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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

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STUDY OF FILMS ON A MERCURY ELECTRODE

(Presented by Academician A. N. Frumkin, 1 II 1958)

Along with the determination of capacitance⁽¹⁻³⁾ and surface tension^(4,5), the method described below may be useful for the study of anodic and cathodic films.

An electrolyzer with the solution under investigation was connected into an ordinary polarographic circuit. When the potential of the mercury dropping electrode is maintained constant, discrete changes in current occur in the circuit. They can be observed on an oscillographic polarograph. The current rises sharply to a certain value and then smoothly falls to zero (Fig. 1). The intervals of potentials at which this effect is observed, as well as the shape and size of the pulse, are different for different substances; a number of solutions give no pulses, while in many solutions the pulses are observed in the anodic

Fig. 1. Oscillograms of solutions:

a—0.1 N KCl, *b*—0.1 N KI, *v*—0.1 N Na₂S.

Potential of the dropping electrode $U = +0.6$ V relative to Hg.

regions and, finally, there are solutions that exhibit them in the cathodic and anodic regions (Table 1).

The potentials at which the pulses disappear and appear are not the same. In both cases the change occurs with some delay. Thus, for KHSO₄, when the positive potential is increased, pulses arise at $U_1 = 3.7$ V and disappear at $U_2 = 1.5$ V when the potential is decreased. During the lifetime of a single drop, the number of pulses for a number of solutions reaches 10,000. The amplitude and duration of the pulse increase as the drop grows.

Table 1

Electrolyte, 0.1 N	U_2 in V (rel. Hg)	U_1 in V (rel. Hg)
NH ₄ F	+1.9	+2.4

Electrolyte, 0.1 N	U_2 in V (rel. Hg)	U_1 in V (rel. Hg)
KCl	+0.02	+0.03
KBr	+0.02	+0.6
KJ	+0.13	+1.5
KHSO ₄	+1.5	+3.7
Na ₂ S	above +3.5 and from -0.1 to -0.9	-

Despite fluctuations of these quantities, in particular of the frequency and number of pulses, their dependence on time is reproduced each time with an accuracy up to the conversion coefficient of the device, which was equal to 64. This means that comparison of the numbers of pulses obtained in two identical experiments reveals a difference not exceeding 64 when the total number of pulses is several thousand. Good reproducibility indicates a stable statistical regularity in the process of film rupture.

In Fig. 1 one can see the difference between the pulse forms for different solutions. However, concentrations and potentials can strongly change the form of the curves and, although the difference is preserved over the predominant interval of potentials, similarity can nevertheless be observed in certain regions. This makes it possible to conclude that the processes described, occurring in different solutions, have one and the same structure in time.

The cause of the appearance of current pulses is the formation of a film on the growing mercury drop. Having formed on the fresh surface of the electrode, the film deforms and, on reaching a critical tension, bursts.

The size of the drop and the number of pulses recorded during the time of drop growth make it possible to estimate the newly liberated surface as being of the order of 10^{-4} mm². The frequency of the process, together with other data, makes it possible to determine the degree of deformation and the mechanical properties of the film. However, a quantitative estimate is complicated by the violation of symmetry. Indeed, spherical symmetry of the drop cannot be used here, since the region of film rupture is hundreds of times smaller than the drop surface. This in turn causes local nonuniformities in the growth of the drop: different regions of the surface grow alternately. Under the microscope the nonuniformity appears as waviness of the surface. The fact that the current pulses do not overlap one another indicates the growth, at a given moment in time, of only one region of the drop. The duration of one-sided growth indicates that the newly formed film has lower strength and, consequently, is thinner. Therefore ruptures occur on one region of the surface until the tension of the film at this place decreases. The reason for its decrease at constant mercury pressure is the decrease in the radius of curvature of the growing region. Indeed, considering the equilibrium of a section of the film (in the case of a slit-like rupture of the film one may restrict oneself to the two-dimensional case), we obtain (Fig. 2):

Fig. 2. Dependence of the number of pulses N and the amplitude, expressed in arbitrary units (A_0), on time

Figure 2: Fig. 2. Dependence of the number of pulses N and the amplitude, expressed in arbitrary units (A_0), on time

Fig. 3

Figure 3: Fig. 3

$$\Sigma_x = -2Py + 2T(x) \frac{1}{\sqrt{1+y'^2}} = 0.$$

Hence

$$T(x) = Py\sqrt{1+y'^2}$$

$$T(0) = P \lim \frac{y'}{\left(\frac{1}{\sqrt{1+y'^2}}\right)'} = -\frac{P}{\frac{y''}{(1+y'^2)^{3/2}}} = -PR.$$

Here T is the tension, P the pressure, and R the radius of curvature. The different thickness of the film at two points of the surface shows that its growth continues even after it becomes monomolecular. This is also indicated by the amount of deposited substance, equivalent to the current of one pulse.

