

1. B.D.Berezin, Zhur.Fiz.Khim., **36**, 494 (1962) [Russ.J. Phys. Chem., 258 (1962)].
2. B.D.Berezin, Zhur.Neorg.Khim., **6**, 2672 (1961) [Russ.J. Inorg.Chem., 1349 (1961)].
3. B.D.Berezin, Zhur.Neorg.Khim., **7**, 2507 (1962) [Russ.J. Inorg.Chem., 1300 (1962)].
4. E.Dent, R.Linstead, and A.Lowe, J.Chem.Soc., 1033 (1934).
5. A.Spryskov and A.Kobenin, Trudy Ivanovsk.Khim.-Tekhnol. Inst., 196 (1955).
6. B.D.Berezin, Zhur.Fiz.Khim., **35**, 2494 (1961) [Russ.J. Phys.Chem., 1234 (1961)].
7. B.D.Berezin, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., **6**, 841 (1963).
8. I.Brand, J.Chem.Soc., 997 (1950).
9. V.Pal'm, Zhur.Fiz.Khim., **32**, 380 (1958).
10. B.D.Berezin, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., **6**, 1016 (1963).
11. N.Deno and R.Taft, J.Amer.Chem.Soc., **76**, 244 (1954).
12. V.N.Vasil'eva and K.B.Yatsimirskii, Zhur.Neorg.Khim., **7**, 2520 (1962) [Russ.J.Inorg.Chem., 1307 (1962)].
13. A.A.Frost and R.G.Pearson, "Kinetics and Mechanism: A Study of Homogeneous Chemical Reactions", Wiley, New York, 1953.

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THEORY OF DIFFERENTIAL CAPACITANCE CURVES IN THE PRESENCE OF ORGANIC COMPOUNDS

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It has been shown¹⁻⁴ that the attraction between adsorbed particles, represented by the quantity a in Frumkin's isotherm¹

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

(where B is the potential-dependent adsorption equilibrium constant and θ the ratio of the adsorption Γ at a given concentration c to the maximum adsorption $\Gamma_{\max}$: $\theta = \Gamma/\Gamma_{\max}$), does not remain constant with variation in the electrode potential φ . Let us therefore examine the relation between the shape of the adsorption peak on the differential capacitance C curves and the quantity a in the most general case, when $a = a(\varphi)$.

The peak on the $C-\varphi$ curves is due to the additional capacitance C_{add} , which, when there is no formation of multilayers or micellar films, is given by

$$C_{\text{add}} = \left(\frac{\partial \epsilon}{\partial \theta} \right)_{\varphi} \frac{d\theta}{d\varphi}, \quad (2)$$

where ϵ is the surface charge on the electrode.

To find $d\theta/d\varphi$ and $(\partial \epsilon / \partial \theta)_{\varphi}$ we take logarithms in Eqn. (1) and then differentiate with respect to φ , obtaining after algebraic rearrangement

$$\frac{d\theta}{d\varphi} = \left(\frac{d \ln B}{d\varphi} + 2\theta \frac{da}{d\varphi} \right) h, \quad (3)$$

where

$$h = \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \quad (4)$$

On the other hand, it follows from Eqn. (1) that

$$\ln c = -\ln B - \ln \left(\frac{\theta}{1-\theta} \right) + 2a\theta, \quad (5)$$

whence

$$\left(\frac{\partial \ln c}{\partial \varphi} \right)_{\theta} = - \left(\frac{d \ln B}{d\varphi} + 2\theta \frac{da}{d\varphi} \right) = -\Phi(1 + \lambda\theta), \quad (6)$$

where

$$\Phi = \frac{d \ln B}{d\varphi} \quad \text{and} \quad \lambda = 2 \frac{da/d\varphi}{d \ln B/d\varphi} = 2 \frac{da}{d \ln B}.$$

Comparison of Eqns. (3) and (6) shows that

$$\frac{d\theta}{d\varphi} = - \left(\frac{\partial \ln c}{\partial \varphi} \right)_{\theta} h. \quad (7)$$

