

15. *The Conductivities of Some Complex Cobalt Chlorides and Sulphates.*

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From the conductivities of dilute solutions at 25° of the chlorides and sulphates of hexamminocobalt, trisethylenediaminocobalt, and trispropylenediaminocobalt, the limiting mobilities of the cobaltic cations, and the dissociation constants of the ion pairs formed between these and chloride and sulphate ions have been determined. The increasing radii of the complex cations are found to alter systematically the limiting mobilities of these ions and the dissociation constants of their sulphates. A comparison is drawn between the sizes of these ion pairs as calculated by Stokes's law and by Bjerrum's method.

AMONG the various factors which influence the extent to which ions associate in solution is their effective size. This may be seen, for instance, by a comparison of similar salts containing organic ions in non-aqueous solvents, where the dissociation constants are found to increase with increasing size of the organic ions (Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 3614; Davies, "Conductivity of Solutions," 1933, Chap. 18). In aqueous solutions, hydration effects distort this generalisation. So far as quantitative relations are concerned, Bjerrum (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9) has proposed, for those cases where the forces are essentially polar, the relation

$$K^{-1} = \frac{4\pi N}{1000} \left(\frac{|z_1 z_2|}{DkT} \right)^3 Q(b) \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (1)$$

where $b = (|z_1 z_2|)^2 / aDkT$; a represents the distance of closest approach of the ions forming

charcoal as catalyst, and 50 ml. of concentrated ammonia solution, then drawing air through the solution for 5 hours. The product was filtered off, dissolved, and the animal charcoal filtered off, the sulphate being precipitated by addition of 100 ml. of concentrated sulphuric acid and cooling to 0°. It was washed with water, dissolved in water, and precipitated with alcohol, this process being repeated six times. Although the salt was dried in a vacuum oven at 50°, it could not be brought to constant weight, being slightly hygroscopic. Consequently, the concentrations of the stock solutions were found by quantitative sulphate analysis. Vogel's method ("Quantitative Analysis," Longmans, Green and Co., p. 478) was used, the barium sulphate being weighed in sintered porcelain crucibles; duplicates agreed to within $\pm 0.03\%$. The stock solutions had a pH of *ca.* 6. Adsorption effects were very small, and it was easy to get consistent resistance readings.

TABLE I.

