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ADSORPTION OF ORGANIC COMPOUNDS [AT THE MERCURY ELECTRODE-SOLUTION INTERFACE]

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Among various direct and indirect methods for the investigation of the adsorption of organic substances on the surface of electrodes, the most widely used are those based on measurements of the interfacial tension (σ) and differential capacitance (C) as a function of electrode potential (φ). Most of these data have been obtained for the mercury–aqueous solution interface in the presence of small amounts of organic additives. In this connection, the theory of the adsorption or organic compounds described below is mainly based on experimental data obtained for the mercury electrode by the measurement of $\sigma-\varphi$ and $C-\varphi$ curves.

Starting with the work of Gouy [1,2] and Frumkin [3,4], the method based on the measurement of electrocapillary curves has been widely used up to the present time for the study of the adsorption on the mercury electrode of a wide variety of organic substances [5-20]. Fig. 1, taken from the paper by Gouy [1], shows that the adsorption of an organic compound (in this case pentanol) appreciably lowers the interfacial tension of mercury, the lowering being a maximum near the zero-charge point (z.c.p.) in a solution of an inorganic electrolyte, decreasing with increase in the negative or positive surface charge. In most cases, when the charge is sufficiently positive or negative, the lowering of the interfacial tension under the influence of an organic substance is not observed and the electrocapillary curve obtained in the presence of the additive coincides with the $\sigma-\varphi$ curve measured in the supporting electrolyte solution (Fig. 1). According to the Gibbs adsorption equation,

$$d\sigma = -RT\Gamma\, d\ln c, \qquad (1)$$

where Γ and c are the extent of adsorption and the concentration of the organic substance. This means that at high surface charges organic molecules are desorbed from the electrode surface. Qualitatively this effect is associated with replacement of a layer of organic molecules, having a low dielectric constant, by a layer of water molecules whose dielectric constant is much higher.

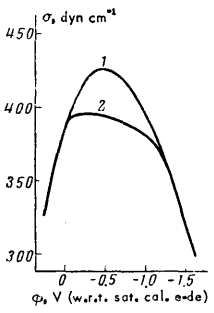


Fig. 1. Electrocapillary curves in different solutions:
1) 1 N Na_2SO_4; 2) 1 N Na_2SO_4 + + 0.1 M $C_5H_{11}OH$ (Gouy's data [1]).

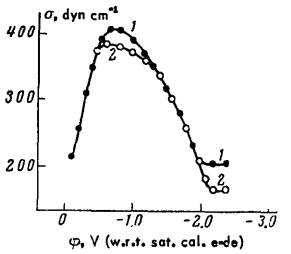


Fig. 2. Electrocapillary curves in different solutions:
1) 0.2 M NaI; 2) 0.2 M NaI + 0.1 M n-$C_5H_{11}OH$ (data of Smirnov and Demchuk [21]).

Fig. 2 shows $\sigma-\varphi$ curves measured by Smirnov and Demchuk [21] in 0.2 M aqueous solution of sodium iodide in the presence of 0.1 M n-pentanol over a wide range of potentials, up to the potential corresponding to the discharge of Na^+ ions with formation of sodium amalgam. In the authors' view, the divergence of the electrocapillary curves at highly negative potentials is due to the same cause as in the vicinity of the zero-charge point of mercury, i.e. it is associated with the adsorption of pentanol near the zero-charge point of the sodium amalgam.

A quantitative theory of the effect of the electric field on the adsorption of neutral molecules was developed by Frumkin [22]; according to Frumkin, when allowance is made for the attractive forces between the adsorbed molecules, the lowering of the interfacial tension ($\Delta\sigma$) and the degree of surface coverage ($\theta = \Gamma/\Gamma_\infty$) by the organic substance are related as follows:

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

where A and a are constants: $A = RT\Gamma_\infty$, while a is a measure of the interaction between the molecules of the adsorbed species (attraction constant).

The equation for the adsorption isotherm can be readily obtained from Eqn. (2) and the Gibbs equation (1):

$$Bc = \frac{\theta}{1-\theta}\exp(-2a\theta), \qquad (3)$$

where B is the adsorption equilibrium constant which determines the variation of the extent of adsorption with electrode potential. Eqn. (3) has been called the Frumkin isotherm.

In order to find the explicit relation between B and φ, Frumkin suggested that the boundary between the electrode and solution may be represented by two condensers connected in parallel: the space between the plates of one of them contains only molecules of the organic substance and that between the plates of the other only the molecules of the solvent (water). The charge of the electrode (ϵ) can then be represented by an equation of the following form:

$$\epsilon = \epsilon_0(1-\theta) + C'\theta(\varphi - \varphi_N), \qquad (4)$$

where $\epsilon_0 = \int_0^{\varphi} C_0 d\varphi$, C_0 and C' are the double layer capacitances at $\theta = 0$ and $\theta = 1$ respectively, φ is the potential reckoned from the zero-charge point at $\theta = 0$, and φ_N is the shift of the zero-charge point on going from $\theta = 0$ to $\theta = 1$.

