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Polarographic Study of Tris-(ethylenediamine)-cobalt(III) Ion

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The polarographic reduction of tris-(ethylenediamine)-cobalt(III) ion is shown to be reversible in the presence of excess ethylenediamine. The anodic half-wave potential for the corresponding cobalt(II) complex is identical with that of the cathodic process. A study of the formation of ion pairs by tris-(ethylenediamine)-cobalt(III) ion with certain anions was made, and the magnitudes of the equilibrium constants for the dissociation reactions were estimated.

Polarographic reduction curves of tris-(ethylenediamine)-cobalt(III) ion were observed by Herda² in potassium nitrate solutions in the presence of gelatin and octyl alcohol, and by Willis, Friend and Mellor³ in potassium sulfate and sodium acetate solutions. In neither case was excess ethylenediamine present and, as will be seen below, the conditions for a reversible reduction were therefore not fulfilled. Bjerrum⁴ evaluated the consecutive formation constants of the complexes of cobalt(II) ion with ethylenediamine in 1 *N* potassium chloride, and evaluated the formal potential of the tris-(ethylenediamine)-cobalt(III)-tris-(ethylenediamine)-cobalt(II) system in 1 *N* potassium chloride at 30° at -0.259 volt (*vs.* the normal hydrogen electrode). Concurrently with and subsequent to the present investigation, Kivalo⁵ has studied the effect of the instability of the tris-(ethylenediamine)-cobalt(II) ion under certain experimental conditions on the cathodic behavior of the cobalt(III) complex. The anomalous faradaic impedance of an electrode caused by the adsorption of both electroactive species at the equilibrium potential has recently been described.⁶ The reduction of hexamminecobalt(III) ion in the presence of excess ethylenediamine has been shown to occur at a potential

characteristic of the reversible potential of the tris-(ethylenediamine)-cobalt(III)-(II) system.⁷

In the present investigation, the conditions for reversible reduction were studied, and ion-pair formation reactions were quantitatively evaluated.

Experimental

Apparatus and Procedure.—A Sargent Model XXI Polarograph, a Leeds and Northrup Model E Electrochemograph, and a Sargent Model III Manual Polarograph were used, together with suitable external potentiometers. For manual observations, the mean current was measured by a galvanometer and the potential was determined by an external potentiometer, corrected for the potential drop due to the average resistance of the cell. Alternatively, manual measurements were made with the recording polarographs, taking as average currents the mean values of the small oscillations of the current recorder operated at maximum damping. Polarograms were recorded with the Sargent Model XXI Polarograph, using a span voltage of 0.5 v., making two potential measurements with a potentiometer, after stopping the instrument, at points on the wave before and after the half-wave potential. Current values were taken corresponding to the envelope of the tops of the fluctuations of the recorder, operated without damping. Potential values were corrected for *iR* drop, using the minimum value of cell resistance at the moment of the fall of the drop, measured with a 1000 cycle a.c. conductivity bridge.

The solution was introduced into both halves of an H-type cell with a fine porosity fritted diaphragm, using no agar plug. The side arm of a saturated calomel electrode was introduced into one side of the cell, in which the solution was maintained at a level below that of the solution to be electrolyzed in the other side. The latter solution was deaerated before the dropping mercury electrode was introduced. The cell and reference electrode were maintained at 25 ± 0.02° by a water thermostat.

Two different capillaries were used. The characteristics of capillary I are given in Table II. Capillary II, with a drop time of 3.52 sec. and mass rate of flow of 2.42 mg.

- (1) Abstracted from the Ph.D. Thesis of M. W. Grieb, 1953.
- (2) M. G. Herda, M.S. Thesis, University of Illinois, 1943.
- (3) J. B. Willis, J. A. Friend and D. P. Mellor, *THIS JOURNAL*, **67**, 1680 (1945).
- (4) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution." P. Haase and Son, Copenhagen, 1941.
- (5) P. Kivalo, Ph.D. Thesis, Åbo Akademi, Åbo, Finland, 1954; *THIS JOURNAL*, **77**, 2678 (1955).
- (6) H. A. Laitinen and J. E. B. Randles, *Trans. Faraday Soc.*, **51**, 54 (1955).

(7) H. A. Laitinen and P. Kivalo, *THIS JOURNAL*, **75**, 2198 (1953).

sec.⁻¹, measured on open circuit in air-saturated 0.1 *M* potassium chloride, was used in a few experiments for which only potential data are reported.

