies have been carried out in this direction (for a list of these see[1] and[64]). It should be emphasized however that the use of this method alone in some cases can lead to erroneous conclusions. In fact comparing Figs. 3 and 4, and observing their outward similarity, one could conclude that aniline molecules, just as those of n-C_4H_9OH, are desorbed from the mercury surface at a large enough positive surface charge. That this conclusion is erroneous is evident from σ,*E*-curves in aniline solutions

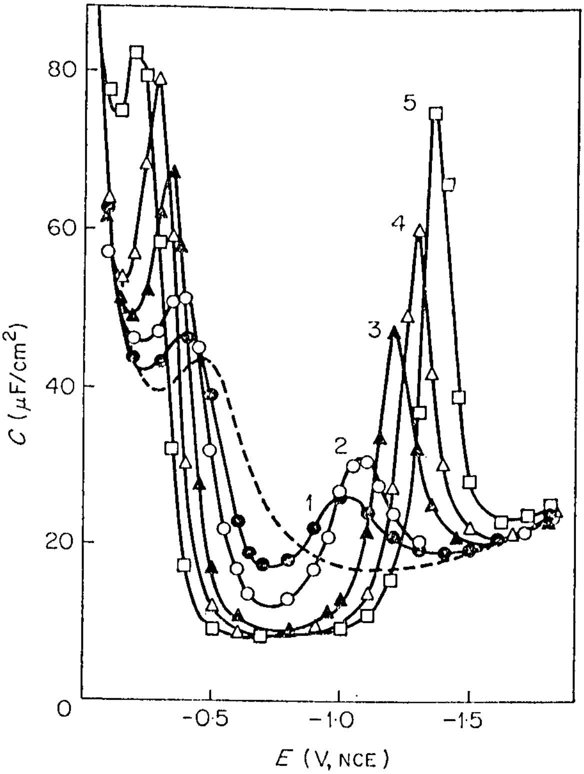

Fig. 4. Differential capacity curves of a mercury electrode in 1 N KCl solution (dashed line) and with additions of aniline in concentrations: 1 — 0·01, 2 — 0·02, 3 — 0·05, 4 — 0·1, and 5 — 0·2 M. Frequency 400 cps.

(Fig. 2). Thus in respect of adsorption the system KCl + aniline proves to be more complex than Na_2SO_4 + *n*-butanol. While in the presence of aliphatic compounds both maxima on the *C*,*E*-curves are connected with the adsorption-desorption processes, only the cathodic maxima correspond to these processes in the case of aniline, whereas anodic maxima are associated with the process of re-orientation of adsorbed aniline molecules: vertical orientation of molecules characteristic of $q < 0$ being replaced by a horizontal one which favours the π-electronic interaction of the benzene ring with the positive charges of the mercury surface.[14]

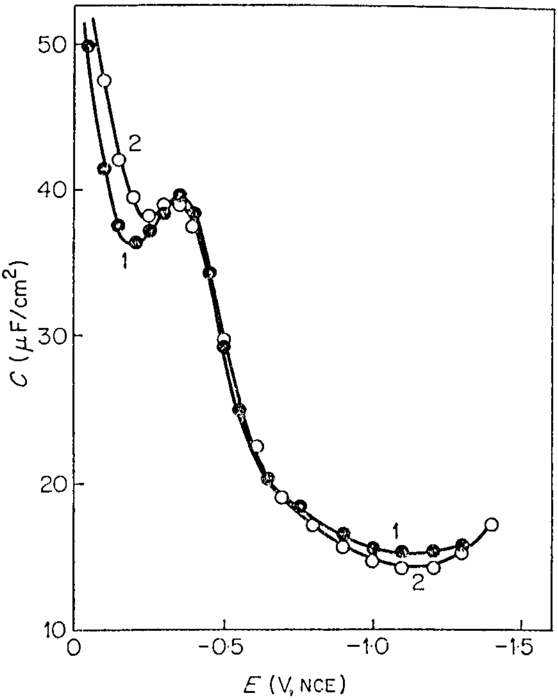

Fig. 5. Differential capacity curves of a mercury electrode in solutions: 1 — 0·1 N HCl, 2 — 0·1 N HCl + 0·1 M aniline. Frequency 400 cps.

An even more interesting example presents the *C*,*E*-curves in acid solutions of aniline,[83] pyridine[46] and phenylenediamine, which, as can be seen from Fig. 5, hardly differ from the *C*,*E*-curve in a pure supporting electrolyte solution. In this case, however, a possible conclusion about the absence of adsorption of organic substance over the whole potential range under investigation would be at variance with the results of electrocapillary measurements.[31,36,39]

The double layer capacity being independent of the organic substance adsorption on a positively charged electrode seems to be due to a strong π-electronic interaction, in the presence of which aniline molecules and anilinium cations horizontally oriented on the electrode surface form, as it were, an extension of the metal surface in the direction of the solution, so that the electrode and the solution sides of the double layer do not move apart and hence its capacity changes insignificantly, if at all. At $q < 0$ the slight influence of the anilinium cations adsorption on the double layer capacity is partly due to the π-electronic interaction and partly due to strong hydration of the $—NH_3^+$ group. The latter conclusion can be inferred from the relatively slight dependence of the differential capacity of the mercury electrode on the adsorption of butyl- and amylammonium cations in which π-electronic bonds are absent.[67]

The shape of the C,E-curves becomes even more complex if adsorption of organic substances on the electrode surface involves the formation of polymolecular layers or micellar films. In many cases polymolecular adsorption

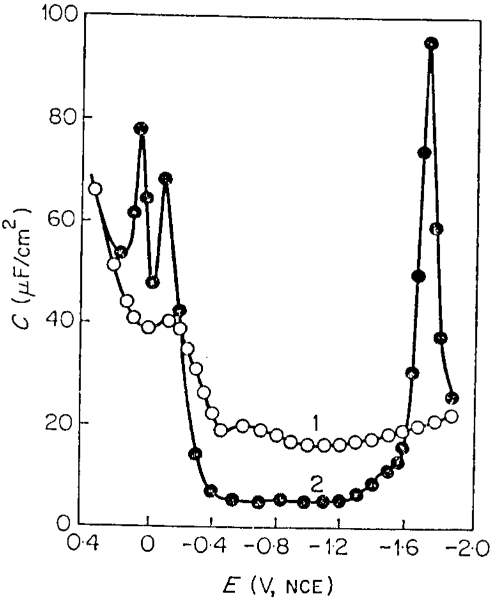

Fig. 6. Differential capacity curves of a mercury electrode in solutions: 1 — 0·05 N Na_2SO_4, 2 — 0·05 N Na_2SO_4 + 0·008 N $C_6H_{13}OSO_3Na$ + 0·001 N $[(C_4H_9)_4N]_2SO_4$. Frequency 400 cps.

leads to a capacity decrease in a certain potential range up to 0·9 μF/cm^2.[84] The processes of formation and destruction of micellar films on the C,E-curves correspond to the appearance of additional peaks,[85,86] the frequency dependence of which differs sharply from that of the adsorption-desorption peaks.[86]

If two organic compounds are present together in the solution, their desorption from the electrode surface as a rule occurs simultaneously and involves the formation of one common peak on the C,E-curve. The position of this peak depends on the adsorption characteristics of each of these substances, on their concentration ratio as well as on the interaction between molecules of these compounds within the adsorption layer.[60,82] In rare instances, the adsorption peaks of two substances become separated. This case is illustrated in Fig. 6 which shows the C,E-curve for co-adsorption of $[(C_4H_9)_4N]^+$ cations and $C_6H_{13}OSO_3^-$ anions. The comparison with the electrocapillary curves for the same system and for solutions with additions of one or the other of these surface-active substances shows that the right hand anodic peak on the C,E-curve corresponds to desorption of $[(C_4H_9)_4N]^+$ cations and the left hand one to desorption of $C_6H_{13}OSO_3^-$ anions.

III. THEORY OF THE EFFECT OF ELECTRIC FIELD ON ADSORPTION OF ORGANIC MOLECULES

This theory was first developed by one of the authors in 1926.[87] Since it is described in detail in our review,[64] we shall dwell here only on the analysis of the basic assumptions and report some new results. Two following assumptions form the basis of this theory.

1. The First Assumption

The electric double layer in the presence of an organic substance whose molecules do not change their orientation on the electrode surface can be represented as two capacitors connected in parallel, with only adsorbate molecules contained between the plates of one of them and only water molecules between those of the other. This model conforms to the equation:

$$q = q_0(1 - \theta) + q_1\theta \tag{14}$$

where θ is the surface coverage with organic substance; q_0 and q_1 the values of q at $\theta = 0$ and $\theta = 1$, respectively.

