

ABSORBED AMOUNTS OF ORGANIC SUBSTANCE COMPUTED FROM MEASUREMENTS OF THE MERCURY ELECTRODE IMPEDANCE

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In a paper of Frumkin and Melik-Gaikazyan [1] it was shown that the following equations:

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

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

hold for the reactive (ωC_i) and active (G_i) components of the admittance (total conductivity) related to the adsorption-desorption process, if the adsorption of a surface-active organic substance is limited by diffusion to the electrode surface. Here, $H = (\partial \Gamma / \partial c)_E$; Γ denotes the concentration of the adsorbate near the surface at equilibrium and $\underline{c}$ the bulk concentration.

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

$\underline{d}$ denotes the diffusion coefficient, ω the angular frequency; $C_1 = C_{\omega \rightarrow 0}$ when $\omega \rightarrow 0$.

In Melik-Gaikazyan's paper [2] it was shown that the gradients $\partial \Gamma / \partial c$ calculated from Eqs. (1) and (2) and from electrocapillary curves and the dependence of Γ on $\underline{c}$ are of the same order of magnitude. However, the accuracy of the calculation from Eq. (2) in the cited paper was restricted by the inaccuracy in the determination of G_i caused by the solution creeping in between the capillary walls and the mercury.

In the cell described in paper [3] the causes of the inaccuracy in the determination of G_i have been eliminated. Hence it was interesting to employ Eqs. (1) and (2) in calculating some adsorption parameters, in particular, $\partial \Gamma / \partial c$ and Γ .

Starting from Eqs. (1) and (2) we may determine $(\partial \Gamma / \partial c)$ in several ways. The choice of the formula to be used in the computation of $\partial \Gamma / \partial c$ is dictated by the conditions of the experiment. If, for instance, the values of C_1 and G_1 at a given frequency are known, it is convenient to employ the formula

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

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

It should be noted that Eq. (3) is applicable only in the frequency range where diffusion of the adsorbate to the electrode constitutes the rate determining step in the adsorption process. At high frequencies the rate of adsorption may be limited by other, nondiffusive processes. As a result the derivative $\partial \Gamma / \partial c$ calculated from formula (3) becomes dependent on the frequency. Hence, the most correct procedure is to determine $\partial \Gamma / \partial c$ from formula (3) at various frequencies and to employ those $\partial \Gamma / \partial c$ values which depend only slightly on the frequency. Using Eq. (3), we may compute $\partial \Gamma / \partial c$ and find Γ at a given concentration by integrating the curve of $\partial \Gamma / \partial c$ versus $\underline{c}$ without having to resort to measurement of the interfacial tension.

We determined C_i and G_i for adsorption of n -amyl alcohol on mercury in 3N KCl at the frequencies of 390, 910, and 1150 Hz. In the measurements we employed the alternating current bridge the diagram of which is shown in Fig. 1. The value of R_1 was determined by extrapolating to $\omega \rightarrow \infty$ the solution conductivities recorded at the various frequencies (in these measurements R_2 was switched off). The R_2 values in 3N KCl at 390, 910, and 1150 Hz were determined later at constant R_1 . The values of $G = 1/R_2$ were computed from the conductivity values measured in the presence of

TABLE 1

Frequency Hz	$C_i, \mu\text{F}/\text{cm}^2$	$C_{\omega \rightarrow 0}, \mu\text{F}/\text{cm}^2$ from Eq. (7)	$\underline{a}$ from Eq. (7)	B from Eq. (10) liter/mole
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		

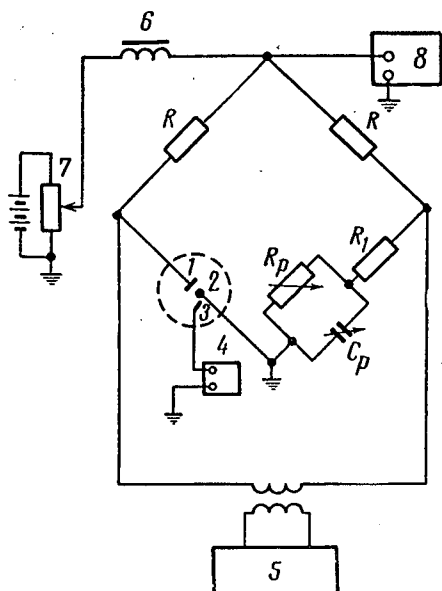


Fig. 1. Alternating-current bridge used in the present study. Notation: 1) Anode, 2) operating electrode, 3) calomel electrode, 4) potentiometer for measuring the potential difference between the calomel electrode and the operating electrode, 5) sound generator of the ZG-12 type, 6) inductor, 7) block for polarization with a constant current, 8) zero indicator, R_s and R_p) inductionless resistance boxes, C_p) capacity box, $R = 100$ ohm.

