STRUCTURE OF THE ELECTRODE-SOLUTION INTERFACE IN THE PRESENCE OF ORGANIC SOLUTIONS ADSORBED IN TWO DIFFERENT POSITIONS

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As was shown in [1-3], the behavior of the mercury–aqueous solution interface in the presence of organic substances adsorbed in one position (saturated aliphatic compounds) can be described with good approximation by a model of two parallel condensers. If the organic substance can be adsorbed on the electrode in two different positions (such as, for example, aromatic compounds), then evidently the model of two parallel condensers should be replaced by a model of three parallel condensers: between the linings of one of them are found water molecules, and between the linings of the second – molecules of the organic substance in the first, for example, vertical position, and between the linings of the third – molecules of the organic substance in the second, for example, planar position. The equation corresponding to this model for the charge of the electrode ε takes the form

$$\varepsilon = \varepsilon_0(1 - \theta_1 - \theta_2) + C_1(\varphi - \varphi_{N1})\theta_1 + C_2(\varphi - \varphi_{N2})\theta_2 \quad (1)$$

where ε_0 is the charge of the electrode in a pure background solution; φ is the electrode potential, read from the point of zero charge in a pure background solution; θ_1 and θ_2 are the degrees of coverage of the surface by the organic substance in the first and second positions, respectively; C_1 and C_2 are the double-layer capacitances in the case of complete coverage of the surface by the organic substance, also for the first and second positions; φ_{N_1} and φ_{N_2} are the shifts of the point of zero charge in the transition from the pure background solution to $\theta_1 = 1$ or $\theta_2 = 1$, respectively.

For practical utilization of Eq. (1), it is necessary to additionally select two adsorption isotherms, which relate the quantities θ_1 and θ_2 to the volume concentration of the organic substance c. The selection of these isotherms cannot be arbitrary, since they are related to function (1) by the basic equation of electrocapillarity

$$d\sigma = -\varepsilon d\varphi - RT\Gamma d \ln c \quad (2)$$

where σ is the interfacial tension; Γ is the adsorbed amount of the organic substance; R is the bath constant; and T is the absolute temperature. The value of Γ for an organic substance adsorbed in two positions can be written in the form

$$\Gamma = \Gamma_\infty^{(1)}\theta_1 + \Gamma_\infty^{(2)}\theta_2 = \frac{\Gamma_\infty^{(H_2O)}}{n_1}\theta_1 + \frac{\Gamma_\infty^{(H_2O)}}{n_2}\theta_2 \quad (3)$$

where $\Gamma_\infty^{(H_2O)}$, $\Gamma_\infty^{(1)}$, and $\Gamma_\infty^{(2)}$ are the limiting adsorbed amounts for water molecules and molecules of the organic substance in the first and second positions, respectively; $n_1 = \Gamma_\infty^{(H_2O)}/\Gamma_\infty^{(1)}$ and $n_2 = \Gamma_\infty^{(H_2O)}/\Gamma_\infty^{(2)}$.

Let us show that the models of three parallel condensers in the simplest case satisfy isotherms of the type

$$B_1 c = \frac{\theta_1}{(1 - \theta_1 - \theta_2)^{n_1}}; \quad B_2 c = \frac{\theta_2}{(1 - \theta_1 - \theta_2)^{n_2}} \quad (4)$$

based upon the Flory-Haggins model [4, 5], in which the constants of adsorption equilibrium B_1 and B_2 are some functions of the electrode potential.*

*It is not difficult to show that the Langmuir equations of the mixed isotherm [6], i.e., Eqs. (4) when $n_1 = n_2 = 1$, do not satisfy function (1), if $\Gamma_\infty^{(1)} \neq \Gamma_\infty^{(2)}$.

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At a constant electrode potential, it follows from Eqs. (2) and (3) that

$$d\sigma = -\frac{A}{n_1}\theta_1 d\ln c - \frac{A}{n_2}\theta_2 d\ln c \tag{5}$$

where $A = RT\Gamma_{\infty}^{(H_2O)}$. From Eqs. (4) at φ = const, it is easy to obtain

$$d\ln c = \frac{d\theta_1}{\theta_1} + n_1\frac{d\theta}{1-\theta} \quad \text{and} \quad d\ln c = \frac{d\theta_2}{\theta_2} + n_2\frac{d\theta}{1-\theta} \tag{6}$$

