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Kinetic Parameters of the Electrode Reaction of Carbonatocobalt(III) Complexes at Mercury Electrodes

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The electroreduction of $[Co(CO_3)(NH_3)_5]^+$, $[Co(CO_3)(NH_3)_4]^+$, $[Co(CO_3)(tn)_2]^+$, $[Co(CO_3)(pn)_2]^+$, $[Co(CO_3)(en)_2]^+$, and $[Co(CO_3)_2(en)]^-$ (tn=trimethylenediamine, pn=propylenediamine, en=ethylenediamine) have been studied at mercury electrodes in weak acid solutions. All complexes exhibit two irreversible reduction waves; the first corresponds to $Co^{III} \longrightarrow Co^{II}$, and the second, to $Co^{II} \longrightarrow Co^0$. The kinetic parameters of the electrode reactions of the first step were determined by means of Tast and pulse polarography in solutions containing 0.005 M sodium acetate–acetic acid buffer (pH=6) and 0.995 M sodium nitrate at 25 °C. The differential pulse polarographic characteristics of these complexes are also given.

The polarography of carbonatocobalt(III) complexes has been briefly reported in the course of the survey of the half-wave potential for mixed ammine cobalt[1,2] and ethylenediamine cobalt[3] complexes. However, a systematic study of a series of carbonatocobalt(III) complexes under the same conditions has not yet been made. Data for electrochemical kinetic parameters are of importance in the discussion not only of the properties of electrode reactions but also the effect of the solvent, the supporting electrolytes and the electrical double layer on the reactions.

In this paper, the kinetic parameters of the electrode reactions of several carbonatocobalt(III) complexes were examined by means of Tast and pulse polarography.

Experimental

Materials. The complexes, $[Co(CO_3)(en)_2]ClO_4$,[4] $[Co(CO_3)(pn)_2]NO_3$,[5] $[Co(CO_3)(tn)_2]ClO_4$,[6] $[Co(CO_3)(NH_3)_4]NO_3 \cdot 0.5H_2O$,[7] $[Co(CO_3)(NH_3)_5]NO_3 \cdot 0.5H_2O$,[8] $K[Co(CO_3)_2(en)]$,[9] $[Co(NH_3)_6](NO_3)_3$,[10] and $Na[Co(edta)]$[11] were prepared by the literature methods. The concentration of 0.001% polyacrylamide (PAA) was used as the maximum suppressor. All the other chemicals used were of a guaranteed reagent-grade.

Electrochemical Measurements. A three-electrode cell[12] equipped with a saturated calomel electrode (Yanagimoto MR-P2-05-1) and a platinum wire electrode was employed. The dropping mercury electrode (flow rate, 1.25 mg s^{-1} and drop time, 2.99 s in 1 M (1 M=1 mol dm^{-3}) sodium nitrate solutions) served as a working electrode. The kinetic parameters of the electrode reactions were determined by means of Tast and pulse polarography. The polarograms were recorded on Yanagimoto Model P-1000 polarograph with a Riken Denshi Model F3EP x-y recorder. A Takeda Riken digital multimeter, Model TR-6355, was used; the current and the potential were thus measured precisely. Electrolytic solutions were deaerated by bubbling purified nitrogen gas through the solution. All measurements were made at 25±0.1 °C.

In a series of determination of the electrochemical kinetic parameters of various cobalt(III) complexes, the electrochemical procedure was as follows. After measurements of residual current of 10 ml of supporting electrolyte solution, a solid sample of the cobalt complex under test was added to the solution. The electrode potential which is premeditatedly selected was applied. The current was then measured. Measurements were made within ten minutes to avoid the decomposition of complexes in the solution.

