A POLAROGRAPHIC STUDY OF ANODIC PEAKS OF COBALT IN THIOGLYCOLIC ACID MEDIUM

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Four anodic peaks are formed on the anodic polarization curves of solutions of thioglycolic acid in an ammonia buffer containing cobalt. It is however necessary to form a suitable electrode deposit by preelectrolysis in a certain narrow potential range, in order to obtain the anodic peaks. Three of the peaks have been ascribed to oxidation of metallic cobalt.

Polarography of systems containing thioglycolic acid has been studied by many authors[1-3]. It was found that if thioglycolic acid (TGA) is present in a buffered solution containing cobaltous ions, the overvoltage of the hydrogen evolution is lowered. The formation of the Brdička catalytic maximum and of the catalytic hydrogen currents, designated by Kolthoff and Mader[4] as A and B, has already been observed on a dropping mercury electrode.

In our previous paper[5] we dealt with the existence of anodic peaks on the anodic polarization curves of solutions containing some thiol compounds (cysteine, cystamine) and divalent cobalt. We found that a similar effect appears in the case of TGA. In this study we again used polarography on a hanging mercury drop electrode (HMDE).

EXPERIMENTAL

Equipment for HMDE according to Kemula (Radiometer, Copenhagen) was used in combination with an LP type polarograph and EZ 2 type pen recorder (Laboratorní přístroje, Prague). The charge passing during the anodic process was estimated by weighing the areas of the peaks. The thioglycolic acid (Reanal, Budapest), cobaltous chloride, ammonium chloride and ammonia (Lachema, Brno) were of analytical grade purity. The mercury used for filling the electrodes was purchased from Lachema, Brno and was labelled "for polarography". Stock solutions of 1M-NH_4Cl; 0·01M-$CoCl_2$ and 1M-NH_4OH were prepared. The solutions used for each determination were freshly prepared before every measurement. All experiments were carried out under nitrogen atmosphere at temperature 20 ± 1°C. The total volume of the solution was always 20 ml; the weight of the mercury drop was 3 mg. All potential values are referred to S.C.E.

RESULTS AND DISCUSSION

Anodic peaks, labelled A, A', B, B', appear on an anodic polarization curve of a solution containing 10^{-6}M-TGA in the Brdička solution (0·1M-NH_4Cl; 0·1M-NH_4OH;

0.001M-CoCl$_2$) which was recorded after electrolysis. Fig. 1 shows anodic polarization curves obtained at different potentials of preelectrolysis. The electrode deposit which is essential for the existence of peak A' is formed in potential range -0.83 to to -0.92 V, and in the ranges -0.89 to -1.38 V, -1.14 to -1.50 V, -1.10 to -1.38 V for peaks A, B', and B respectively.

In order to obtain further information we followed the dependence of the charge passing during anodic oxidation on the electrolysis time. We found that the charge increases with time to a limit, the value of which is $7.3 \cdot 10^{-5}$ C, $1.3 \cdot 10^{-4}$ C and $7.3 \cdot 10^{-5}$ C for peaks A', A and B respectively (electrolysed at the potential -0.89 V in the case of peaks A' and A, at -1.25 V for peak B). The value of the charge passing during the anodic process in the potential range of peak B' is $7.3 \cdot 10^{-5}$ C and does not change with the electrolysis time (electrolysed at -1.25 V). We further followed the change in charge as a function of cobalt concentration in the solution, after thirty seconds' preelectrolysis and with the same potentials as in the previous case. The results are very similar; the charge passing during oxidation increases with increasing cobalt concentration to a limit ($4 \cdot 10^{-5}$ C, $3 \cdot 10^{-5}$ C, $8 \cdot 10^{-5}$ C and $7.9 \cdot 10^{-5}$ C for peaks A', A, B and B' respectively).

Further experiments showed that the potential of the summits of the anodic peaks ($-E_p$) shifts with increasing TGA concentration to more negative values (electrolysed for 30 s at -0.89 V for peaks A and A' and at -1.25 V for peaks B and
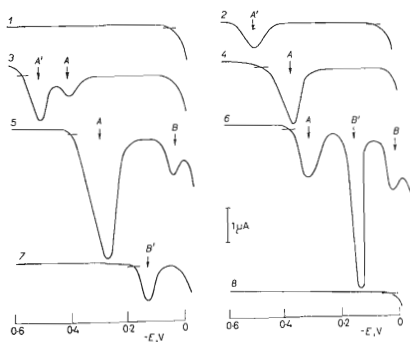

Fig. 1

Anodic Polarization Curves of the Brdička Solution Containing 10^{-6}M-TGA

Preelectrolysis 30 s at: *1* -0.80 V; *2* -0.83 V; *3* -0.89 V; *4* -1.00 V; *5* -1.12 V; *6* -1.25 V; *7* -1.145 V; *8* -1.60 V.

B'). At higher concentrations the potential of the summit of the anodic peaks A and A' coincides very nearly with the standard redox potential of the Co°/Co^{2+} system (-0.525 V vs S.C.E. ref.[6]):

[TGA] . 10^6M	0.5	1	5	10	50	100
$-E_{p,A'}$, V	0.40	0.50	0.52	0.53	0.55	0.55
$-E_{p,A'}$, V	0.35	0.40	0.45	0.45	0.50	0.50
$-E_{p,B'}$, V	0.18	0.20	0.26	0.26	0.28	0.28
$-E_{p,B'}$, V	0.02	0.05	0.05	0.05	—	—

The anodic peaks labelled A', A, B' and B are a new phenomenon in polarographic studies of systems containing TGA and divalent cobalt in a buffered solution. Peaks A', A and B are similar to the peaks produced by cysteine and cystamine[5]. The charge passing during the anodic process increases both with the time of electrolysis and the concentration of cobaltous ions in solution. The shape of curves is typical for inversion voltametric techniques[7]. These peaks therefore most likely correspond to anodic oxidation of metallic cobalt on the electrode shown in our previous paper[5]. The greater number of anodic peaks may be explained by the presence of various cobalt complexes in the solution[8].

Peak B' is an exception among these peaks (A and B in cysteine, one peak in cystamine, peaks A, A', B and B' in TGA). It is exceptional in that it reaches the limit value of charge with relatively short times of preelectrolysis. To explain this phenomenon, which seems to be of a catalytic nature, further study is required.

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