ANODIC DISSOLUTION OF PLATINUM IN METHANOLIC SOLUTIONS UNDER CONDITIONS OF KOLBE-TYPE ELECTROCHEMICAL CONDENSATION

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Anodic dimerization by the Kolbe reaction ($2RCOO^- = R-R + 2CO_2 + 2e$) takes place most effectively at platinum in methanolic solutions. A technology for sebacic acid production has now been developed on the basis of this reaction and is being introduced to industry. There is however very little information on the stability of platinum anodes in these solutions. In the present work the dissolution of platinum anodes during reactions of the Kolbe type in methanolic solutions of acetates and salts of dicarboxylic monomethyl esters has been investigated.

The platinum dissolution rate was determined by radiochemical and gravimetric methods [1, 2] in flow-type glass cells at 30 ± 0.5°C. The reference electrode was a palladium half-cell which had been saturated with hydrogen in a 3 N aqueous solution of perchloric acid or an aqueous saturated calomel electrode. Replacement of the water in these half-cells with methanol did not lead to any appreciable change in the measured potential. All the potentials are referred to the normal hydrogen electrode.

The platinum dissolution rate (i_{Pt})* in methanolic acetate solutions and in the region where the Kolbe synthesis occurs depends little on the potential and only increases an order of magnitude when the potential is charged from 2.0 to 2.8 V; it is also practically unaffected by the presence of acetic acid in the solution (Fig. 1). Attention is also drawn to the similarity in form between the partial platinum dissolution curves (1 and 2) and the overall anodic curves (3 and 4), which was observed earlier in aqueous solutions of inorganic acids [3].

Comparison shows that the platinum dissolution rate at $\varphi \geq 2.0$ V is 10-40 times greater in aqueous acetate solutions [1] than in methanolic solutions, and the sharpest change in i_{Pt} (as shown by experiments with mixed aqueous methanolic solutions) occurs at low concentrations of the second solvent (Fig. 2). Small additions of other alcohols (2 mole/liter) to aqueous solutions leads to the same changes in i_{Pt} as additions of methanol (Table 1).

TABLE 1. Dissolution Rate (i_{Pt}) and Current Yield of Platinum ($A_{Pt} = i_{Pt} \cdot 100 / i_a$ %) at φ = 2.85 V in Aqueous Solutions of 1.5 N Sodium Acetate and 1.5 N Acetic Acid in the Presence of Alcohols

Alcohol (2 mole /liter)	i_{Pt}, μA/cm²	$A_{Pt} \cdot 10^{-3}$, %
Methyl.....	3.5	1.6
Ethyl.....	3.6	1.5
Propyl.....	3.6	1.6
Ethylene glycol	3.6	1.7
Glycerol	3.5	1.8

The platinum dissolution rate in the industrially important methanolic solutions of monomethyl glutarate and adipate differs little from i_{Pt} in methanolic acetate solutions (Fig. 1).

As in the case of acetate solutions, addition of water (5%) to a methanolic electrolyte containing glutaric and adipic mono esters leads to an increase in i_{Pt}. At the same time, as shown by experiments carried out under galvanostatic

* In the calculation of i_{Pt} it was assumed that the platinum passes into solution with the removal of four electrons.

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TABLE 2. Dependence of i_{Pt} and $A_{Pt} = i_{Pt} \cdot 100/i_a$ % in Methanolic Solutions of 1.5 M $CH_3OOC(CH_2)_nCOOH$ + 0.5 M $CH_3OOC(CH_2)_nCOONa$ on Magnitude of n, with $i_a = 5 \cdot 10^{-2}$ A/cm^2.

n	2	3	4	5	6	7	8
$i_{Pt} \cdot 10^{-7}$, A/cm^2	2,1	1,5	1,6	3,2	$\leqslant 5,6$	2,7	3,2
$A_{Pt} \cdot 10^{-4}$, %	6,8	4,9	5,2	10,0	$\leqslant 18,0$	8,8	10,0

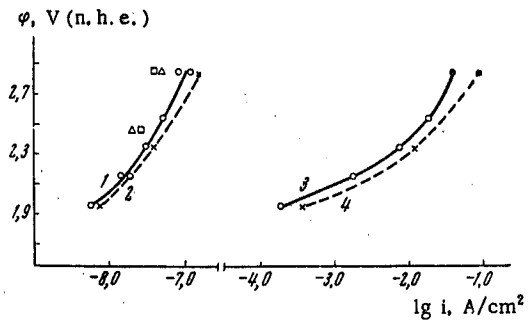

Fig. 1

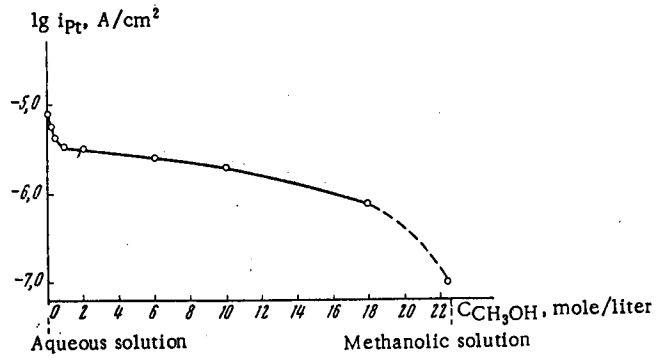

Fig. 2

Fig. 1. Dependence of i_{Pt} (1, 2) and rate of overall anodic process i_a (3, 4) on potential: 1) and 3) In methanolic solution of 0.86 M sodium acetate +0.86 M acetic acid; 2) and 4) in methanolic solution of 0.86 M sodium acetate; Δ) in methanolic solution of monomethyl glutarate; □) in methanolic solution of monomethyl adipate.

Fig. 2. Platinum dissolution rate in aqueous methanolic acetate solutions (1.5 M sodium acetate + 1.5 M acetic acid) at $\varphi = 2.85$ V.

conditions, change in the chain length of the original monoester has no substantial effect on the magnitude of i_{Pt} (Table 2).

Unsaturated compounds of the butadiene type are capable of being adsorbed on platinum at high anodic potentials [4, 5]. It is natural to assume that such adsorption can be reflected in the magnitude of i_{Pt}. However, experiments carried out in methanolic acetate solutions at $\varphi > 2.5$ V with additions (0.08 mole/liter) of benzene, naphthalene, cyclohexene, isoprene, styrene, and nonyl and allyl alcohols did not give any substantial deviations in the values of i_{Pt} and $A_{Pt} = i_{Pt}/i_a$ compared with the acetate electrolyte without additions.

It follows from the results that water has a deciding effect on the platinum dissolution process in the region of potentials corresponding to the Kolbe synthesis. This conclusion confirms the proposal which we made earlier about the determining effect of the composition and properties of surface oxygen compounds of platinum on its anodic dissolution. In fact, under conditions where the formation of surface oxide layers is difficult (in methanolic solutions), i_{Pt} is extremely low and increases sharply on the addition of even small quantities of water. Here account should also be taken of the fact that the investigations in the methanolic electrolytes (without additions of water) were carried out in air, and the working solutions contained 0.1-0.5% water in spite of the careful dehydration of the original components. This amount of moisture could be sufficient to form an oxide film during the polarization process. According to the available published data [6], even the slight amounts of moisture which are adsorbed on the walls of the electrolytic cell are sufficient to form oxygen compounds of platinum on the surface.

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