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## Abstract

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# Measurement of the Capacitance of a Platinum Electrode in Sodium Acetate Solutions with Additions of Methanol and 1,3-Butadiene

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In the electrochemistry of organic compounds, processes occurring with the participation of radicals generated on the electrode surface are of great interest. A particular case of such processes is the reaction of electrochemical additive dimerization—the addition of alkyl radicals, which are intermediate products of the Kolbe electrosynthesis, to an acceptor molecule, for example, 1,3-butadiene, followed by dimerization of the alkenyl radicals formed ([1],[2] ).

As a result of the reaction of electrochemical additive dimerization, compounds of important practical significance may be obtained ([3]). To elucidate the mechanism and to regulate this process purposefully, it is first of all necessary to establish whether the reaction has a homogeneous character ([4]), or whether the radicals formed in the Kolbe reaction interact with acceptor molecules adsorbed on the electrode surface. The present work is devoted to solving this question. As the method for studying the electrode-solution boundary, capacitance measurement was chosen, based on the potential decay after opening the circuit of the polarizing current; this method has been successfully used in recent years for the study of solid electrodes ([5–7]).

A system was investigated in which the source of radicals formed during electrolysis at the anode was sodium acetate acidified with acetic acid to pH 6. The acceptor of methyl radicals was 1,3-butadiene. A platinum wire was used as the anode.

The reaction of electrochemical additive dimerization is usually carried out in methanolic solutions of a carboxylate in the presence of a diene. However, since in aqueous solutions the same condensation products are obtained as in alcoholic ones, we considered it expedient to study the behavior of the platinum anode while gradually complicating the composition of the electrolyte, namely by going from aqueous-diene solutions to aqueous-methanolic and then to methanolic-diene acetate solutions.

The apparatus for measuring capacitance did not differ essentially from those described in the literature ([8]) and consisted of potentiometric and oscillographic

Figure 1

Figure 1: Figure 1

circuits connected in parallel to the electrochemical cell. Recording of the potential decay after interruption of the current was carried out with a CI-19 oscillograph, having minimum time marks of $5 \cdot 10^{-6}$ sec and a sensitivity of 2 mV/mm. The sweep of the oscillograph before switching off the current was started by an electromagnetic relay.

The reagents used in the work were purified by double distillation or recrystallization; aqueous solutions were prepared with bidistilled water; methanol was purified from carbonyl compounds ([9]) and thoroughly dehydrated. To obtain reproducible results, the platinum anode was subjected to preliminary anodic polarization in 15% $H_2SO_4$ at a current of $2 \cdot 10^{-3}$ A/cm$^2$ for 30 min.

The discrepancy in the potential values in parallel experiments did not exceed 5-8 mV, and in the values of the coefficient $b = \dfrac{\partial \varphi}{\partial \lg i}$ it was on average 0.006.

Figure 1 presents, in the coordinates $\varphi$—$\lg i$, the polarization curves obtained by the compensation method in aqueous solutions of sodium acetate in the presence of 1,3-butadiene.

The form of the background curve—that is, that of a pure sodium acetate solution (curve 1)—has been discussed in the literature ([10,11]), and it was shown that, up to the potential jump in the region 1.9-2.1 V, the only product of the electrochemical reaction is oxygen. Kolbe electrosynthesis begins to proceed only at the potentials of the upper portion of the $\varphi$—$\lg i$ curve.

It follows from Fig. 1 that, upon introduction of 1,3-butadiene into the solution, a "hump" appears on the second lower rectilinear segment of the background curve, increasing

**Fig. 1.** Dependence of the potential of a platinum anode on the logarithm of the current density in a 1 M aqueous solution of sodium acetate with additions of 1,3-butadiene (mol/l): 1—without additive; 2—$8.35 \cdot 10^{-5}$; 3—$4.175 \cdot 10^{-4}$; 4—$8.35 \cdot 10^{-4}$; 5—$4.175 \cdot 10^{-3}$; 6—$8.35 \cdot 10^{-3}$.

with increasing diene concentration. Significant inhibition of the oxygen-evolution process in this potential region already occurs at a 1,3-butadiene concentration of $5 \cdot 10^{-4}$—$1 \cdot 10^{-3}$ mol/l. With increasing diene concentration, moreover, the beginning of the upper rectilinear segment, corresponding to Kolbe electrosynthesis, shifts into the region of lower current densities, while the potential jump decreases in magnitude and then disappears completely (curves 5, 6, Fig. 1). The character of the upper portion of the $\varphi$—$\lg i$ curve in the presence of the diene is practically unchanged.