The quantity q_0 is determined using the experimental C,E-curve in the supporting electrolyte solution, so that

$$q_0 = \int_0^E C_0\,\mathrm{d}E \tag{15}$$

where C_0 is the value of C at $\theta = 0$ and the potential E (henceforth as well) is read from the point of zero charge in the pure supporting electrolyte solution.

The quantity q_1 is determined by means of an approximate formula

$$q_1 = C_1(E - E_N) \tag{16}$$

where C_1 and E_N are constants: C_1 is the value of C at $\theta = 1$ and E_N is the shift of the point of zero charge when passing from $\theta = 0$ to $\theta = 1$. In the case of adsorption of organic substances for which $C_1 \ll C_0$ (e.g. aliphatic compounds with one polar group) the errors in the estimation of q_1 by means of eqn (16) are relatively insignificant, the change of the charge in the process of adsorption for high values of the charge being primarily determined by the term $q_0(1 - \theta)$ in eqn (14). In principle, however, it would be possible to take into consideration the dependence of C_1 on E as well.

2. The Second Assumption

Adsorption of organic substance on the electrode surface can be described by Langmuir's equation corrected for intermolecular interaction of adsorbed particles. It was admitted that this interaction can be taken into account by introducing the term $a\theta^2$ into the equation of state of the adsorbed layer by analogy with the three-dimensional van der Waals equation of state.[88] This gives the equation

$$Bc = \frac{\theta}{1 - \theta} \exp(-2a\theta) \tag{17}$$

in which B is the adsorption equilibrium constant, c is the organic substance concentration and a is the attraction constant: if $a > 0$ it is the attraction forces between adsorbed molecules that predominate, while if $a < 0$ the repulsion forces are stronger. The quantity a, increasing with the length of hydrocarbon chain, takes account of the increase of the gain in free energy in adsorption (linear with θ), which is associated with two factors:

(*a*) dispersion interaction between parallel oriented hydrocarbon chains;

(*b*) expulsion of hydrocarbon chains from the bulk of the solution, which also makes the drawing together of nonpolar parts of molecules more favourable.

The application of eqn (17) to non-localized adsorption from solution is justified since in this case adsorption of the solute involves the displacement of the solvent.[89] The importance of the last point was emphasized by Bockris *et al.*[62] When deriving eqn (17) it is necessary to assume however that the solvent and adsorbate molecules occupy equal areas on the surface. If the adsorbate molecules occupy an n times larger area on the surface than the solvent molecules, two different equations can be obtained, depending on the assumptions made in the derivation:[90,110,142]

$$Bc = \frac{\theta}{n(1-\theta)^n} \exp(-2a\theta) \tag{18}$$

and

$$Bc = \frac{\theta}{n(1-\theta)^n} \left(1 - \theta + \frac{\theta}{n}\right) \exp(-2a\theta) \tag{19}$$

It can be readily seen that at $n = 1$ both the equations reduce to the isotherm eqn (17).

It should be noted that the basic assumptions of the theory in eqns (14) and (17) proved to be quite sufficient for expressing quantitatively, in conjunction with strictly thermodynamic relations, the shape of the electrocapillary curves in the presence of tert. amyl alcohol.[64,87] However, the verification of the theory under more rigid conditions, which involved the comparison of calculated and experimentally measured C,E-curves,[69,76-80] as well as the discussion of the main statements of the theory made a more detailed analysis of assumptions one and two necessary.

The analysis of the first assumption by means of Gibbs thermodynamics shows[95,98] that eqn (14) is strictly equivalent to the condition of the congruence of the adsorption isotherm with respect to the electrode potential. This condition implies that the adsorption isotherms measured at different E are similar and can be written in the form

$$B(E) \, . \, c = f(\theta) \tag{20}$$

where $B(E)$ is a function of the electrode potential and $f(\theta)$ is a function of the coverage independent of E.

An alternative to condition eqn (20) is the assumption about the congruence of the adsorption isotherm with respect to the electrode charge, which can be written as:

$$B(q) \, . \, c = f(\theta) \tag{21}$$

where $B(q)$ is a function of the electrode charge. The analysis of eqn (21) shows[95,98] it to be equivalent to the relation

$$E = E_0(1 - \theta) + E_1\theta \tag{22}$$

where the potentials E, E_0, and E_1 correspond to a certain q = constant at the surface coverages with organic substance, $\theta = 0$ and $\theta = 1$, respectively.

The question of the choice of one of the models of the double layer in the presence of organic substance leads to a discussion on the choice of the electric variable.[91-94,97] With such a statement of the problem, a number of arguments were adduced in favour of eqn (21) to the effect that the choice of the electrode charge as an independent electric variable would be more convenient and suitable (see e.g.[94,99]). In reality, however, as we have pointed out earlier, with a strictly thermodynamic approach to the investigation of adsorption on electrodes, the choice of the electric variable is of no fundamental importance. But when the thermodynamic approach to investigation of adsorption on electrodes is supplemented by some model assumptions, e.g. by those of eqns (20) or (21), the choice of one of them should be dictated by the agreement of the relevant models with the experimental data. It should be noted that under the condition $C_0 = C_1$, which to the first approximation is realized in the case of adsorption on mercury of thiourea molecules[13] or those of benzene *m*-disulphonate ions,[56] eqns (20) and (21) are compatible. The difference between them can be experimentally established only under the condition $C_0 \gg C_1$, e.g. in the case of adsorption on mercury of aliphatic compounds with one polar group. Under these conditions the verification of the model of two parallel capacitors was carried out by various methods[69,71,95,96,98] showing this model to ensure better agreement with experimental data than the model based on eqn (21). The strongest argument in favour of the model of two parallel capacitors seems to be the dependence of the adsorption potential drop $E_{q=0}$ on the extent of adsorption (or on $\theta = \Gamma/\Gamma_m$). It follows from eqns (14)–(16) under the assumption that $C_0 =$ constant and $q = 0$ that:

$$E_{q=0} = \frac{E_N\theta}{(C_0/C_1)(1-\theta)+\theta} \tag{23}$$

i.e. according to the two parallel capacitors model the dependence of $E_{q=0}$ on θ (or on Γ) should deviate from linearity, the stronger the more the ratio C_0/C_1 differs from unity. From eqn (22) at $q = 0$, when $E_0 = 0$ and $E_1 = E_N$, we obtain a different relation

$$E_{q=0} = E_N\theta \tag{24}$$

The use of the two parallel capacitors model is justified if the condition of equipotentiality is valid both on the metal surface and at the boundary between the inner part of the double layer and the bulk of the solution.[95,96] In the former case this condition is trivial, whereas in the latter it is only approximately valid due to the high value of the dielectric constant outside the inner layer.[100] But on the free surface of the solution one of the equipotential surfaces (i.e. the metal surface) is absent. Therefore, in this case, in the absence of effects caused by changes in the orientation of adsorbed molecules, in accordance with eqn (24) an additive summation of dipole effects is to be expected. Figure 7 shows the experimental dependences of $E_{q=0}$ on Γ for the case of adsorption at the two interfaces of *n*-propyl alcohol and *n*-caproic acid obtained by different methods. As is clear from the figure, in the case of the solution/mercury interface these dependences deviate markedly from the straight line and agree well with eqn (23). The same result was obtained[95] for the case of adsorption on mercury of *n*-valeric acid and *n*-amylamine. It should be noted that similar forms of the curves of the dependence of $E_{q=0}$ on Γ were found for camphor,[34] *n*-butylamine[42] and some other aliphatic compounds,[40] although they were explained by a change in the orientation of adsorbed dipoles. The dependence of the adsorption potential drop on θ being approximately linear in these systems at the solution/gas interface (see Fig. 7), this explanation cannot be considered correct.

