INVESTIGATION OF THE STRUCTURE OF THE DOUBLE LAYER DURING ELECTROCHEMICAL INITIATION OF METHYLMETHACRYLATE POLYMERIZATION

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In the present communication we report the results obtained in studying the structure of the double layer near the mercury-solution boundary during the cathodic initiation of methylmethacrylate (MMA) polymerization. In the investigation of the electrode-solution boundary we employed the method of measuring the differential capacitance of the double layer by means of an impedance bridge. Most results were obtained by using a mercury drop electrode. Some measurements were performed by applying the procedure of paper [1] to a mercury drop suspended from a platinum filament. Application of a drop electrode alters the conditions under which electrochemical initiation is usually carried out, since electrolysis of the solution is effected at a stationary electrode when rapid detection of the polymer is desired. However, this does not impede comparison of our results with the data obtained in paper [2].

The mercury which has fallen on the cell bottom and has formed a ring served as the auxiliary electrode. This enabled us directly to measure the rate at which mercury flowed from the capillary during the experiment. No dispersion of the differential capacitance in a 1 N electrolyte solution was detected at frequencies up to 10,000 Hz. The auxiliary mercury electrode was employed to avoid possible contamination of the solution by traces of platinum [3]; this is particularly important in polymerizations sensitive to impurity traces. The measurements were carried out in an 1 N solution of sulfuric acid at 22°C and at potentials up to −1.80 to −1.82 V by employing a normal sulfate electrode (n. s. e.) at the frequency of 1000 Hz. Since an irreversible reaction proceeds on the electrode, the electrode impedance is equivalent to a capacitance with a leak [4]. The measuring branch of the operating bridge consisting of capacitance and resistance units arranged in series, the capacitances and the ohmic components were calculated from the measured total impedance by applying the scheme of Fig. 1a. Bridge balance was determined in the same way as in [5]. The purification of the reagents, the preparation of the monomer solutions and the procedure of filling the cell were described in papers [2, 6].

The differential capacitance curves (Fig. 1, curves 2-5) measured at various concentrations of the monomer in the solution and at potentials ranging from positive values to the cathodic desorption peaks, show shapes typical of of adsorption of simple aliphatic compounds containing a small number of carbon atoms in the chain [7]. To avoid incompleteness of the equilibrium as a result of diffusion limitations, the capacitance in the range of maximum adsorption was measured by means of a pending drop mercury electrode; the adsorption isotherm was computed from the data obtained by using the equation $\theta = (C_0 - C)/(C_0 - C')$, where θ denotes the degree of coverage of the surface by the adsorbed substance, C_0 and C' are the capacitances of the double layer at $\theta = 0$ and $\theta = 1$, respectively, and C is the double layer capacitance at θ. The isotherm has a slightly pronounced S-shape and obeys Frumkin's equation of the adsorption isotherm [8]: $Bc = \theta/1 - \theta \exp(-2a\theta)$, where $\underline{c}$ denotes the concentration of the organic substance, B is the adsorption equilibrium constant, θ the degree of coverage of the surface by the organic substance. The attraction constant $\underline{a}$ equals 1.1.

At potentials more negative than the cathodic desorption peaks the differential capacitance curves have an anomalous shape, which is particularly clearly marked in curve 2 of Fig. 1. Neatly reproducible shoulders and drops in capacitance are visible in the falling branch of the desorption peak of curve 2. The capacitance falls sharply at more negative potentials. The higher the MMA concentration of the solution, the more negative are the potentials at which the capacitance starts falling. We note that the differential capacitance curve measured in a neutral solution of MMA has the normal shape typical of adsorption of aliphatic compounds [7].