Results and Discussion

Many mixed cobalt(III) complexes with various ligands have been prepared, but the kinetic parameters of the electrode reactions have been studied only for a few.[13] For the carbonatocobalt(III) complexes, the polarographic half-wave potentials in neutral solutions have been reported only for carbonatopentaamminecobalt(III),[1] carbonatotetraamminecobalt(III),[2] and carbonatobis(ethylenediamine)cobalt(III)[3] complexes. These cobalt(III) complexes are reduced in two steps: the first corresponds to $Co^{III} \rightarrow Co^{II}$ and the second, to $Co^{II} \rightarrow Co^0$. This work reports extensive kinetic studies of carbonatocobalt(III) complex ions, such as $[Co(CO_3)(en)_2]^+$, $[Co(CO_3)(pn)_2]^+$, $[Co(CO_3)(tn)_2]^+$, $[Co(CO_3)(NH_3)_4]^+$, $[Co(CO_3)(NH_3)_5]^+$, and $[Co(CO_3)_2(en)]^-$. They are made in acid solutions at mercury electrodes.

The carbonatocobalt(III) complexes gave two polarographic waves. The limiting currents of both the first and the second wave were diffusion-controlled and were proportional to the concentration of the complex. The limiting current of the second wave was twice that of the first one, which suggests that a one-electron reduction is followed by a two-electron reduction. From a polarographic log-plot analysis[14] and other polarographic experiments, both steps are considered to be totally irreversible. The present investigation is concerned only with the reduction of cobalt(III) to cobalt(II).

Figure 1 shows the Tast polarogram of the first wave of several carbonatocobalt(III) complexes obtained in solutions containing 0.005 M sodium acetate–acetic acid buffer (pH=6) and 0.995 M sodium nitrate. In the carbonatocobalt(III) complexes studied, the CO_3^{2-} acts as a bidentate ligand, except for $[Co(CO_3)(NH_3)_5]^+$, in which the carbonate ions are unidentate ligands. An examination of Fig. 1 shows the half-wave potentials for the first wave of the complex depend on the types of coordination. The order of the half-wave potential in the series of complexes is:

$$[Co(CO_3)(NH_3)_5]^+ > [Co(CO_3)(NH_3)_4]^+ > [Co(CO_3)_2(en)]^-$$

and

$$[Co(CO_3)(tn)_2]^+ > [Co(CO_3)(pn)_2]^+ > [Co(CO_3)(en)_2]^+.$$

In the first series, carbonatopentaamminecobalt(III)

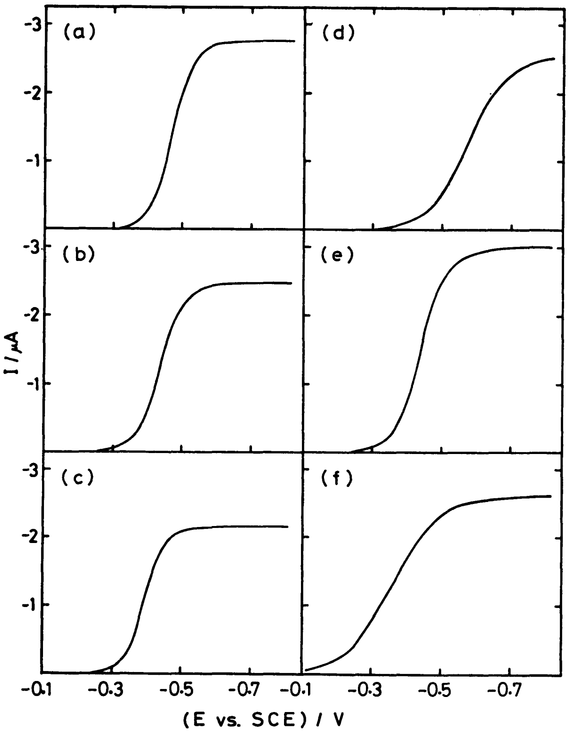

Fig. 1. Tast polarograms for the first wave of several carbonatocobalt(III) complex ions obtained in 0.005 M acetate buffer (pH=6), 0.995 M sodium nitrate and 0.001% PAA at 25 °C.
(a) $[Co(CO_3)(en)_2]^+$, (b) $[Co(CO_3)(pn)_2]^+$, (c) $[Co(CO_3)(tn)_2]^+$, (d) $[Co(CO_3)_2(en)]^-$, (e) $[Co(CO_3)(NH_3)_4]^+$, (f) $[Co(CO_3)(NH_3)_5]^+$.