where

$$\theta = \theta_1 + \theta_2 \tag{7}$$

Introducing (6) into (5), we find

$$d\sigma = -A\left(\frac{d\theta_1}{n_1} + \frac{d\theta_2}{n_2}\right) - A\frac{\theta d\theta}{1-\theta} \tag{8}$$

from which, after integration, it follows that

$$\sigma = \sigma_0 + A\left[\ln(1-\theta) + \frac{n_1-1}{n_1}\theta_1 + \frac{n_2-1}{n_2}\theta_2\right] \tag{9}$$

where σ_0 is the integration constant, equal to the interfacial tension in a pure solution of the background, since $\sigma = \sigma_0$ when $\theta = \theta_1 = \theta_2 = 0$.

Differentiation of Eq. (9) with respect to the potential gives

$$\varepsilon = -\frac{d\sigma}{d\varphi} = \varepsilon_0 + A\left[\frac{1}{1-\theta}\frac{d\theta}{d\varphi} - \frac{n_1-1}{n_1}\frac{d\theta_1}{d\varphi} - \frac{n_2-1}{n_2}\frac{d\theta_2}{d\varphi}\right] \tag{10}$$

Let us use Eq. (4) to find the derivatives $d\theta/d\varphi$; $d\theta_1/d\varphi$, and $d\theta_2/d\varphi$; from these equations, considering (7), it follows that

$$\theta_1 = B_1 c(1-\theta)^{n_1} \tag{11}$$

$$\theta_2 = B_2 c(1-\theta)^{n_2} \tag{12}$$

and

$$\theta = B_1 c(1-\theta)^{n_1} + B_2 c(1-\theta)^{n_2} \tag{13}$$

Differentiating Eq. (13) with respect to φ and solving the equation obtained with respect to $d\theta/d\varphi$, after algebraic transformations considering Eqs. (11) and (12), we can obtain

$$\frac{d\theta}{d\varphi} = \frac{(1-\theta)\left(\theta_1\frac{d\ln B_1}{d\varphi} + \theta_2\frac{d\ln B_2}{d\varphi}\right)}{1+(n_1-1)\theta_1+(n_2-1)\theta_2} \tag{14}$$

Differentiating Eq. (11) with respect to the potential, we obtain the relationship of the derivatives $d\theta_1/d\varphi$ and $d\theta/d\varphi$, after which, considering expression (14), we find

$$\frac{d\theta_1}{d\varphi} = \frac{d\ln B_1}{d\varphi}\theta_1 - \frac{n_1\theta_1\left(\theta_1\frac{d\ln B_1}{d\varphi} + \theta_2\frac{d\ln B_2}{d\varphi}\right)}{1+(n_1-1)\theta_1+(n_2-1)\theta_2} \tag{15}$$

By an analogous method, from Eqs. (12) and (14) we obtain

$$\frac{d\theta_2}{d\varphi} = \frac{d\ln B_2}{d\varphi}\theta_2 - \frac{n_2\theta_2\left(\theta_1\frac{d\ln B_1}{d\varphi} + \theta_2\frac{d\ln B_2}{d\varphi}\right)}{1+(n_1-1)\theta_1+(n_2-1)\theta_2} \tag{16}$$

Substitution of the functions (14)-(16) into Eq. (10) after algebraic transformations gives

$$\varepsilon = \varepsilon_0 + \frac{A}{n_1}\theta_1\frac{d\ln B_1}{d\varphi} + \frac{A}{n_2}\theta_2\frac{d\ln B_2}{d\varphi} \tag{17}$$

which is equivalent to the model of three parallel condensers [see Eq. (1)] under the condition

$$\frac{d\ln B_1}{d\varphi} = -\frac{n_1[\varepsilon_0 - C_1(\varphi-\varphi_{N1})]}{A} \tag{18}$$

$$\frac{d\ln B_2}{d\varphi} = -\frac{n_2[\varepsilon_0 - C_2(\varphi - \varphi_{N2})]}{A} \tag{19}$$

and consequently

$$B_1 = B_{01}\exp\left\{-\frac{n_1\left[\int_0^{\varphi}\varepsilon_0 d\varphi + C_1\varphi\left(\varphi_{N1} - \frac{\varphi}{2}\right)\right]}{A}\right\} \tag{20}$$

$$B_2 = B_{02}\exp\left\{-\frac{n_2\left[\int_0^{\varphi}\varepsilon_0 d\varphi + C_2\varphi\left(\varphi_{N2} - \frac{\varphi}{2}\right)\right]}{A}\right\} \tag{21}$$

Equations (20) and (21) concretize the dependence of the constants of adsorption equilibrium contained in the isotherm (4) upon the potential.