On combining Eqn. (4) with the principal equation of electrocapillarity,

$$d\sigma = -\varepsilon d\varphi - RT\Gamma d\ln c, \quad (5)$$

the following relation between B and the potential is obtained:

$$B = B_0 \exp\left[-\frac{E + C'\varphi\left(\varphi_N - \frac{\varphi}{2}\right)}{A}\right], \quad (6)$$

where $E = \int_0^{\varphi} \epsilon_0 d\varphi$, i.e. the lowering of σ under the influence of the adsorption of inorganic ions only.

Eqns. (6) and (3) permit the calculation of the dependence of the degree of coverage θ on the potential φ and then the determination from Eqn. (2) of the lowering of the interfacial tension under the influence of the adsorption of organic molecules on the surface of the electrode. Such calculations have been made by Frumkin[22] for the adsorption of t-pentanol from 1 N NaCl solution and showed satisfactory agreement with experimental $\sigma-\varphi$ curves.

However, even in these experiments a more detailed comparison of the calculated and experimental $\sigma-\varphi$ curves showed that the break in the experimental electrocapillary curves at $\epsilon > 0$ is more pronounced than would follow from theory. This result was explained[22] by a decrease in the area occupied by one adsorbed alcohol molecule as θ increases, which is equivalent to a parabolic relation between the potential and the attraction constant a.

In Butler's theory[23] an attempt was made to interpret electrocapillary curves on the basis of the molecular properties of the adsorbed substances, in particular by taking into account the polarisability of organic molecules. However, in Butler's theory the dipole moments of the adsorbed molecules are determined from experimental data on interfacial tension. Furthermore, this theory gives an incorrect variation of the extent of adsorption of the organic substance with its concentration in the solution, since it is based on the hypothesis that Henry's law holds.

Further development of the theory of the adsorption of organic compounds was possible on the basis of experimental measurements of the differential capacitance of the mercury electrode in the presence of organic additives, since differential capacitance is a much more sensitive function of the double-layer structure than interfacial tension[24]. On the basis of the electrocapillary data and Lippman's equation, it was to be expected that the differential capacitance curves obtained in the presence of organic additives would include a region of low capacitance (of the order of 4–5 μF cm^{-2}) bounded on either side by desorption peaks. Proskurnin and Frumkin[24] were able to demonstrate for the first time that $C-\varphi$ curves measured in the presence of n-octanol have indeed this shape (Fig. 3). Capacitance curves of similar shape were also obtained subsequently by a number of other investigators. Thus, starting with the work of Proskurnin and Frumkin[24], the method based on the measurement of differential capacitance has been widely used to study the adsorption of various organic substances on mercury[25–44].

However, quantitative application of these data has been limited in practice only to the range of potentials corresponding to maximum adsorption, where the $C-\varphi$ curves show a decrease in capacitance in the presence of organic

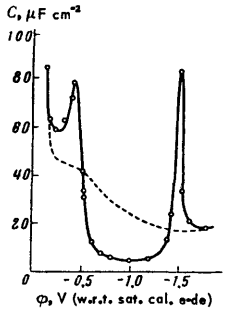


Fig. 3. Differential capacitance curves in 1 N Na_2SO_4 solution and in 1 N Na_2SO_4 solution saturated with n-$C_8H_{17}OH$ (data of Proskurnin and Frumkin[24]).

substances (Fig. 3) and where the following relation obtains between the capacitance and the degree of surface coverage:

$$C = C_0(1-\theta) + C'\theta. \quad (7)$$

This equation has been used[34,38,42] for the calculation of the adsorption isotherms on mercury of various organic compounds. Recently the variation of the capacitance at the potential of maximum adsorption with the degree of coverage was used by Dobren'kov to develop a theory for the simultaneous adsorption of two organic substances on the electrode surface[45,46].

In order to interpret the overall differential capacitance curve in the presence of an organic substance, it is necessary to choose an independent electrical variable and a particular equation for the adsorption isotherm. The controversy which has arisen concerning these problems[47–49] makes it necessary to examine them in greater detail.