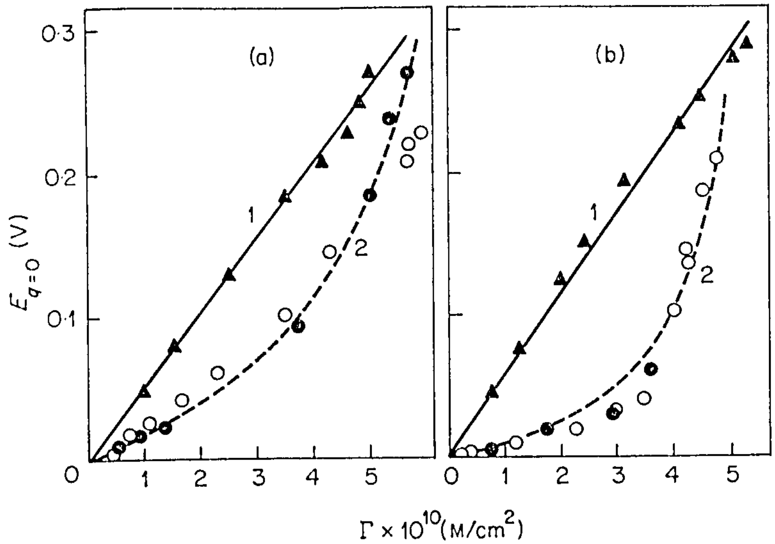

Fig. 7. Dependence of the adsorption potential drop on adsorption of *n*-propyl alcohol (a) and caproic acid (b) at the solution/gas (1) and solution/mercury (2) interfaces. Data obtained: from the maximum on σ, E curves (open circles) and from the minimum on C,E-curves in dilute supporting electrolyte solutions (full circles). Dashed curves calculated by means of eqn (23) under the condition that: $E_N = 0{\cdot}31$ V, $C_0/C_1 = 3{\cdot}5$, $\Gamma_m = 6 \times 10^{-10}$ mol/cm^2 (a) and $E_N = 0{\cdot}29$ V, $C_0/C_1 = 7$, $\Gamma_m = 5 \times 10^{-10}$ mol/cm^2 (b). Supporting electrolyte –0·01 N H_2SO_4.

It follows from eqn (23) that the dependence of $E_{q=0}$ on log c can be linear only with $C_0 \approx C_1$ and a logarithmic adsorption isotherm, which is obtained from isotherm eqn (17) at $a < 0$. These conditions are realized in the case of adsorption on mercury of organic ions and thiourea molecules. The Esin–Markov effect observed in their presence (see[40,101]) can serve as an additional proof of the validity of eqn (23).

Good agreement between the $E_{q=0}$–Γ-curves with eqn (23), as well as some other considerations,[98] shows that the structure of the interface between the electrode and an aqueous solution containing small additions of organic substance agrees much better with eqn (20) than with eqn (21). The clear physical significance of the two parallel capacitors model also points in favour of eqn (20).

Although the assumption expressed by eqn (14) (or eqn (20), which is the same) to the first approximation agrees well enough with experimental data, a more detailed analysis based on the comparison of experimental and calculated C,E-curves shows that the shape of the experimental adsorption isotherms is not exactly similar at different E and, hence, real systems deviate somewhat from the two parallel capacitors model. At least three possible reasons for this deviation can be given:[87,102]

(*a*) the outer side of the electric double layer facing the solution is not strictly equipotential due to the discrete nature of adsorbed dipoles of organic substance;

(*b*) with increasing coverage the component of the dipole moment of adsorbed molecules perpendicular to the surface changes (usually increases) due to their changed orientation;

(*c*) with increasing coverage the surface area per adsorbed molecule decreases.

The shape of the adsorption isotherm described by eqn (17) being determined by the value of the attraction constant a, in using this isotherm the deviation of the system from the two parallel capacitors model can be formally represented in terms of the dependence of a on E. An analysis shows that the first two reasons for the deviations of real systems from this model correspond to a linear dependence of a on E:[102,150]

$$a = a_0 + kE \tag{25}$$

in case '*a*', $k > 0$ (adsorption on mercury of alcohols and amines of the fatty series[76,79,80]) and in case '*b*', $k < 0$ (adsorption on mercury of phenol[15] and pyridine[46,77]). The third reason for the deviation of real systems from the two parallel capacitors model given above corresponds to a parabolic dependence of a on E.[64,87] Such a dependence was observed in the case of the system $Na_2SO_4 + [(C_4H_9)_4N]_2SO_4$.[103]

It is evident that in the general case any deviation of the system from the two parallel capacitors model can be formally expressed by means of a dependence of the attraction constant contained in eqn (17) on the electrode potential: $a = a(E)$. The introduction of this dependence appears justified, since, as has been pointed out above, it is only a slight correction to the first basic assumption of the theory.

It remains now to substantiate the second basic assumption of the theory, viz. the applicability of eqn (17) for the description of real systems. As was shown by one of the authors,[104] a convenient criterion in the choice of the adsorption isotherm is the dependence of $(\partial \log c/\partial\theta)_E$ on θ, which at the potential of maximum adsorption $E = E_m$, when $d\theta/dE = 0$, can be readily determined experimentally from the experimental C,E-curves by means of the relation

$$\theta = \frac{C_0 - C}{C_0 - C_1} \tag{26}$$

It can be shown that the $(\partial \log c/\partial\theta)_E$ vs. θ curve always passes through a minimum at a certain value of $\theta = \theta^*$, which, being a function of

$$n = S_{\mathrm{org}}/S_{\mathrm{H_2O}},$$

is at the same time independent of the value of the attraction constant. It can be also readily shown that in the case of eqn (18)

$$\theta^* = \frac{1}{1 + \sqrt{n}} \tag{27}$$

and in the case of eqn (19)

$$\theta^* = \frac{2n - 1 - \sqrt{(n^2 - n + 1)}}{3(n - 1)} \tag{28}$$

The dependence of θ^* on n calculated by means of these equations is shown in Fig. 8. It was experimentally established[104] from the dependence of $(\partial \log c/\partial\theta)_E$

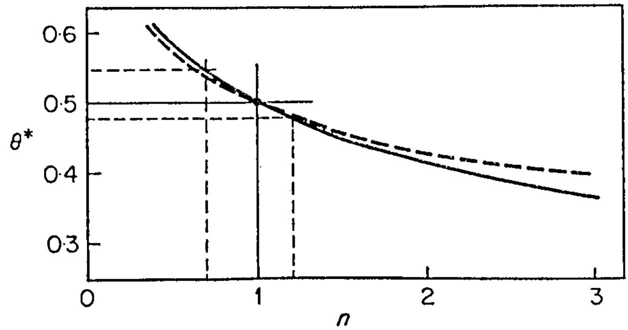

Fig. 8. Dependence of θ^* on n calculated by means of eqn (27)—solid line and eqn (27)—dashed line.

on θ for some aliphatic compounds (alcohols, acids, amines, tetrabutylammonium cation) as well as for aniline, that the values of θ^* lie within the range 0·48–0·55 (see Fig. 9). As follows from Fig. 8, this range corresponds to the values of n from 0·7–1·2. Considering the rather small sensitivity of the shape of the isotherm to the change of n within this range, we can set $n = 1$ to a good enough approximation.

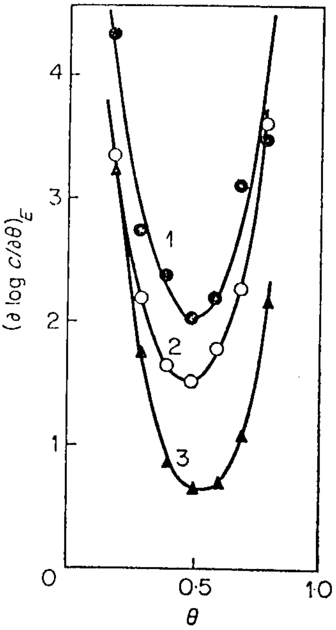

Fig. 9. Dependence of $(\partial \log c/\partial\theta)_E$ on θ obtained from experimental adsorption isotherms: 1—aniline, 2—n-amylamine and 3—tert-amyl alcohol.

At first glance, this experimental result is inconsistent with the difference in dimensions of water and adsorbate molecules. To eliminate this discrepancy it is necessary to assume an adsorption site on the mercury surface to be occupied by a group of associated H_2O molecules rather than by one water molecule.[105] From a thermodynamic point of view, this can mean that the work due to the transfer of such a group of molecules as a whole from the surface to the bulk is less than the total work of transfer of each of the molecules separately. The S-shaped adsorption isotherm of water vapour on mercury obtained,[106–108] demonstrating a considerable attractive interaction between adsorbed H_2O molecules, supports this conclusion.

The concept of the association of water molecules adsorbed on the mercury surface theoretically justifies the use of eqn (17) as a semi-empirical basis for the consideration of adsorption of organic molecules at the mercury/electrolyte interface.

