POLAROGRAPHIC INVESTIGATION OF THE SYSTEM Co(II)–THIOL WITH RESPECT TO ANODIC DISSOLUTION OF DEPOSITED COBALT

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The existence of anodic peaks of oxidation of metal cobalt depends on the presence of thiols in the solution, and on the formation of a suitable electrode deposit of cobalt in a narrow range of potentials in the vicinity of $-1 \cdot 0$ V (s.c.e.). A mechanism of the anodic oxidation of cobalt deposited on the electrode was suggested. Photographs taken of the drop of mercury give evidence of a solid phase of cobalt being deposited.

For many years now, systems containing Co(II) and several thiols (*e.g.* cysteine) in buffered solutions have been investigated with respect to the catalytic evolution of hydrogen first reported by Brdička[1]. Aside from the mercury dropping electrode, the hanging mercury drop electrode (HMDE) was used by Kalous[2] and Březina[3] for investigating catalytic currents. The properties of deposited cobalt were studied by Hovsepian and Shain[4], those of deposited nickel by Kemula, Jeftić, and Galus[5]. Contrary to Ivanov and Iofa[6] and Astley and Harrison[7], who assumed a solid cobalt existing on the electrode, the former authors[4,5] postulated the formation of a cobalt amalgam.

The present paper is devoted to investigating the properties of cobalt deposited electrolytically from the system Co(II)–thiol, using the HMDE.

EXPERIMENTAL

An equipment for the HMDE after Kemula (Radiometer, Copenhagen) was used in combination with an LP 60 type polarograph and an EZ 2 type recorder (Laboratorní přístroje, Prague). The mass of the mercury drop was $3 \cdot 0$ mg. Measurements were made in a nitrogen atmosphere in a vessel with a separated saturated calomel electrode (S.C.E.) to which all potential values are referred. A Kalousek switch combined with a mercury dropping electrode of $2 \cdot 82$ s dropping time and $2 \cdot 94$ mg/s flow rate, and two LP 60 type polarographs and an EZ 2 type recorder were used.

All chemicals used, cysteine hydrochloride (Výzkumný ústav sér a očkovacích látek, Prague), cystamine dihydrochloride (Labaz, Brussels), cobalt(II) chloride, ammonium chloride, and ammonium (Lachema, Brno) were of reagent grade. The mercury used for filling the electrodes was labelled "for polarography" (Lachema, Brno). Stock solutions of 1M-NH$_4$Cl, 0·1M-CoCl$_2$, and 1M-NH$_4$OH were prepared, and from these a Brdička solution of 10^{-3}M-CoCl$_2$ + 0·1M-NH$_4$OH + 0·1M-NH$_4$Cl was freshly prepared before each determination.

RESULTS

Systems Co(II)–*Cysteine*

Four anodic peaks[8] (A, B, C, and D, Fig. 1) were observed on anodic polarization curves recorded after a preceding electrolysis of a solution containing cysteine in Br- dička solution at potentials corresponding to the summit of the cathodic peak of cobalt reduction. Anodic peaks C and D appear also on anodic polarization curves of a pure ammoniacal buffer solution, on anodic polarization curve obtained after a preceding electrolysis of cobalt from Brdička solution free of cysteine, and also on anodic polarization curve of a solution containing cysteine in Brdička solution (without preceding electrolysis).
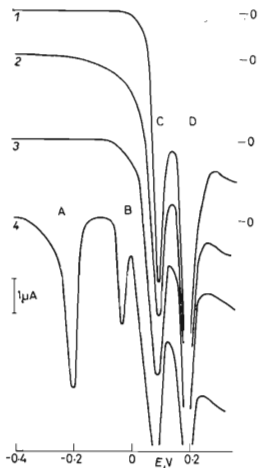

Fig. 1

Anodic Polarization Curves

1 Ammoniacal buffer ($1 . 10^{-1}$M-NH_4Cl, $1 . 10^{-1}$M-NH_4OH); *2* Brdička solution ($1 . 10^{-3}$M-$CoCl_2$ in ammoniacal buffer) after 30 s electrolysis at -1.20 V; *3* $1 . 10^{-6}$M cysteine in Brdička solution; *4* $1 . 10^{-6}$M cys- teine in Brdička solution after 30 s electrolysis at -1.15 V.
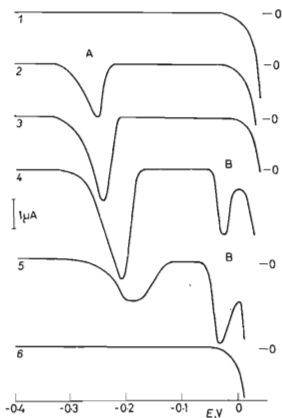
Fig. 2

Anodic Polarization Curves of Solution Con- taining $1 . 10^{-6}$M Cysteine in Brdička Solu- tion

Pre-electrolysis 30 s at potential: *1* -1.00 V; *2* -1.05 V; *3* -1.10 V; *4* -1.14 V; *5* -1.16 V; *6* -1.20 V.