From the reciprocity relation for the main electrocapillary equation it follows that

$$\left(\frac{\partial \epsilon}{\partial \theta} \right)_{\varphi} = -A \left(\frac{\partial \ln c}{\partial \varphi} \right)_{\theta}, \quad (8)$$

where $A = RT\Gamma_{\max}$. Hence from Eqns. (2), (7), and (8) we obtain

$$C_{\text{add}} = A \left(\frac{\partial \ln c}{\partial \varphi} \right)_{\theta} h. \quad (9)$$

Since experiment shows that $(\partial \ln c / \partial \varphi)_{\theta}$ and hence also $(\partial \ln c / \partial \varphi)_{\theta}^2$ vary monotonically in the region of peaks in the potential, the position of the maximum $C_{\text{add}}^{\max}$ is determined by the maximum in h [see Eqn. (4)]. In this case²

$$\theta^{\max} = 0.5; \quad h^{\max} = \frac{1}{4-2a}, \quad (10)$$

while the degree of coverage at a given relative height $h/h^{\max}$ is

$$\theta_i = \frac{1}{2}(1 \pm r); \quad i = 1, 2, \quad (11)$$

where

$$r_{1/2} = \sqrt{\frac{6-3a}{8-6a}}; \quad r_{1/4} = \sqrt{\frac{2-a}{4-a}}; \quad r_{3/4} = \sqrt{\frac{2-a}{8-a}}; \quad r_{1/8} = \sqrt{\frac{2-a}{16-a}} \quad (12)$$

the subscript following r giving the ratio $h/h^{\max}$.

Combination of the condition $\theta^{\max} = 0.5$ with Eqn. (6) gives

$$\frac{\partial \ln c}{\partial \varphi} = \left(\frac{\partial \ln c}{\partial \varphi} \right)_{\theta=0.5} = - \left(\frac{d \ln B}{d\varphi} + \frac{da}{d\varphi} \right) = -\Phi \left(1 + \frac{\lambda}{2} \right). \quad (6a)$$

From Eqns. (7), (6), and (4) it follows that

$$d\varphi = \frac{1}{\Phi} \frac{1-2a\theta(1-\theta)}{\theta(1-\theta)(1+\lambda\theta)} d\theta. \quad (13)$$

On integrating this equation from θ_1 to θ_2 , defined by Eqn. (11), we have, in view of Eqn. (6a),

$$\Delta\varphi \left| \frac{\partial \ln c}{\partial \varphi} \right| = \frac{(2+\lambda)^2}{2(1+\lambda)} \left[\ln \frac{1+r}{1-r} - \frac{2a(1+\lambda)+\lambda^2}{(2+\lambda)\lambda} \ln \frac{2+\lambda(1+r)}{2+\lambda(1-r)} \right], \quad (14)$$

where the values of r are given by Eqns. (12). This is the general expression for the widths of the capacitance peaks.

Analysis of Eqn. (14) shows that, at $h/h^{\max} = \frac{3}{4}$, its right-hand side varies little with λ if $|\lambda| < 1$ (see Table 1). The latter condition follows from the monotonic variation in $(\partial \ln c / \partial \varphi)_{\theta}$ in the region of the peak potentials [see Eqn. (6)]. Indeed, if $|\lambda| > 1$, the quantity $(\partial \ln c / \partial \varphi)_{\theta}$

TABLE 1.

λ	a		
	1.0	1.5	1.8
1.0	0.8397	0.3084	0.08004
0.5	0.8350	0.3078	0.07983
0.0	0.8348	0.3073	0.07962
-0.5	0.8398	0.3082	0.07974
-0.7	0.8475	0.3099	0.07978
-0.9	0.8675	0.3137	0.08024
-0.99*	0.8856	0.3244	0.08103

* The function defined by the right-hand side of Eqn. (14) is discontinuous at $\lambda = -1$.

may change sign with a change in θ : i.e. the θ - φ curves for different concentrations may intersect, and consequently a decrease in θ with increase in c is possible at constant φ . Thus instead of Eqn. (14), it is possible to use, with an acceptable degree of approximation, the considerably simpler equation obtained by putting $\lambda = 0$ on the right-hand side of Eqn. (14):

$$\Delta\varphi \left| \frac{\partial \ln c}{\partial \varphi_{\max}} \right| \approx 2 \left(\ln \frac{1+r}{1-r} - ar \right). \quad (15)$$

When a is constant, $da/d\varphi = 0$, $|\partial \ln c / \partial \varphi_{\max}| = |\Phi|$, and Eqn. (15) passes into the expression obtained previously [Eqn. (12) in Ref. 2].

