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POLAROGRAPHIC BEHAVIOUR OF SOME COBALT(III) COMPLEXES WITH ETHYLENEDIAMINE

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Abstract

The polarographic behaviour of various cobalt(III)–amine complexes with ethylenediamine were studied in Britton–Robinson buffer solutions and also in the presence of 1,2-cyclohexane dione dioxime. It was observed that the cobalt(III)–amine complexes, generally, are reduced in two steps. The first wave (Co(III) → Co(II)) has an irreversible character, the second one corresponds rather to a Co(II)–ligand → Co(0) step, than to a $[Co(H_2O)_6]^{2+}$ → Co(0) reduction, as presumed earlier. In the presence of dioximes the hexamine and monoacidopentamine type cobalt(III) complexes do not undergo substitution reactions under the above mentioned experimental conditions.

Keywords: polarographic behaviour of ethylene-diamine-cobalt (III) complexes.

Introduction

The reduction of various cobalt(III)–amine complexes with ammonia and various chelating agents on the dropping mercury electrode in aqueous solutions [1 – 4] and in some organic solvents [5] was the subject of some papers. The classical hexamine complex: $[Co(NH_3)_6]Cl_3$ presents two waves, the first corresponding to a monoelectronic — and the second one to a bielectronic process. The height of the second wave is twice that of the first one.

$$[Co(NH_3)_6]^{3+} + e = [Co(NH_3)_6]^{2+} \,, \qquad (I)$$

$$[Co(NH_3)_6]^{2+} + 2e = Co + 6NH_3 \,. \qquad (II)$$

The polarographic reduction of a great number of amine complexes ($[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5X]^{n+}$ (X = H_2O, Cl, Br, NO_2, NCS, etc., $[Co(NH_3)_4X_2]^+$, $[Co(NH_3)_3(NO_2)_3]$, etc.) was studied in various supporting electrolytes, and also in the presence of capillary active substances [1 – 3]. The $E^{I}_{1/2}$(Co(III) → Co(II) varies between −0.03 – 0.47 V (vs.

SCE). In some cases differences are observed in the $E_{1/2}$ values of the geometric isomers, too, e. g. cis–$[Co(NH_3)_4(NO_2)_2]^+$ ... −0.04 V, trans–$[Co(NH_3)_4(NO_2)_2]^+$ ... −0.21 V (vs. SCE). For the optical isomers of the cobalt(III) chelates the $E^I_{1/2}$ — values are identical.

Willis [2] presumed the formation of $[Co(H_2O)_6]^{2+}$ after the Co(III) → Co(II) step.

The majority of the mentioned amine complexes present approximately the same value for $E^{II}_{1/2}$ (Co(II) → Co(0), i. e. −1.28 V (vs. SCE).

$$[Co(NH_3)_{6-n}X_n]^{3-n} + 6H_2O + e = [Co(H_2O)_6]^{2+} + (6-n)NH_3 + nX^- .$$

The $[Co(H_2O)_6]^{2+}$ is reduced to Co(0).

This presumption is in disagreement with the $E_{1/2}$ value of the reduction step of $[Co(H_2O)_6]^{2+}$ (i. e. −1.43 V vs. SCE), which is by −0.14 V more negative than the $E^{II}_{1/2}$ values of the above mentioned cobalt(III) amine complexes [6].

Yamaoka [4] observed that the first reduction step Co(III) → Co(II) is totally irreversible and the rate of the charge transfer at the dropping mercury electrode cannot be determined polarographically.

The polarographic behaviour of some 1,2– and 1,6–$[Co(en)_2X_2]^+$ type complexes (X = Cl, NCS, NO_2, CO_3, acetate) in various supporting electrolytes was studied by Kékedy et al. [7], Maki et al. [8] and Carunchio [9].

The polarographic reduction of cobalt(III) chelates with aliphatic di- and triamines [10, 11], with heterocyclic diamines [12], with terpyridyl [13], and with tetradentate Schiff bases leads, generally, to the formation of two waves.