The two basic assumptions of the theory with account taken of possible deviations of real systems from the two parallel capacitors model (by introducing the dependence $a = a(E)$) lead to the following formula for the adsorption equilibrium constant B, the differential capacity C and the decrease of the surface tension $\Delta\sigma$ due to organic substance adsorption:[109]

$$B = B_0 \exp\left[-\frac{\int_0^E q_0\, \mathrm{d}E + C_1 E\left(E_N - \frac{E}{2}\right)}{A}\right] \exp(a_0 - a) \qquad (29)$$

$$\begin{aligned} C = {} & C_0(1-\theta) + C_1\theta - A\frac{\mathrm{d}^2 a}{\mathrm{d}E^2}\theta(1-\theta) \\ & + \frac{1}{A}\left[q_0 + C_1(E_N - E) + A\frac{\mathrm{d}a}{\mathrm{d}E}(1-2\theta)\right]^2 \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \end{aligned} \qquad (30)$$

$$\Delta\sigma = -A[\log(1-\theta) + a\theta^2] \qquad (31)$$

in which $A = RT\Gamma_m$, B_0 and a_0 are the values of the functions $B(E)$ and $a(E)$ at $E = 0$, respectively. In the case of a linear dependence of a on E (see eqn (25)) or at a = constant, eqns (29) and (30) are simplified accordingly.

The theory based on the above assumptions is applicable in the first instance to adsorption on mercury of aliphatic compounds, in the presence of which, with account taken for the small linear dependence of a on E, there is good agreement between calculated and experimentally measured differential capacity curves. This is illustrated in Fig. 10 for the case of adsorption on mercury of iso-amylamine.[79] Good agreement between calculated and experimental C,E-curves is observed in the case of adsorption on mercury of n-C_3H_7OH, n-C_4H_9OH, n-$C_5H_{11}OH$, iso-$C_5H_{11}OH$, tert-$C_5H_{11}OH$, n-$C_4H_9NH_2$, n-$C_5H_{11}NH_2$, n-C_4H_9COOH, and $C_2H_5COC_2H_5$.[76,78-80]

The picture is more complicated in the case of aromatic and heterocyclic compounds, which can be adsorbed in two different positions: horizontal and vertical. The number of molecules adsorbed in either position depends, in its turn, both on the organic substance concentration and on the electrode potential. For these systems the two parallel capacitors model cannot be applied over the whole range of adsorption potentials.[14] It must be substituted by the model of three parallel capacitors, with water molecules contained between the plates of one of them, organic substance molecules in the first, say vertical, position between the plates of the second, and organic substance molecules in the second, say horizontal, position between the plates of the third capacitor.[59] This model corresponds to

$$q = q_0(1 - \theta_1 - \theta_2) + q_1\theta_1 + q_2\theta_2 \tag{32}$$

where θ_1 and θ_2 are the coverages for vertical and horizontal orientations of adsorbed molecules, respectively; q_1 is the value of q at $\theta_1 = 1$ and $\theta_2 = 0$; q_2 is the value of q at $\theta_2 = 1$ and $\theta_1 = 0$.

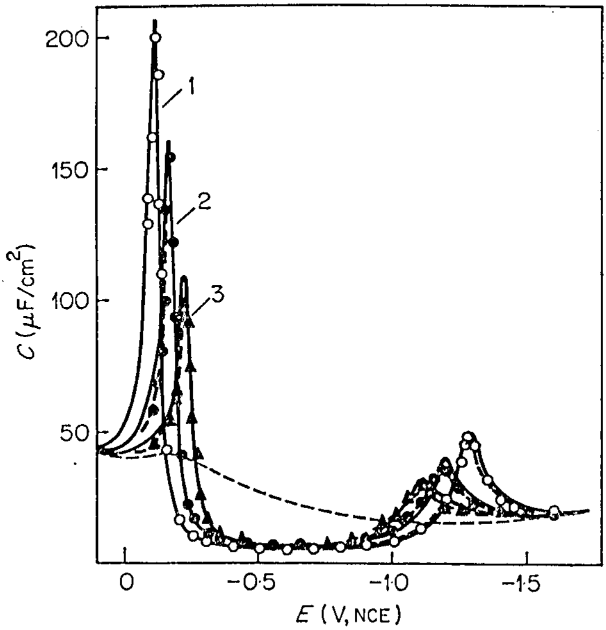

Fig. 10. Differential capacity curves of a mercury electrode in 1 N Na_2SO_4 solution (dashed line) and with additions of isoamylamine in concentrations: 1—0·04, 2—0·02, and 3—0·01 M. Solid lines—calculated curves (different symbols) and dashed lines—experimental data at the frequency 400 cps.

In using eqn (32), however, it is necessary to choose in addition two adsorption isotherms relating the quantities θ_1 and θ_2 with the bulk concentration of organic substance. It should be stressed that the choice of these isotherms cannot be arbitrary since they are related to eqn (32) by the basic equation of electrocapillarity eqn (1). It can be shown that in the general case the following isotherms are consistent with the three parallel capacitors model

$$\left.\begin{aligned} B_1c &= \frac{\theta_1}{n_1(1-\theta_1-\theta_2)^{n_1}}\exp(-2a_{11}n_1\theta_1 - 2a_{12}n_1\theta_2) \\ B_2c &= \frac{\theta_2}{n_2(1-\theta_1-\theta_2)^{n_2}}\exp(-2a_{22}n_2\theta_2 - 2a_{12}n_2\theta_1) \end{aligned}\right\} \tag{33}$$

in which the adsorption equilibrium constants B_1 and B_2 are some functions of the electrode potential; the attraction constant a_{11} takes account of the interaction between vertically adsorbed molecules, a_{22} between horizontally adsorbed molecules and a_{12} between the adsorbed molecules in different positions; n_1 is the ratio of the area occupied by a vertically oriented organic substance molecule to the area per an associate of adsorbed water molecules; n_2 is the similar ratio for the case of horizontal orientation of adsorbate molecules.* By means of eqn (32) it is possible to find the explicit dependence of B_1 and B_2 on E. In fact, if we assume

$$q_1 = C_1(E - E_{N1})$$

and

$$q_2 = C_2(E - E_{N2}),$$

we obtain for B_1 and B_2:

$$B_1 = B_{01}\exp\left[-\frac{\int_0^E q_0\,dE + C_1E\left(E_{N1} - \frac{E}{2}\right)}{RT\Gamma_{m1}}\right] \tag{34a}$$

$$B_2 = B_{02}\exp\left[-\frac{\int_0^E q_0\,dE + C_2E\left(E_{N2} - \frac{E}{2}\right)}{RT\Gamma_{m2}}\right] \tag{34b}$$

The set of eqn (33) can be exactly solved only with the help of an electronic computer. There is an additional difficulty due to the fact that in eqns (33) and (34), apart from organic substance concentration, it is possible to vary relatively arbitrarily 12 parameters: B_{01}, B_{02}, C_1, C_2, E_{N1}, E_{N2}, n_1, n_2, a_{11},

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* Parry and Parsons[57] also used the set of eqn (33) to describe such systems; they assume however the quantities B_1 and B_2 to be some functions of the electrode charge rather than of its potential. The analysis of this assumption shows that it is equivalent to the model of three capacitors connected in series and filled with water molecules and adsorbate molecules in two different positions, respectively. Apparently, it is difficult to give a physical interpretation to such model, although it is not inconsistent with the experimental dependence of θ on q in sodium *p*-toluenesulphonate solutions.

a_{22}, a_{12}, and $A = n_1RT\Gamma_{m1} = n_2RT\Gamma_{m2}$. In order to avoid these difficulties, we tried to use for the evaluation of the three parallel capacitors model a first rough approximation, according to which $a_{11} = a_{12} = a_{22} = 0$. Since under these conditions the comparison of theory with experiment can be only semi-quantitative, it appeared justified to make the following additional assumptions: $C_0 = C_2 =$ constant, $n_1 = 1$, and $n_2 = 2$. Even with all these simplifications, the expression for the differential capacity of the double layer in the presence of an organic substance adsorbed in two different positions is rather cumbersome:

$$C = C_0 - 2A\alpha\theta_1 + \frac{A}{2(1+\theta_2)}\{8\alpha^2(E-E_m)^2\theta_1(1-\theta_1) + \beta^2\theta_2(1-\theta_2) + 8\theta_1\theta_2[\alpha^2(E-E_m)^2 + \alpha\beta(E-E_m)]\} \quad (35)$$

where $\alpha = (C_0 - C_1)/2A$; $E_m = -C_1E_{N1}/(C_0 - C_1)$; $\beta = -2C_0E_{N2}/A$; $A = RT\Gamma_{m1} = 2RT\Gamma_{m2}$.