Figure 2 illustrates the change in the capacitance of the double layer with po-

Fig. 2. Change in the capacitance of the double layer with potential in a 1 M aqueous solution of sodium acetate with additions of 1,3-butadiene (mol/l): 1 —without addition; 2—$8.35 \cdot 10^{-5}$; 3—$4.175 \cdot 10^{-4}$; 4—$8.35 \cdot 10^{-4}$; 5—$4.175 \cdot 10^{-3}$; 6—$8.35 \cdot 10^{-3}$.

Figure 2: Fig. 2. Change in the capacitance of the double layer with potential in a 1 M aqueous solution of sodium acetate with additions of 1,3-butadiene (mol/l): 1—without addition; 2—$8.35 \cdot 10^{-5}$; 3—$4.175 \cdot 10^{-4}$; 4—$8.35 \cdot 10^{-4}$; 5—$4.175 \cdot 10^{-3}$; 6—$8.35 \cdot 10^{-3}$.

tential in the same solutions in which the polarization curves were recorded. All curves have a maximum at a potential of approximately 1.4 V relative to the normal calomel electrode, which decreases with increasing concentration of the 1,3-butadiene additive.

$C$—$\varphi$ curves with maxima have been observed on platinum anodes in acid solutions by V. I. Veselovskii and co-workers ($^{12}$), and by V. L. Kheifets and I. Ya. Rivlin ($^{13}$), with the high capacitance values being associated by these authors with an increase in the amount of chemisorbed oxygen; i.e., the maximum on the $C$—$\varphi$ curve has the character of a pseudo-capacitance. The decrease observed on the $C$—$\varphi$ curve with increasing potential is associated with strengthening of the metal-oxygen bond. On the basis of these considerations, the decrease in the height of the oxygen pseudo-capacitance peak can be explained by preferential adsorption of diene molecules and, correspondingly, by a decrease in the number of adsorption centers for oxygen atoms. Since the curves are located one below another with increasing additive concentration, it follows that 1,3-butadiene is adsorbed over the entire measured range of potentials.

The adsorption of neutral organic molecules at such high positive potentials is apparently associated with the presence in the molecule of

of the diene—a readily polarizable conjugated system of double bonds whose $\pi$-electrons interact with the positive charges of the electrode ($^{14}$). Anion-like behavior of organic compounds containing multiple bonds had previously been observed by M. A. Gerovich and co-workers ($^{15}$), and by Bockris and co-workers ($^{16}$), on anodically polarized mercury; however, the deviation from the potential of zero charge in these cases did not exceed 0.3 V.

From the curves presented in Fig. 2 it is also evident that, at the potential corresponding to the jump on the polarization curve, there is a sharp decrease in capacitance, analogous to that observed by A. N. Frumkin and V. V. Sobol ($^{17}$) in hydrochloric-acid solutions. The minimum capacitance measured in a solution of pure sodium acetate is lower than the double-layer capacitance, which may possibly be connected with the presence on the electrode surface of adsorbed $CH_3COO\cdot$ radicals.

**Fig. 2.** Change in the capacitance of the double layer with potential in a 1 *M* aqueous solution of sodium acetate with additions of 1,3-butadiene (mol/l): 1—

Fig. 3. Change in the capacitance of the double layer with potential in aqueous-methanol solutions of 1 M sodium acetate: 1—0% $CH_3OH$; 2—16.7% $CH_3OH$; 3—48.7% $CH_3OH$; 4—97.3% $CH_3OH$; 5—100% $CH_3OH$.

Figure 3: Fig. 3. Change in the capacitance of the double layer with potential in aqueous-methanol solutions of 1 M sodium acetate: 1—0% $CH_3OH$; 2—16.7% $CH_3OH$; 3—48.7% $CH_3OH$; 4—97.3% $CH_3OH$; 5—100% $CH_3OH$.

without addition; 2—$8.35 \cdot 10^{-5}$; 3—$4.175 \cdot 10^{-4}$; 4—$8.35 \cdot 10^{-4}$; 5—$4.175 \cdot 10^{-3}$; 6 —$8.35 \cdot 10^{-3}$.