Eqn. (15) enables a to be found from experimental data on the widths of the capacitance peaks and on the slope of the plot of $\log c$ against $\varphi_{\max}$. For this purpose it is convenient to change to common logarithms, and introduce a function $f(a)$:

$$\frac{f(a)}{1000} = \log \frac{1+r}{1-r} - \frac{a}{2.3} r = \frac{\Delta\varphi}{2} \left| \frac{\partial \log c}{\partial \varphi_{\max}} \right|. \quad (15a)$$

The left-hand side of this equation is readily calculated as a function of a , while the right-hand side is determined experimentally. In this way the quantity a can be found from the graph of $f(a)$ against a . Table 2 gives values of the function $f(a)$ at various values of a with the ratio $h/h^{\max}$ being $\frac{1}{2}$ and $\frac{3}{4}$.

If the character of the adsorption of an organic compound on an electrode surface does not change (for example, as a result of π -electron interaction) within the potential range investigated, the expression given by Frumkin's theory¹ for the dependence of B on electrode potential can be assumed to hold whatever the relation between a and φ :

$$B = B_0 \exp \left[- \frac{E + C'\varphi(\varphi_N^* - \varphi/2)}{A} \right], \quad (16)$$

where $E = \int_0^\varphi \epsilon_0 d\varphi$, $\epsilon_0 = \int_0^\varphi C_0 d\varphi$, and C_0 and C' represent the capacitance at $\theta = 0$ and $\theta = 1$ respectively. Both in this equation and in all cases henceforward, the potentials φ are reckoned from the zero-charge point at $\theta = 0$; B_0 and φ_N^* are constants, the former determining the standard free energy of adsorption at $\theta = 0$ and $\varphi = 0$: $-\Delta G_{\text{ads}}^0 = RT \ln 55.5 B_0$, while φ_N^* will be shown below to represent the adsorption potential difference extrapolated to $\theta = 0$.

TABLE 2.

a	$h/h_0(a)$	$f_{1/2}(a)$	a	$h/h_0(a)$	$f_{3/4}(a)$
2.0	0.0	0.0	1.0	321.21	181.27
1.9	12.60	6.16	0.8	406.30	234.71
1.8	34.59	17.30	0.6	493.82	291.41
1.7	61.88	31.53	0.4	583.15	350.96
1.6	92.83	48.13	0.2	673.9	412.95
1.5	126.65	66.72	0.0	765.6	477.12
1.4	162.64	86.96	-0.5	997.8	645.3
1.3	200.35	108.71	-1.0	1232.6	822.7
1.2	239.50	131.76	-1.5	1468.3	1006.9
1.1	279.87	156.00	-2.0	1704.8	1196.9

It follows from Eqns. (6) and (16) that

$$\left(\frac{\partial \ln c}{\partial \varphi} \right)_\theta = \frac{\epsilon_0 + C'\varphi_N^* - C'\varphi}{A} - 2\theta \frac{da}{d\varphi} \quad (17)$$

and from Eqn. (8) that

$$\left(\frac{\partial \epsilon}{\partial \theta} \right)_\varphi = -\epsilon_0 + C'\varphi - C'\varphi_N^* + 2A\theta \frac{da}{d\varphi}. \quad (18)$$

Integrating this equation with respect to θ , remembering that $\epsilon = \epsilon_0$ when $\theta = 0$, we obtain

$$\epsilon = \epsilon_0(1 - \theta) + C'\theta \left[\varphi - \left(\varphi_N^* - \frac{A}{C'} \theta \frac{da}{d\varphi} \right) \right] = \epsilon_0(1 - \theta) + C'\theta(\varphi - \varphi_N^*). \quad (19)$$