Under the same conditions the decrease in surface tension due to organic substance adsorption can be written as

$$\Delta\sigma = -A\left[\log(1-\theta_1-\theta_2) + \frac{\theta_2}{2}\right] \quad (36)$$

In Figs. 11–13 calculations by means of these equations are compared with the experimental C,E- and σ,E-curves for the mercury electrode in the

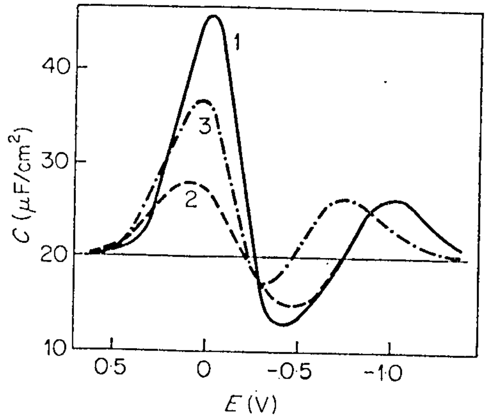

Fig. 11. Theoretically calculated differential capacity curves: 1—$E_{N1} = 0{\cdot}5$ V and $E_{N2} = -0{\cdot}5$ V; 2—$E_{N1} = 0{\cdot}5$ V and $E_{N2} = 0{\cdot}25$ V; 3—$E_{N1} = 0$ and $E_{N2} = -0{\cdot}5$ V.

presence of ortho- and para-phenylenediamines.[59] It was assumed in the calculations that: $C_0 = 20\,\mu\text{F/cm}^2$; $C_1 = 7\,\mu\text{F/cm}^2$; $A = 1{\cdot}6\,\mu\text{F/cm}^2$; $B_{01} = 100$ l./mole; $B_{02} = 500$ l./mole; $c = 0{\cdot}02$ M; $E_{N1} = +0{\cdot}5$ V, and 0; $E_{N2} = -0{\cdot}25$, and $-0{\cdot}5$ V. As is clear from Fig. 12, when passing from

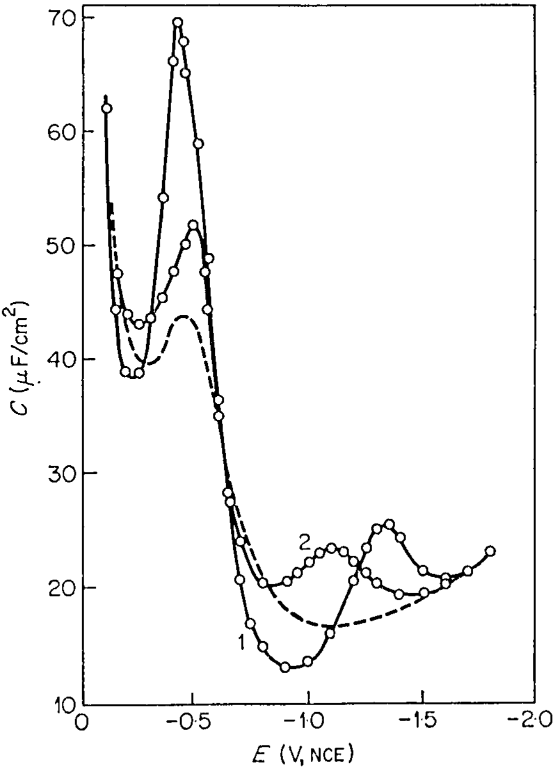

Fig. 12. Differential capacity curves of a mercury electrode in 1 N KCl solution (dashed line) and with 0·02 M addition of: 1—para-phenylenediamine, 2—ortho-phenylenediamine. Frequency 400 cps.

ortho- to para-phenylenediamine, the anodic peak grows appreciably, the decrease of capacity in the middle part of the C,E-curve compared to the curve of the supporting electrolyte becomes greater and the cathodic peak shifts in the direction of more negative potentials. All these phenomena can be observed in Fig. 11 when passing from curve 3 calculated for $E_{N1} = 0$ to curve 1, which was calculated assuming $E_{N1} = +0{\cdot}5$ V. Thus the difference in the adsorption behaviour of ortho- and para-phenylenediamines can be connected with the change in the dipole moment component perpendicular to the surface observed in the case of their vertical orientation, whereas the quantity E_{N2} due to π-electronic interaction of these molecules with the mercury surface remains unchanged. This conclusion is supported by the comparison of the theoretically calculated and experimental electrocapillary curves (Fig. 13).

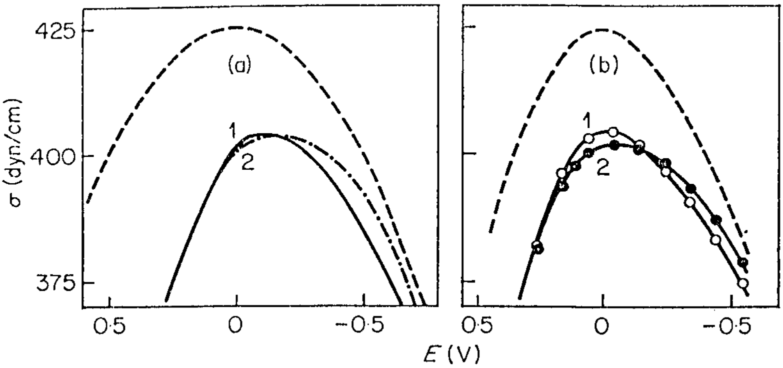

Fig. 13. Electrocapillary curves theoretically calculated (a) and experimentally measured (b): (a) 1—$E_{N1} = 0{\cdot}5$ V and $E_{N2} = -0{\cdot}5$ V; 2—$E_{N1} = 0$ and $E_{N2} = -0{\cdot}5$ V. (b) 1—1 N KCl + 0·03 M para-phenylenediamine; 2—1 N KCl + 0·03 M ortho-phenylenediamine. Dashed lines are σ,E—curves in supporting electrolyte solution.

The above results show that the three parallel capacitors model is a good semi-quantitative basis for describing the systems in which organic substance can be adsorbed on the electrode in two different positions. It can be readily shown[150] that if the two positions in which molecules of organic substance are adsorbed differ mainly in the values of the adsorption potentials, the behaviour of such systems can be described by means of eqns (14), (17), and (25) with $k < 0$, the k-values being in this case however larger than in the case of aliphatic substances adsorption. This gives a theoretical basis for the application of the two parallel capacitors model to the description of adsorption on mercury of phenol[15] and pyridine.[46,77]

The three parallel capacitors model in conjunction with the set of isotherms (eqn (33)) can be also used as a basis in describing the simultaneous adsorption on the electrode of two surface-active organic substances. Only in that case in the first of the equations (eqn (33)) the total concentration c should be substituted by c_1 (the concentration of the first substance), and in the second equation by c_2 (the bulk concentration of the second organic substance). The physical significance of other quantities appearing in eqns (32) and (33) will be changed accordingly: all the quantities with the subscript 1 refer to the first substance and with the subscript 2 to the second.

An accurate solution of the set of eqn (33) in the case of the simultaneous adsorption on the electrode of two organic substances presents the same difficulties as in the case of one substance adsorbed in two different positions. For some particular cases where these difficulties could be avoided the three parallel capacitors model was successfully used by Tedoradze. Arakeljan and Belokolos.[82] An essentially similar theoretical approach to the description of such systems was developed also by Kastening and Holleck.[110]

IV. PROBLEMS OF THEORY OF MOLECULAR ADSORPTION OF ORGANIC SUBSTANCES

In two recent papers,[62,99] the second of which is further development of the first, Bockris and collaborators advanced a molecular theory of adsorption of organic substances and of its dependence on the electrode charge. Bockris and collaborators contrast their theory as a molecular one with our concepts, which are of a thermodynamic nature and involve finding the necessary values of the constants from experiments.

There is no doubt that a theory entirely based on molecular data is a considerable advance over a thermodynamic theory supplemented with a macromodel (the two or three parallel capacitors models). It seems to us however that in developing such a theory one should determine first from a thermodynamic analysis which quantities appearing in mathematical expressions should be treated from the molecular point of view. In point of fact, Butler's theory[23] can be considered as an example of an approach of that kind, since Butler's relations can be obtained from the equations of Frumkin's initial theory[87] if the double layer capacity is calculated as the capacity of a flat capacitor of constant thickness from molecular polarizabilities, the shift of the point of zero charge—from dipole moments of adsorbed molecules, and the adsorption isotherm is approximated by means of the Henry equation.

We would like to discuss here the possibilities, as it appears to us, of further development of the theory of adsorption of organic substances on the basis of thermodynamic relations, which would bring us to an accurate molecular theory, at least for simplest aliphatic compounds.