**Fig. 3.** Change in the capacitance of the double layer with potential in aqueous-methanol solutions of 1 *M* sodium acetate: 1—0% $CH_3OH$; 2—16.7% $CH_3OH$; 3 —48.7% $CH_3OH$; 4—97.3% $CH_3OH$; 5—100% $CH_3OH$.

Before proceeding to the study of sodium acetate solutions in absolute methanol in the presence of the diene, we investigated the effect of methanol additions to aqueous solutions.

The introduction of methanol into aqueous sodium acetate solutions affects the polarization curves only in the oxygen region, i.e., up to the potentials of the upper segment. Up to current densities of $1 \cdot 10^{-1}$—$5 \cdot 10^{-1}$ mA/cm$^2$, depolarization of the anode occurs, and then a sharp inhibition of the process sets in up to the potential corresponding to the onset of Kolbe electrosynthesis. In potentiostatic recording of the curves in the oxygen region, a maximum is found similar to that observed for aqueous solutions of alcohols on platinized platinum ([18]).

In absolute methanol, the upper linear portion on the curve

$\varphi$—lg $i$ begins at a potential 200 mV more negative, and at current densities 30 times smaller than in aqueous acetate solutions. The $C$—$\varphi$ curves recorded in aqueous-methanol acetate solutions are shown in Fig. 3; it follows from them that, with increasing methanol concentration, the height of the maximum on the curves first increases, in the concentration interval from 16.7 to 89% decreases somewhat, and then decreases sharply. The change in capacitance at the maximum point of the $C$—$\varphi$ curve ($C_{\max}$) as a function of methanol concentration is presented below.

| Conc. $CH_3OH$, vol. % | 0 | 0.81 | 3.3 | 16.7 | 48.7 | 89 | 97.3 | 99.8 | 100 |
|---|---|---|---|---|---|---|---|---|---|
| $C_{\max}$, $\mu$F/cm$^2$ | 471 | 599 | 694 | 843 | 775 | 640 | 391 | 250 | 174 |

The anode potential corresponding to the maximum on the $C$—$\varphi$ curve shifts in the cathodic direction with increasing methanol concentration.

An increase in the capacitance of the platinum electrode during anodic polarization as a result of adding methanol to hydrochloric acid solutions was noted by Breiter and co-workers (19), who explained this phenomenon by an increase in the amount of adsorbed oxygen formed during the discharge of water molecules. However, since the shapes of the capacitance curves in absolute methanol and in an aqueous solution containing acetate are analogous, such an explanation can hardly be considered exhaustive. Indeed, in absolute methanol an electromotor-active formation must also be present on the anode surface, giving rise to high capacitance values. Such formations may probably be adsorbed radicals $CH_3O^\bullet$ or $^\bullet CH_2OH$ (20). The presence of these radicals evidently also increases the pseudocapacitance at the maximum point on the $C$—$\varphi$ curves.

When 1,3-butadiene is added to a solution of sodium acetate in absolute methanol, the nature of the changes in the $\varphi$—lg $i$ and $C$—$\varphi$ curves is the same as in aqueous solutions: the presence of the diene inhibits the electrochemical reactions occurring at the potentials of the lower branch of the polarization curve and has practically no effect on the nature of the upper section. The onset potential of Kolbe electrosynthesis is almost not shifted, while the current density already at a diene concentration of $4 \cdot 10^{-2}$ mol/L decreases by more than a factor of 10. From the $C$—$\varphi$ curves recorded in methanolic acetate solutions in the presence of diene, it follows that 1,3-butadiene, as in aqueous solutions, lowers the capacitance at all potentials, and this decrease in capacitance is the more pronounced the higher the diene concentration. Consequently, butadiene, both in an aqueous and in an alcoholic medium, is present in the adsorbed state on the electrode surface up to high positive potentials (2.0–2.1 V relative to the saturated calomel electrode).

The experimental data obtained allow one to conclude that the reaction of electrochemical additive dimerization is heterogeneous in character.

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