In [7], Eqs. (4) were also used to describe the behavior of the electrode-solution interface in the presence of an organic substance, adsorbed in two positions, but in this case it was assumed that the constants of adsorption equilibrium are some arbitrarily selected functions not of the electrode potential, but of its charge. An analysis of this assumption by the method described above shows that it is equivalent to the model of three condensers connected in series, between the linings of which are: 1) only water molecules; 2) only molecules of the organic substance in the first position; 3) only molecules of the organic substance in the second position. Such a model, as is readily seen, cannot have a physical substantiation, although it does not contradict the experimental dependence of Γ upon ε in solutions of sodium p-toluenesulfonate (see [7]). The parameters entering into Eqs. (20) and (21) directly reflect the properties of the electrical double layer in the presence of adsorbed organic molecules.

Equations (4) do not take into consideration the attraction interaction among the adsorbed organic molecules. In view of this, a comparison of theory and experiment can be only semiquantitative; moreover, the following supplementary simplifying assumptions are found to be justified: 1) the capacitance in the background solution C_0 does not depend upon the potential; 2) the capacitance in the case of planar orientation of the adsorbed molecules is equal to the capacitance in the background solution, i.e., $C_2 = C_0$ [8, 9]; 3) a molecule of the organic substance in the vertical position occupies one adsorption place, corresponding to an associate of water molecules adsorbed on mercury; under these conditions $n_1 = 1$ [10]; 4) a molecule of the organic substance in the planar position occupies two adsorption sites and, consequently, $n_2 = 2$.

When conditions (1)-(4) are fulfilled, Eqs. (20) and (21) take the form

$$B_1 = B_m\exp\left[-\alpha(\varphi - \varphi_m)^2\right] \tag{22}$$

and

$$B_2 = B_{02}\exp(\beta\varphi) \tag{23}$$

where

$$\alpha = \frac{C_0 - C_1}{2A};\quad \varphi_m = -\frac{\varphi_{N1}C_1}{C_0 - C_1};\quad B_m = B_{01}\exp(\alpha\varphi_m^2)$$

and

$$\beta = -2C_0\varphi_{N2}/A.$$

Then, from Eq. (13), it follows that

$$\theta = B_1c(1-\theta) + B_2c(1-\theta)^2 \tag{13a}$$

from which, after solving with respect to θ, we find

$$\theta = 1 + \frac{1 + B_1c}{2B_2c} - \sqrt{\frac{1}{B_2c} + \left(\frac{1 + B_1c}{2B_2c}\right)^2} \tag{24}$$

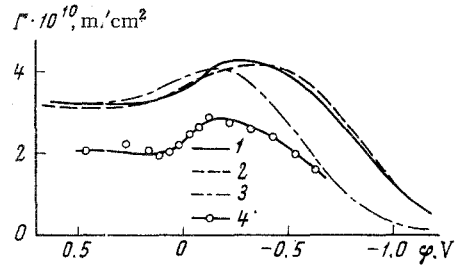

Fig. 1. Dependence of the adsorbed amount on the potential, calculated at: 1) $\varphi_{N1} = 0.5$ and $\varphi_{N2} = 0.25$ V; 2) $\varphi_{N1} = 0.5$ and $\varphi_{N2} = -0.5$ V; 3) $\varphi_{N1} = 0$ and $\varphi_{N2} = -0.5$ V; 4) experimental curve in a solution of 1 M KCl + 0.02 M p-phenylendiamine.

Equations (22), (23), and (24) permit the calculation of θ at any set potential. Then θ_1 and θ_2 can be found according to Eqs. (11) and (12). Knowing θ_1 and θ_2, we can calculate the value of Γ according to Eq. (3), and from Eq. (9), in which $\sigma_0 = \frac{1}{2} C_0 \varphi^2$, we can find the dependence of the interfacial tension upon the potential.

