**A.N. Frumkin, V.I. Melik-Gaikazyan**

**Determination of the kinetics of adsorption of organic substances using the measurements of the capacitance and conductance of the electrode-solution interface under alternating current**

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Let us consider the behavior of the electrode-solution interface with adsorbed organic substance when the alternating current of various frequencies is applied. We assume that all electrochemical processes in the bulk <*they mean Faradaic processes*> are excluded, and the charge is only spent for the double layer charging. We also assume that current amplitude is small, and correspondingly the induced deviations from initial state are small. Let us call charge of surface unit of the double layer plate located from solution side $\varepsilon$, potential difference between solution and metal $\varphi$, current density flowing from solution to metal *i,* time *t*, and the amount of adsorbate at 1 cm$^2$ $\Gamma$. Then

$$i = \frac{d\varepsilon}{dt} = \left(\frac{\partial\varepsilon}{\partial\varphi}\right)_\Gamma \frac{\partial\varphi}{\partial t} + \left(\frac{\partial\varepsilon}{\partial\Gamma}\right)_\varphi \frac{\partial\Gamma}{\partial t} = C_e \frac{\partial\varphi}{\partial t} + i', \qquad (1)$$

$$i' = \left(\frac{\partial\varepsilon}{\partial\Gamma}\right)_\varphi \frac{\partial\Gamma}{\partial t}. \qquad (1a)$$

The quantity $C_e$ should be considered as the “real” electrode capacitance, which correspond to certain constant adsorption $\Gamma$. The dependence of $\Gamma$ on t under electrode polarization results in additional consumption of electricity (current *i*’). If the charging is infinitely slow (the frequency of the alternating current *n* = 0), the value of $\Gamma$ at any moment corresponds to equilibrium value for given potential $\varphi$ and bulk concentration of adsorbing substance *c*. In this case

$$i' = \left(\frac{\partial\varepsilon}{\partial\Gamma}\right)_\varphi \frac{\partial\Gamma}{\partial t} = \left(\frac{\partial\varepsilon}{\partial\Gamma}\right)_\varphi \left(\frac{\partial\Gamma}{\partial\varphi}\right)_c \frac{\partial\varphi}{\partial t} = C_{i\,(n=0)} \frac{\partial\varphi}{\partial t}. \qquad (2)$$

Hence, the changes of $\Gamma$ with potential results in appearance of “additional” capacitance [1], which is denoted $C_{i(n=0)}$. As follows from (2),

$$C_{i\,(n=0)} = \left(\frac{\partial\varepsilon}{\partial\Gamma}\right)_\varphi \left(\frac{\partial\Gamma}{\partial\varphi}\right)_c. \qquad (3)$$

In case of finite charging rate, the changes of $\Gamma$ are delayed as compared to $\varphi$ changes, and the quantity $\partial\Gamma/\partial t$ depends not only on $\partial\varphi/\partial t$, but also on adsorption kinetics. Let us consider two limiting cases.

1. <u>The rate of adsorption process itself is high, and adsorption kinetics is determined by diffusion of adsorbing substance towards the electrode surface or from it</u>. In this case, the alternating current induces periodic oscillations of the concentration of dissolved adsorbing substance, which are damping in the direction from the electrode surface towards solution bulk. Let us call concentration at distance *x* at time *t* as $c_{x,t}$. Then

$$\frac{\partial c_{x,t}}{\partial t} = D \frac{\partial^2 c_{x,t}}{\partial x^2}, \qquad (4)$$

where *D* is diffusion coefficient for adsorbing substance. We limit ourselves by considering diluted solutions exclusively, so D can be assumed to be constant. The solution of Eq. (4) should satisfy the boundary conditions

$$D\left(\frac{\partial c_{x,t}}{\partial x}\right)_{x=0} = \frac{\partial \Gamma}{\partial t}, \tag{5}$$

$$c_{\infty,t} = c. \tag{6}$$

As we assumed the equilibrium between adsorbed species and solution layer near the electrode, $\Gamma$ only depends on $c_{0,t}$ and $\varphi$. Hence,

$$\frac{\partial \Gamma}{\partial t} = \left(\frac{\partial \Gamma}{\partial \varphi}\right)_c \frac{\partial \varphi}{\partial t} + \left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \frac{\partial c_{0,t}}{\partial t} = D\left(\frac{\partial c_{x,t}}{\partial x}\right)_{x=0}. \tag{7}$$