Materials.⁸—Tris-(ethylenediamine)-cobalt(III) chloride was recrystallized from concentrated aqueous solution by addition of concentrated HCl and ethanol, and was dried for two hours at 100°. Stock solutions (0.05 *M*) were stored over periods up to three months with no evidence of decomposition.

Tris-(ethylenediamine)-cobalt(III) perchlorate was prepared from the sulfate, previously recrystallized by a procedure similar to that used for the chloride, by metathesis with a slight excess of barium perchlorate solution acidified with a drop of perchloric acid, followed by filtration of the barium sulfate. It was purified by repeated recrystallization and washing with small portions of distilled water, until the washings showed no turbidity upon addition of sulfuric acid and were nearly neutral to litmus. The salt, unlike the chloride and sulfate, is soluble in ethanol and only moderately soluble in water.

A stock solution, approximately 0.5 *M* of cobalt(II) chloride was made from Mallinckrodt Analytical Reagent grade hexahydrate product.

Seventy per cent. ethylenediamine-water azeotrope (Union Carbon and Carbide) was distilled after addition of a few pellets of sodium hydroxide, a middle constant boiling fraction being collected. A 1 *M* stock solution was standardized by potentiometric titration with standard acid. Upon prolonged standing, the stock solutions showed evidence of oxidation in a slight rise in the diffusion current at -0.55 v. vs. S.C.E.

Results and Discussion

Effect of Ethylenediamine Concentration.—The cathodic curves of millimolar tris-(ethylenediamine)-cobalt(III) chloride in 0.1 *M* potassium chloride and various concentrations of ethylenediamine were studied using capillary I, with a mercury column height of 70.0 cm., and recording the curves with the Sargent Model XXI polarograph.

To determine the anodic curves of the cobalt(II) complex, a residual current curve was first recorded. Then to 25 ml. of air-free solution was added one drop of cobalt(II) chloride stock solution, with passage of purified nitrogen through the solution. This procedure yielded an approximately millimolar solution of tris-(ethylenediamine)-cobalt(II) ion. The trace of oxygen introduced with the drop of cobalt(II) solution caused sufficient oxidation of the cobalt(II) complex to be detected, but compensation was made in the calculation by appropriate adjustment of the residual current.

The half-wave potentials and reciprocal slope values obtained from the logarithmic plots are given in Table I.

The constancy of the half-wave potential at ethylenediamine concentrations greater than 0.03 *M* indicates that under these conditions both cobalt(III) and cobalt(II) are coordinated with an equal number of ethylenediamine molecules, *viz.*, three. The reciprocal slopes show satisfactory agreement with the theoretical value for a reversible reaction at least down to 0.005 *M* ethylenediamine. In the absence of excess ethylenediamine, the behavior is not reversible.⁹

In each case, except that of the cobalt(II) solution in 0.004 *M* ethylenediamine, the plot of $\log [(i_d)_c - i] / [i - (i_d)_a]$ vs. *E* gave very good straight lines. The excepted case exhibited only slight deviations at potentials more negative than that of the half-wave. Diffusion currents in the various solu-

(8) The samples of complex compounds used in this study were generously supplied by Professor J. C. Bailar, Jr.

TABLE I

VARIATION WITH CONCENTRATION OF ETHYLENEDIAMINE OF HALF-WAVE POTENTIALS AND REVERSIBILITY VALUES OF [Co en₃]⁺⁺⁺ ION AND [Co en₃]⁺⁺ ION FORMED IN THE SUPPORTING ELECTROLYTE

Concn. en, <i>M</i>	Cathodic wave		Anodic wave	
	<i>E</i> _{1/2} , v. vs. S.C.E.	Reciprocal slope, v.	<i>E</i> _{1/2} , v. vs. S.C.E.	Reciprocal slope, v.
0.5	-0.459	0.0604	-0.457	0.0594
.4	-.461	.0587	-.459	.0567
.2	-.456	.0564	-.457	.0578
.1	-.457	.0570	-.457	.0570
.1	-.458	.0602	-.456	.0586
.07	-.457	.0580	-.455	.0585
.05	-.457	.0570	-.455	.0583
.03	-.457	.0585	-.455	.0582
.02	-.456	.0572	-.453	.0589
.01	-.454	.0581	-.450	.0584
.007	-.452	.0584	-.446	.0574
.005	-.450	.0578	-.434	.0595
.004	-.429	.0639
.003	-.444	.0575
.001	-.430	.0626

tions were constant within the accuracy of the method. Cobalt(II) solutions in the two lowest concentrations of ethylenediamine, for which data are not reported, showed progressively much reduced diffusion currents, indicating that all available cobalt was not complexed.