TABLE 1. DIFFERENTIAL-PULSE POLAROGRAPHIC CHARACTERISTICS OF THE ONE-ELECTRON REDUCTION OF 1 mM COBALT(III) COMPLEXES OBTAINED IN 0.005 M ACETATE BUFFER (pH=6), 0.995 M SODIUM NITRATE AND 0.001% PAA AT 25 °C.

Complex	E_p vs. SCE / V	I_p / µA	ΔW / mV
$[Co(CO_3)_2(en)]^-$	−0.630	−0.45	194
$[Co(CO_3)(en)_2]^+$	−0.470	−1.5	106
$[Co(CO_3)(pn)_2]^+$	−0.436	−1.4	111
$[Co(CO_3)(tn)_2]^+$	−0.410	−1.1	90
$[Co(CO_3)(NH_3)_4]^+$	−0.495	−1.0	123
$[Co(CO_3)(NH_3)_5]^+$	−0.382	−0.59	218
	(−0.57)[a]	(−0.38)[a]	—
$[Co(NH_3)_6]^{3+}$	−0.363	−1.3	113
$[Co(edta)]^-$	+0.145	−3.2	102

a) Corresponds to the second peak.

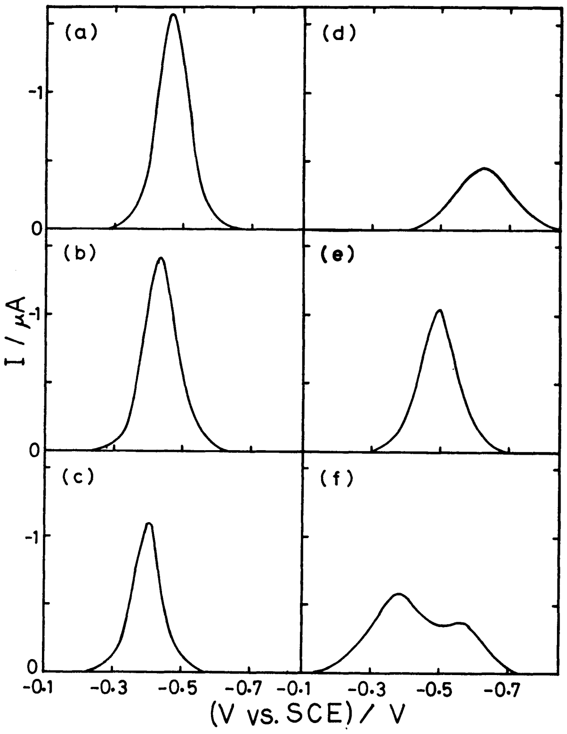

Fig. 2. Differential pulse polarograms for the first wave of several carbonatocobalt(III) complex ions obtained in 0.005 M acetate buffer (pH=6), 0.995 M sodium nitrate and 0.001% PAA at 25 °C.
(a) $[Co(CO_3)(en)_2]^+$, (b) $[Co(CO_3)(pn)_2]^+$, (c) $[Co(CO_3)(tn)_2]^+$, (d) $[Co(CO_3)_2(en)]^-$, (e) $[Co(CO_3)(NH_3)_4]^+$, (f) $[Co(CO_3)(NH_3)_5]^+$.

may be less stable than carbonatotetraamminecobalt(III) since the ligand CO_3^{2-} acts as unidentate in $[Co(CO_3)(NH_3)_5]^+$. Dicarbonatoethylenediaminecobaltate(III) may be more stable than carbonatotetraamminecobalt(III) because the CO_3^{2-} ligand occupies four coordination positions in the former, but only two in the latter. In the second series, the order of the half-wave potential is in accordance with that of the tris-type complexes ($[Co(tn)_3]^{3+} > [Co(pn)_3]^{3+} > [Co(en)_3]^{3+}$).[15] The trimethylenediamine chelate ring is more bulky than the ethylenediamine chelate ring, and carbonatobis(trimethylenediamine)cobalt(III) may be less stable than carbonatobis(ethylenediamine)cobalt(III).