In the case of $[Co(C_2O_4)_3]^{3-}$ and $[Co(EDTA)(H_2O)]^-$ only the Co(III) → Co(II) reduction step appears. The cyanocomplexes $[Co(CN)_5(H_2O)]^{2-}$ and $[Co(CN)_5X]^{3-}$ are reduced in a bielectronic process to Co(I), in a single, irreversible wave [14 – 16].

Results and Discussion

In the present paper a comparative study of the reduction on the dropping mercury electrode of some ethylenediamine complexes of cobalt(III) at various pH values was carried out. The polarograms were taken in Britton–Robinson buffers as well as in borax buffer solution. The polarograms of $[Co(en)_3]Cl_3$ as compared with those of $[Co(NH_3)_6]Cl_3$ are presented in *Fig. 1.*

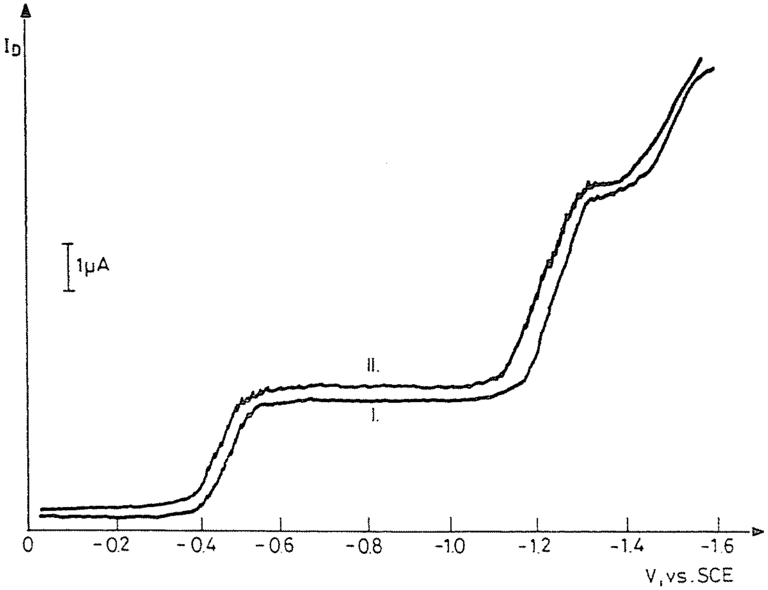

Fig. 1. Polarogram of $[Co(en)_3]Cl_3$: (I) $[Co(NH_3)_6]Cl_3$: (II). Conc. $4 \cdot 10^{-4}$ mol/l, Britton–Robinson soln. pH = 4.10 gelatine: 0.12%

As seen, the polarograms present two waves, with approximately identical $E^{I}_{1/2}$ and $E^{II}_{1/2}$ values. The height of the second wave is twice that of the first one, indicating a bielectronic reduction process. The second $E^{II}_{1/2}$ is more positive than the value for hydrated Co(II) ($[Co(H_2O)_6]^{2+}$).

Therefore we can presume that this step corresponds to the reduction of a complexed form of the Co^{2+}-ion.

The polarograms of a series of bis-ethylenediamine – cobalt(III) complexes of the monoacido-pentamine type: cis-$[Co(en)_2X(Am)]^{2+}$ were also recorded at various pH values (ph = 1.8, 2.56 ... 11.70).

It was observed that in acidic media only a single well formed wave appears with $E_{1/2} = -1.24$ V (vs. SCE). This wave seems to have a more reversible character than the $[Co(H_2O)_6]^{2+} \rightarrow Co(0)$ step. The half-wave potential $E^{II}_{1/2}$ is practically independent of the composition of the $[Co(en)_2X(Am)]^{2+}$ type cations and is equal to that of the second wave of $[Co(en)_3]^{3+}$. With increasing pH this potential is shifted towards more negative values.

Comparing the height of this wave with the composition of different $[Co(en)_2XY]^{n+}$ type complexes, one can consider that the polarographic step mentioned is the result of the Co(II)compl → Co(0) reduction.

