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Abstract

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CALCULATION OF THE ADSORBED AMOUNT OF ORGANIC SUBSTANCE FROM IMPEDANCE MEASUREMENTS OF A MERCURY ELECTRODE

(Presented by Academician A. N. Frumkin, March 3, 1964)

In the work of Frumkin and Melik-Gaikazyan (^{1}) it was shown that if the rate of adsorption of a surface-active organic substance is limited by the stage of its diffusion to the electrode surface, then for the reactive (ωC_i) and active (G_i) components of the admittance (total conductance) associated with the adsorption—desorption process, the following equations are valid:

$$C_i = C_{\omega\to 0}\,(HA+2)/[(HA+1)^2+1], \tag{1}$$

$$G_i = \omega C_{\omega\to 0}\,HA/[(HA+1)^2+1]. \tag{2}$$

Here $H = (\partial\Gamma/\partial c)_E$, Γ is the surface concentration of the adsorbate under equilibrium conditions, and c is its bulk concentration.

$$A = \sqrt{\frac{2\omega}{D}},$$

D is the diffusion coefficient, ω is the angular frequency, and $C_i = C_{\omega\to 0}$ when $\omega \to 0$.

In Melik-Gaikazyan' s work it was indicated (^{2}) that the values of $\partial\Gamma/\partial c$ calculated from equations (1) and (2) are, in order of magnitude, in agreement with the same values calculated from electrocapillary curves and from the dependence of Γ on c. However, the accuracy of the calculation by equation (2) in the cited work was limited by the error in determining G_i because of leakage of solution between the capillary walls and the mercury.

In the cell described in (^{3}), the causes leading to inaccuracy in the determination of G_i were eliminated. Therefore it seemed of interest to use equations (1) and (2) for calculating certain adsorption parameters, in particular $\partial\Gamma/\partial c$ and Γ.

On the basis of equations (1) and (2), $(\partial\Gamma/\partial c)$ can be determined in several ways. The choice of one formula or another for calculating $\partial\Gamma/\partial c$ will be dictated by the experimental conditions. If, for example, the values of C_i and G_i at a given frequency are known, it is convenient to use the formula

$$(\partial\Gamma/\partial c)_E = G_i\sqrt{2D/\omega}/(\omega C_i - G_i), \tag{3}$$

which is obtained by dividing (1) by (2) and carrying out simple transformations.

It should be noted that the use of equation (3) is permissible only in the frequency range in which the limiting stage of the adsorption process is the diffusion of the adsorbate to the electrode. At high frequencies the adsorption rate may be limited by other, non-diffusion processes. When formula (3) is used, this will lead to a dependence of $\partial\Gamma/\partial c$, calculated by this formula, on frequency. Therefore the most correct procedure is to determine $\partial\Gamma/\partial c$ by formula (3) for different frequencies and to use those values of $\partial\Gamma/\partial c$ that depend little on frequency. Thus, by applying equation (3), one can calculate $\partial\Gamma/\partial c$ and, by carrying out graphical integration of the curve of the dependence of $\partial\Gamma/\partial c$ on c, find Γ at a given concentration, without resorting to measurements of the boundary tension.

We determined C_i and G_i for the adsorption of n-amyl alcohol on mercury in $3N$ KCl at frequencies of 390, 910, and 1150 Hz. The measurements used an alternating-current bridge, whose circuit is shown in Fig. 1. The value R_1 was determined by extrapolating to $\omega \to \infty$ the values of the solution resistance obtained at different frequencies (R_2 was disconnected in this case). Then, with R_1 unchanged (equal to the solution resistance at $\omega \to \infty$), the values of R_2 were determined for $3N$ KCl at 390, 910, and 1150 Hz. The obtained values $G = 1/R_2$ were subtracted from the conductance values measured in the presence of n-amyl alcohol. To determine C_i, it was necessary to subtract from the measured capacitance C the capacitance of the double layer in the presence of amyl alcohol at the given potential. Since we did not have these values available, as a first approximation we assumed that the dependence of the degree of coverage by n-amyl alcohol on the adsorbate concentration is described by the Frumkin isotherm:

$$Bc = \Theta(1-\Theta)^{-1}\exp(-2a\Theta), \tag{4}$$

where Θ is the degree of coverage, and a and B are constants.