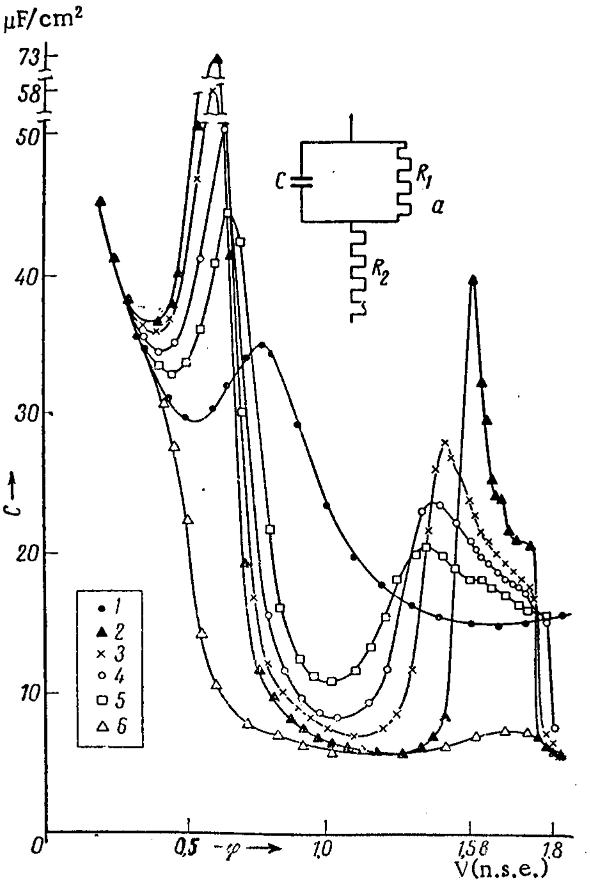

Fig. 1. Differential capacitance curves of the solutions: 1)1 NH_2SO_4; 2) saturated solution of MMA in 1 NH_2SO_4; 3) 1 N H_2SO_4 + saturated solution of MMA in 1 N H_2SO_4 (5: 2); 4) 1 N H_2SO_4 + saturated solution of MMA in 1 NH_2SO_4 (3 :1); 5) 1 N H_2SO_4 + saturated solution of MMA in 1 H_2SO_4 (5 :1); 6) explained in the text. R_1 denotes the polarization resistance, R_2 the resistance of the solution, C the double layer capacitance.

Comparison of the C versus φ curve (curve 2, Fig. 1) and the polarization curve of hydrogen ion reduction [2] measured under the same conditions reveals that the distinct maximum in the falling branch of the former curve corresponds to the range where catalytic liberation of hydrogen starts. This suggests that the maximum considered is due to the pseudocapacitance produced by the liberation of hydrogen. The range of low capacitances in the polarization curves of hydrogen ion reduction in the presence of MMA, at potentials more negative than the cathodic desorption peaks,corresponds to the region where the polymer is formed and adsorbed. The changes in the electrode surface state are graphically demonstrated by the I versus *t* curves measured at various potentials (Fig. 2).

The polymer film formed on the surface of the pending mercury drop electrode at $\varphi = -1.80$ V (n. s. e.) is so firmly bound to the surface that after a positive shift of the potential to $\varphi = -0.5$ V (n. s. e.) the double layer capacitance is still determined by adsorption of the polymer (curve 6, Fig. 1).

Analysis of the polarization curves of hydrogen ion reduction measured in the presence of monomer [2], and, in particular, inspection of the I versus *t* curves (Fig. 2) reveals that the rise in hydrogen overvoltage produced by the formation and adsorption of polymer on the electrode surface precedes the process which causes the overvoltage to drop and is due to the catalytic activity of MMA. Formation of polymer is evidently a consequence of this process. This consideration is confirmed by the experiment. As is well-known, a rise in concentration of neutral salt

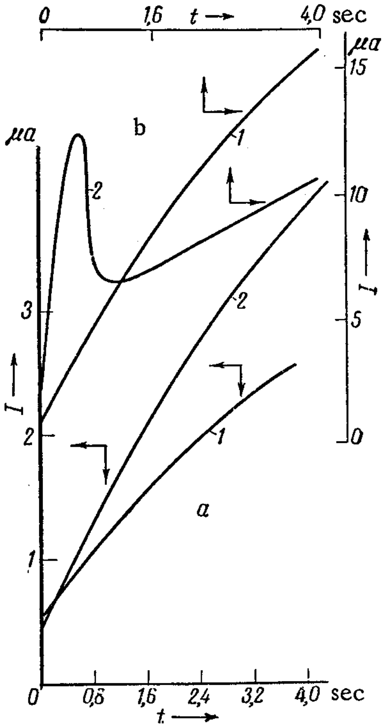

Fig. 2. I versus t curves measured by means of a mercury drop electrode in 1 N H_2SO_4 (1) and in a saturated MMA solution in 1 N H_2SO_4 (2). a) φ = −1.65 V (n. s. e.); b) φ = −1.73 (n. s. e.)

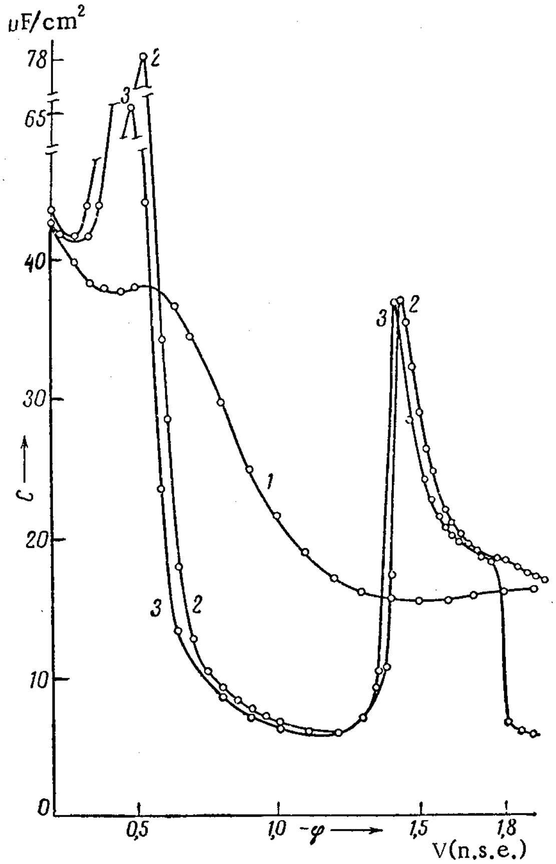

Fig. 3. Differential capacitance curves measured in the solutions: 1) 0.1 N H_2SO_4; 3,2) in 0.1 N H_2SO_4 and 0.1 N H_2SO_4 + 0.9 N Li_2SO_4, respectively, with one and the same MMA concentration.