Anodic peaks C *and* D. The dependence of the height of peak C on the concentration of individual components of a pure ammoniacal buffer solution was followed. The height of peak C was found to increase linearly with ammonium concentration; no change was registered in dependence on ammonium chloride concentration. As reported in the literature[9], a hydroxocomplex Hg^{2+} appears in the potential region of peak C, and in the region of peak D mercurous chloride was observed; this is in agreement with observations made on the mercury drop whose surface became dull at potentials corresponding to peak D as it got covered with a grey layer of the forming precipitate.

Formation of peaks A *and* B. A series of investigations revealed that anodic peaks A and B appear only after an electrode deposit has been formed in the potential region of approximately -1.0 to -1.3 V. By scanning this region (Fig. 2) it was found that the electrodeposit which induces peak A is produced in a narrow range of potentials -1.05 to -1.18 V, and in the region -1.11 to -1.18 V another deposit is formed which may be oxidized at potentials corresponding to peak B.

Kalousek switch. The existence of anodic currents was further verified with a Kalousek switch on a dropping mercury electrode. During the first experiment, (arrangement I) the auxiliary potential was set to -1.15 V and the polarographic curve was registered (Fig. 3a). A well-defined anodic wave with a visible diffusion current was obtained; compared to experiments made with the HMDE, no distribution corresponding to anodic peaks A and B was obtained. In arrangement II, anodic current at a chosen potential is registered (here -0.20 V), the auxiliary potential varying continuously during the experiment. The experiment confirmed (Fig. 3b) that a system which is capable of oxidation is produced only in a narrow range of potentials.
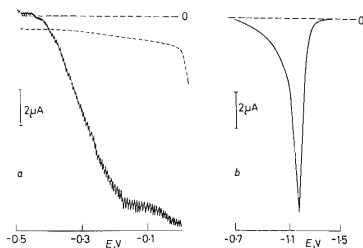

FIG. 3

Measurements with Kalousek Switch on a Dropping Mercury Electrode

a Arrangement I, Auxiliary potential -1.15 V; $1 . 10^{-5}$M cysteine; $1 . 10^{-3}$M-CoCl$_2$; 0.1M-NH$_4$OH; 0.1M-NH$_4$Cl. *b* Arrangement II. Auxiliary potential from -0.7 to -1.5 V, anodic current registered at -0.20 V. The same solution as that in Fig. 3a.

Dependence of the charge involved in anodic oxidation on the time of electrolysis of cobalt. For both peaks, the course of the dependence is analogous and tending to a limit (for peak A at $1\cdot8 . 10^{-4}$C, and for peak B at $0\cdot7 . 10^{-4}$ C). Electrolyses above 90 s make the peaks coincide and no separation is possible. For this reason, the dependence of the overall oxidation charge of cobalt in the potential region of both the peaks was followed. This dependence points to the limiting nature of the process. The limiting nature is also apparent from the dependence of the charge of cobalt oxidation on the concentration of cobalt in the solution. For peak A, the limiting value is approximately $4 . 10^{-4}$ C and for peak B $1 . 10^{-4}$ C. For peak A, the dependence of the charge on the cobalt concentration is linear in the concentration range $2\cdot5 . 10^{-4}$ to $1\cdot25 . 10^{-3}$, which makes the peak suitable for quantitative estimation by stripping voltammetry.

The effect of deposit ageing. The cobalt deposited at $-1\cdot15$ V was kept at $-0\cdot4$ V for a period of time and then oxidized anodically. The quantity of metal which was capable of oxidation at the potential of peak A fell during the first two minutes to 60% (to $1\cdot5 . 10^{-4}$ C) and remained unchanged afterwards.