Figure 2 shows the differential pulse polarograms of the first wave of several carbonatocobalt(III) complexes. The wave height of $[Co(CO_3)_2(en)]^-$ was about one-third of $[Co(CO_3)(en)_2]^+$. The differential pulse polarogram of $[Co(CO_3)(NH_3)_5]^+$ showed two peaks while the Tast polarogram gave a single wave as is seen in Fig. 1. Tast and pulse polarograms of this complex were observed over a wide potential range.

Various parameters which characterize a differential pulse polarogram were obtained; they are shown in Table 1 together with those of hexaamminecobalt(III) and ethylenediaminetetraacetatocobaltate(III) ions. The electrode reaction of $[Co(NH_3)_6]^{3+}$ at a mercury electrode is recognized as a typical key reaction for an irreversible electron-transfer process.[13] On the contrary, the electrode reaction of $[Co(edta)]^-$ is known to proceed reversibly at a mercury electrode.[16] For all the complexes studied, the peak currents of the first wave were found to be much smaller than that expected for a reversible electron-transfer process indicating that the electrode reaction is irreversible.

The reduction of carbonatocobalt(III) to cobalt(II) species in an acid solution was considered to be irreversible from the facts described above. For a totally irreversible electrode reaction, the following relations of the Tast polarography are derived:[17,18]

$$(\boldsymbol{R}T/\alpha n\boldsymbol{F})\ln[2x(3-x)/5(1-x)] = E_{1/2} - E, \quad (1)$$

with:

$$x = I/I_d, \quad (2)$$

and:

$$E_{1/2} = (\boldsymbol{R}T/\alpha n\boldsymbol{F})\ln[1.35\,k_c^\circ(t_d/D)^{1/2}], \quad (3)$$

where I is the current at the potential E; I_d the diffusion-controlled current; D, the diffusion coefficient; t_d, the drop time; α, the transfer coefficient; k_c°, the cathodic rate constant at $E=0$; n, the number of electrons; $\boldsymbol{R}$, $\boldsymbol{F}$, and T have usual meanings. According to Eq. 1, a plot of $\ln[2x(3-x)/5(1-x)]$ *vs.* E should be a straight line. The transfer coefficient, α, can be obtained from $E_1/_2$ by applying Eq. 3. These relations are derived under the assumptions that a transfer coefficient is independent on electrode potentials and extrapolation to $E=0$ is possible for the rate constants. The analysis of electrode kinetics by these relations, therefore, may be limited to a first approximation. However, such kinetic parameters of electrode reactions play an important role in the interpretation of electrode kinetics, because the available data have been reported only few.[13]

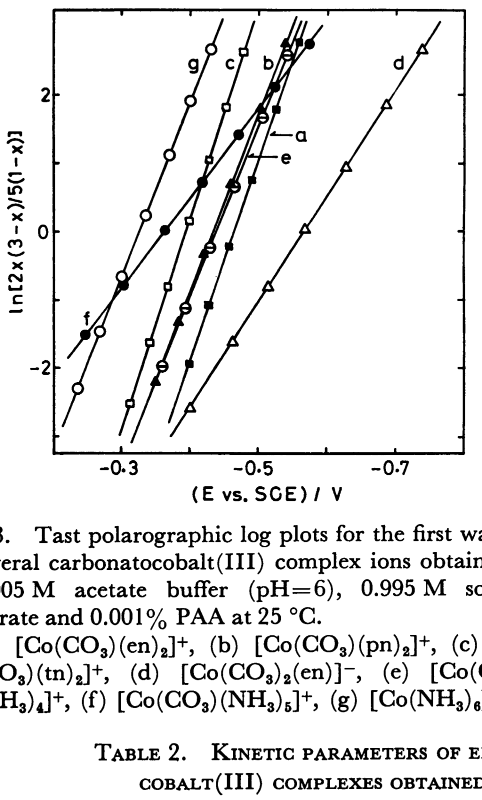

Fig. 3. Tast polarographic log plots for the first wave of several carbonatocobalt(III) complex ions obtained in 0.005 M acetate buffer (pH=6), 0.995 M sodium nitrate and 0.001% PAA at 25 °C.
(a) $[Co(CO_3)(en)_2]^+$, (b) $[Co(CO_3)(pn)_2]^+$, (c) $[Co[CO_3)(tn)_2]^+$, (d) $[Co(CO_3)_2(en)]^-$, (e) $[Co(CO_3)(NH_3)_4]^+$, (f) $[Co(CO_3)(NH_3)_5]^+$, (g) $[Co(NH_3)_6]^{3+}$.