Diffusion Current Constants.—Extensive data were obtained to verify that the limiting currents for both the cathodic and anodic processes were diffusion controlled. The average diffusion currents and drop times were measured at constant potential on the plateau of the waves, with the mercury reservoir at various heights. The mass rate of flow of mercury was determined under similar conditions. Appropriate back-pressure corrections were made.⁹ A few typical data are presented in Table II. The anodic diffusion current constants could not be evaluated precisely because of uncertainty in the absolute concentration of cobalt(II) complex, but the data showed similar consistency at various values of the height of reservoir.

TABLE II
CONSTANCY OF $i_d/h^{1/2}$ AND *I*

(a) 1.00 mM [Co en₃]Cl₃ in 0.1 *M* KCl, 0.1 *M* en; capillary I.
(b) 2.50 mM [Co en₃]Cl₃ in 2.0 *M* KCl, 0.1 *M* en; capillary I.

<i>h</i> , cm.	<i>m</i> _p , mg./sec.	<i>t</i> _p , sec.	<i>i</i> _d , μa.	<i>i</i> _d / <i>h</i> ^{1/2} cor., μa./cm. ^{1/2}	<i>I</i> , μa. sec. ^{1/2} / mM. mg. ^{2/3}
(a) 70.0	1.690	4.41	2.78		1.530
70.0	1.690	4.34	2.79		1.539
(b) 50.0	1.190	6.21	5.87	0.8435	1.543
60.0	1.440 ^a	5.12	6.45	.8439	1.541
70.0	1.690	4.35	6.96	.8414	1.536
80.0	1.937 ^a	3.76	7.46	.8424	1.539
90.0	2.183 ^a	3.35	7.93	.8433	1.541
100.0	2.430	3.01	8.36	.8428	1.539

^a Values by interpolation.

(9) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, New York, N. Y., 1952, p. 81.

Effect of Supporting Electrolyte.—Using a 1.00 millimolar solution of tris-(ethylenediamine)-cobalt(III) chloride, in 0.1 *M* ethylenediamine, and capillary I at a mercury column height of 70.0 cm., the effect of various concentrations of supporting electrolytes on the half-wave potentials and diffusion current constants was determined. All half-wave potentials were corrected for potential drop due to cell resistance. Anodic half-wave potentials were found to coincide with those of the cathodic waves within an experimental error of about 1 mv. and are not separately reported.

a. Sodium Perchlorate.—From polarograms recorded with the Sargent Model XXI polarograph, the half-wave potentials were found to remain essentially constant at an average value of -0.441 v. *vs.* S.C.E. as the concentration of sodium perchlorate was varied from 0.1 to 4.0 *M*. However, precipitation of potassium perchlorate occurred at the junction with the saturated KCl-agar salt bridge, causing a moderate increase in cell resistance and lowering the reproducibility of the potentials. The apparent constancy of half-wave potential with sodium perchlorate concentration has no particular theoretical significance, having arisen presumably through cancellation of relatively small junction potentials and activity coefficient effects.

The experiment was repeated with capillary II and a solution of tris-(ethylenediamine)-cobalt(III) perchlorate, estimated by comparison of diffusion currents to be 0.5 millimolar, in 0.03 *M* sodium perchlorate. The agar plug was protected by saturated potassium chloride in the bridge side of the H-cell. No precipitation of potassium perchlorate was observed, and the cell resistance was normal. The half-wave potential thus obtained was -0.4414 v. *vs.* S.C.E., and was used to calculate the "standard" half-wave potential $(E_{1/2}^{\circ})_s$ used in subsequent calculations.

b. Potassium Chloride.—The half-wave potential data in Table III were obtained with the Sargent Model III manual polarograph.

TABLE III

ANALYSIS OF DEPENDENCE OF $E_{1/2}$ ON POTASSIUM CHLORIDE CONCENTRATIONS IN SOLUTIONS CONTAINING 1.00 mM $[\text{Co en}_3]\text{Cl}_3$ AND 0.1 *M* en.