Differentiation of Eq. (17) with respect to the potential gives a value of the electrical double-layer capacitance, which, after algebraic transformations considering Eqs. (15) and (16), as well as the conditions described above, can be represented in the form

$$C = C_0 - 2A\alpha\theta_1 + \frac{A}{2(1+\theta_2)}\Big\{8\alpha^2(\varphi-\varphi_m)^2\theta_1(1-\theta_1) + \beta^2\theta_2(1-\theta_2) + 8\theta_1\theta_2[\alpha^2(\varphi-\varphi_m)^2 + \alpha\beta(\varphi-\varphi_m)]\Big\} \quad (25)$$

Knowing the dependence of θ_1 and θ_2 upon the electrode potential, we can calculate the complete C versus φ curve in the presence of an organic substance adsorbed in two different positions according to Eq. (25).

Finally, it is of interest to calculate the dependence of the point of zero charge upon the adsorption of the organic substance Γ. For this let us rewrite Eq. (3) at $n_1 = 1$ and $n_2 = 2$ in the form

$$x = RT\Gamma / A = \theta_1 + \theta_2 / 2 \quad (26)$$

and let us solve it with respect to θ_1 and θ_2 simultaneously with the equation

$$\theta_1 / \theta_2 = z / (1 - \theta_1 - \theta_2) \quad (27)$$

which is obtained from Eqs. (4) when $n_1 = 1$ and $n_2 = 2$, and in which, according to (22) and (23)

$$z = \frac{B_1}{B_2} = \frac{B_m}{B_{02}} \exp[-\alpha(\varphi-\varphi_m)^2 - \beta\varphi] \quad (28)$$

The solution gives

$$\theta_1 = x - \left(z + \frac{1}{2}\right) + \sqrt{\left(z+\frac{1}{2}\right)^2 - x(1-x)} \quad (29)$$

and

$$\theta_2 = (2z+1) - \sqrt{(2z+1)^2 - 4x(1-x)} \quad (30)$$

Then these values of θ_1 and θ_2 should be substituted into Eq. (17), which is set equal to zero according to the condition $\varepsilon = 0$. As a result of such a substitution, after certain algebraic transformations, considering the simplifying conditions introduced above, we can obtain the following quadratic equations with respect to x:

$$x^2(1-Q^2) - [1 - 2PQ - Q(2z+1)]x - P[(2z+1) + P] \quad (31)$$

in which

$$Q = \frac{2\alpha(\varphi-\varphi_m)}{\beta + 2\alpha(\varphi-\varphi_m)}, \qquad P = \frac{C_0\varphi}{A[\beta + 2\alpha(\varphi-\varphi_m)]},$$

while z is given by expression (28).

Thus, by setting different values of the potential φ, we can find the dependence of the point of zero charge upon the value of x according to Eq. (31), and consequently its dependence upon the total adsorption of the organic substance Γ [see Eq. (26)]. In using Eq. (31), it should be considered that the real values of x should satisfy the condition $0 \leq x \leq 1$.

In performing calculations of the adsorption, electrocapillary curves, differential capacitance curves, as well as the dependence of the point of zero charge upon Γ, we selected the following values of the parameters of the double layer: $C_0 = 20\ \mu F/cm^2$; $C_1 = 7\mu F/cm^2$; $A = 1.6\ \mu J/cm^2$; $B_m = 100$ liters/mole; $B_{02} =$

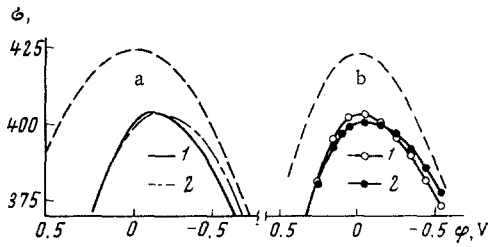

Fig. 2

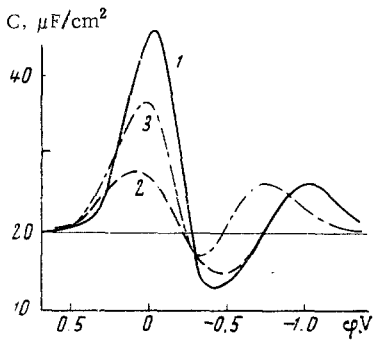

Fig. 3

Fig. 2. Electrocapillary curves calculated theoretically (a) and measured experimentally (b). a: 1) $\varphi_{N1} = 0.5$ and $\varphi_{N2} = -0.5$ V; 2) $\varphi_{N1} = 0$ and $\varphi_{N2} = -0.5$ V. b: 1) 1 M KCl + 0.03 M para-phenylendiamine; 2) 1 M KCl + 0.03 M ortho-phenylendiamine. Dashed lines are the electrocapillary curves in the background solution.