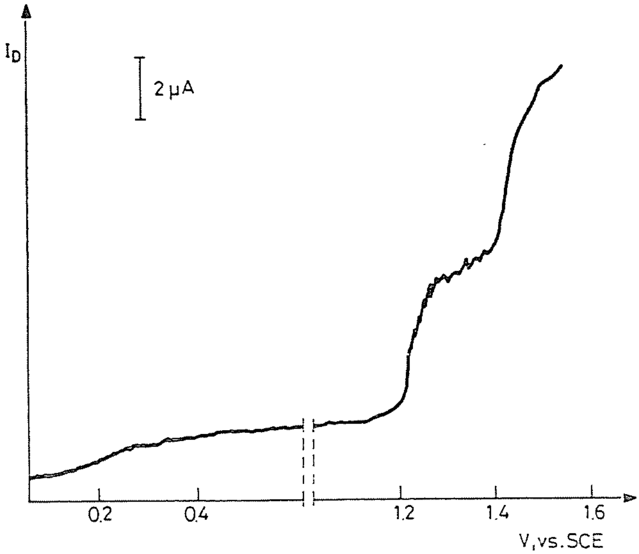

Fig. 2. Polarogram of cis-$[Co(en)_2Cl(\gamma\text{-picoline})](ClO_4)_2)$. Conc. $4 \cdot 10^{-4}$ M/l, Britton–Robinson soln., pH = 4.10

As for the Co(III) → Co(II) step, this appears on the polarograms of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ at -0.4 – 0.6 V (vs. SCE) depending on the pH-value of the supporting electrolyte.

In the case of the bis-ethylenediamine derivatives this wave can be observed only in alkaline solutions (e. g. pH = 11.7).

One can presume that in the case of $[Co(en)_2XY]^{n+}$ type complexes the $E^{I}_{1/2}$ values of the first reduction steps are shifted towards more positive potential values as compared to that of the $[Co(en)_3]^{3+}$, up to 0 … −0.1, 0.2 V (vs. SCE), corresponding to the anodic dissolution wave of mercury. This overlaps the Co(III) → Co(II) reduction wave.

An analogous phenomenon was also observed in some cases for the $[Co(NH_3)_nX_{(6-n)}]^m$ derivatives (X = Cl, Br).

The polarographic behaviour of some hexamine type complexes ($[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$) was studied also in the presence of a water-soluble α–dioxime, 1,2-cyclohexane dione dioxime (nyoxime). In this case, as supporting electrolyte, borax solution was used. (In Britton–Robinson solutions slightly soluble $[Co(en)_3]PO_4$ and $[Co(NH_3)_6]PO_4$ are formed.).

The polarograms of $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ in the presence and absence of nyoxime are presented in *Fig. 5.*

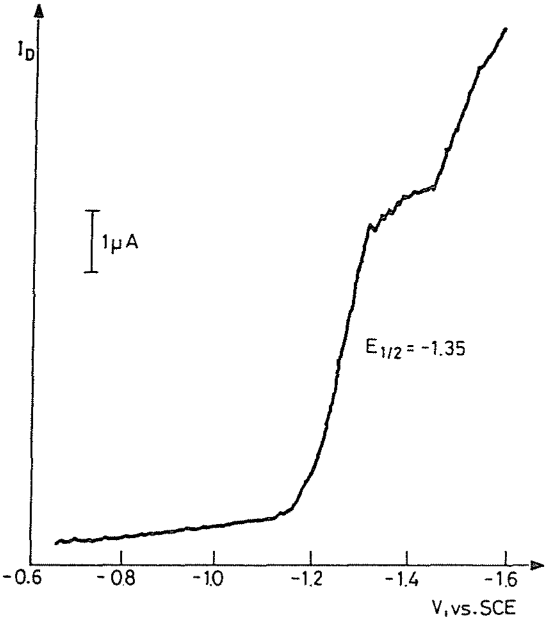

Fig. 3. Polarogram of cis-[Co(en)$_2$Cl(benzylamine)](N0$_3$)$_2$. Conc. 4·10^{-4} M/l, Britton–Robinson soln., pH = 11.70