An example of the plots for Eq. 1 is given in Fig. 3. Table 2 summarizes the kinetic parameters of the electrode reactions corresponding to the first wave for various carbonatocobalt(III) complexes. The diffusion coefficients required for the calculation of kinetic parameters were taken from the earlier work.[19] These kinetic parameters obtained were checked by calculating the current according to the relation:

$$2x(3-x)/5(1-x) = 1.35\,k_c^\circ(t_d/D)^{1/2}\exp(-\alpha n\boldsymbol{F}E/\boldsymbol{R}T). \quad (4)$$

The calculated currents were in agreement with the observed ones except for the case of $[Co(CO_3)(NH_3)_5]^+$. The order of a specific rate constant (k_c°) was found to be 10^{-6}—10^{-9} cm s^{-1}. The transfer coefficients were found to be above 0.5 except for the cases of $[Co(CO_3)(NH_3)_5]^+$ and $[Co(CO_3)_2(en)]^-$.

The kinetic parameters of electrode reactions for these carbonatocobalt(III) complexes are also determined by means of pulse polarography. To a pulse response of totally irreversible system, the following equations are applied:[17,18]

$$(\boldsymbol{R}T/2\alpha n\boldsymbol{F})\ln[x^2(1.75+x)/(1-x)] = E_{1/2} - E, \quad (5)$$

with:

$$E_{1/2} = (\boldsymbol{R}T/\alpha n\boldsymbol{F})\ln[2.31\,k_c^\circ(t_d/D)^{1/2}]. \quad (6)$$

where x is defined by Eq. 2. In this case a plot of $\ln[x^2(1.75+x)/(1-x)]$ *vs.* E should give a straight line. The transfer coefficient (α) and the specific rate constant (k_c°) can be claculated if a linear plot is obtained.

Examples of the plot of Eq. 5 obtained at various electrode potentials are given in Fig. 4. A linear plot was obtained except for $[Co(CO_3)(NH_3)_5]^+$. The log plot for $[Co(CO_3)(NH_3)_5]^+$ is somewhat sigmoid in shape. The kinetic parameters obtained from these plots are given in Table 3. The half-wave potentials obtained by means of pulse polarography were found to shift to more negative potentials. This is expected from the magnitude of the sampling time as is given by Eqs. 3 and 6. The measurements were made at sampling times of 2.99 and 0.04 s for the Tast and the pulse polarography, respectively.

The transfer coefficients obtained by means of those

TABLE 2. KINETIC PARAMETERS OF ELECTRODE REACTIONS OF THE ONE-ELECTRON REDUCTION OF COBALT(III) COMPLEXES OBTAINED BY TAST POLAROGRAPHY IN 0.005 M ACETATE BUFFER (pH=6), 0.995 M SODIUM NITRATE AND 0.001% PAA AT 25 °C.

Complex	$E_{1/2}$ *vs.* SCE / V	α	$k_c^\circ/\sqrt{D}$ / s$^{-1/2}$	k_c° / cm s^{-1}	$D^{a)}$ / 10^{-6} cm^2 s^{-1}
$[Co(CO_3)_2(en)]^-$	−0.567	0.40	5.9×10^{-5}	1.5×10^{-7}	6.74
$[Co(CO_3)(en)_2]^+$	−0.465	0.74	6.4×10^{-7}	1.8×10^{-9}	7.85
$[Co(CO_3)(pn)_2]^+$	−0.435	0.68	4.3×10^{-6}	1.1×10^{-8}	6.21
$[Co(CO_3)(tn)_2]^+$	−0.395	0.79	2.3×10^{-6}	5.0×10^{-9}	4.76
$[Co(CO_3)(NH_3)_4]^+$	−0.439	0.65	6.7×10^{-6}	2.0×10^{-8}	9.04
$[Co(CO_3)(NH_3)_5]^+$	−0.360	0.34	3.6×10^{-3}	9.6×10^{-6}	7.09
$[Co(NH_3)_6]^{3+}$	−0.327	0.65	1.1×10^{-4}	3.1×10^{-7}	8.06

a) Taken from the previous work.[19]