It follows from eqn (29) at $a =$ constant that the dependence of adsorption on the potential is determined by the expression:

$$B = B_0 \exp\left[-\frac{\int_0^E q_0\,\mathrm{d}E + C_1 E\left(E_N - \frac{E}{2}\right)}{RT\Gamma_m}\right] \tag{37}$$

This expression takes full account of the effect of the free energy stored in the electric double layer undisturbed by the adsorption process since this energy is determined by numerical integration of the experimental C,E-curves in a pure supporting electrolyte solution. As is evident from eqn (37), the adsorption is determined by the following parameters: C_1, E_N, Γ_m, and B_0, which depend on the nature of the adsorbate. In addition, a relation must be established between the adsorbate nature and the value of the attraction constant a contained in the adsorption isotherm eqn (17). Thus in order to pass from the thermodynamic to the molecular theory it is necessary to interpret the experimental dependence of C_0 on E, to estimate the parameters C_1, Γ_m. E_N and B_0 as well as to interpret the intermolecular interaction of adsorbed particles. Let us consider each of these problems in more detail.

1. The Dependence of C_0 on E

A number of investigators aimed at solving this problem completely or partially.[62,111–116] Bockris, Gileadi, and Müller[99] did not take up the question of the adequacy of the double layer model used by them when treating the adsorption of organics, for the solution of the above problem, although earlier[62] they pointed to the necessity of resorting to more complex concepts for explaining the dependence of C_0 on E at $q \geqslant 0$. In principle we can suppose that it will be possible to develop an adequate molecular theory of the C,E-curves in not too distant future.

2. The Quantity C_1

This quantity depends primarily on the thickness of the hydrocarbon layer between the double layer ions and metal and on its dielectric constant. Difficulties arise because this layer can contain water molecules as well.[80] The physical significance of the parameters contained in the quantity C_1 is quite clear, but their quantitative determination requires further experimental work on the dependence of C_1 on the hydrocarbon chain length.

3. The Quantity Γ_m

The determination of this quantity involves establishing the geometric dimensions and orientation of adsorbed organic molecules. In calculating Γ_m however, it is necessary to take into consideration the possibility of embedding of water molecules between adsorbate molecules as well, since adsorption saturation is usually established before water molecules are completely expelled from the mono-molecular layer at the interface.[117] Nevertheless, the calculation of Γ_m can be considered as being the simplest problem in the molecular adsorption theory of organic compounds.

4. The Quantity E_N

For better understanding of the physical significance of this quantity it can be conveniently represented as the difference of Galvani potentials at the point of zero charge at the metal/solution interface $\varphi_{q=0}$ after its coverage with adsorbed organic molecules and in a pure solvent, respectively:

$$E_N = (\varphi_{q=0})_{\text{org}} - (\varphi_{q=0})_{\text{H}_2\text{O}} \tag{38}$$

The effect of adsorbed substance upon the change of $\varphi_{q=0}$ is usually associated with the change in the dipole effect upon substitution of adsorbate molecules for those of the solvent. This approach is to a certain degree justified due to the existence of an approximate parallelism between E_N and the adsorption potential at the solution/gas interface at $\theta = 1$ in the case of adsorption of fatty acids, alcohols and amines.[21] It should be borne in mind however that along with this dipole effect the quantity $\varphi_{q=0}$ can also vary owing to the change in the electron density distribution in the metal surface layer depending on the medium the metal is in contact with. Judging by the influence of adsorption of noble gases on metal electron work functions,[118] this effect, about which little is known, can become quite appreciable.

The attempts to calculate the dipole effect, to the consideration of which we have to confine ourselves at present, meet difficulties owing to the following two circumstances:

(*a*) at present there is no general agreement about the sign of the dipole component of the quantity $(\varphi_{q=0})_{\text{H}_2\text{O}}$,[119,120] although many workers, Bockris *et al.*[62] included, suppose that at $q = 0$ there is a certain preferred orientation of water dipoles with their negative ends turned towards mercury, as was suggested by Frumkin.[21] There is no doubt however that the potential drop caused by this orientation is not large in absolute value (of the order of 0·1 V);

(*b*) a quantitative calculation of the potential drop in the adsorbed dipole layer from the dipole moments by means of the well-known elementary formula is possible under exceptional conditions, as follows from the surface potential measurements of films of long chain ω-bromosubstituted fatty acids and alcohols.[121] The reasons for these difficulties have already been discussed.[22] However, attempts[122,123] to interpret semi-quantitatively the surface potentials of monolayers of long-chain substances at the solution/gas interface on the basis of dipole moments of individual bonds lead to useful results.

It should be noted that in a model of the *n*-butanol molecule directed normal to the surface (as suggested[99]) the dipole moment is oriented almost parallel to the surface and cannot affect the potential drop in the adsorption layer. It is known, however, that the presence on the surface of monolayers of aliphatic alcohols, e.g. hexadecyl alcohol, causes the surface potential to shift by ∼400 mV in the positive direction. In these condensed layers the molecules are oriented normal to the surface and the dipole structure of the polar group should not differ from that in the *n*-butanol molecule. The polar group being far removed from the interface in the case of solution/mercury and solution/gas interfaces, there should be no difference in its dipole structure. Thus if we adopted the model used,[99] we should have to assume the potential drop between the gas phase and water to be about −400 mV. But such high negative values of this potential difference lead to improbable relations between chemical hydration energies of cations and anions.[66]

5. The Quantity B_0

This quantity is a measure of the free energy of adsorption at the uncharged mercury/solution interface $-\Delta G_A^0$, since in sufficiently dilute organic substance solutions, where the mole fraction of the solvent can be equated with unity,

$$B_0 = \frac{1}{55{\cdot}5} \cdot \exp\left(-\frac{\Delta G_A^0}{RT}\right) \qquad (39)^*$$

As is well known, calculations of the adsorption energy of simple molecules on various adsorbents from the gas phase have been carried out on the basis of molecular data. In principle such a calculation is possible for the case under consideration. For this purpose, however, in addition to taking account of the image work and the dispersion interaction at the interface with metal both for water and adsorbate, and in the case of unsaturated and aromatic compounds also of the π-electronic interaction between metal and adsorbed particle, it is necessary to give a molecular interpretation of the interaction between solvent and solute in the bulk of the solution, i.e. to calculate from molecular quantities the standard free energy of evaporation and the free energy of hydration.

Apparently, we are far as yet from solving these problems. Bockris *et al.*[99] introduce an empirical component of the free adsorption energy ('chemical' term), which limits the 'molecular' nature of their theory.

6. The Adsorption Isotherm

As shown above, at a given number of constants eqn (7) fits best the experimental data, though the interaction between adsorbed molecules is

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* As has been many times rightly emphasized by Bockris *et al.*,[37,62,99] the quantity ΔG_A^0 appearing in eqn (39) is strictly speaking the difference between the standard free energies of adsorption of organic substance and of water molecules. This fact is of essential importance for understanding the comparative behaviours of organic substances at the solution/mercury and solution/gas interfaces.

allowed for in this isotherm in a semi-empirical manner. A molecular interpretation requires more rigid account to be taken of the dependence of the interaction between adsorbed particles on the coverage and hence will lead to a more complex expression for the adsorption isotherm, which will make more difficult its use with a simultaneous allowance for the field effect.

Bockris *et al.*[99] used the isotherm expressed by eqn (19) at $a = 0$, and treated the intermolecular interaction within the adsorption layer entirely as an interaction between oriented water dipoles. Taking into consideration the interaction between these dipoles seems in a certain sense to be equivalent to our conclusion about the association of water molecules adsorbed on mercury, since it gives an approximately Langmuir dependence of θ on the adsorbate concentration at the values of n corresponding to the relation between the geometric dimensions of water and organic substance molecules. However, by ignoring the direct interaction between adsorbed organic substance molecules as Bockris *et al.* do, it is impossible to explain the dependence of the shape of the isotherm on the chain length (the S-shape becoming more pronounced with increasing chain length), which is observed in the case of adsorption both at the solution/mercury and solution/gas interfaces, and with a sufficient chain length leads to characteristic condensation phenomena.

In conclusion, we would like to make the following remark regarding the level of experimental verification attempted in the case of both thermodynamic and molecular theories. In developing the theory the basic assumptions of which were considered in the previous section we sought to obtain exact agreement between calculated and experimental quantities under the conditions of a most rigorous verification, viz. a confrontation of calculated and experimentally measured C,E-curves. Therefore, the theory was made more complicated (by taking account of the dependence of a on E), which would be quite unnecessary if we considered as it was done by Bockris *et al.* as sufficient the statement of some similarity between the calculated and experimentally found dependence of adsorption on potential.