in the solution causes the catalytic wave of hydrogen to drop, and at rather high concentrations of neutral salt this wave may be sharply depressed [9]. It is found that depression of the catalytic hydrogen wave by addition of neutral salt to the monomer solution stops the formation of polymer during electrolysis of the solution. Figure 3 shows differential capacitance curves measured in a 0.1 N H_2SO_4 solution at one and the same monomer concentration with and without added salt. As can be seen from the plots, admixture of Li_2SO_4, which changes the pH of the solution only slightly; completely suppresses the formation of polymer.

As pointed out above, the pseudocapacitance which masks the right-hand desorption peak and produces the maximum and the shoulder in the left-hand branch (curve 2, Fig. 1) corresponds to the potential range of catalytic hydrogen liberation. The apperance of the pseudocapacitance can be explained by the reversible stage of the electrochemical reduction of $MMAH^+$:

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

and we suggest that polymerization is initiated by the MMAH radicals.

Our views are not shared by some other authors [10, 11] who believe that polymerization of a monomer in acid solutions during reduction of hydrogen ions is produced by adsorbed H-atoms. However, this point of view does not agree with the experimental data. In fact, at a given current density the concentration of adsorbed hydrogen ions (H_{ads}) should remain constant, or (depending on the supposed desorption mechanism of H_{ads}) rise even slightly upon addition of a neutral salt. If the polymer is supposed to form at a definite value of H_{ads}, then, after admixture of neutral salt to the acid solution and the resulting rise in hydrogen overvoltage, only a slightly more negative potential would be required to reach the previous rate of polymerization. However, as can be seen in Fig. 3, no polymerization is observed up to potentials much more negative than the potential corresponding to the rise in overvoltage caused by addition of the neutral salt. 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 the polymerization by adsorbed atomic hydrogen does not take place.

If the monomer contains autooxidation products, then, formation of a polymer film on the electrode surface at a potential more positive than that in the absence of autooxidation products, strongly affects the shape of the differential capacitance curves.

Curves of C versus φ as measured in MMA solutions containing various concentrations of autooxidation products are shown in Fig. 4. Curves 1, 2 and 3 correspond to the monomer kept in contact with air for 1, 2 and 3 days, respectively. The shape of the C versus φ curve measured in an acid MMA solution containing added hydrogen peroxide (curve 4, Fig. 4) is similar to that of curve 3. As can be seen in Fig. 4, the presence of autooxidation products leads to disappearance of the cathodic desorption peaks and to a general drop of the capacitance which, as appears from a comparison with curve 6 of Fig. 1, points to preferential adsorption of the polymer forming at potentials more positive than the cathodic desorption peak.

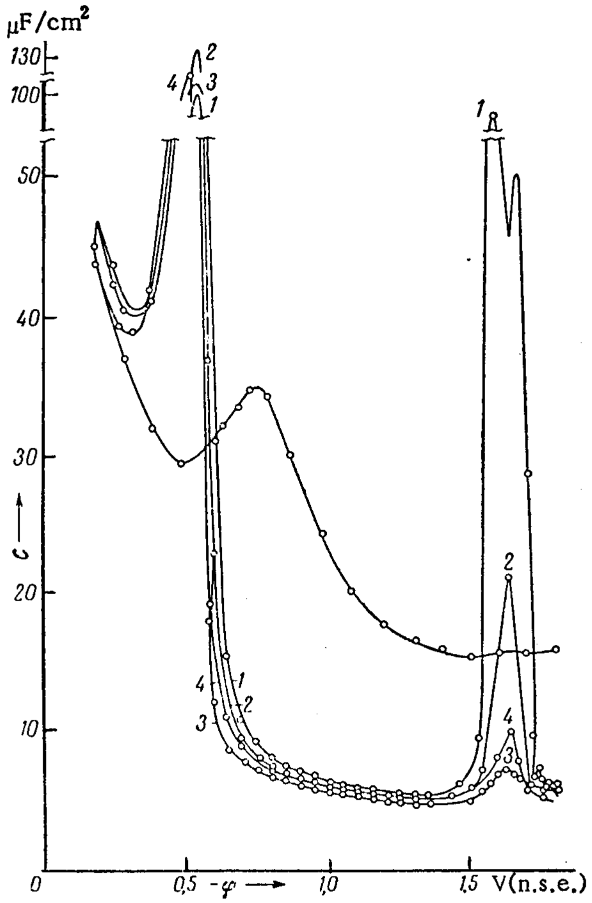

Fig. 4. Differential capacitance curves measured in 1 N H_2SO_4 saturated with MMA and containing autooxidation products (1, 2, 3); 4) saturated MMA solution in 1 N H_2SO_4 containing $5 \cdot 10^{-3}$ N H_2O_2.

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