TABLE 3. KINETIC PARAMETERS OF ELECTRODE REACTIONS OF THE ONE-ELECTRON REDUCTION OF COBALT(III) COMPLEXES OBTAINED BY PULSE POLAROGRAPHY IN 0.005 M ACETATE BUFFER (pH=6), 0.995 M SODIUM NITRATE AND 0 001% PAA AT 25 °C.

Complex	$E_{1/2}$ vs. SCE / V	α	$k_c^\circ/\sqrt{D}$ / $s^{-1/2}$	k_c° / cm s^{-1}
$[Co(CO_3)_2(en)]^-$	−0.624	0.48	1.8×10^{-5}	4.7×10^{-8}
$[Co(CO_3)(en)_2]^+$	−0.490	0.82	3.4×10^{-7}	9.5×10^{-10}
$[Co(CO_3)(pn)_2]^+$	−0.456	0.75	3.8×10^{-6}	9.5×10^{-9}
$[Co(CO_3)(tn)_2]^+$	−0.437	0.80	2.6×10^{-6}	5.7×10^{-9}
$[Co(CO_3)(NH_3)_4]^+$	−0.508	0.67	4.0×10^{-6}	1.2×10^{-8}
$[Co(CO_3)(NH_3)_5]^+$	−0.430	0.35	7.9×10^{-3}	2.1×10^{-5}
$[Co(NH_3)_6]^{3+}$	−0.379	0.67	1.1×10^{-4}	3.1×10^{-7}

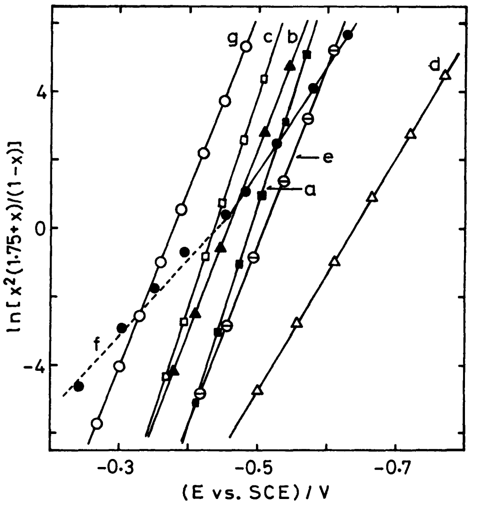

Fig. 4. Pulse polarographic log plots for the first wave of several carbonatocobalt(III) complex ions obtained in 0.005 M acetate buffer (pH=6), 0.995 M sodium nitrate and 0.001% PAA at 25 °C.
(a) $[Co(CO_3)(en)_2]^+$, (b) $[Co(CO_3)(pn)_2]^+$, (c) $[Co(CO_3)(tn)_2]^+$, (d) $[Co(CO_3)_2(en)]^-$, (e) $[Co(CO_3)(NH_3)_4]^+$, (f) $[Co(CO_3)(NH_3)_5]^+$, (g) $[Co(NH_3)_6]^{3+}$.

Tast polarography, however, were found to be smaller than those of the pulse polarography. In the Tast polarography, the electrolysis proceeds simultaneously during the drop life, while in the pulse polarography the faradaic current is negligibly small before the pulse is applied. Therefore, the differencies of the kinetic parameters obtained by the two electrochemical methods may be mainly attributed to the depletion effect as was pointed out by Hans *et al.*[20] Furthermore, the electrode reactions of the cobalt complex studied here are followed by chemical reactions as described below. This may enhance the depletion effect. The evaluated specific rate constant (k_c°) may be smaller when the transfer coefficient increases as is seen from Eqs. 3 and 6.

