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Abstract

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STUDY OF THE STRUCTURE OF THE DOUBLE LAYER DURING ELECTROCHEMICAL INITIATION OF THE POLYMERIZATION OF METHYL METHACRYLATE

The present communication sets forth results obtained in studying the structure of the double layer at the mercury–solution interface under conditions of cathodic initiation of the polymerization of methyl methacrylate (MMA). To investigate the electrode–solution boundary, the method of measuring the differential capacitance of the double layer with an impedance bridge was used. A mercury dropping cathode served as the electrode under investigation; with it the main part of the results was obtained. Some measurements were carried out on a mercury drop suspended from a platinum wire according to the method of ([1]). The use of a dropping electrode changes the conditions under which electrochemical initiation is usually carried out, since electrolysis of the solution, when the task is rapid detection of polymer, is performed on a stationary electrode. However, this does not create difficulty in comparing the results with the data obtained in ([2]).

The auxiliary electrode was mercury poured onto the bottom of the cell in the form of a ring. This made it possible to measure the rate of outflow of mercury from the capillary directly during the experiment. Dispersion of the differential capacitance in a normal electrolyte solution was not detected up to 10,000 Hz. The use of a mercury auxiliary electrode was motivated by the desire to avoid possible contamination of the solution by traces of platinum ([3]), which is especially undesirable in the case of carrying out a polymerization reaction sensitive to traces of impurities. Measurements were performed at a temperature of 22° C in a normal solution of sulfuric acid down to potentials of -1.80–-1.82 V versus the normal sulfate electrode (n.s.e.) at a frequency of 1000 Hz. In view of the occurrence of an irreversible process at the electrode, its impedance is equivalent to a capacitor with leakage ([4]). Since the measuring arm of the working bridge consisted of successively connected capacitance and resistance boxes, for correct separation of the capacitive and ohmic components of the total impedance the experimental data were recalculated to the circuit of Fig. 1a. The bridge-balance time was determined as in ([5]). Purification of the reagents and the procedure for preparing monomer solutions and introducing

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

them into the cell are described in (^{2}, ^{6}).

The differential-capacitance curves measured at different concentrations of monomer in the solution (Fig. 1, curves 2–5), from positive values of the potential to the potentials of the cathodic desorption peaks, have the form characteristic of adsorption of simple aliphatic compounds with a small number of carbon atoms in the chain (^{7}). To avoid incomplete establishment of equilibrium because of diffusion limitations, the capacitance in the region of maximum adsorption was measured on a hanging mercury drop, and on the basis of the data obtained the adsorption isotherm was calculated from the equation $\theta = C_0 - C / C_0 - C'$, where θ is the degree of surface coverage by the adsorbed substance, C_0 and C' are the double-layer capacitances respectively at $\theta = 0$ and $\theta = 1$, and C is the double-layer capacitance at θ. The isotherm has a weakly expressed S-shaped form and obeys the Frumkin adsorption-isotherm equation (^{8}): $Bc = \theta / 1 - \theta \exp(-2a\theta)$, where c is the concentration of the organic substance, B is the adsorption-equilibrium constant, and θ is the degree of surface coverage by the organic substance. The value of the attraction constant a is equal to 1.1.

At potentials more negative than the cathodic desorption peaks, the differential-capacitance curves have an anomalous appearance, which is especially clearly expressed for curve 2 in Fig. 1. On the descending side of the desorption peak of curve 2, well reproducible lags in the decrease of capacitance are visible. At more neg-

at negative potentials the capacitance decreases sharply. The lower the concentration of MMA in the solution, the more negative the potential at which the decrease in capacitance occurs. Let us note that the differential-capacitance curve measured in a neutral solution in the presence of MMA has the normal form characteristic of the adsorption of aliphatic compounds (^{7}).

Fig. 1. Differential-capacitance curves in solutions:
1 –1 *N* H_2SO_4; 2 –saturated solution of MMA in 1 *N* H_2SO_4; 3 –1 *N* H_2SO_4 + $^2/_5$ of a saturated solution of MMA in 1 *N* H_2SO_4; 4 –1 *N* H_2SO_4 + $^1/_3$ of a saturated solution of MMA in 1 *N* H_2SO_4; 5 –1 *N* H_2SO_4 + $^1/_5$ of a saturated solution of MMA in 1 *N* H_2SO_4; 6 –explained in the text. R_1 –polarization resistance; R_2 –solution resistance; C –double-layer capacitance.

Fig. 2. I–t curves on a dropping mercury electrode in 1 *N* H_2SO_4 (1) and in a saturated solution of MMA in 1 *N* H_2SO_4 (2).
a: $\varphi = -1.65$ V (N.H.E.),
b: $\varphi = -1.73$ V (N.H.E.).