Thus the true value of the adsorption potential difference φ_N is found to depend on the surface coverage and the potential, since $da/d\varphi$ is in general a function of φ :

$$\varphi_N = \varphi_N^* - \frac{A}{C'} \theta \frac{da}{d\varphi}. \quad (20)$$

It follows directly from Eqn. (20) that

$$\varphi_N = \varphi_N^* \quad \text{when } \theta = 0, \quad (20a)$$

$$\varphi_N = \varphi_N^* = \varphi_N^* - \frac{A}{C'} \theta \frac{da}{d\varphi} \quad \text{when } \theta = 1. \quad (20b)$$

Eqn. (20b) shows that in general the adsorption potential difference at limiting surface coverage φ_N^* also should depend on the electrode potential (through the quantity $da/d\varphi$). In particular cases, however, constant values of φ_N^* are obtained:

$$\varphi_N^* = \varphi_N^* \quad \text{when } a = \text{const}, \quad (20c)$$

i.e. in this case the adsorption potential difference does not depend on θ , as was to be expected¹. Provided that

$$a = a_0 + \beta\varphi, \quad (21)$$

where a_0 and β are constants,

$$\varphi_N^* = \varphi_N^* - \frac{\beta A}{C'}. \quad (20d)$$

When the condition (21) is satisfied, Eqn. (20) shows that the adsorption potential difference varies linearly with the surface coverage³:

$$\varphi_N = \varphi_N^* - \frac{\beta A}{C'} \theta. \quad (20e)$$

On differentiating Eqn. (19) with respect to φ and bearing in mind Eqns. (3) and (16), we obtain the following expression for the total differential capacitance of the double layer in the presence of an organic substance:

$$C = C_0(1 - \theta) + C'\theta + \left[\epsilon_0 + C'(\varphi_N^* - \varphi) - 2A\theta \frac{da}{d\varphi} \right] \frac{h}{A}. \quad (22)$$

When a is constant, Eqn. (22) passes into the equation first obtained by Hansen *et al.*⁵, and used by the present writer³ as first and second approximations [taking into account the dependence of a on φ only through the quantity h , see Eqn. (9) in Ref. 5 and Eqn. (7) in Ref. 3].

Eqn. (22) can be used to calculate C - φ curves in the presence of an organic substance provided that the constants C' , A , φ_N° , and B_0 and also the relation between a and φ are known. Actually Eqn. (16) is first used to calculate the dependence of B on φ , then isotherms plotted from Eqn. (1) for various values of a are used to determine graphically the relation between θ and φ for each concentration of organic substance chosen†, and finally the complete differential capacitance curves are calculated from Eqn. (22) taking into account the expression for h [see Eqn. (4)].

The values of a at the potential maxima on the C - φ curves can be determined by the above method from the width of the peaks and the slope of the curve of $\log c$ against $\varphi^{\max}$. In the region of the potentials of maximum adsorption, it is convenient to find a from the formula for the reduced adsorption isotherm which derives from Eqn. (1):

$$y = \frac{c}{c_{0.5}} = \frac{\theta}{1-\theta} \exp[a(1-2\theta)]. \quad (23)$$

On solving this equation for a we obtain

$$a = \frac{2.3}{1-2\theta} \log \frac{y(1-\theta)}{\theta}. \quad (23a)$$

From Eqn. (23) it follows that

$$\frac{dy}{d\theta} = \exp[a(1-2\theta)] \frac{1-2a\theta(1-\theta)}{(1-\theta)^2}; \quad (24)$$

$$\left(\frac{dy}{d\theta}\right)_{\theta=0} = e \text{ when } \theta = 0; \quad (24a)$$

$$\left(\frac{dy}{d\theta}\right)_{\theta=0.5} = 4 - 2a \text{ when } \theta = 0.5. \quad (24b)$$

The relations (24a) and (24b) thus give two further graphical methods for determining a from the shape of the experimental adsorption isotherm (see Fig. 1).