KCl, <i>M</i>	a_{KCl}	$E_{1/2}$, v. <i>vs.</i> S.C.E.	E_j , v.	$E_{1/2}$, cor., v. <i>vs.</i> S.C.E.	$\Delta E_{1/2}$, v.
0	0			-0.420	
0.01	0.009	-0.436	0.0031	-0.433	0.013
.025	.021	-0.442	.0027	-0.439	.019
.05	.041	-0.448	.0024	-0.446	.026
.10	.077	-0.456	.0020	-0.454	.034
.20	.144	-0.4652	.0017	-0.4635	.0435
.40	.269	-0.4765	.0013	-0.4752	.0552
.70	.447	-0.4880	.0010	-0.4870	.0670
1.0	.623	-0.4956	.0008	-0.4948	.0748
2.0	1.225	-0.5125	.0004	-0.5121	.0921
3.0	1.899	-0.5266	.0002	-0.5264	.1064
4.0	2.686	-0.5390	.0000	-0.5390	.1190

The activities of potassium chloride in the various solutions were calculated from an equation expressing the mean activity coefficients as reported by Shedlovsky.¹⁰ The effect of the 0.1 *M* ethylene-

diamine was ignored. To estimate values of the junction potentials, the formula of MacInnes¹¹ was used, with the e.m.f. data of Shedlovsky and MacInnes.¹² When plotted against logarithm of molar concentration, the junction potentials gave a smooth, nearly linear plot.

To evaluate the formation constants of ion-pair or higher ion-cluster complexes, the method of DeFord and Hume¹³ was used, assuming that the divalent complex ion does not form ion-pairs. The functions $F_0(X)$, $F_1(X)$ and $F_2(X)$ are defined as by DeFord and Hume, but regarding the tris-(ethylenediamine)-cobalt(III) ion as the central ion. To calculate these functions, it is necessary to adopt a value of the half-wave potential of the system in the absence of complexing anions. The best reference value seems to be that measured in 0.03 *M* sodium perchlorate, corrected for liquid junction potential and for activity coefficient ratio of the trivalent and divalent cobalt complex ions. The junction potential is estimated to be 2.5 mv., due principally to diffusion of the saturated potassium chloride, giving -0.4839 v. *vs.* S.C.E. for the corrected potential. Estimating the activity coefficients by a formula used by Kielland,¹⁴ taking an ionic radius of 3.68 Å. for each ion, we estimate the "standard" half-wave potential at unit activity ratio to be -0.420 v. *vs.* S.C.E. The figure 3.68 Å. was obtained from limiting equivalent ionic conductance of the tris-(ethylenediamine)-cobalt(III) ion as determined by Jenkins and Monk,¹⁵ and is consistent with crystallographic interatomic distances in both complexes.¹⁶⁻¹⁹

The values of $F_0(X)$ and $F_1(X)$ are plotted in Fig. 1. Extrapolation of the $F_1(X)$ to zero concentration of supporting electrolyte gives the value 28 for the formation constant of the $[\text{Co en}_3]\text{Cl}^{++}$ ion pair. The dissociation constant is the reciprocal, 0.036.

The slight upward trend of $F_1(X)$ at high concentration indicates the beginning of association of two chloride ions with each cation. The marked upward trend of $F_1(X)$ values at the lowest concentrations may be due to ignoring the activity coefficient ratio of the ion-pair and the divalent cobalt complex in the calculation (it was assumed that the ion pair behaves more nearly as a divalent ion than as a trivalent one, so that this ratio could be neglected). Over-correction of activity coefficients in estimating the "standard" half-wave potential would also cause such an effect. For example, if the value -0.430 v. *vs.* S.C.E. is adopted for $(E_{1/2}^{\circ})_s$, the $F_1(X)$ values at low concentrations are brought much closer to the extrapolated portion of the curve, the formation constant is estimated to be 18, and the dissociation constant to be 0.056.

(11) D. A. MacInnes, *ibid.*, **37**, 2301 (1915).(12) T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).(13) D. D. DeFord and D. N. Hume, *ibid.*, **73**, 5321 (1951).(14) J. Kielland, *ibid.*, **59**, 1675 (1937).(15) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, 68 (1951).(16) M. Atoji and T. Watanabe, *J. Chem. Phys.*, **20**, 1045 (1952).(17) D. P. Mellor and R. J. Goldacre, *J. Proc. Roy. Soc. N. S. Wales*, **73**, 233 (1940).