1. CHOICE OF ELECTRICAL VARIABLE

Either the electrode potential[22] or the electrode charge[47] can be chosen as the electrical variable in the investigation of adsorption of organic substances on electrodes. It will be assumed initially that the experimental variation of the extent of adsorption of an organic substance Γ with its bulk concentration and the potential may be written thus:

$$Bc = f(\Gamma), \quad (8)$$

where B is a function of φ only and $f(\Gamma)$ a function of Γ only. It is evident that under these conditions it is useful to choose the potential as the independent electrical variable, since the shape of the isotherm [Eqn. (8)] in dimensionless coordinates is then independent of φ. It follows from Eqn. (8) that

$$\frac{d\ln B}{d\varphi} = -\left(\frac{\partial \ln c}{\partial \varphi}\right)_{\Gamma} = \frac{1}{RT}\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_{\varphi}, \quad (9)$$

where the second equality is a consequence of the basic equation of electrocapillarity [Eqn. (5)]. On integrating Eqn. (9), we find

$$\varepsilon = RT\left(\frac{d\ln B}{d\varphi}\right)\Gamma + \varepsilon_0 = A\left(\frac{d\ln B}{d\varphi}\right)\theta + \varepsilon_0, \quad (10)$$

where, as before, $A = RT\Gamma_\infty$.

Let the charge at $\theta = 1$ and the given potential be ϵ', so that

$$\varepsilon' = A\left(\frac{d\ln B}{d\varphi}\right) + \varepsilon_0. \quad (11)$$

It follows from Eqns. (10) and (11) that

$$\varepsilon = \varepsilon_0(1-\theta) + \varepsilon'\theta. \quad (12)$$

On differentiating Eqn. (12) with respect to the potential at θ = const, we obtain Eqn. (7). Thus representation of the sorption isotherm by Eqn. (8) and hence the choice of the electrode potential as the independent electrical variable are consistent with the model of the electrical double layer previously proposed by Frumkin [22].

If it is assumed as a first approximation that the capacitance C_0 is independent of φ, then evidently $\epsilon_0 = C_0\varphi$ and for $\epsilon = 0$ Eqn. (4) yields

$$\varphi_{\varepsilon=0} = \frac{\varphi_N\theta}{\frac{C_0}{C'}(1-\theta)+\theta}, \quad (13)$$

where $\varphi_{\epsilon=0}$ is the difference between the zero-charge point at a given θ and the zero-charge point at $\theta = 0$, i.e. the jump in potential due to adsorption. Eqn. (13) shows that the variation of $\varphi_{\epsilon=0}$ with θ (or Γ) is not linear when the potential is chosen as the electrical variable, and deviates from linearity to a greater extent the higher the value of C_0/C'.

It will be assumed first that the experimental data can be described by an equation of the type

$$Gc = f(\Gamma), \quad (14)$$

where G is a function of ϵ only and $f(\Gamma)$ a function of Γ only. In this case it is reasonable to choose the electrode charge as the independent electrical variable, since the shape of the isotherm defined by Eqn. (14), in dimensionless coordinates, is then independent of ϵ. It follows from Eqn. (14) that

$$\frac{d\ln G}{d\varepsilon} = -\left(\frac{\partial\ln c}{\partial\varepsilon}\right)_\Gamma = -\frac{1}{RT}\left(\frac{\partial\varphi}{\partial\Gamma}\right)_\varepsilon, \quad (15)$$

where the second equality is due to the basic equation of electrocapillarity corresponding to ϵ = const. [50] On integrating Eqn. (15), we obtain

$$\varphi = -RT\left(\frac{d\ln G}{d\varepsilon}\right)\Gamma + \varphi_0 = -A\left(\frac{d\ln G}{d\varepsilon}\right)\theta + \varphi_0, \quad (16)$$

where φ_0 is the value of φ, when $\theta = 0$, corresponding to the given value of ϵ.

If the potential at a given ϵ and $\theta = 1$ is denoted by φ', then

$$\varphi' = -A\left(\frac{d\ln G}{d\varepsilon}\right) + \varphi_0. \quad (17)$$

Eqns. (16) and (17) show that

$$\varphi = \varphi_0(1-\theta) + \varphi'\theta. \quad (18)$$

On differentiating Eqn. (18) with respect to ϵ for θ = const, we obtain

$$\frac{1}{C} = \frac{1-\theta}{C_0} + \frac{\theta}{C'}. \quad (19)$$

Thus when the adsorption isotherm is represented by Eqn. (14), and therefore when the electrode charge is chosen as the electrical variable, we have a model corresponding to two condensers with capacitances $C_0/(1-\theta)$ and C'/θ connected in series. The physical interpretation of this model appears to be difficult.