The dependence of potential of anodic oxidation (E_p) on concentration of cysteine in the solution. Cobalt was deposited at the potential of the summit of the anodic peak of reduction of Co(II) ions. This deposit was then anodically dissolved. The results obtained are summarized in the following table:

Thiol. concentration ($c . 10^6$M)	0·5	1	5	10	20	30	50
$-E_p$, V (cysteine)	0·05	0·05					
		0·20	0·30	0·47	0·47	0·47	0·47
$-E_p$, V (cystamine)	0·32	0·40	0·43	0·44	0·47	0·47	0·45

System Co(II)–Cystamine

Systems containing cystamine $(H_2N.CH_2.CH_2.SS.CH_2.CH_2.NH_2)$ are, to a large extent, analogous to systems containing cysteine. A deposit capable of oxidation also forms on the electrode in a narrow potential region of $-0\cdot95$ to $-1\cdot175$ V. Contrary to cysteine, only one peak corresponding to anodic oxidation appears on the anodic polarization curves. The dependence of the quantity of charge involved in the anodic oxidation on the time of the electrolysis of cobalt and on the concentration of cobalt in the solution tends to limit which in both cases amounts to approximately $2\cdot5 . 10^{-4}$ C. The anodic oxidation potential of the electrode deposit shifts to more negative potentials as the cystamine concentration increases. The results are tabulated.
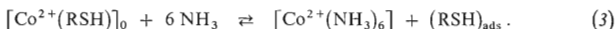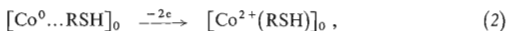
DISCUSSION

Anodic peaks A and B appearing on polarization curves of solutions containing Co(II) and cysteine or cystamine in buffered solutions have so far not been reported in literature although Brdička catalytic currents of these systems have long been known. The dependence of the charge involved in the oxidation on both the electrolysis time and the Co(II) ion concentration implies that peaks A and B correspond to anodic dissolution of cobalt.

Similar anodic peaks of cobalt have been reported by Kemula and Galus[10] in a potassium chloride supporting electrolyte in connection with utilization of the HMDE. Experiments more similar to those reported in the present paper were made by Hovsepian and Shain[4]. These authors deposited cobalt on the HMDE from solutions containing pyridine in a large excess. They also studied the dependence of the behaviour of the anodic peak of cobalt (at -0.2 V) on the potential at which they changed the sense of polarization during cyclic voltammetry. The anodic peak disappeared when the potential reached the region of catalytic evolution of hydrogen. A similar phenomenon was observed by Ivanov and Iofa[6] in the case of anodic peaks of Co and Ni in solutions containing excess quantities of chlorides.

In contrast to these observations, anodic peaks A and B are produced at very low cysteine and cystamine concentrations (10^{-6}M), a thousand times lower than that of cobalt. Besides that, peaks A and B exhibit an important selectivity with respect to potential. The fact that only part of cobalt deposited during the pre-electrolysis in a narrow range of potentials undergoes oxidation points to the influence of various complex compounds of two-valent cobalt with cysteine and/or cystamine present. It is known[8,11,12] that deposition of cobalt (in potential regions of -0.95 to -1.20 V) is catalyzed by organic catalyst molecules e.g. cysteine present in the solution. This region shows good agreement with the potential region observed by us, in which a cobalt deposit capable of anodic oxidation was formed. The anodic peaks evidently correspond to a "catalytically deposited cobalt", i.e. to cobalt which was deposited in a catalytic way, and at a lower overpotential. At more negative potentials, cobalt is reduced also from other complexes, in the first place from an ammoniacal one. The concentration of cysteine being low, the major part of cobalt ions is present in the ammoniacal complex. The "ammoniacal cobalt" formed during reduction is not anodically dissolved as was shown by experiments with pure (cysteine free) Brdička solution (Fig. 1, curve 2). Also, another electrode reaction may be of importance, namely the reduction of hydrogen; its influence may increase with the shift of potential to more negative values.