The adsorption isotherm at the potentials of maximum adsorption which is required for these calculations can be readily obtained⁴ on the basis of the equation

$$C = C_0(1-\theta) + C'\theta, \quad (25)$$

C' being determined graphically by extrapolation of the plot of $1/C^{\min}$ against $1/c$ to $1/c = 0$, where $C^{\min}$ is the minimum capacitance on the C - φ curve in the presence of the organic substance⁵.

Let us consider the determination of the constants φ_N° , A , and B_0 from experimental data on the differential capacitance. Since at $\varphi^{\max}$ we have $\theta \approx 0.5$ and $h = 1/(4-2a)$, it follows from Eqns. (9) and (6a) that the additional capacitance at the peak ($C_{\text{add}}^{\max}$) is

$$C_{\text{add}}^{\max} = \left(\frac{\partial \ln c}{\partial \varphi^{\max}}\right)^2 \frac{A}{4-2a}, \quad (9a)$$

while according to Eqn. (22) the total capacitance at $\varphi^{\max}$ is

$$C^{\max} = \frac{C_0 + C'}{2} + \frac{A}{4-2a} \left(\frac{\partial \ln c}{\partial \varphi^{\max}}\right)^2. \quad (22a)$$

† In practice it is more convenient to calculate the dependence of $\log B$ on φ by means of Eqn. (16), and then, from the graphs of $\log Bc$ against θ plotted from Eqn. (1) for different values of a , to determine the dependence θ on φ for each of the concentrations of organic substance chosen.

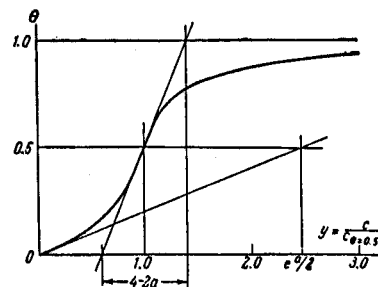


Fig. 1. Determination of a from shape of reduced adsorption isotherm.

Eqn. (22a) enables A to be determined from the height of the capacitance peak, since all the remaining quantities which it contains are already known from experiment.

Since at $\varphi^{\max}$ the value of $\theta \approx 0.5$, it follows from Eqns. (5) and (16) that

$$\ln c = -a(\varphi) - \ln B_0 + \frac{E + C'\varphi^{\max}(\varphi_N^\circ - \varphi^{\max}/2)}{A}. \quad (26)$$

This is the equation to the curve of $\ln c$ against $\varphi^{\max}$, which is easily obtained experimentally. From the points of intersection of this curve with the straight line $\ln c = \text{const}$ (see Fig. 2) we obtain, in conformity with Eqn. (26),

$$\varphi_N^\circ = \frac{\varphi_2 + \varphi_1}{2} - \frac{E_2 - E_1}{C'(\varphi_2 - \varphi_1)} + \frac{A}{C'} \frac{a(\varphi_2) - a(\varphi_1)}{\varphi_2 - \varphi_1}. \quad (27)$$

The values of A and φ_N° obtained from Eqns. (22a) and (27) are to be regarded as a first approximation, since this method of determining A [and hence also φ_N° , as Eqn. (27) contains A] is extremely inexact, because it is difficult to measure accurately the height of a peak, especially if the latter is high and narrow. Let us therefore examine a more precise method for determining A , based on the experimental curve of $\ln c$ against $\varphi^{\max}$.

Application of Eqn. (26) for this curve to two concentrations of the organic substance (high c_h and low c_l , Fig. 3) shows that A can be found from the formula

$$A = \frac{\Delta E + C'\varphi_N^\circ(\varphi_h - \varphi_l) - (C'/2)(\varphi_h^2 - \varphi_l^2)}{\Delta \ln c + [a(\varphi_h) - a(\varphi_l)]} \quad (28)$$

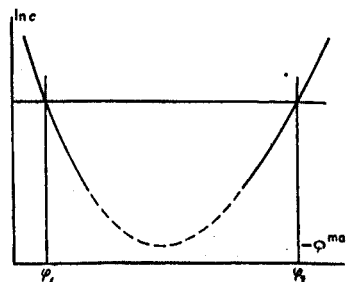


Fig. 2. Determination of φ_N° from experimental curve of $\ln c$ against $\varphi^{\max}$.