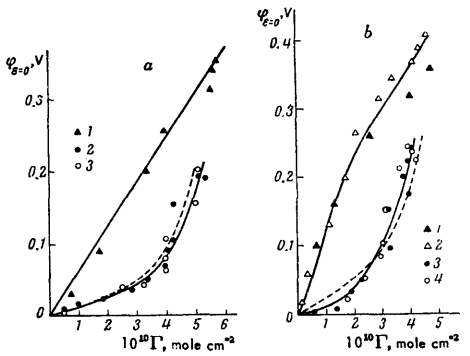


Fig. 4. Variation of the adsorption-induced potential jump with the extent of adsorption of the organic substance: *a*) adsorption of n-C_4H_9COOH; 1) at the solution/air interface, supporting electrolyte 0.01 N H_2SO_4; 2) and 3) at the mercury/solution interface [2] supporting electrolyte 0.01 N H_2SO_4; 3) supporting electrolyte 1 N Na_2SO_4 + 0.01 N H_2SO_4]; dashed line — calculated by Eqn. (13) for φ_N = 0.02 V, Γ_∞ = $= 5 \times 10^{-10}$ mole cm^{-2}, and $C_0/C' = 5$; *b*) adsorption of n-$C_5H_{11}NH_2$: 1) and 2) at the solution/air interface [1] supporting electrolyte 0.05 N KOH; 2) supporting electrolyte 1 N Na_2SO_4 + 0.05 N KOH]; 3) and 4) at the mercury/solution interface [3] supporting electrolyte 0.05 N KOH; 4) supporting electrolyte 1 N Na_2SO_4 + 0.05 N KOH]; dashed line — calculated by Eqn. (13) for φ_N = 0.4 V, Γ_∞ = $= 5 \times 10^{-10}$ mole cm^{-2}, and $C_0/C' = 5$.

On the other hand, if the capacitances C_0 and C' are independent of ϵ, then evidently $\varphi_0 = \epsilon/C_0$ and $\varphi' = \epsilon/C' + \varphi$. In this case Eqn. (18) can be rewritten thus:

$$\varepsilon = \frac{\varphi - \theta\varphi_N}{\frac{1-\theta}{C_0} + \frac{\theta}{C'}}. \quad (20)$$

Putting $\epsilon = 0$ in Eqn. (20), we obtain a linear variation of the adsorption-induced potential jump with θ (or Γ):

$$\varphi_{\varepsilon=0} = \theta\varphi_N. \quad (21)$$

Thus the variation of the adsorption-induced potential jump with Γ makes it possible to decide whether condition (8) or condition (14) holds, and hence which choice of the electrical variable (φ or ϵ) is more reasonable in the investigation of the adsorption of an organic substance at the interface.

Fig. 4 shows the variation of $\varphi_{\epsilon=0}$ with Γ for the adsorption of n-butyric acid and n-pentylamine at the mercury/solution and solution/air interfaces [51]. It is evident that the relation between $\varphi_{\epsilon=0}$ and Γ at the mercury/solution interface is satisfactorily consistent with Eqn. (13), regardless of the concentration of the supporting electrolyte, and sharply deviates from the linear variation predicted by Eqn. (21). At the same time at the solution/air interface the relation is approximately consistent with Eqn. (21)†. Similar results were obtained by the present author also for the adsorption of n-propanol and n-butanol at both interfaces.

† Certain deviations of the $\varphi_{\epsilon=0}$–Γ plot from linearity for the solution/air interface may be associated with a change in the orientation of the adsorbed molecules as Γ increases.

It follows from these results that both the physical interpretation of the model of the double layer and the experimental variation of the adsorption-induced potential jump with the extent of adsorption suggest that the electrode potential and not the electrode charge be chosen as the electrical variable in the investigation of the adsorption of organic compounds at the mercury/solution interface.

2. CHOICE OF ADSORPTION ISOTHERM

Since experimental adsorption isotherms for organic compounds can have both the form of a logarithmic curve and the characteristic S-shape (Fig. 5), in choosing the equation for the adsorption isotherm it is reasonable to consider only those equations which can represent various shapes of the experimental isotherms, depending on the quantity a (the attraction constant). This condition is satisfied by the following equations for adsorption isotherms:

(1) Frumkin's isotherm — Eqn. (3).

(2) de Boer's isotherm[52]:

$$Bc = \frac{\theta}{1-\theta}\exp\left(\frac{\theta}{1-\theta}\right)\exp(-2a\theta), \qquad (22)$$

(3) Parsons' isotherm[47]:

$$Bc = \frac{\theta}{1-\theta}\exp\left[\frac{2-\theta}{(1-\theta)^2}\right]\exp(-2a\theta), \qquad (23)$$

(4) The general equation of Frumkin's isotherm:

$$Bc = \frac{\theta}{(1-\theta)^n}\exp(-2a\theta), \qquad (24)$$

obtained by the present author[53] and taking into account both the forces of interaction between the adsorbed molecules and the organic substance (via the quantity a), and the displacement by the adsorbed species of n molecules of the solvent (water).

Apart from the theoretical justification of a particular type of equation for the adsorption isotherm[47,48], it appears that experimental criteria must be the deciding factor. Such criteria were proposed by Parsons[47] and Tedoradze[54], but, as shown by the present author[55], they do not allow a choice among the four equations for adsorption isotherms given above. Let us therefore consider another criterion which does permit such a choice.