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(19) T. Watanabe and J. Atoji, *Science (Japan)*, **20**, 422 (1950); *C. A.*, **45**, 9972^b (1951).(10) T. Shedlovsky, *THIS JOURNAL*, **72**, 3680 (1950).

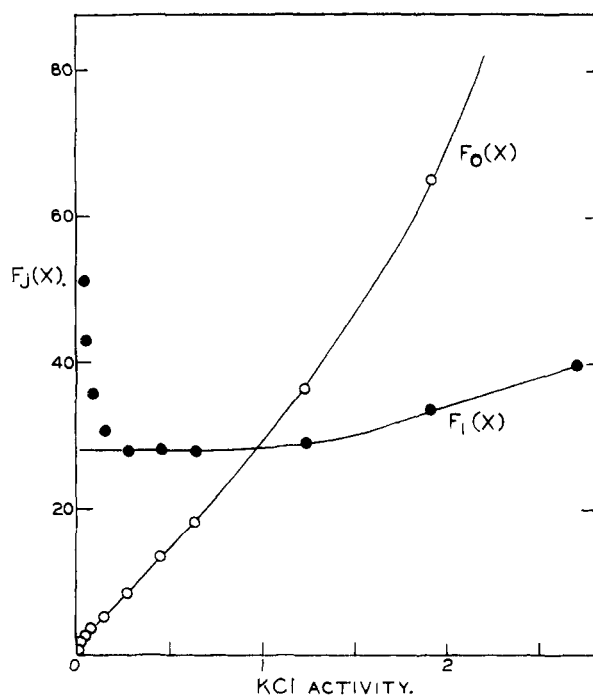


Fig. 1.—Variation of $F_j(X)$ with activity of KCl.

These values are in reasonably good agreement with the value of 0.019 for the dissociation constant, calculated from conductance data by Jenkins and Monk,¹⁵ who regard it as approximate to an order of magnitude. From the present data, it appears fairly certain that 0.036 is a minimum value for this constant.

Sodium Sulfate.—The half-wave potentials in Table IV were obtained with the Sargent Model XXI recording polarograph operated by the manual method previously described.

Although it is seen that sulfate ion causes a very large shift of half-wave potential, it has not been possible to attempt an accurate calculation of its formation constant. No suitable method is known to correct for the junction potential between saturated potassium chloride and concentrated sodium sulfate solutions. The effect on potential of the activity coefficients of the ion pair and the reduced ion cannot be expected to cancel, because they differ in charge. The activity of the sulfate ion in concentrated solutions remains in doubt.

TABLE IV
EFFECT OF Na_2SO_4 CONCENTRATION ON HALF-WAVE POTENTIAL

1.00 mM[Co en ₃] cl ₃ and 0.1 M en					
Molar Conc.	SO_4^{2-}	$E_{1/2}$	$\Delta E_{1/2}$	$F_0(X)$	$F_1(X)$
Na_2SO_4		v. vs. S.C.E.	v.		
		-0.420			
0.01	0.0095	- .477	0.057	9.19	862.2
.025	.0230	- .493	.073	17.13	701.3
.05	.0442	- .505	.085	27.32	595.5
.1	.0844	- .518	.098	45.31	525.0
.25	.182	- .537	.117	94.91	515.9
.5		- .557	.137	206.6	
1.0		- .580	.160	505.8	
2.5		- .630	.210	3540	

As an approximation to the latter problem the $F_1(X)$ values in Table IV have been calculated on the basis of free sulfate ion concentrations found in data of Righellato and Davies²⁰ for 18°. These authors concluded from conductance data that sodium and sulfate ions in solution undergo ionic association. Because in the region for which the conductance data were available, the $F_1(X)$ values decrease rather than increase with increasing concentration it would not be meaningful to attempt an extrapolation.

If, by analogy with the case of the chloride, the first values are disregarded, the formation constant may be estimated as about 525. The corresponding dissociation constant is 1.9×10^{-3} . This value is in only fair agreement with the value 3.55×10^{-4} calculated by Jenkins and Monk¹⁵ from conductance data.

Sodium Nitrate.—Qualitative evidence for a weak ion-pair complex with nitrate ions was obtained from the fact that the half-wave potential varied from -0.451 to -0.524 v. vs. S.C.E. as the concentration of sodium nitrate was varied from 0.1 to 4.0 M in the presence of 0.1 M ethylenediamine. From the fact that the shift of potential is smaller than with chloride ion, we may infer that the nitrate ion forms a less stable ion pair.

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