The Polarography of Ethylenediaminetetraacetato-Cobaltate(III) and Cobaltate(II) Complexes

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For analytical purposes the EDTA salts, $Na_2H_2\,edta \cdot 2H_2O$ and $Na_4\,edta \cdot 1/2\ H_2O$, have often been used as a masking or a complexing reagent in polarography.[1] However, there have been few reports on the relationship between the structure of EDTA complexes and their polarographic behavior in the absence of an excess $edta^{4-}$ ions.[2]

The present communication deals mainly with the polarography of EDTA cobalt(III) complexes of the $[Co^{III}\,edta\,X]$ type in the absence of an excess $edta^{4-}$ ion, where the unidentate ligand, X, denotes the ion, Cl^-, Br^-, NO_2^-, OH^- or OH_2.

The complex, $K[Co^{III}\,edta] \cdot 2H_2O$, was found to give rise to only one wave, corresponding to an acceptance of one electron, in a 0.5 F sodium sulfate solution at the dropping mercury electrode (DME). The wave was present in the positive region of the potential. The limiting current of the wave was proportional to the concentration of the complex in the range of $10^{-2} \sim 10^{-4}$ F and was diffusion-controlled.

The process of the electrode reaction was concluded to be as follows:

$$[Co^{III}\,edta]^- + e^- \rightarrow [Co^{II}\,edta]^{2-}$$

The cobalt(II) complex, $Na_2[Co^{II}\,edta] \cdot 3/2H_2O$, gave no reduction wave at all in a 0.5 F sodium sulfate solution without an excess $edta^{4-}$ ion.

The hexaquocobalt(II) chloride, $[Co^{II}(OH_2)_6] \cdot Cl_2$, also gave no reduction wave in the presence of 1/4 F sodium ethylenediaminetetraacetate at the DME.

The chloro-, bromo-, nitro- and hydroxo-ethylenediaminetetraacetato-cobaltate(III) complexes, $K_2[Co^{III}\,edta \cdot Cl] \cdot 3H_2O$, $Na_2[Co^{III}\,edta \cdot Br] \cdot 4H_2O$, $Na[Co^{III}\,edta(NO_2)] \cdot 3H_2O$, and $Na_2[Co^{III}\,edta(OH)] \cdot 3H_2O$,[3] were found to be irreversibly reduced in two steps to the metal through cobalt(II) complexes in a 0.5 F sodium sulfate solution at the DME.

The ratio of the height of the first wave to that of the second was roughly 1:2 for all the complexes. All the first waves existed in the positive region of potential except the hydroxo-complex. The limiting current of each wave was proportional to the concentration of the complex in the range between 10^{-4} and 8×10^{-3} F and was diffussion-controlled.

The nitro-EDTA cobalt(III) ion, $[Co\,edta \cdot (NO_2)]^{2-}$, was found to be reduced up to the cobalt(II) state in a 1 F potassium nitrite solution, not reduced to the metal. Therefore, the second wave obtained in a 0.5 F sodium sulfate solution is due to the reduction of the

TABLE I. HALF-WAVE POTENTIALS OF THE WAVES FOR THE EDTA COBALT(III) AND COBALT(II) COMPLEXES

Compound	$E_{1/2}$ of the 1st wave $Co(III) \rightarrow Co(II)$	$E_{1/2}$ of the 2nd wave $Co(II) \rightarrow Co(0)$	Supporting electrolyte
$Na_2[Co^{II}\,edta] \cdot 3/2H_2O$	——	No reduction	0.5 F Na_2SO_4 (25°C)
$K[Co^{III}\,edta] \cdot 3H_2O$	+	No reduction	0.5 F Na_2SO_4
$K_2[Co\,edta \cdot Cl] \cdot 3H_2O$	+	ca. −1.6	0.5 F Na_2SO_4
$Na_2[Co\,edta \cdot Br] \cdot 4H_2O$	+	−1.62	0.5 F Na_2SO_4, 0.0058% Triton X 100
$Na_2[Co\,edta\,(NO_2)] \cdot 3H_2O$	+	-1.05_6	0.5 F Na_2SO_4
	+	No reduction	1 F $NaNO_2$
$Na_2[Co\,edta\,(OH)] \cdot 3H_2O$	-0.10_3	-1.05_5	0.5 F Na_2SO_4 (0°C)*
$[Co^{II}(OH_2)_6]Cl_2$	——	No reduction	1/4 F Na_4 edta (25*C)

Voltage unit: V. vs. SCE. Concentration of the complex: 5×10^{-3} F

* The ion, $[Co\,edta\,(OH)]^{2-}$, is unstable in solution and tends to become the ion, $[Co\,edta \cdot (OH_2)]^-$ in neutral unbuffered solution.

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[1] $edta = (OCOCH_3)_2N \cdot CH_2CH_2 \cdot N(CH_3COO)_2{}^{4-}$

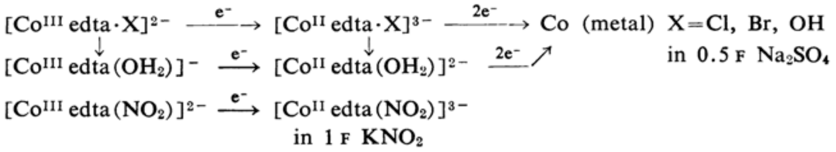
[2] More exactly, the ions, $edtaH_3{}^-$, $edtaH_2{}^{2-}$, etc., are usually present together in solutions.

[3] I. A. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, **1958**, **260**.

aquated species of this complex.

Table I shows the half-wave potentials of the waves for these complexes. All the waves were irreversible.

The following processes of the electrode reaction are considered to be most plausible:



$$\begin{tikzcd}
{[\mathrm{Co^{III}\,edta\cdot X}]^{2-}} \arrow[r, "e^-"] \arrow[d] & {[\mathrm{Co^{II}\,edta\cdot X}]^{3-}} \arrow[r, "2e^-"] \arrow[d] & \text{Co (metal)} & X{=}\mathrm{Cl,\ Br,\ OH} \\
{[\mathrm{Co^{III}\,edta(OH_2)}]^{-}} \arrow[r, "e^-"] & {[\mathrm{Co^{II}\,edta(OH_2)}]^{2-}} \arrow[ur, "2e^-"] & & \text{in } 0.5\,\mathrm{F\ Na_2SO_4} \\
{[\mathrm{Co^{III}\,edta(NO_2)}]^{2-}} \arrow[r, "e^-"] & {[\mathrm{Co^{II}\,edta(NO_2)}]^{3-}} & & \\
 & \text{in } 1\,\mathrm{F\ KNO_2} & &
\end{tikzcd}$$

From these results it can be said that the EDTA-cobalt(II) ion in solution usually contains the edta^{4-} ion as a hexadentate ligand in its coordination sphere.

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