Fig. 3. Theoretically calculated differential capacitance curves: 1) $\varphi_{N1} = 0.5$ and $\varphi_{N2} = -0.5$ V; 2) $\varphi_{N1} = 0.5$ and $\varphi_{N2} = -0.25$ V; 3) $\varphi_{N1} = 0$ and $\varphi_{N2} = -0.5$ V.

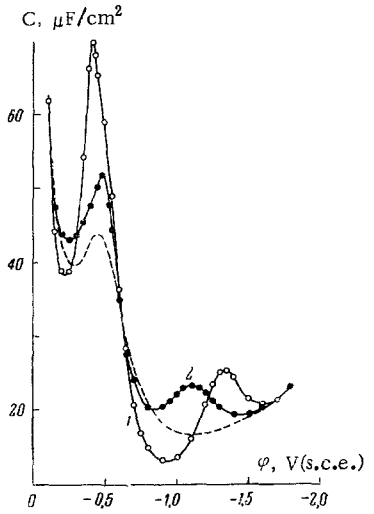

Fig. 4. Differential capacitance curves in 1 M KCl solution (dashed line), as well as with 0.02 M of the additive: 1) para-phenylendiamine; 2) ortho-phenylendiamine. Frequency 400 Hz.

1000 liters/mole; $\varphi_{N1} = +0.5$ V and 0; $\varphi_{N2} = -0.25$ and -0.5 V. The Γ versus φ, σ versus φ, and C versus φ curves were calculated for the concentration c = 0.02 M. The results of the calculation were compared with the experimental data on the adsorption of ortho- and para-phenylendiamines on mercury from solutions of them against a background of 1 M KCl. Some of the results obtained are presented in Figs. 1-5.

As can be seen from Fig. 1, the theoretically calculated Γ versus φ curves are in qualitative agreement with the shape of the Γ versus φ curve in the presence of p-phenylendiamine. Γ versus φ curves of an analogous shape were obtained earlier in solutions of aniline against a background of 1 M KCl and 1 M KI [9]. From Fig. 1 it also follows that the shape of the Γ versus φ curve in the case of an organic substance adsorbed in two positions is practically independent of the value of φ_{N2}, while a change in φ_{N1} leads to a shift of the Γ versus φ curve along the X axis.

Figure 2a presents electrocapillary curves, calculated theoretically at two values of φ_{N1}: +0.5 V and 0, and at the same value of $\varphi_{N2} = -0.5$ V. As can be seen from Fig. 2a, these curves intersect close to the potential of zero charge, while at $\varepsilon > 1$ they merge. In contrast to these curves, the σ versus φ curve calculated at $\varphi_{N2} = -0.25$ V is situated between the background curve and curves 1 and 2 in Fig. 2a when $\varepsilon > 0$. A comparison of Fig. 2a and Fig. 2b shows that from ortho- to para-phenylendiamine there is an increase in the positive value of φ_{N1}, whereas the value of φ_{N2}, determined by the π-electronic interaction of these molecules with the surface of mercury, remains unchanged.

This conclusion is confirmed by a comparison of the theoretically calculated and experimental curves of the differential capacitance (see Figs. 3 and 4). Actually, from ortho- to para-phenylediamine there is an appreciable increase in the anodic peak, an increase in the reduction of the capacitance in comparison with the background curve in the middle portion of the C versus φ curve, and a shift of the cathodic peak in the direction of more negative potentials (see Fig. 4). All these phenomena can be observed in Fig. 3, in the transition from curve 3, calculated theoretically for $\varphi_{N1} = 0$, to curve 1, in the calculation of which it was assumed that $\varphi_{N1} = +0.5$ V. At the same time, as is evident from Fig. 3, an increase in the negative value of φ_{N2} with a constant value of φ_{N1} (curves 2 and 3) has no effect upon the position of the cathodic peak, although it is also accompanied by a substantial increase in the anodic peak and a certain decrease in the capacitance at the minimum of the C versus φ curve.