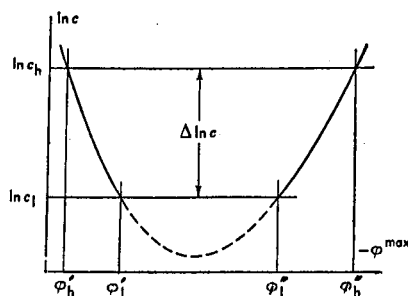


Fig. 3. Determination of A from experimental curve of $\ln c$ against $\varphi^{\max}$.

if φ_N° is known. For the general case, therefore, a method of successive approximations can be used: Eqn. (22a) is first used to find A_1 , at which $(\varphi_N^\circ)_1$ is then determined from Eqn. (27); the resulting value is then used to find A_2 from Eqn. (28), and hence $(\varphi_N^\circ)_2$ is determined at A_2 from Eqn. (27); and so on. The determination of A and φ_N° is considerably simplified in the particular case when condition (21) is satisfied. In fact, in this case $[a(\varphi_2) - a(\varphi_1)]/(\varphi_2 - \varphi_1) = \beta$, and it follows from Eqn. (27) combined with Eqn. (20d) that

$$\varphi_N^\circ - \frac{\beta A}{C'} = \varphi_N^\circ = \frac{\varphi_2 + \varphi_1}{2} - \frac{E_2 - E_1}{C'(\varphi_2 - \varphi_1)}. \quad (27a)$$

On the other hand, on substituting $a(\varphi_h) - a(\varphi_1) = \beta(\varphi_h - \varphi_1)$ and $\varphi_N^\circ = \varphi_N^\circ + \beta A/C'$ in Eqn. (28), we obtain for A

$$A = \frac{\Delta E + C'\varphi_N^\circ(\varphi_h - \varphi_1) - (C'/2)(\varphi_h^2 - \varphi_1^2)}{\Delta \ln c}. \quad (28a)$$

Thus in this case the experimental relation between $\ln c$ and $\varphi^{\max}$ is first used to determine φ_N° from Eqn. (27a), then A from Eqn. (28a), and only then φ_N° from Eqn. (20d). Eqns. (27a) and (28a) are used also to find φ_N° and A in the case in which a is constant, when $\beta = 0$ and $\varphi_N^\circ = \varphi_N^\circ$ [see Eqn. (20c)].

In order to determine B_0 it is again convenient to use the experimental curve of $\ln c$ against $\varphi^{\max}$ together with Eqn. (26). Actually, from a knowledge of C' , A , φ_N° , and the function $a(\varphi)$ it is possible to calculate some $f(\varphi)$ curve by using the equation

$$f(\varphi) = -a(\varphi) + \frac{E + C'\varphi(\varphi_N^\circ - \varphi/2)}{A}. \quad (29)$$

It follows from Eqn. (26) that this curve is displaced with respect to the experimental curve of $\ln c$ against $\varphi^{\max}$ by $\ln B_0$, from which the value of B_0 can be readily obtained. In the particular case in which condition (21) is satisfied, calculation of the function $f(\varphi)$ is somewhat simplified, and from Eqns. (21) and (20d) together with Eqn. (29) we obtain

$$f(\varphi) = -a_0 + \frac{E + C'\varphi(\varphi_N^\circ - \varphi/2)}{A}. \quad (29a)$$

Knowledge of the constants C' , A , φ_N° , and B_0 , together with the function $a(\varphi)$, enables us to calculate electrocapillary curves in the presence of the organic substance in addition to the $C-\varphi$ curves, by using Frumkin's equation of state¹ for the adsorbed layer:

$$\sigma = \sigma_0 - \Delta\sigma = \sigma_0 + A [\ln(1 - \theta) + a\theta^2], \quad (30)$$

where $\sigma_0 = \sigma_0^{\max} - E$ is the interfacial tension in a pure solution of the supporting electrolyte ($\sigma_0^{\max}$ corresponds to the electrocapillary maximum) and $\Delta\sigma$ is the decrease in surface tension due to adsorption of the organic substance.