It is readily seen that the above equations are all of the form

$$Bc = F(\theta)\exp(-2a\theta), \qquad (25)$$

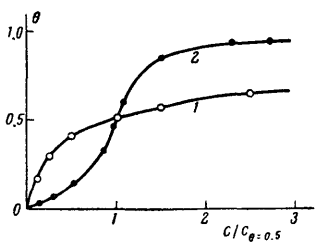


Fig. 5. Adsorption isotherms on mercury: 1) triethylammonium cations; 2) t-pentanol (data of Lorenz and coworkers[42,43]).

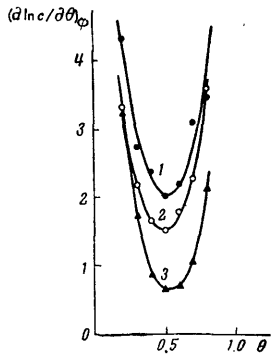


Fig. 6. Variation of $(\partial \ln c/\partial\theta)_\varphi$ with θ obtained from experimental adsorption isotherms:
1) aniline; 2) n-$C_5H_{11}NH_2$; 3) t-$C_5H_{11}OH$.

where $F(\theta)$ is a function of θ independent of a. On taking logarithms in Eqn. (25) and then differentiating it with respect to θ with φ = const, we obtain

$$\left(\frac{\partial \ln c}{\partial\theta}\right)_\varphi = \frac{d\ln F(\theta)}{d\theta} - 2a. \qquad (26)$$

Analysis shows that at a certain value $\theta = \theta^*$, determined by the condition

$$\frac{d^2 \ln F(\theta)}{d\theta^2} = 0, \qquad (27)$$

the relation between $(\partial \ln c/\partial\theta)\varphi$ and θ passes through a minimum whose position is determined only by the function $F(\theta)$ and is independent of the attraction constant a.

As shown elsewhere[55], the values of θ^* for Eqns. (3), (22), (23), and (24) are respectively 0.500, 0.333, 0.215, and $1/(1+\sqrt{n})$. Thus the position of the minimum on the experimental curve for the variation of $(\partial \ln c/\partial\theta)_\varphi$ with θ may serve as a convenient criterion for choosing one of the four isotherms. When this method is used, only de Boer's equation [Eqn. (22)] and Eqn. (24) with $n = 4$ are virtually indistinguishable.

Experimental $(\partial \ln c/\partial\theta)_\varphi - \theta$ curves can be obtained as follows. Initially, using the value of the capacitance at the minimum on the $C-\varphi$ curves, the $\theta-c$ adsorption isotherm is plotted in terms of Eqn. (7), which, as we have seen, is valid for any isotherm of the type represented by Eqn. (8) or (25). Since $d\ln c/d\theta = dc/cd\theta$, the values of $(\partial \ln c/\partial\theta)_\varphi$ can be found from the slope of this isotherm for various θ, and the $(\partial \ln c/\partial\theta)-\theta$ curve can be plotted.

The characteristic curves obtained for the adsorption of aniline, n-pentylamine, and t-pentanol on the mercury electrode are presented in Fig. 6, which shows that the minimum on these curves corresponds to $\theta^* \simeq 0.5$ and therefore the adsorption of these compounds follows Frumkin's isotherm [Eqn. (3)]. Similar $(\partial \ln c/\partial\theta)_\varphi-\theta$ curves were obtained also for n-propanol, n-pentanol, isopentanol, isopentylamine, phenol, and tetrabutylammonium cations. For all these compounds the experimental values of θ^* are in the range between 0.45 and 0.55.[55]

Thus the adsorption on mercury of most organic compounds which lower the double-layer capacitance follows the equation of Frumkin's isotherm [Eqn. (3)]. Recently

Dobren'kov and Golovin [56] showed that this equation is also valid for the adsorption of dibutylnaphthalenesulphonic acid and isopentanol on the cadmium electrode‡. Therefore the equation of Frumkin's isotherm [Eqn. (3)] should be used as a basis for the theory of differential capacitance curves in the presence of organic substances.

3. QUANTITATIVE THEORY OF DIFFERENTIAL CAPACITANCE CURVES IN THE PRESENCE OF ORGANIC ADDITIVES

The fact that experimental data suggest the choice of the electrode potential as the electrical variable and of Frumkin's equation (3) as the equation of the adsorption isotherm means that the theoretical relations obtained by Lorenz and coworkers [42,43] and Parsons [47] and also the Devanathan [60] and Bockris–Devanathan–Müller [61] theories must be rejected, particularly as the last two theories have a number of significant disadvantages, which are discussed in detail in Ref. 62.