The constants a and B can be calculated from the values of the additional capacitance. Indeed, under equilibrium conditions the additional capacitance is equal to $^{(4)}$:

$$C_{\omega\to 0} = \{C_0E - C_1(E-E_N)\}^2\Theta(1-\Theta) : RT\Gamma_\infty[1 - 2a\Theta(1-\Theta)]. \tag{5}$$

Fig. 1. Alternating-current bridge used in this work. Designations: 1—anode, 2—working electrode, 3—calomel electrode, 4—potentiometer for measuring the potential difference between the calomel electrode and the working electrode, 5 —sound generator of type ZG-12, 6—choke, 7—circuit for polarization with direct current, 8—null indicator, R_s and R_p—inductance-free resistance boxes, C_p—capacitance box, $R = 100\ \Omega$.

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Here C_0 and C_1 are the double-layer capacitances at $\Theta = 0$ and $\Theta = 1$, respectively; E is the potential, measured from the potential of the maximum of the electrocapillary curve of the background solution; E_N is the potential of the maximum of the electrocapillary curve in the solution of the surface-active substance at $\Theta = 1$, measured from the potential of the maximum of the electrocapillary curve of the background solution. Γ_∞ is the value of Γ at $\Theta = 1$. At the potential of the maximum of the additional capacitance (if $a \geq 1$ and Θ at the potential of maximum adsorption is close to unity), $\Theta \simeq 0.5$. Therefore

$$C^{\max}_{\omega\to 0} = \{C_0E - C_1(E - E_N)\}^2 / RT\Gamma_\infty(4 - 2a)$$

and

$$a = 2 - \{C_0E - C_1(E - E_N)\}^2 / 2C^{\max}_{\omega\to 0}RT\Gamma_\infty, \tag{6}$$

consequently, to calculate the attraction constant it is necessary to know $C_{\omega\to 0}$.

For determining $C_{\omega\to 0}$, the values of C_i are usually extrapolated to $\omega = 0$, and the criterion of the correctness of the results obtained is the agreement of the charge values in the background solution and in the solution of the surface-active substance (4). However, in the case of narrow adsorption peaks, a significant change in the peak height has little effect on the calculated value

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charge. This method therefore does not always give reliable results. Combining equations (3) and (1) or (2), it is easy to obtain an analytical expression for

$C_{\omega\to 0}$:

$$C_{\omega\to 0} = \frac{\omega^2 C_i^2 + G_i^2}{\omega(\omega C_i - G_i)}. \tag{7}$$

Taking equation (7) into account, we reduce formula (6) to the form:

$$a = 2 - \frac{[C_0 E - C_1(E - E_N)]^2(\omega^2 C_i - \omega G_i)}{2RT\Gamma_\infty(\omega^2 C_i^2 + G_i^2)}, \tag{7a}$$

where

$$C_i = C - C \quad = C - C_0 + \Theta(C_0 - C_1) \tag{8}$$

(C is the measured differential capacitance).

If $\Theta = 0.5$ (at the potential of the maximum of the additional capacitance), equations (4) and (8) take the form:

Table 1

Frequency, Hz	C_i, μF/cm^2	$C_{\omega\to 0}$, μF/cm^2, by equation (7)	a by equation (7a)	B by equation (10), l/mol
390	69.2	94.1	1.67	6.3
910	61	93.0	1.67	6.3
1150	56.5	90.5	1.66	6.3
		92.5$±$2		

$$C_i = C - C_0 + 0.5(C_0 - C_1), \tag{9}$$

$$Bc = \exp(-a). \tag{10}$$

We determined a and B from equations (7a) and (10) at the potential of the maximum of the additional capacitance, assuming that $\Gamma_\infty = 5.34 \cdot 10^{-10}$ mol/cm^2, $C_1 = 5.4$ μF/cm^2 (^{2}), and $E_N = 0.345$ V. Table 1 presents the values of a and B, calculated at $c = 3 \cdot 10^{-2}$ mol/l (the potential of the maximum of the additional capacitance was equal to -1.1 V in the N.C.E.).