From a comparison of the C–φ curve (Figs. 1, 2) and the polarization curve for

Fig. 3. Differential-capacitance curves

Figure 2: Fig. 3. Differential-capacitance curves

the reduction of hydrogen ions (^{2}), measured under the same conditions, it is seen that the beginning of the region of catalytic hydrogen evolution corresponds to the clearly expressed delay. This leads one to suppose that the delay in the decrease of capacitance is caused by the pseudocapacitance of the latter reaction. The regions of low capacitance values at potentials more negative than the cathodic desorption peaks on the polarization curves for hydrogen-ion reduction in the presence of MMA correspond to the region of formation and adsorption of the polymeric product. Changes in the state of the electrode surface are clearly recorded by the I—t curves measured at different potentials (Fig. 2).

The polymer film formed on the surface of the hanging mercury drop at $\varphi = -1.80$ V (N.H.E.) is so firmly bound to the surface that, when the potential is shifted in the positive direction to $\varphi = -0.5$ V (N.H.E.) ···

the capacitance of the double layer continues to be determined by adsorption of the polymeric product (Fig. 1, 6).

In analyzing the polarization curves for the reduction of hydrogen ions in the presence of monomer (^{2}), and especially from consideration of the I—t curves (Fig. 2), it is seen that an increase in the hydrogen overvoltage caused by the formation and adsorption of the polymeric product on the electrode surface is preceded by a process leading to a decrease in the overvoltage and due to the catalytic activity of MMA. The formation of the polymeric product is, apparently, a consequence of this process. The latter consideration finds experimental confirmation. As is known, an increase in the concentration of a neutral salt in solution leads to a decrease in the catalytic wave of hydrogen, which at a significant salt concentration may be strongly suppressed (^{9}). It turns out that, as a result of suppression of the catalytic wave of hydrogen when a neutral salt is added to the monomer solution, formation of the polymeric product during electrolysis of the solution ceases. Figure 3 presents curves of differential capacitance measured in a solution of $0.1N$ H_2SO_4 with and without added salt at the same monomer concentration. As is seen from the graph, addition of Li_2SO_4, which causes only a slight change in the pH of the solution, completely removes the formation of the polymeric product.

Fig. 3. Curves of differential capacitance in solutions: 1 —0.1 N H_2SO_4; 3, 2 —respectively in 0.1 N H_2SO_4 and 0.1 N $H_2SO_4 + 0.9$ N Li_2SO_4 with one and the same concentration of MMA.

As indicated above, the pseudocapacitance, masked by the right desorption peak and expressed by steps on its right branch (Figs. 1, 2), corresponds in potentials to the region of catalytic hydrogen evolution. Its appearance can be explained by a reversible stage of electrochemical reduction of $MMAH^+$:

Figure 4

Figure 3: Figure 4

$$\mathrm{MMAH}^+_{\mathrm{ads}} + e^- \rightleftarrows \mathrm{MMAH}$$

and it may be assumed that polymerization is initiated by MMAH radicals.

In contrast to the considerations set forth, the authors of a number of works (^{10,11}) believe that polymerization of the monomer in acid solutions during reduction of hydrogen ions is caused by adsorbed H atoms. However, this viewpoint is not consistent with the experimental data. Indeed, at a given current density the concentration of adsorbed hydrogen atoms ($\mathrm{H}_{\mathrm{ads}}$) upon addition of a neutral salt should remain constant or even increase somewhat (depending on assumptions about the mechanism of removal of $\mathrm{H}_{\mathrm{ads}}$). If one assumes that polymer-

···product is formed at a certain value of H_{ads}, then, upon addition to the acid solution of a neutral salt causing an increase in the overvoltage of hydrogen, only a somewhat more negative potential will be required to achieve the same polymerization effect. However, as is evident from Fig. 3, up to potentials considerably more negative than the potential corresponding to the increased overvoltage caused by the addition of the neutral salt, polymerization is not observed. Apparently, the rate of electrochemical desorption—the most probable mechanism for the removal of adsorbed hydrogen atoms from the mercury surface—is so high that initiation of polymerization by adsorbed atomic hydrogen does not occur.

If the monomer contains autoxidation products, the formation of a polymer film on the electrode surface, which occurs at a more positive potential than in the absence of autoxidation products, has a stronger effect on the shape of the differential-capacitance curves.

Fig. 4. Differential-capacitance curves in $1\,N\ H_2SO_4$ saturated with MMA and containing autoxidation products (1, 2, 3); 4—saturated solution of MMA in $1\,N$ H_2SO_4 containing $5 \cdot 10^{-3}\,N\ H_2O_2$

Figure 4 shows C—φ curves obtained with solutions of MMA containing different concentrations of autoxidation products. Curve 1 was obtained with monomer that had been in contact with atmospheric oxygen for 1 day, curve 2 for 2 days, curve 3 for 3 days. The C—φ curve obtained with an acid-saturated solution of MMA after addition of hydrogen peroxide (Fig. 4, 4) has a form analogous to that of curve 3. As is evident from Fig. 4, in the presence of oxidation products the cathodic desorption peaks disappear and there is an overall decrease in capacitance, which, as follows from comparison with curve 6 of Fig. 1, indicates the preferential adsorption of the polymer formed at potentials more positive than the cathodic desorption peak.

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Note: Figure translations are in progress. See original paper for figures.