If $\varphi = \varphi_0 + a\cos nt$, solution of Eq. (4) under boundary conditions (6) and (7) looks as follows:

$$c_{x,t} = c + \alpha \exp\left(-\sqrt{\frac{n}{2D}}\,x\right)\cos\left(nt - \sqrt{\frac{n}{2D}}\,x\right) + \\ + \beta \exp\left(-\sqrt{\frac{n}{2D}}\,x\right)\sin\left(nt - \sqrt{\frac{n}{2D}}\,x\right), \tag{8}$$

where

$$\alpha = -a\left(\frac{\partial \Gamma}{\partial \varphi}\right)_c \sqrt{\frac{2n}{D}}\left[\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \sqrt{\frac{2n}{D}} + 1\right] : \left\{\left[\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \sqrt{\frac{2n}{D}} + 1\right]^2 + 1\right\}; \tag{9}$$

$$\beta = a\left(\frac{\partial \Gamma}{\partial \varphi}\right)_c \sqrt{\frac{2n}{D}} : \left\{\left[\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \sqrt{\frac{2n}{D}} + 1\right]^2 + 1\right\}. \tag{9a}$$

Using elementary transformations, it is easy to derive from Eqs (1a), (7), (8), (9), (9a), and (3)

$$i' = -C_i a n \sin nt + \Pi_i a \cos nt, \tag{10}$$

where

$$C_i = C_{i\,(n=0)}\left[\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \sqrt{\frac{2n}{D}} + 2\right] : \left\{\left[\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \sqrt{\frac{2n}{D}} + 1\right]^2 + 1\right\}; \tag{11}$$

$$\Pi_i = C_{i\,(n=0)}\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \sqrt{\frac{2n}{D}}\, n : \left\{\left[\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi \sqrt{\frac{2n}{D}} + 1\right]^2 + 1\right\}. \tag{12}$$

As one can see from Eq. (10), the quantities $C_i$ and $\Pi_i$ present, respectively, "additional" capacitance and conductance, which appear as the result of $\Gamma$ dependence on $\varphi$. Phase shift $\theta = \mathrm{arctg}(nC_i/\Pi_i)$ is changing from 90 to 45° when n is changing from 0 to $\infty$.

As, according to Gibbs formula, the quantity

$$d\sigma = -\varepsilon d\varphi - \frac{RT\Gamma}{c}\,dc,$$

where σ is surface tension at metal/solution interface, expresses the total differential [2], one can write

$$\left(\frac{\partial \Gamma}{\partial \varphi}\right)_c = \frac{c}{RT}\left(\frac{\partial \varepsilon}{\partial c}\right)_\varphi = \frac{c}{RT}\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_\varphi \left(\frac{\partial \Gamma}{\partial c}\right)_\varphi . \qquad (13)$$

From (3) and (13), a useful relationship can be obtained (see below)

$$\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi = \frac{RT}{c}\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_\varphi^{-2} C_{i\,(n=0)} . \qquad (14)$$

At high enough $n\,(\sqrt{2n\,/\,D} \gg (\partial\Gamma\,/\,\partial c)_\varphi^{-1})$, it follows from (11), (12), (3), and (14)

$$C_i = \frac{1}{n}\Pi_i = C_{i\,(n=0)}\left(\frac{\partial \Gamma}{\partial c}\right)_\varphi^{-1}\sqrt{\frac{D}{2n}} = -\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_\varphi \left(\frac{\partial c}{\partial \varphi}\right)_\Gamma \sqrt{\frac{D}{2n}} =$$

$$= \frac{c}{RT}\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_\varphi^2 \sqrt{\frac{D}{2n}} . \qquad (15\text{-}$$

It is easy to see that, according to Eq. (15), at high n the capacitance and conductance are determined by the quantity of adsorbing substance being in time to diffuse towards the electrode surface or from it, if under condition of potential change the concentration near the surface always keeps its equilibrium value in respect to initially adsorbed quantity Γ.

2. The rate of adsorption process is low, and adsorption kinetics is determined by adsorption step exclusively. In this case concentration of adsorbing substance in solution remains constant. Let us call the rate of adsorption process Φ(*c*, Γ, φ):

$$\frac{\partial \Gamma}{\partial t} = \Phi\,(c,\ \Gamma,\ \varphi). \qquad (16)$$