TABLE 2

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

n-amyl alcohol. To find C_i the capacity of the double layer in the amyl alcohol solution at the given potential had to be subtracted from the measured capacity values. Since these values were not available, we assumed as a first approximation that the degree of coverage of *n*-amyl alcohol as a function of the adsorbate concentration is given by the Frumkin isotherm:

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

here Θ denotes the degree of coverage, $\underline{a}$ and B are constants.

The constants $\underline{a}$ and B can be calculated from the additional capacity. In fact, the additional capacity at equilibrium equals [4]:

$$C_{\omega \rightarrow 0} = [C_0 E - C_1 (E - E_N)]^2 \Theta (1 - \Theta) / RT \Gamma_{\infty} [1 - 2a\Theta (1 - \Theta)]. \quad (5)$$

Here, C_0 and C_1 denote the capacities of the double layer at $\theta = 0$ and $\theta = 1$, respectively, E is the potential referred to the potential of the maximum in the electrocapillary curve of the solution back ground, E_N the potential of the maximum of the electrocapillary curve in the solution of the surface active substance at $\theta = 1$ referred to the potential of the maximum in the electrocapillary curve of the solution back ground. Γ_{∞} denotes the value Γ at $\theta = 1$. At the potential of the maximum of the additional capacity (if $a \geq 1$) and θ at the potential of maximum adsorption is close to unity) $\theta \approx 0.5$. Consequently,

$$C_{\omega \rightarrow 0}^{\max} = [C_0 E - C_1 (E - E_N)]^2 / RT \Gamma_{\infty} (4 - 2a) \quad (6)$$

and

$$a = 2 - [C_0 E - C_1 (E - E_N)]^2 / 2 C_{\omega \rightarrow 0}^{\max} RT \Gamma_{\infty},$$

hence it is necessary to know the value of $C_{\omega \rightarrow 0}$ in order to calculate the attraction constant.

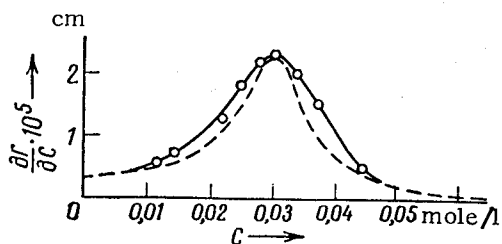


Fig. 2 The gradient $\partial\Gamma/\partial c$ as a function of the n -amyl alcohol concentration at the potential of -1.1 V referred to the normal calomel electrode. The dashed curve is the theoretical curve for $a = 1.6$ and $B = 6.3$ liter/mole.

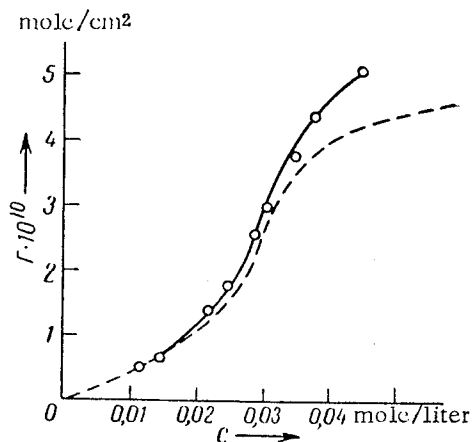


Fig. 3 Γ as a function of c at the potential of -1.1 V referred to the normal calomel electrode. The dashed curve is the curve corresponding to the equation $6.3c = 0(1-\theta)^{-1} \exp(-3.3\theta)$ at $\Gamma_\infty = 5.34 \cdot 10^{-10}$ mole/liter.