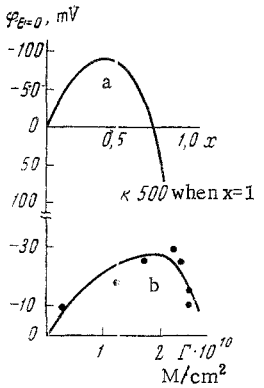

Fig. 5. Dependence of the adsorption potential drop $\varphi_{\varepsilon=0}$ upon the adsorbed amount Γ or the quantity x = RTΓ/A: a) calculated theoretically at $\varphi_{N1} = 0.5$ and $\varphi_{N2} = -0.25$ V; b) experimental data for the system 1 M KCl + para-phenylendiamine.

As can be seen from Fig. 3, the theoretically calculated C versus φ curves also give a good rendering of the experimentally observed coincidence of the capacitance at $\varepsilon > 0$ in background solutions and with an organic additive (see Fig. 4), although under these conditions there is no desorption of the organic molecules from the electrode surface (see Figs. 1 and 2). This phenomenon, detected earlier and explained quantitatively in the case of the adsorption of pyridine and aniline on mercury [8, 9], leads to the fact that the area under the differential capacitance curve in the presence of an organic substance may differ substantially from the area under the capacitance curve in a pure background solution. This result is especially distinctly illustrated by curve 3 in Fig. 3 and by curve 2 in Fig. 4.

If the values of φ_N for two different positions of the adsorbed substance possess different signs, just as in the case that we are considering, the dependence of the shift of the point of zero charge ($\varphi_{\varepsilon=0}$) upon the adsorption Γ may pass through a maximum. This conclusion, which is indicated by the theoretically calculated curve of the dependence of $\varphi_{\varepsilon=0}$ upon x = RTΓ/A (see Fig. 5a), is well confirmed by the experimental data obtained in the adsorption of para-phenylendiamine on mercury (see Fig. 5b). The dependence of the point of zero charge of the mercury electrode upon the adsorption of para-toluenesulfonate anions upon it, which can be constructed on the basis of the data cited in [7], is also analogous.

It should be mentioned that the original shift of the point of zero charge in the negative direction can be observed even under the condition $|\varphi_{N2}| < |\varphi_{N1}|$ (see Fig. 5b), if only $B_{02} \gg B_m$, i.e., if the energy of adsorption of organic molecules in the planar position substantially exceeds the energy of adsorption in the vertical position (in the calculation, it was assumed that $B_{02}/B_m = 10$). If, however, the energies of adsorption in two positions differ negligibly (for example, $B_{02}/B_m \approx 2$), then the shift of the point of zero charge is determined by the orientation of the adsorbed molecules, to which a larger value of $|\varphi_N|$ corresponds. Thus, in the case of the adsorption of aniline on mercury [9], the shift of the point of zero charge occurs only in positive direction.

The data cited show that the model of three parallel condensers is a good semiquantitative basis for describing the behavior of the electrode-solution interface in the presence of organic compounds adsorbed in two different positions.

CONCLUSIONS

1. Quantitative functions permitting calculation of the dependence of the adsorption, interfacial tension, and differential capacitance upon the electrode potential, as well as the dependence of the point of zero charge upon the adsorption in systems where the organic substance can be adsorbed on the electrode in two different positions, were obtained on the basis of a model of three parallel condensers.

2. A comparison of the results of the calculation with the experimental data on the adsorption of ortho- and para-phenylendiamines on mercury shows that the model of three parallel condensers is a good semiquantitative basis for describing systems of this type.

LITERATURE CITED

1. A. N. Frumkin, Z. Physik, 35, 792 (1926).
2. B. B. Damaskin, Uspekhi Khimii, 34, 1764 (1965).
3. A. N. Frumkin and B. B. Damaskin, Collection: Modern Aspects of Electrochemistry [in Russian], "Mir," (1967).
4. P. J. Flory, J. Chem. Phys., 10, 51 (1942).
5. M. L. Haggins, J. Phys. Chem., 46, 151 (1942).
6. E. Hückel, Adsorption und Kapillarkondensation, Leipzig (1928), pp. 218-219.
7. J. M. Parry and R. Parsons, J. Electrochem. Soc., 113, 992 (1966).

8. L. D. Klyukina and B. B. Damaskin, Izv. AN SSSR, Otd. khim. n. (1963), 1022.
9. B. B. Damaskin, I. P. Mishutushkina, V. M. Gerovich, and R. I. Kaganovich, Zh. fiz. khimii, 38, 1797 (1964).
10. B. B. Damaskin, Élektrokhimiya, 1, 63 (1965).