It is evident that equilibrium is determined by condition

$$\Phi\,(c,\ \Gamma,\ \varphi) = 0. \qquad (17)$$

If deviations from equilibrium are small, and *c* = const,

$$\frac{\partial \Gamma}{\partial t} = \left(\frac{\partial \Phi}{\partial \Gamma}\right)_{\varphi,\,c}\Delta\Gamma + \left(\frac{\partial \Phi}{\partial \varphi}\right)_{\Gamma,\,c}\Delta\varphi = A\left[\Delta\Gamma - \left(\frac{\partial \Gamma}{\partial \varphi}\right)_c \Delta\varphi\right], \qquad (18)$$

where $A = (\partial\Phi/\partial\Gamma)_{\varphi,c}$; ΔΓ and Δφ are deviations of Γ and φ from equilibrium values; $\Delta\varphi = a\cos nt$. It is evident that $A > 0$. Solution of Eq. (18), which satisfies physical conditions of the problem, takes a form

$$\Delta\Gamma = p\cos nt + q\sin nt, \qquad (19)$$

where

$$p = \frac{aA^2}{n^2 + A^2}\left(\frac{\partial \Gamma}{\partial \varphi}\right)_c, \quad q = -\frac{anA}{n^2 + A^2}\left(\frac{\partial \Gamma}{\partial \varphi}\right)_c . \qquad (20)$$

According to (1a), (19), (20), and (3),

$$i' = -C_i an \sin nt + \Pi_i a \cos nt,$$

where

$$C_i = C_{i\,(n=0)} \frac{A^2}{n^2 + A^2}, \quad \Pi_i = -C_{i\,(n=0)} \frac{An^2}{n^2 + A^2}. \qquad (21)$$

<*note that the exponent 2, right-hand part of the first formula, is corrected by hand*; *this is a scan of reprint from the persona Frumkin's collection of his reprints*>

In this case, phase shift for the current *i*' $\theta$ = arctg(n$C_i/\Pi_i$) is changing from 90° to 0° when n is changing from 0 to $\infty$.

As one can see comparing Eqs (11) and (12) with Eqs (21), two considered assumptions about adsorption kinetics result in essentially different dependences of $C_i$ and $\Pi_i$ vs. *n*. This is illustrated by two curves in Fig.1. Curve *1* shows the dependence of $C_i/C_{i(n=0)}$ vs. *n* for arbitrary *n* scale, according to Eq. (11). Curve 2 demonstrates the dependence of the same ratio vs. *n* according to Eq. (21), with *A* value chosen to have the intersection of curves 1 and 2 at $C_i/C_{i(n=0)} = 0.5$.

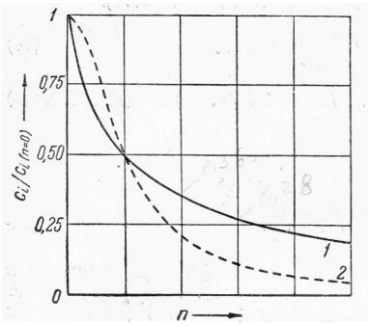

Fig.1 <*there is no Caption, only discussion in the text*>

As one can see from the Figure, the shapes of curves 1 and 2 are crucially different. Limitation of adsorption process by diffusion is more noticeable at small *n*, when limitation by adsorption step as is more visible at high *n*.

The difference in the curves shape allows to determine, on the basis of experimental $C_i/C_{i(n=0)}$ vs. *n* dependences, what step is the slowest. As was demonstrated in experiments of V.I. Melik-Gaikazyan, for adsorption of the normal aliphatic alcohols (butyl, amyl, and hexyl alcohols) at mercury-solution interface, the kinetics as a whole is purely determined by diffusion in solution, when adsorption step as is appears to be much faster. The dependences of $C_i$ and $\Pi_i$ vs. *n* allow, according to Eqs (11) and (12), to find $(\partial\Gamma/\partial c)_\varphi$. Another independent way to determine this quantity is provided by Eq. (14), because $(\partial\varepsilon/\partial\Gamma)_\varphi$ can be more or less easily determined from comparison of $\varepsilon$ for mercury with and without adsorbed molecules*. Satisfactory agreement of $(\partial\Gamma/\partial c)_\varphi$ found by these two methods also confirms that the conclusion about slow diffusion is correct.

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[1] V.I. Melik-Gaikazyan, P.I. Dolin, Doklady AN SSSR **66**, 409 (1949). [2] G. Gouy, Ann. De phys. (9), **7**, 134 (1917); A.N. Frumkin, Trudy khim. In-ta im. Karpova **5**, 6 (1926).

* According to Gibbs adsorption formula, $\left(\frac{\partial\Gamma}{\partial c}\right)_\varphi = -\frac{1}{RTc}\frac{\partial^2\sigma}{(\partial \ln c)^2}$. Unfortunately, the accuracy of measurements of the surface tenson $\sigma$ does not allow to determine $(\partial\Gamma/\partial c)_\varphi$ even approximately.