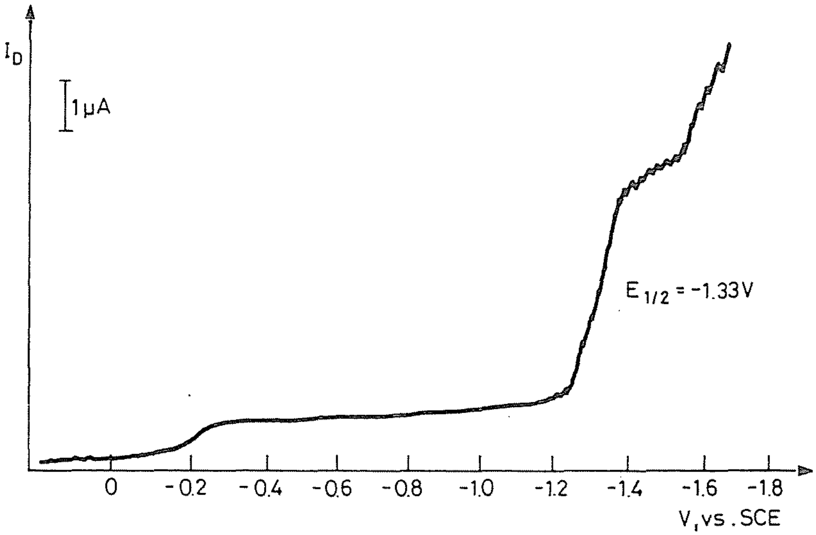

Fig. 4. Polarogram of cis-[Co(en)$_2$Cl(o-toluidine)]Cl$_2$. Conc. 4 · 10^{-4} M/l, Britton–Robinson soln. pH = 11.70

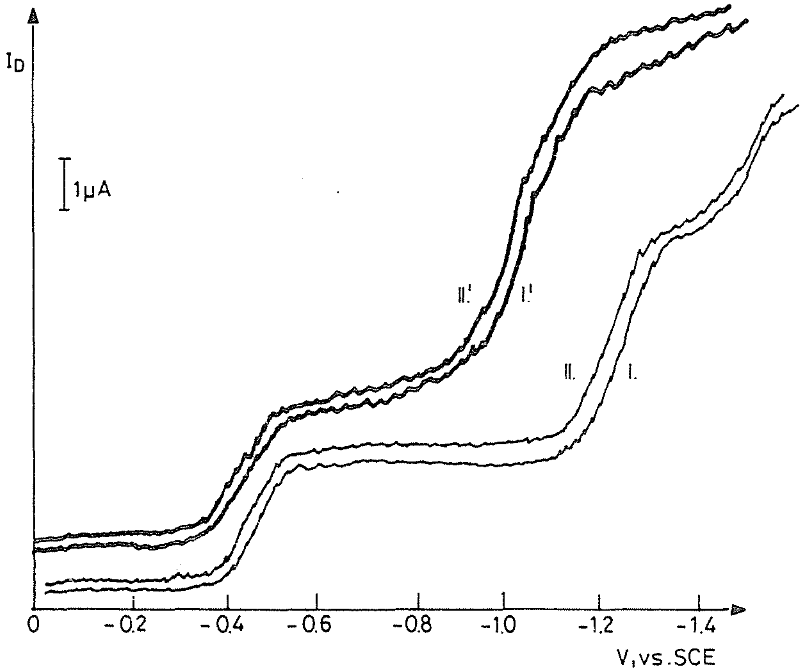

Fig. 5. Polarograms of $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ in the absence (I, II) and in the presence of nyoxime (I', II ')

As seen, the $E^{I}_{1/2}$ values of the first waves are approximately equal, independent of the presence or the absence of dioxime. The $E^{II}_{1/2}$ value of the second wave (Co(II) compl → Co(0) is shifted towards more positive values (−1.1 - 1.15 V (vs. SCE)), in comparison with $[Co(en)_3]^{3+}$ and $[Co(en)_2XY]^n$ type complexes (−1.24 - 1.25 V (vs. SCE)). The height of the second wave is much higher in the presence of oxime. This phenomenon shows that the $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ are not engaged in substitution reactions. The reduced $[Co(NH_3)_6]^{2+}$ and $[Co(en)_3]^{2+}$ take part in a rapid substitution process, probably with the formation of $[Co(oxime)_3(NH_3)_2]$ and $[Co(oxime)_2(en)]$, respectively.