If the potential is chosen as the independent electrical variable, then under the condition that the adsorption of the organic substance on the electrode surface is not complicated by the formation of multilayers and micellar films, the electrode charge is a function of electrode potential and degree of coverage only:

$$\varepsilon = \varepsilon(\varphi, \theta). \tag{28}$$

Thus the overall expression for the differential capacitance can be put in the following form:

$$C = \frac{d\varepsilon}{d\varphi} = \left(\frac{\partial \varepsilon}{\partial \varphi}\right)_\theta + \left(\frac{\partial \varepsilon}{\partial \theta}\right)_\varphi \frac{d\theta}{d\varphi}. \tag{29}$$

The quantities $(\partial\epsilon/\partial\varphi)_\theta$ and $(\partial\epsilon/\partial\theta)_\varphi$ in this equation can be found immediately from Eqn. (4):

$$\left(\frac{\partial \varepsilon}{\partial \varphi}\right)_\theta = C_0(1-\theta) + C'\theta, \tag{30}$$

$$\left(\frac{\partial \varepsilon}{\partial \theta}\right)_\varphi = -[\varepsilon_0 + C'(\varphi_N - \varphi)]. \tag{31}$$

The derivative $d\theta/d\varphi$ is found from Eqn. (3). On taking logarithms in this equation and then differentiating it with respect to φ, we obtain after algebraic rearrangement,

$$\frac{d\theta}{d\varphi} = \frac{d\ln B}{d\varphi} \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \tag{32}$$

It follows from Eqn. (6) that

$$\frac{d\ln B}{d\varphi} = -\frac{\varepsilon_0 + C'(\varphi_N - \varphi)}{A} \tag{33}$$

and therefore

$$\frac{d\theta}{d\varphi} = -\frac{\varepsilon_0 + C'(\varphi_N - \varphi)}{A} \frac{\theta(1-0)}{1-2a\theta(1-\theta)}. \tag{34}$$

On substituting the values of the derivatives from Eqns. (30), (31), and (34) in Eqn. (29), we obtain the final expression for the differential capacitance in the presence of an organic substance:

$$C = C_0(1-\theta) + C'\theta + \frac{[\varepsilon_0 + C'(\varphi_N - \varphi)]^2}{A} \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \tag{35}$$

This equation was obtained for the first time by Hansen and coworkers [28].

As already pointed out above, Eqns. (3) and (6) make it possible to calculate the variation of θ with φ at a given concentration of the organic substance. Once this variation has been found, and the constants C', A, a, and φ_N are known, the total differential capacitance curve in the presence of an organic substance may be calculated by Eqn. (35). Such calculations, made by Hansen and coworkers [28] and by the present author [63], show that, despite the qualitative agreement between the calculated and experimental $C-\varphi$ curves, there is a very significant quantitative discrepancy between them. Analysis shows that the discrepancy is evidence of a change with potential of the attraction constant in the equation of Frumkin's isotherm [Eqn. (3)]. Furthermore, in contrast to Frumkin's hypothesis [22], the variation of a with φ for most organic compounds is linear and not parabolic.

Thus it is of interest to develop a theory assuming an arbitrary variation of a with φ [$a = a(\varphi)$].

In this case on taking logarithms in Eqn. (3) and differentiating with respect to the potential, we obtain, after rearrangement, the following expression instead of Eqn. (32):

$$\frac{d\theta}{d\varphi} = \left(\frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}\right) \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \tag{36}$$

At the same time differentiation with respect to φ when θ = const gives

$$\left(\frac{\partial \ln c}{\partial \varphi}\right)_\theta = -\left(\frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}\right). \tag{37}$$

Taking into account the second equality in Eqn. (9), we obtain

$$\frac{1}{A}\left(\frac{\partial \varepsilon}{\partial \theta}\right)_\varphi = \frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}. \tag{38}$$

On integrating this equation and remembering that the integration constant is ϵ_0, we obtain

$$\varepsilon = \varepsilon_0 + A\frac{d\ln B}{d\varphi}\theta + A\theta^2\frac{da}{d\varphi}. \tag{39}$$

Since $\epsilon = \epsilon' = C'(\varphi - \varphi_N)$ when $\theta = 1$, it follows from Eqn. (39) that

$$\frac{d\ln B}{d\varphi} = -\frac{\varepsilon_0 + C'(\varphi_N - \varphi)}{A} - \frac{da}{d\varphi}. \tag{40}$$

After integrating this equation from 0 to φ and taking antilogarithms, we have

$$B = B_0 \exp\left[-\frac{E + C'\varphi\left(\varphi_N - \frac{\varphi}{2}\right)}{A}\right] \exp(a_0 - a), \tag{41}$$

where a_0 is the value of a when φ = 0.