The θ values at the various concentrations were calculated from the equation

$$6.3c = \theta(1-\theta)^{-1} \exp(-3.3\theta) \quad (11)$$

and C_{true} was determined by means of the relationship $C_{\text{true}} = C_0 - \theta(C_0 - C_1)$. Formula (8) made it possible to calculate C_1 , and the values of $\partial\Gamma/\partial c$ at the various adsorbate concentrations were computed from Eq. (2). The diffusion coefficient of amyl alcohol, which is needed in this calculation, was taken from [5]: $D = 0.88 \times 10^{-5}$ cm²/sec.

The gradient $\partial\Gamma/\partial c$ as a function of c at the potential of -1.1 V referred to the normal calomel electrode is plotted in Fig. 2. The dashed curve in this same figure was constructed from the equation

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

which is obtained by differential of Eq. (4) and substitution of $\partial\theta/\partial c = \frac{1}{\Gamma_\infty} \partial\Gamma/\partial c$; a was taken equal to 1.6; $\Gamma_\infty = 5.34 \cdot 10^{-10}$.

In Fig. 3 the amount adsorbed Γ (determined by graphical integration of the curve of Fig. 2) is plotted versus the concentration (drawn curve). The dashed curve corresponds to the theoretical relationship between Γ (obtained by multiplying the θ values computed from Eq. (11) by $\Gamma_\infty = 5.34 \cdot 10^{-10}$) and the concentration. In this plot it can be seen that at $\theta = 0.5$ the experimental points lie nearly on the theoretical curve. The discovery that at large degrees of coverage the experimental amounts adsorbed slightly exceed the theoretical values may be ascribed to a rise of Γ_∞ with θ [6].

$C_{\omega \rightarrow 0}$ is usually determined by extrapolating C_i to $\omega = 0$; agreement between the values of the charges in the solution background and in the solution of the surface-active substance is a criterion of the correctness of the results obtained by this extrapolation [4]. However, if the adsorption peaks are narrow, a considerable change in the peak height only slightly affects the calculated value of the charge. Therefore, the above method does not always yield reliable results. An analytic expression for $C_{\omega \rightarrow 0}$ is easily derived by combining Eqs. (3) and (1):

$$C_{\omega \rightarrow 0} = (\omega^2 C_i^2 + G_i^2) / \omega(\omega C_i - G_i). \quad (7)$$

Utilizing Eq. (7), we transform formula (6) to:

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

where

$$C_i = C - C_{\text{нст}} = C - C_0 + \theta(C_0 - C_1) \quad (8)$$

(C denotes the measured differential capacity).

If $\theta = 0.5$ at the additional capacity, Eqs. (4) and (8) become:

$$C_i = C - C_0 + 0.5(C_0 - C_1), \quad (9)$$

$$Bc = \exp(-a). \quad (10)$$

We determined the values of a and B at the potential of maximum additional capacity by employing Eqs. (7a) and (10) and assuming that $\Gamma_\infty = 5.34 \cdot 10^{-10}$ mole/cm², $C_1 = 5.4 \mu\text{F/cm}^2$ [2], and $E_N = 0.345$ V. The a and B values calculated with $c = 3 \cdot 10^{-2}$ mole/liter are reported in Table 1 (the potential of maximum additional capacity equaled -1.1 V referred to the normal calomel electrode).

Finally, one possible way of determining Γ_∞ should be mentioned. Differentiation of (4) yields:

$$\begin{aligned} (\partial\Theta/\partial c)_E &= \frac{1}{\Gamma_\infty} (\partial\Gamma/\partial c)_E = \\ &= \Theta (1 - \Theta) / \{c [1 - 2a\Theta (1 - \Theta)]\}, \end{aligned}$$

when combined with (3), (5) and (7) this leads to

$$\begin{aligned} \Gamma_\infty^2 &= [C_0E - \\ &- C_1(E - E_N)]^2 c (\partial\Gamma/\partial c)_E / RTC_{\omega \rightarrow 0} = \\ &= [C_0E - C_1(E - E_N)]^2 c\omega / RT (\omega^2 C_i^2 + G_i^2). \end{aligned} \quad (13)$$

The Γ_∞ values computed from equations (13) are reported in Table 2.

As mentioned above, the value $\Gamma_\infty = 5.34 \cdot 10^{-10}$ mole/cm² agrees with the experimental data up to $\theta = 0.5$.

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