When discussing the mechanism of anodic oxidation a complex of metal with thiol $[Co^0...RSH]$ will be postulated. The possibility of the existence of such complexes was studied by Vlček[13] and employed to explain the catalytic Brdička reaction by Kolthoff and Mader[14]. Following equation (1) the complex on the electrode is in equilibrium with its components. Complex $[Co^0...RSH]$ can, in contrast to cobalt

deposited from an ammoniacal buffer solution in the absence of thiol, be oxidized at potentials more negative than that of dissolution of mercury. With two electrons remaining on the electrode, a complex ion $[Co^{2+}(RSH)]$ (reaction (2)) is formed. As a consequence of a large surplus of ammonium (usually one hundred thousand fold) an exchange of ligands takes place and thiol is set free to participate in the formation of a metal cobalt complex:

$$Co_0^0 + (RSH)_{ads} \rightleftarrows [Co^0...RSH]_0, \qquad (1)$$

$$[Co^0...RSH]_0 \xrightarrow{-2e} [Co^{2+}(RSH)]_0, \qquad (2)$$

$$[Co^{2+}(RSH)]_0 + 6\,NH_3 \rightleftarrows [Co^{2+}(NH_3)_6] + (RSH)_{ads}. \qquad (3)$$

RSH stands for a molecule of thiol, the subscript o stands for the electrode surface. Aside from this, a strong adsorption of cysteine[12] on the electrode surface shifts the equilibrium in equation (3) to the right-hand side. In the presence of thiocompounds, a situation on the electrode arises, where the deposited cobalt is in a permanent equilibrium with the complex $[Co^0...RSH]$ and it consequently is not fully available to take place in the formation of a metal lattice. It is also possible that the formation of the metal lattice accounts for the decrease of the quantity of dissolved cobalt with time in the potential region of peak A.

To verify the mechanism given above two experiments were made. The first one was aimed at proving the necessity of the presence of thiol from the very start, namely during the deposition of metal cobalt. Cobalt was deposited from an ammoniacal buffer solution free of cysteine which was added only after the electrolysis. No anodic oxidation took place in this case. The other experiment consisted in first electrolysing a suitable deposit of cobalt from a solution containing thiol and in exchanging the initial solution for a solution containing cysteine in an ammoniacal buffer solution, or for a pure ammoniacal buffer, in either case free of cobalt ions. The mercury drop was rinsed with distilled water. In either case anodic peaks of cobalt oxidation were again recorded.

The shift of the anodic peak to more negative potentials taking place at increasing concentrations of thiols points to its participation in the mechanism of cobalt dissolution. An increase in the concentration of thiol thus facilitates the dissolution of cobalt. The occurrence of two anodic peaks may be due to various species of cobalt depositing on the electrode, or to various species of the complex $[Co^0...RSH]$.

The present discussion postulates a solid phase of cobalt deposit forming in mercury under the given experimental conditions. This postulate is supported by results of Astley and Harrison[7], and by our own observations of the mercury drop. Cobalt was electrolyzed two minutes (at -1.20 V) from 0.1M aqueous solution of $CoCl_2$ in the presence and absence of cysteine (cysteine concentration was 10^{-6}M).

In the case of absence of cysteine, formation of metallic cobalt clusters was observed but in the presence of cysteine, traces of rust-coloured coating of cobalt appeared on the electrode surface. The cobalt coating was then completely dissolved at the potentials of anodic peaks.

REFERENCES

1. Brdička R.: This Journal *8*, 366 (1936).
2. Kalous V. in the book: *Advances in Polarography* (I. S. Longmuir, Ed.), Vol. 2, p. 924. Pergamon Press, London 1960.
3. Březina M.: Cit. 2, p. 921.
4. Hovsepian B. K., Shain I.: J. Electroanal. Chem. *12*, 397 (1966).
5. Kemula W., Jeftić L., Galus Z.: J. Electroanal. Chem. *10*, 387 (1965).
6. Ivanov V. F., Iofa Z. A.: Dokl. Akad. Nauk SSSR *140*, 1368 (1961).
7. Astley D. J., Harrison J. A.: Electrochim. Acta *15*, 2007 (1970).
8. Anzenbacher P.: *Thesis*, Charles University, Prague 1971.
9. Heyrovský J., Kůta J.: *Základy polarografie*. Published by Nakladatelství ČSAV, Prague 1962.
10. Kemula W., Galus Z.: Bull. Acad. Pol. Sci., Ser. Sci. Chim., Geol., Geograph. *7*, 729 (1958).
11. Zielinski M., Kůta J.: *Prinzipen in der Molekularen Biologie*, III. Jenaer Symposium 1965, Akad. Verlag, Berlin 1966.
12. Mader P., Kolthoff I. M., Khalafalla S. E.: J. Electroanal. Chem. *18*, 315 (1968).
13. Vlček A. A.: Z. Elektrochem. *61*, 1014 (1957).
14. Kolthoff I. M., Mader P.: Anal. Chem. *42*, 1762 (1970).