Eqn. (41) represents the variation of the adsorption equilibrium constant with potential for any relation between a and φ. It is readily seen that it becomes identical with Eqn. (6) when a = const.

On substituting Eqn. (40) in Eqn. (39), we obtain the equation for the electrode charge in the general case, when $a = a(\varphi)$:

$$\varepsilon = \varepsilon_0(1-\theta) + C'\theta(\varphi - \varphi_N) - A\frac{da}{d\varphi}\theta(1-\theta). \tag{42}$$

‡ The satisfactory agreement of Eqn. (3) with experimental data implies that in the more general equation (24) n = 1 and therefore one adsorption site on the surface of the electrode is occupied by a group of several water molecules [53]. When allowance is made for the considerable attractive interaction between the H_2O molecules adsorbed on mercury [57-59], this result may be explained by the fact that the work associated with the transfer of this group of molecules, taken as a whole, from the surface into the bulk of the solution is smaller than the overall work of transfer of each of these molecules separately.

As was to be expected, Eqn. (42) becomes identical with Eqn. (4) when a = const.

Finally, we shall find an expression for the differential capacitance in the presence of an organic substance under the condition that $a = a(\varphi)$. From Eqn. (42), we have

$$\left(\frac{d\varepsilon}{\partial\varphi}\right)_\theta = C_0(1-\theta) + C'\theta - A\frac{d^2a}{d\varphi^2}\theta(1-\theta), \quad (43)$$

$$\left(\frac{\partial\varepsilon}{\partial\theta}\right)_\varphi = -\varepsilon_0 + C'(\varphi-\varphi_N) - A\frac{da}{d\varphi}(1-2\theta). \quad (44)$$

On substituting Eqn. (40) in Eqn. (36), we find

$$\frac{d\theta}{d\varphi} = -\left[\varepsilon_0 - C'(\varphi-\varphi_N) + A\frac{da}{d\varphi}(1-2\theta)\right]\frac{1}{A}\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \quad (45)$$

If we now substitute the values of the derivatives from Eqns. (43), (44), and (45) in Eqn. (29), we obtain the final expression for the differential capacitance:

$$C = C_0(1-\theta) + C'\theta - A\frac{d^2a}{d\varphi^2}\theta(1-\theta) + \frac{1}{A}\left[\varepsilon_0 + C'(\varphi_N-\varphi) + A\frac{da}{d\varphi}(1-2\theta)\right]^2\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \quad (46)$$

Evidently Eqn. (46) becomes identical with Eqn. (35) when a = const.

Earlier the present author obtained expressions for the adsorption equilibrium constant B, the electrode charge ϵ, and the differential capacitance C under the condition that the attraction constant is a linear function of electrode potential:

$$a = a_0 + \beta\varphi. \quad (47)$$

In the expressions for B, ϵ, and C the variation of a with φ was allowed for by introducing a new constant:

$$\varphi_N^0 = \varphi_N + \frac{\beta A}{C'}. \quad (48)$$

Eqns. (41), (42), and (46) obtained in this work are free from the limitations imposed by condition (47), and are valid for any relation between the attraction constant and the electrode potential. Since the experimental variation of the attraction constant with potential satisfied condition (47) in most cases, the formulae obtained in Ref. 64 led to satisfactory agreement between calculated and experimental $C-\varphi$ curves[63,65-68]. Fig. 7 illustrates this result using as an example the adsorption of n-valeric acid on mercury[68]. Similar satisfactory agreement between calculation and experiment was observed by the author for the adsorption on mercury of n-propanol, n-butanol, n-pentanol, isopentanol, t-pentanol, n-butylamine, n-pentylamine, isopentylamine, and diethyl ketone.

The calculated and experimental $C-\varphi$ curves for the adsorption of aniline[69] and pyridine[70] on mercury coincide only in the range of negative surface charges (Fig. 8). On going from $\epsilon < 0$ to $\epsilon > 0$, there is a change in the orientation accompanied by partial desorption of aniline or pyridine molecules due to their π-electron interaction with the positive charges on the surface of mercury. It is this process and not total desorption of the molecules of the organic substance from the electrode surface which corresponds to the anodic maxima on the $C-\varphi$ curves in the presence of aniline or pyridine. Clearly, under these conditions when $\epsilon > 0$ theoretical $C-\varphi$ curves, which do not take account of the above anomalies in the adsorption of an organic substance, cannot coincide with the experimental differential capacitance curves.