Let us turn to quantities capable of characterizing the process described. Experimentally, the amplitude and duration of the pulses as functions of time can be determined (oscillographic polarograph), as well as their number and frequency (counting device), and their amplitude distribution (pulse analyzer). The change in the number of pulses with time is well reproduced from drop to drop, which makes it possible to rely on this quantity in quantitative calculations. Graphs of the number of pulses and of the amplitude distribution for KHSO_4 are shown in Fig. 3.

Fig. 3

For small thickness, the film does not change the growth rate of the drop. Let us introduce the notation: S_0 and S are the areas of the region before and after deformation, σ_0 is the critical stress of the film, N is the number of pulses from the moment the drop appears, τ is the duration of a pulse, t is time, and i_0 is the pulse amplitude. Then $S \sim t^{2/3}$.

To make a first approximation in the theoretical determination of $\frac{dN}{dt}(t)$, i_0 , and τ , let us assume the deformation of the film to be elastic and the thickness to be the same over the entire surface.

Then

$$\sigma = k \frac{S - S_0}{S_0}$$

or

$$\frac{d\sigma}{dt} = \frac{k}{S_0} \frac{dS}{dt}; \quad \frac{dN}{dt} = \frac{1}{\sigma_0} \frac{d\sigma}{dt} = \frac{k}{\sigma_0 S_0} \frac{dS}{dt}.$$

Taking into account that $S_0 \simeq S \sim t^{2/3}$, we obtain

$$\frac{dN}{dt} = \frac{2}{3} \frac{k}{\sigma_0} \frac{1}{t}; \quad \tau = \frac{dt}{dN} = \frac{3}{2} \frac{k}{\sigma_0} t.$$

The size of the surface freed after destruction of the film is

$$\delta = \frac{dS}{dt} \tau \sim t^{2/3}.$$

Since the current i_0 is proportional to the free surface, $i_0 \sim t^{2/3}$. From the experimental data,

$$\frac{dN}{dt} \sim t^{-3/5}; \quad i_0 \sim t^{1/2}.$$

Thus, the simplified calculation makes it possible to explain qualitatively the change with time of the amplitude and frequency of the pulses. For exact quantitative agreement, it would be necessary to take into account the residual deformation of the film, the distribution of its thickness, and the curvature of the drop. Because of fluctuations, the solution of such a problem presents difficulties.

However, from the kinetic point of view, greater interest is presented by considering a single pulse, or a process occurring once on the freshly freed surface of the electrode. Since this surface amounts to about 0.0001 of the average surface of the drop, the region may be considered plane. The monotonic decrease of the current observed on the oscillograms-

maxima for 0.1 N KCl and 0.1 N Na₂S, is easily explained if it is assumed that the rate-determining stage of the process is not diffusion, but an electrochemical

reaction. In this case the current $i(t)$ is proportional to the concentration of the solution C_0 and to the active surface of the electrode $S_0 - S(t)$:

$$i(t) = kC_0[S_0 - S(t)], \quad (1)$$

where k is the proportionality coefficient, S_0 is the fresh surface, and $S(t)$ is the surface occupied by the film:

$$S(t) = \frac{m}{lhd} \int_0^t i(t) dt. \quad (2)$$

Here m is the electrochemical equivalent of one of the ions participating in the formation of the film, l is the content of this ion in the substance of the film, d is the specific weight, and h is the thickness of the film.

Substituting (2) into (1) and solving the resulting equation with respect to $i(t)$, we arrive at an expression for the pulse current:

$$i(t) = i(0) \exp \left[-\frac{km}{lhd} C_0 t \right]. \quad (3)$$

From (2), $S(0) = 0$, therefore from 1 it follows that:

$$i(0) = kC_0 S_0.$$

The proportionality between the initial concentration C_0 and the maximum pulse current $i(0)$ is well confirmed experimentally for concentrations below 0.1 N .

The similarity of the oscillograms of 0.1 N KCl and 0.1 N Na₂S with an exponential at $U = 0.6$ V does not, however, permit one to conclude that the assumptions adopted in deriving (3) are absolutely correct. Indeed, at lower potentials the exponential law of current decay for KCl and Na₂S solutions is violated. For 0.1 N KJ it is not obeyed at any potentials: from Fig. 1b it is seen that in the middle part of the pulse the current decay is sharply slowed down and then increases again. The causes of the appearance of this wave in the central part of the pulse are not yet sufficiently clear. It may be assumed that here the influence of nonstationary diffusion is manifested, i.e., an increase with time in the flux of substance to the electrode. The influence of other phenomena is also possible, for example, crystallization of the film ⁽⁶⁾ and the associated increase in its porosity.

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