As for $[Co(CO_3)(NH_3)_5]^+$, the current-potential curves between −0.25 and −0.45 V *vs.* SCE were used in this calculation. The alternative value of $\alpha=0.44$, and $k_c^\circ/\sqrt{D}=7.8\times10^{-4}\ s^{-1/2}$ were obtained for the use of the current between −0.45 and −0.60 V *vs.* SCE. If the whole data are used the following values can be determined: $\alpha=0.32$, and $k_c^\circ/\sqrt{D}=1.1\times10^{-2}\ s^{-1/2}$. N. Maki *et al.*[1] have reported the half-wave potential of carbonato- and dicarbonatoethylenediaminecobalt(III) complex in solution of 0.5 M K_2SO_4: $E_{1/2}=-0.50_0$ V *vs.* SCE for $[Co(CO_3)(NH_3)_5]^+$ and $E_{1/2}=-0.50_2$ V *vs.* SCE for $[Co(HCO_3)(NH_3)_5]^{2+}$. The hydrogencarbonate complex may exist partly in the solution, but no further experiments were done.

Among the cobalt complexes used here, cobalt(III) is substitution-inert towards solvolysis, while cobalt(II) is substitution-labile. In general, dissociation of the inert cobalt(III) complexes can be neglected from the standpoint of polarography, whereas that of the labile cobalt(II) complexes occurs rapidly compared with the scanning rate of the applied potential. Therefore, the cobalt(II) complex results in the formation of an aquacobalt(II) mixture in an equilibrium state with water molecules in aqueous solutions.

The overall electrode reaction for the first wave was evaluated by a comparison of its electrode reaction with that of other cobalt(III) complexes.[13] Thus,

$$[Co(CO_3)(NH_3)_5]^+ + e \longrightarrow [Co(CO_3)(NH_3)_5], \tag{7a}$$

$$[Co(CO_3)(NH_3)_5] + pH_2O \longrightarrow [Co(H_2O)_p(NH_3)_{6-p}]^{2+} + CO_3^{2-} + (p-1)NH_3, \tag{7b}$$

for the pentaammine complex, and

$$[Co(CO_3)(NH_3)_4]^+ + e \longrightarrow [Co(CO_3)(NH_3)_4], \tag{8a}$$

$$[Co(CO_3)(NH_3)_4] + (p+2)H_2O \longrightarrow [Co(H_2O)_{p+2}(NH_3)_{4-p}]^{2+} + CO_3^{2-} + pNH_3, \tag{8b}$$

for the tetraammine complex. With the bis(diamine) complex:

$$[Co(CO_3)(N)_2]^+ + e \longrightarrow [Co(CO_3)(N)_2], \tag{9a}$$

$$[Co(CO_3)(N_2)] + (2p+2)H_2O \longrightarrow [Co(H_2O)_{2+2p}(N)_{2-p}]^{2+} + CO_3^{2-} + p(N). \tag{9b}$$

$$((N)=en,\ pn,\ tn)$$

The electrode reaction of dicarbonatoethylenediaminecobaltate(III) complex may be:

$$[Co(CO_3)_2(en)]^- + e \longrightarrow [Co(CO_3)_2(en)]^{2-}, \tag{10a}$$

$$[Co(CO_3)_2(en)]^{2-} + (2p+q)H_2O \longrightarrow [Co(H_2O)_{2p+2q}(en)_{1-p}]^{2-} + pCO_3^{2-} + q\,en. \tag{10b}$$

The kinetic parameters given in Table 2 and 3 correspond to the electrode reactions $Co^{III} \rightarrow Co^{II}$ (Eqs. 7a, 8a, 9a, and 10a). Furthermore, the experimental data obtained for complexes $[Co(CO_3)(en)_2]^+$, $[Co(CO_3)(pn)_2]^+$, $[Co(CO_3)(tn)_2]^+$, $[Co(CO_3)(NH_3)_4]^+$, and [Co-

$(NH_3)_6]^{3+}$ show transfer coefficients above 0.5, indicating that the electrode process follows outer-sphere pathways.[21]

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