V. INFLUENCE OF THE NATURE OF THE METAL ON ADSORPTION OF ORGANIC MOLECULES

The dependence of adsorption of organic substances on the nature of the metal can be determined by the following factors: change of the difference between the energies of interaction of adsorbate and water with the metal surface, heterogeneity of the solid electrode surface, adsorption of hydrogen and oxygen atoms on the metal surface and finally by chemisorption processes leading to deep changes in the structure of adsorbate molecules (e.g. to the breaking of the C—H and even C—C bonds). Let us discuss briefly each of these factors.

1. The Change in the Energy of Interaction of Adsorbate and Water Molecules with Metal Surface

If, when passing from one metal to another, only this factor comes into play, the main regularities in adsorption of organic molecules established for the mercury electrode (sections 2 and 3) should be valid for other metals as well. In fact, the shape of the electrocapillary curves on 57·5 per cent indium amalgam and liquid gallium electrode in the presence of iso-amyl alcohol[124,125] is similar to corresponding σ,E-curves of the mercury electrode (Fig. 14),

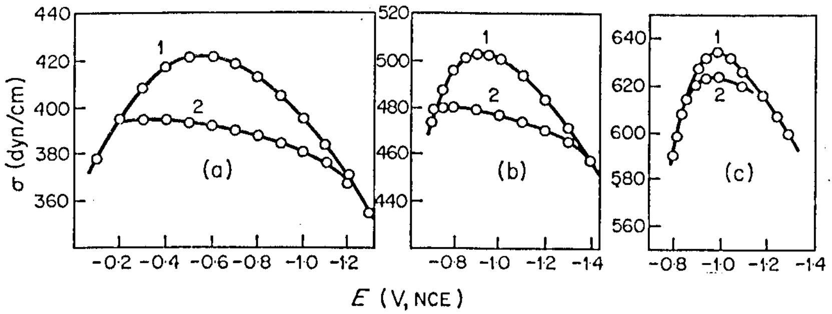

Fig. 14. Electrocapillary curves on various metals. (a) On mercury: 1—1 N KCl + 0·1 N HCl; 2—1 N KCl + 0·1 N HCl + 0·1 M iso-$C_5H_{11}OH$. (b) On 57·5 per cent indium amalgam: 1—1 N Na_2SO_4 + 0·01 N H_2SO_4; 2—1 N Na_2SO_4 + 0·01 N H_2SO_4 + 0·14 M iso-$C_5H_{11}OH$. (c) On gallium: 1—1 N KCl + 0·1 N HCl; 2—1 N KCl + 0·1 N HCl + 0·1 M iso-$C_5H_{11}OH$.

and the differential capacity curves of the solid bismuth electrode obtained recently by Palm, Past and Pullerits[132] (Fig. 15) are quite similar to corresponding C,E-curves on mercury (cf. Fig. 3). Characteristic shapes of the C,E-curves with decreasing capacity near $E_{q=0}$ and adsorption-desorption peaks in the presence of various organic substances were observed also on electrodes from thallium amalgam, gallium, lead, tin, silver, and antimony.[125–132]

Of course, when passing from one metal to another, the change in the interaction of the electrode both with adsorbate and water molecules involves a change in the parameters contained in eqn (37), but a quantitative comparison is yet possible, owing to the scarcity of experimental data, in few

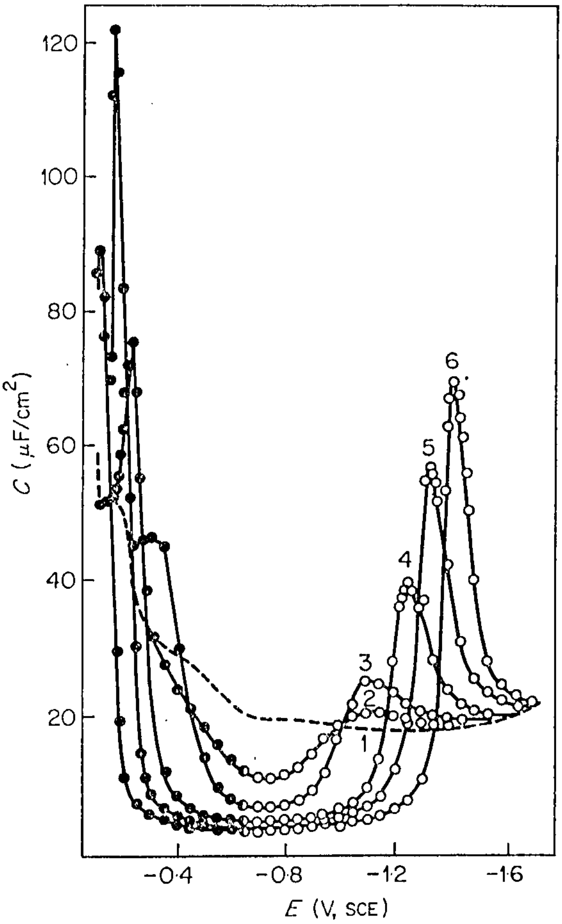

Fig. 15. Differential capacity curves of a bismuth electrode in n-amyl alcohol solutions of varying concentration: 1—0, 2—0·01, 3—0·02, 4—0·05, 5—0·1 and 6—0·2 M. Supporting electrolytes—0·1 N K_2SO_4 (open circles) and H_2SO_4 (full circles). Frequency 1000 cps.

cases only.[132] As is clear from Fig. 14, the adsorptivity of iso-$C_5H_{11}OH$ on indium amalgam and especially on gallium is markedly less than on mercury. In the latter case this can be accounted for by a stronger adsorption of water molecules on gallium surface at $q \geqslant 0$.[125] It should be pointed out, however, that at large enough negative surface charges, where this kind of adsorption of water on gallium is not observed, the differential capacity values in the presence of n-C_3H_7OH and tert-$C_5H_{11}OH$ at equal q are practically the same on mercury and gallium.[131] On passing to the iron electrode, the interaction of water molecules with the metal surface increases to such an extent that hexyl alcohol, which has a high surface activity in the case of Hg, Ga, Pb, Bi, Sn, Tl, Ag, and Sb, is practically not adsorbed on iron.[133] No adsorption of aliphatic compounds (cyclohexane, fatty acids) could be observed on the gold electrode.[134] According to Hillson,[135] hexyl alcohol has a very low surface activity on the nickel electrode.

2. Surface Heterogeneity

In itself the change in the state of aggregation of the electrode upon transition from liquid to solid metal has no pronounced effect on its adsorption properties. This is evident from the coincidence of the cathodic branches of the C,E-curves in the presence of organic substance for liquid and solid mercury electrodes.[129,136] Unlike a liquid electrode, however, the surface of a solid one can be heterogeneous with respect to adsorption energy. This is due to the fact that the free surface energy depends on the orientation of metal crystals and increases with increasing concentration of flaws at the interface (dislocations, vacancies, microdistortions of crystal lattice, etc.).

The adsorption isotherm on a heterogeneous surface must be different from that on a homogeneous surface. As shown by Temkin,[137] in the case of uniform heterogeneity the adsorption energy decreases linearly with the coverage (Temkin isotherm). In the case of a formal use of eqn (17) under these conditions, an increase in surface heterogeneity should lead to a decrease of the positive value of a down to zero (Langmuir isotherm) and then to an increase in the negative value of this constant. This explains why in some cases the dependence of adsorption of organic substances on solid electrodes with a heterogeneous surface upon the bulk concentration of adsorbate obeys formally the Langmuir isotherm. As follows from eqn (30), the decrease of a should lead to a lowering and widening of the adsorption-desorption peaks on the C,E-curves. Thus the experimental fact that the adsorption-desorption peaks on the C,E-curves are much less pronounced in the case of some solid electrodes, e.g. Ag and Sb, than on mercury[128,129] can be accounted for by heterogeneity of the surface of these metals.

The surface heterogeneity can change significantly as the result of annealing or mechanical treatment of the metal. Consequently, the pre-treatment of solid electrodes can be expected to affect their adsorption properties. Figure 16 shows the adsorption isotherms of allylphenylthiourea on a high purity iron electrode calculated for $E = -0{\cdot}35$ V (NHE) by means of eqn (26) from the experimental C,E-curves.[138] It is clear from the figure that the surface activity of allylphenylthiourea decreases sharply upon transition from iron annealed at 600°C to iron annealed at 750°C.