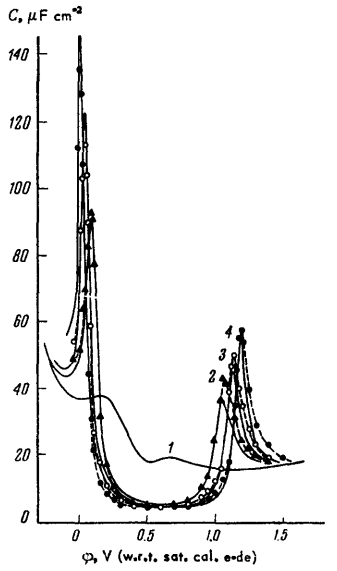


Fig. 7. Differential capacitance curves for 0.05 N Na_2SO_4 solution with different concentrations of added n-C_4H_9COOH (M): 1) 0; 2) 0.05; 3) 0.08; 4) 0.12; continuous lines — experimental data for 400 c/s; symbols and dashed lines — calculated values.

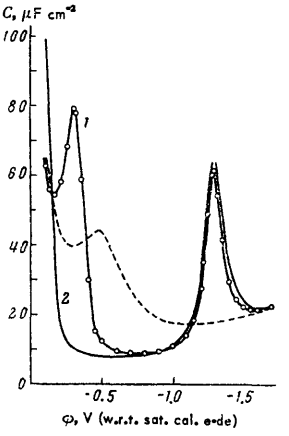


Fig. 8. Differential capacitance curves for 0.1 N KCl solution alone (dashed curve) and in the presence of 0.1 M aniline: 1) experimental data; 2) calculated curve.

Finally, in the adsorption of phenol on mercury[71] the planar disposition of molecules, associated with strong π-electron interaction, is characteristic of the entire range of its adsorption potentials. In this case the constants which enter into the equations for the quantity B [Eqn. (41)] and the differential capacitance [Eqn. (46)] characterise the planar configuration of the phenol molecules in the adsorbed state, so that the calculated and experimental $C-\varphi$ curves agree with one another over the entire range of potentials (Fig. 9). However, the effect of the π-electron interaction

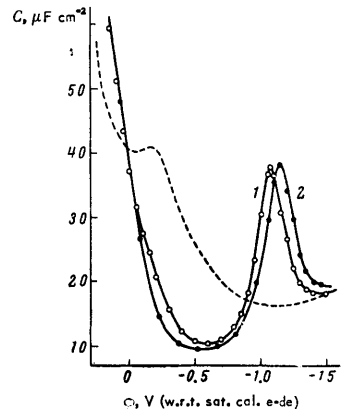


Fig. 9. Differential capacitance curves for 1 N Na_2SO_4 solution alone (dashed curve) and in the presence of 0.05 M phenol: 1) experimental data; 2) calculated curve.

leads nevertheless to less satisfactory agreement between calculation and experiment for phenol than for the adsorption of aliphatic compounds (Fig. 7).

Apart from the quantitative interpretation of the differential capacitance curves in the presence of an organic substance, Eqns. (3), (41), and (46) make it possible to investigate certain general features of equilibrium (i.e. extrapolated to zero frequency) and non-equilibrium $C-\varphi$ curves, in particular the dependence of the potentials corresponding to the peaks on the $C-\varphi$ curves and the height of these peaks on the concentration of the organic substance. Study of these relations is very important, since it leads to methods for the determination of the principal constants in Eqns. (41) and (46) and the relations between a and φ from experimental differential capacitance curves. Recently the present author and Tedoradze [72-76] considered the problems involved in the determination of such general relations, which are of independent scientific interest.

I should like to take this opportunity to express my profound gratitude to A. N. Frumkin for continued interest in this work and discussion of the results obtained.

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THEORY OF HOMOGENEOUS AND HETEROGENEOUS ELECTRONIC PROCESSES IN LIQUIDS

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I. INTRODUCTION

The theory of electronic processes in liquids occupies a very specific place in the general theory of chemical kinetics. A comparison of various electronic processes occurring in the liquid phase and in solids reveals a great similarity of physical mechanisms. Yet, no such analogy is normally found between gas-phase and liquid-phase reactions. For example, we may consider the electron exchange reaction between ions of the same sign. If we compare the rate of charge transfer between ions in gases with the rate of analogous oxidation–reduction reactions in water, we find that charge transfer in gases not only occurs significantly faster than in solutions, but also, and this is less trivial, that the phenomenon of resonance charge transfer is in general absent in solutions. It is well known that charge transfer between similar ions differing only in valence state proceeds much faster in the gas phase than reactions between unlike ions[1]. At the same time, the reaction $Fe^{2+} + Fe^{*3+} \rightarrow Fe^{3+} + Fe^{*2+}$ is much slower, in solutions, than a reaction like $Fe^{2+} + FeOH^{2+} \rightarrow \rightarrow Fe^{3+} + FeOH^{+}$. On the other hand, it has been possible[2-7] to apply the theory of F-centres and polarons, which was developed for crystals[4], in the study of the absorption spectra and of the conductivity of solutions of metals in liquid ammonia.