From the equation

$$6.3\,c = \Theta(1 - \Theta)^{-1}\exp(-3.3\Theta) \tag{11}$$

Figure 2: graph of $\partial\Gamma/\partial c$ versus c, with a solid experimental curve and a dashed theoretical curve.

Figure 2: Figure 2: graph of $\partial\Gamma/\partial c$ versus c, with a solid experimental curve and a dashed theoretical curve.

Figure 3: graph of Γ versus c, with experimental points and a dashed theoretical curve.

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for each concentration the values of Θ were calculated and, using the equation

Fig. 2. Dependence of $\partial\Gamma/\partial c$ on the concentration of n-amyl alcohol at a potential of -1.1 V in the N.C.E. The dashed line is the theoretical curve for $a = 1.6$ and $B = 6.3$ l/mol

Fig. 3. Dependence of Γ on c at a potential of -1.1 V in the N.C.E. The dashed line is the curve corresponding to the equation $6.3c = \Theta(1-\Theta)^{-1}\exp(-3.3\Theta)$ at $\Gamma_\infty = 5.34 \cdot 10^{-10}$ mol/cm^2

$$C \quad = C_0 - \Theta(C_0 - C_1),$$

C was determined. Formula (8) made it possible to calculate C_i, and from equation (2) we calculated $\partial\Gamma/\partial c$ at various adsorbate concentrations. The diffusion coefficient of amyl alcohol required for this calculation was taken by us from work (5): $D = 0.88 \cdot 10^{-5}$ cm^2/s.

Fig. 2 presents a plot of the dependence of $\partial\Gamma/\partial c$ on c at a potential of -1.1 on the n.h.s. There, the dashed line shows the curve constructed on the basis of the equation

$$\partial\Gamma/\partial c = \Gamma_\infty\Theta(1-\Theta)/\{c[1-2a\Theta(1-\Theta)]\}, \tag{12}$$

which is obtained by differentiating equation (4) with the subsequent substitution $\partial\Theta/\partial c = (1/\Gamma_\infty)\,\partial\Gamma/\partial c$; here a was taken equal to 1.6; $\Gamma_\infty = 5.34 \cdot 10^{-10}$.

Fig. 3 gives a plot of Γ (determined by graphical integration of the curve in Fig. 2) versus concentration (solid line). The dashed curve corresponds to the theoretical dependence of Γ (which was determined by multiplying Θ, calculated from equation (11), by $\Gamma_\infty = 5.34 \cdot 10^{-10}$) on concentration. It follows from this figure that up to $\Theta = 0.5$ the experimental points fit the theoretical curve well. A certain increase of Γ at large coverages in comparison with the theoretical value may be explained by an increase of Γ_∞ with increasing Θ (^{6}).

In conclusion, one should point out one possibility for determining Γ_∞. Differentiation of (4) gives:

$$(\partial\Theta/\partial c)_E = \frac{1}{\Gamma_\infty}(\partial\Gamma/\partial c)_E =$$

$$= \Theta(1-\Theta)/\{c[1-2a\Theta(1-\Theta)]\},$$

which, in combination with (3), (5), and (7), gives:

$$\Gamma_\infty^2 = [C_0 E -$$

$$-C_1(E-E_N)]^2 c(\partial\Gamma/\partial c)_E/RTC_{\omega\to 0} =$$

$$= [C_0 E - C_1(E-E_N)]^2 c\omega/RT(\omega^2 C_i^2 + G_i^2). \tag{13}$$

Table 2

Frequency, Hz	$c \cdot 10^3$, mol/l	$\Gamma_\infty \cdot 10^{10}$
390	25	5.35
910	25	5.65
1150	25	5.05
	25	5.35 ± 0.3
390	30.5	5.8
910	30.5	5.1
1150	30.5	5.5
	30.5	5.5 ± 0.3
390	34	5.05
910	34	5.42
1150	34	5.35
	34	5.27 ± 0.2
Average value		5.34 ± 0.3

The values of Γ_∞ calculated from equations (13) are presented in Table 2. As was already indicated above, up to $\Theta = 0.5$ the value $\Gamma_\infty = 5.34 \cdot 10^{-10}$ mol/cm^2 agrees with the experimental data.

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