This equation shows that with variable a the potential of maximum adsorption $\varphi_{\max}$, defined by the condition $d\theta/d\varphi = 0$ and corresponding to a minimum on the differential capacitance curve [since $C_{\text{add}} = 0$ at $\varphi_{\max}$, see Eqn. (2)], no longer corresponds to the maximum decrease in surface tension $\Delta\sigma$. Actually,

$$\frac{d(\Delta\sigma)}{d\varphi} = -A \left(-\frac{1}{1-\theta} \frac{d\theta}{d\varphi} + 2a\theta \frac{d\theta}{d\varphi} + \frac{da}{d\varphi} \theta^2 \right) \quad (31)$$

and hence

$$\left[\frac{d(\Delta\sigma)}{d\varphi} \right]_{\varphi_{\max}} = -A\theta_{\max}^2 \frac{da}{d\varphi}, \quad (31a)$$

which vanishes only when $da/d\varphi = 0$ ($\theta_{\max}$ being the value of θ at $\varphi = \varphi_{\max}$). When $da/d\varphi > 0$ the potential $\varphi_{\max}$ lies at more positive values than the maximum in $\Delta\sigma$, and when $da/d\varphi < 0$ at more negative values.

On the other hand, when a is not constant, the potential of maximum adsorption does not remain unchanged with change in the concentration of organic substance. Actually, it follows from Eqns. (3) and (16) that, when $(d\theta/d\varphi)_{\varphi_{\max}} = 0$,

$$\varphi_{\max} = -\varphi_N^\circ \frac{C'}{K_0 - C'} + \frac{2A}{K_0 - C'} \frac{da}{d\varphi} \theta_{\max}, \quad (32)$$

where K_0 is the integral capacitance at $\theta = 0$. The dependence of $\varphi_{\max}$ on C is determined by the variation in the maximum coverage $\theta_{\max}$ with the concentration of the organic substance.

It must be noted that the present theory cannot give a quantitative interpretation of the $C-\varphi$ curves over the whole potential range investigated if the character of the adsorption of the organic compound at the electrode-solution interface changes with change in the electrode potential, for example owing to the occurrence of π -electron interaction. This fact can be used to establish the limits within which adsorption of the organic substance is not complicated by such interaction².

In conclusion I wish to express my sincere gratitude to Academician A. N. Frumkin for discussing the present paper.

SUMMARY

Relations have been obtained which enable the dependence of adsorption, differential capacitance, and interfacial tension on electrode potential in the presence of an organic compound to be calculated when the attractive interaction between the adsorbed particles does not remain constant with change in the potential. The theory is not applicable when the character of the adsorption of the organic substance undergoes a change with variation in the potential.

1. A. N. Frumkin, Trudy Inst. Karpova, No. 5, 3 (1926); Z. Physik, **35**, 792 (1926).
2. B. B. Damaskin, Dokl. Akad. Nauk SSSR, **144**, 1073 (1962).
3. B. B. Damaskin and N. B. Grigor'ev, Dokl. Akad. Nauk SSSR, **147**, 135 (1962).

4. B.B.Damaskin, S.Wawrzyszka, and N.B.Grigor'ev, Zhur. Fiz.Khim., **36**, 2530 (1962) [Russ.J.Phys.Chem., 1376 (1962)].
5. R.S.Hansen, R.E.Minturn, and D.A.Hickson, J.Phys.Chem., **60**, 1185 (1956).
6. L.D.Klyukina and B.B.Damaskin, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, No.6, 1022 (1963).

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APPLICATION OF DIFFUSE REFLECTANCE SPECTROPHOTOMETRY TO THE SORPTION OF DYES ON CELLULOSIC FIBRES

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The two main problems in the study of dyeing processes are associated with the physical state of the sorbed compound and the quantitative determination of the dye on the polymer. It is difficult to use spectrophotometry by transmitted light directly on the fibre because of the intense scattering. The most promising method is diffuse reflectance spectrophotometry. Many theoretical papers have appeared on the interaction of radiation and scattering materials¹⁻⁴.