The formed Co(II) mixed complexes are reduced at the dropping mercury electrode together with the coordinated oxime ligands in a multielectronic parallel process.

Table 1
Polarographic data on the reduction of some cobalt(III)-complexes

Formula	Buffer	Conc. $M/l \cdot 10^4$	$E^{I}_{1/2}$	I^{I}_{D} uA	$E^{II}_{1/2}$	I^{II}_{D} uA
$[Co(NH_3)_6]Cl_3$	(borax)	2	-0.49	2.1	-1.24	4.2
$[Co(en)_3]Cl_3$	(borax)	2	-0.50	2.2	-1.26	4.3
		8		5.24		10.3
trans-$[Co(en)_2Cl_2]Cl$		2	-0.1	—	-1.23	2.72
	B.R.	8		—		11.05
cis-$[Co(en)_2Cl$-		2	-0.1 - 0.2	—	-1.24	2.69
pyridine$]Cl_2$	B.R.	8		—		10.80
cis-$[Co(en)_2Cl$-		2	-0.1 - 0.2	—	-1.24	2.63
γ-picoline] $(ClO_4)_2$		8		—		10.62
cis-$[Co(en)_2Cl$-						
(o-toluidine)$]Cl_2$	B.R.	2	-0.1 - 0.2	—	-1.24	2.60
		8		—		10.40
cis-$[Co(en)_2Cl$-		4				
(benzylamine)$](NO_3)_2$	B.R.					
pH 1.81		4	-0.05 - 0.2	—	-1.18	5.10
2.56				—	-1.20	5.20
4.10				—	-1.24	5.25
6.80				—	-1.24	5.25
9.0				—	-1.30	5.30
11.70				—	-1.35	5.30

B.R. — Britton–Robinson solution pH = 4.10

Experimental

Synthesis of cis-$[Co(en)_2Cl(amine)]X_2$ (X = Cl, ClO_4, NO_3) 28.5 g (0.1 mole) of trans-$[Co(en)_2Cl_2]Cl$ in 60 – 80 ml water is treated with 0.11 mole of amine in 15 – 25 ml alcohol. Under continuous stirring (4 – 6 hours) the green solution becomes gradually violet-red. After standing about 24 h the solution is diluted with 100 – 150 ml water, filtered and treated with an excess of solid NaCl ($NaNO_3$ or $NaClO_4$). Red crystals of cis-$[Co(en)_2Cl(amine)]X_2$ are filtered off, washed with a little ice water and dried in air. Yield: 40 – 50%.

For the assignment of geometrical configurations we used the IR absorption spectra of the cobalt-ethylenediamine ring systems. BALDWIN [17] observed that the most consistent differences between the spectra of cis- and trans isomers of $[Co(en)_2XY]X$ appear in the CH_2-rocking region (i. e. 870 – 900 cm^{-1}). Here complexes with a cis-configuration show two bands, while those with trans-structure show one. The splitting of the IR band in this region arises from the lower symmetry of the cis isomer (trans-$[Co(en)_2Cl_2]Cl$: 888 cm^{-1}, cis-$[Co(en)_2Cl(pyridine)]Cl_2$: 899, 883; $[Co(en)_3]Cl_3$: 895, 873; cis-$[Co(en)_2Cl(benzylamine)]Cl_2$ 890, 879 cm^{-1}).

The *polarograms* were taken on a Radelkis–type OH–120 polarograph using a conventional polarographic cell with a saturated calomel reference electrode, connected to the cell by means of an agar-agar bridge (1 M KNO_3). The oxygen was eliminated from the solutions with purified methane. The dropping mercury electrode had a flow rate of 1.30 m·s^{-1} and a drop time of 5 sec in 0.10 M $NaClO_4$ solution and with a mercury reservoir height of 60 cm (at 20°C).

The supporting electrolytes were prepared from Britton–Robinson solutions (and satd. borax soln) with addition of $NaClO_4$ to ensure an ionic strength of 0.2 M. The maximum suppressor was 0.5% gelatine solution.

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