3. Effect of Adsorption of Hydrogen and Oxygen Atoms

Let us consider this problem assuming that the adsorption of hydrogen and organic substance can be treated as a reversible process.[139,140] Under these conditions the basic equation of electrocapillarity eqn (1) can be written as:

$$\mathrm{d}\sigma = -\Gamma_{\mathrm{H}}\,\mathrm{d}\mu_{\mathrm{H}} - \Gamma_{\mathrm{org}}\,\mathrm{d}\mu_{\mathrm{org}} \tag{40}$$

Let us denote by A_{H} the amount of hydrogen adsorbed per unit surface. The quantity A_{H} is not identical with Γ_{H}, since a fraction of hydrogen disappearing upon formation of unit surface is ionized and expended in its charging. A_{H} and Γ_{H} are related by the following expression:

$$\Gamma_{\mathrm{H}} = A_{\mathrm{H}} - \frac{q}{F} \tag{41}$$

In a solution of a constant composition the equilibrium potential of the electrode is determined by the quantity μ_{H}, and hence

$$\mathrm{d}\mu_{\mathrm{H}} = -F\,\mathrm{d}E \tag{42}$$

Substituting expression eqns (41) and (42) into eqn (40), we obtain

$$\mathrm{d}\sigma = (FA_{\mathrm{H}} - q)\,\mathrm{d}E - \Gamma_{\mathrm{org}}\,\mathrm{d}\mu_{\mathrm{org}} \tag{43}$$

It follows from eqn (43) that

$$F\left(\frac{\partial A_{\mathrm{H}}}{\partial \mu_{\mathrm{org}}}\right)_E - \left(\frac{\partial q}{\partial \mu_{\mathrm{org}}}\right)_E = -\left(\frac{\partial \Gamma_{\mathrm{org}}}{\partial E}\right)_{\mu_{\mathrm{org}}} \tag{44}$$

The quantity Γ_{org} being a function of μ_{org} and E, we can write the following general equation:

$$\left(\frac{\partial \mu_{\mathrm{org}}}{\partial E}\right)_{\Gamma_{\mathrm{org}}} = -\left(\frac{\partial \mu_{\mathrm{org}}}{\partial \Gamma_{\mathrm{org}}}\right)_E \left(\frac{\partial \Gamma_{\mathrm{org}}}{\partial E}\right)_{\mu_{\mathrm{org}}} \tag{45}$$

It follows from eqns (44) and (45) that

$$\left(\frac{\partial \mu_{\mathrm{org}}}{\partial E}\right)_{\Gamma_{\mathrm{org}}} = -\left(\frac{\partial q}{\partial \Gamma_{\mathrm{org}}}\right)_E + F\left(\frac{\partial A_{\mathrm{H}}}{\partial \Gamma_{\mathrm{org}}}\right)_E \tag{46}$$

which can be re-written as

$$\left[\frac{\partial(\Delta G_A^0)}{\partial E}\right]_{\Gamma_{\mathrm{org}}} = -\left(\frac{\partial q}{\partial \Gamma_{\mathrm{org}}}\right)_E + F\left(\frac{\partial A_{\mathrm{H}}}{\partial \Gamma_{\mathrm{org}}}\right)_E \tag{47}$$

where ΔG_A^0 is the standard free adsorption energy of organic substance.

In the case of the mercury electrode the change in adsorbability of organic substance with potential is determined by the first term in the right hand side of eqn (47). In the case of hydrogen-adsorbing metals it is also necessary to take into account the second term $F(\partial A_{\mathrm{H}}/\partial \Gamma_{\mathrm{org}})_E$.

In order to compare the first and the second terms let us assume that eqn (14) is valid on the electrode under investigation and that it is possible to write an analogous expression for A_{H}:

$$A_{\mathrm{H}} = A^{0}_{\mathrm{H}}(1 - \theta) + A'_{\mathrm{H}}\theta \tag{48}$$

Taking into consideration eqns (14) and (48), it is possible to write eqn (47) as:

$$\left[\frac{\partial(\Delta G^{0}_{A})}{\partial E}\right]_{\Gamma_{\mathrm{org}}} = \frac{q_0 - q_1}{\Gamma_m} - F\frac{A^{0}_{\mathrm{H}} - A'_{\mathrm{H}}}{\Gamma_m} \tag{49}$$

For many organic substances over a wide potential range $|q_1|$ in the case of the mercury electrode is known to be several times as little as $|q_0|$, which determines the effect of the electric field. Judging by the few experimental data available,[141] there probably exists a similar relation between A'_{H} and A^{0}_{H}. Thus the relative value of the first and the second terms in the right hand side of eqn (49) as factors determining the value of $[\partial(\Delta G^{0}_{A})/\partial E]_{\Gamma_{\mathrm{org}}}$ depends on the relation between FA^{0}_{H} and $|q_0|$.

The maximal value of FA^{0}_{H} in the hydrogen region being $\sim 2 \times 10^{-4}$ C/cm^2 and the maximal value of q_0 for the platinum electrode (e.g. in acid sulphate solutions)—a quantity of the order of 10^{-5} C/cm^2, it is evident that the second term in the right hand side of eqn (49) is of decisive importance. Even at the positive boundary of the hydrogen region and within the double layer region, in which in the case of solutions containing no surface-active anions the amounts of $\mathrm{H_{ads}}$ and $\mathrm{O_{ads}}$, if small, are not equal to zero, $|q_0|$ and FA^{0}_{H} can be of the same order of magnitude and the presence of the term $F(\partial A_{\mathrm{H}}/\partial \Gamma_{\mathrm{org}})_E$ must be allowed for in the determination of the dependence of ΔG^{0}_{A} on E.

It follows from the above that the relations derived for the mercury electrode are not applicable for the determination of the position of the adsorbability maximum of neutral molecules relative to $E_{q=0}$ in the case of the platinum electrode and apparently also for other hydrogen-adsorbing metals. Whereas $E_{q=0}$ for platinum lies in the hydrogen region,[140] the potential of maximum adsorption, due to the desorbing action of hydrogen must be shifted into the double layer region (see the data on naphthalene adsorption on platinum[142]). The magnitude of this shift is limited by the appearance of the surface not only of positive charges, but also of adsorbed oxygen, there being no doubt that the presence of oxygen also reduces the adsorbability of organic molecules.

4. Dissociative Adsorption

Until the beginning of the sixties, in most studies on adsorption of organic substances on platinum metals, a review of which was given by Sokolsky,[143] organic molecules were assumed to be physically adsorbed or reversibly chemisorbed on the electrode surface. In his review Sokolsky first suggested that adsorption of organic substances on platinum metals can involve chemical reactions. In fact, beginning with 1964, various investigators[144–148] established by independent methods that adsorption on platinum of aliphatic alcohols and hydrocarbons involves the dissociation of organic molecules with the breaking of the C—H and even C—C bonds. Thus, in the case of methanol adsorption on platinum three hydrogen atoms break away from the CH_3OH molecule, so that the composition of the chemisorbed particle corresponds to the formula HCO.[145]* In recent years dissociative adsorption of organic molecules has been experimentally established also for other platinum metals: palladium, ruthenium, rhodium and their alloys. Moreover, research has been considerably extended to include many organic substances belonging to different classes.

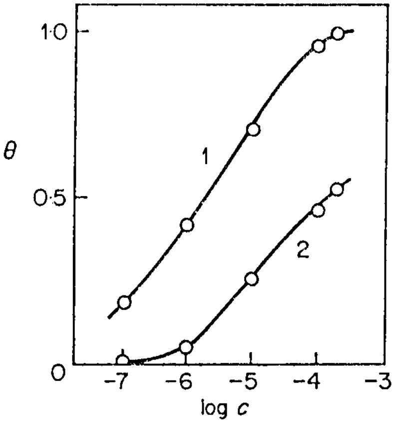

Fig. 16. Adsorption isotherms of allylphenylthiourea at $E = -0{\cdot}35$ V (NHE) on an iron electrode annealed at: 1—600°C and 2—at 750°C.

The data on the adsorption of organic substances from electrolyte solutions obtained so far do not permit us to give a full description of the adsorbed layer structure and in most cases lead only to definite conclusions regarding the stoichiometry of the adsorbed layer (relative amounts of carbon, oxygen,

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* According to Breiter $C_2H_2O_3$.[151]

and hydrogen on the surface). A more detailed discussion of the regularities in dissociative adsorption on the basis of the experimental evidence available now can be found in Reference 1. As follows from direct measurements of ion adsorption, carried out with radioactive tracers, the adsorption of organics on platinum exerts a very strong influence on the composition of the ionic side of the double layer at the platinum/solution interface.[152]

To conclude our discussion of the effect of the nature of the metal on adsorption of organic molecules, we would like to emphasize that the application of experimental data on adsorption of organic compounds obtained for mercury to other metals (see e.g.[35–37,149]), as follows from the above discussion, is possible only in certain particular cases and even then with great caution.

After completion of the manuscript the concepts discussed above have been developed further in References 153–158.

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