The aim of the present work was to study the applicability of the relation^{1,2}

$$K/S = (1 - R)^2 / 2R \quad (1)$$

to the determination of the true absorption spectra of various classes of dyes adsorbed on modified cellulosic fibres. K and S are the absorption and scattering factors of a layer of unit thickness, and R is the reflection factor of an infinite layer. A study has also been made of the concentration dependence of the "absorption spectra"† of dyes adsorbed on various celluloses over a wide range of concentrations.

EXPERIMENTAL

The diffuse reflectance spectra were determined on an apparatus based on an SF-4, which will be described in detail elsewhere⁵. Patterns showing a high quantum efficiency of luminescence (Direct White†) were placed in front of the entry slit of the monochromator to avoid distortion of the reflectance spectra by the light due to the luminescence. The relative reflection factors R of the dyed patterns were measured. Corresponding undyed specimens were used for comparison. From the measured values of R values of K/S were calculated by means of formula (1). The use of undyed celluloses as standards eliminates possible errors due to geometrical peculiarities

in the structure of the fibrous specimens, surface properties, etc. It also eliminates the influence of the slight wavelength dependence of K/S for undyed celluloses on the shape of the "absorption band".

The materials examined were both unoxidised purified cotton cellulose and monocarboxycellulose obtained from it, and also chromatographic paper based on wood cellulose. The dyes studied were Rhodamine 6G, Congo Red, and Direct White. Dyeing was carried out by treating the celluloses with aqueous dyebaths of various concentrations for 4 h, withdrawing the patterns, and drying them in air. The amounts of dye on the celluloses were determined spectrophotometrically from the difference in concentration of the baths before immersion of the samples and after withdrawal of the latter. NaCl was added to the solutions of Direct White to improve the selectivity of the dye. Dyeing was carried out at 70°-80°. Samples of cotton cellulose were obtained as a gauze by compression under 1 atm. A layer of infinite thickness required 10-15 layers of gauze. The patterns were kept and measured in an atmosphere of constant r.h. 0.32 at room temperature.

It was first necessary to establish how far the "absorption spectra" calculated by means of formula (1) from the diffuse reflectance spectra corresponded to the absorption spectra obtained by transmission measurements. For this purpose use was made of regenerated cellulose film, which has no absorption bands and scatters practically no light in the visible region of the spectrum, while its chemical composition is identical with that of cotton cellulose. It was dyed by the same technique as the latter. Fig. 1 shows the absorption spectra of (a) Direct White, (b) Congo Red, and (c) Rhodamine 6G, adsorbed on the regenerated cellulose film (from measurements of the transmitted light) and on cotton cellulose [from reflectance measurements by calculation based on Eqn. (1)]. The dye concentrations were about the same on the film and on the cotton cellulose. It is evident from the diagram that the "absorption spectra" of the adsorbed dyes on the cotton cellulose practically coincide with the spectra of these dyes on the regenerated cellulose film. The spectra of the monocarboxycellulose dyed with Rhodamine 6G also coincide. Hence with the dyed fibrous cellulosic materials examined, the "absorption spectra" can be successfully employed to study all those properties which, in the case of non-scattering materials, are usually studied by means of the absorption spectra.

Fig. 1 shows also the absorption spectra of aqueous solutions of these dyes. The considerable displacement to

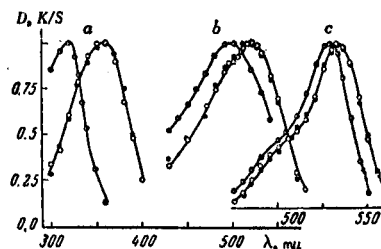


Fig. 1. Absorption spectra of: a) Direct White; b) Congo Red; c) Rhodamine 6G: 1) adsorbed on regenerated cellulose film; 2) adsorbed on cotton cellulose; 3) in aqueous solution.

† The term "absorption spectrum" denotes a spectrum obtained from the reflectance spectrum by means of formula (1).

‡ It has not proved possible to trace the constitution of this fluorescent brightening agent (Ed. of Translation).