10°C.	10°C [‡] .	Λ .	$\Lambda + bC^{\ddagger}$.	<i>a</i> .	10 ⁵ κ .	10°C.	10°C [‡] .	Λ .	$\Lambda + bC^{\ddagger}$.	<i>a</i> .	10 ⁵ κ .
(i) Conductivity of hexamminocobalt(III) chloride solutions.											
1.5374	1.240	171.44	175.33	0.9970	45	6.6539	2.578	166.29	174.38	0.9840	32
2.2421	1.498	170.46	175.16	0.9947	38	7.0800	2.661	165.85	174.19	0.9817	29
2.7957	1.670	169.75	174.99	0.9928	33	7.9998	2.828	165.35	174.12	0.9819	33
4.4657	2.113	168.10	174.73	0.9891	33	8.4888	2.915	164.93	174.07	0.9799	31
4.5705	2.138	168.03	174.74	0.9892	34	9.4439	3.070	164.20	173.83	0.9767	29
5.7812	2.405	166.94	174.48	0.9857	31						
(ii) Conductivity of trisethylenediaminocobalt(III) chloride solutions.											
2.1450	1.465	146.33	150.71	0.9917	22	5.8170	2.412	142.80	150.01	0.9779	18
2.3865	1.545	145.83	150.45	0.9876	16	6.1207	2.474	142.44	149.84	0.9749	17
2.5895	1.609	145.52	150.33	0.9854	15	7.2284	2.689	141.72	149.76	0.9729	20
3.4420	1.855	144.89	150.44	0.9864	21	7.8923	2.809	141.23	149.63	0.9704	18
3.8508	1.962	144.38	150.25	0.9838	18	10.090	3.177	139.79	149.29	0.9634	19
4.4106	2.100	144.00	150.28	0.9834	21	10.143	3.185	139.86	149.38	0.9647	20
5.4216	2.328	142.95	149.91	0.9767	18	12.158	3.487	138.63	149.06	0.9584	20
(iii) Conductivity of trispropylenediaminocobalt(III) chloride solutions.											
1.9246	1.387	137.18	141.01	0.9929	23	6.5440	2.558	133.31	140.36	0.9813	27
2.2269	1.492	136.93	141.04	0.9936	30	7.4520	2.730	132.50	140.03	0.9751	22
3.5599	1.887	135.48	140.68	0.9873	23	8.3983	2.898	132.05	140.04	0.9750	24
4.3626	2.087	134.93	140.69	0.9872	27	9.0360	3.006	131.57	139.82	0.9710	22
5.9195	2.433	133.77	140.48	0.9835	28	10.115	3.180	131.05	139.82	0.9709	24
10°C.	10°C [‡] .	Λ .	10 ⁵ κ .	10 ⁴ κ .	10°C.	10°C [‡] .	Λ .	10 ⁵ κ .	10 ⁴ κ .		
(iv) Conductivity of hexamminocobalt(III) sulphate solutions.											
0.755	0.869	161.04	0.239	2.80	5.384	2.320	123.12	5.96	2.71		
1.483	1.218	150.99	0.769	2.80	8.406	2.899	113.65	10.94	2.84		
2.557	1.599	140.44	1.84	2.79	9.033	3.006	110.55	12.36	2.72		
3.335	1.826	134.57	2.88	2.75	12.70	3.564	103.18	19.38	2.78		
4.369	2.090	128.16	4.36	2.73	14.84	3.852	99.22	23.88	2.75		
4.671	2.161	126.85	4.79	2.75							
(v) Conductivity of trisethylenediaminocobalt(III) sulphate.											
1.278	1.130	136.32	0.457	3.88	8.604	2.932	101.16	10.5	3.25		
3.048	1.746	124.11	1.95	3.92	9.082	3.013	103.74	10.3	3.65		
3.584	1.893	117.74	2.92	3.18	10.68	3.208	97.11	14.1	3.29		
4.667	2.160	116.13	3.88	3.96	13.12	3.623	91.89	19.1	2.94		
6.141	2.480	111.18	5.82	3.86							
(vi) Conductivity of trispropylenediaminocobalt(III) sulphate.											
1.858	1.363	133.77	0.240	16.6	7.847	2.801	120.98	2.49	19.1		
2.407	1.551	132.78	0.306	21.0	7.993	2.827	119.74	2.86	16.9		
3.662	1.914	129.02	0.698	19.2	9.541	3.089	117.48	3.76	17.0		
4.924	2.219	126.32	1.14	19.5	11.27	3.357	116.23	4.46	18.9		
5.733	2.394	124.02	1.62	17.5	14.61	3.826	112.56	6.61	19.0		

Trisethylenediaminocobalt(III) sulphate. 61 ml. of 70% ethylenediamine in water were partly neutralised with 1.5 ml. of concentrated sulphuric acid in 10 ml. of water. To this, a solution of 24 g. of cobalt sulphate in 75 ml. of water was added, and a vigorous stream of air passed through for 5 hours. The mixture was evaporated on a water-bath until a crust formed on the surface. On addition of 15 ml. of concentrated sulphuric acid and 30 ml. of ethyl alcohol, the salt was precipitated. It was filtered off and washed with alcohol until the washings were colourless. The sulphate was recrystallised by dissolving it in water and adding alcohol, this process being repeated five times. The stock solutions were analysed gravimetrically as in the previous case, duplicates agreeing within $\pm 0.03\%$. The stock solutions had a pH of *ca.* 4, which in spite of the numerous recrystallisations was probably due to traces of free acid. In place of the usual solvent correction, a pH-concentration curve was obtained and the pH's of the solutions whose resistances were measured were obtained by interpolation. Since hydrogen

ions contribute to the major part of the solvent conductivity, and the specific conductivity due to these is given by $\kappa = 350[H^+] \times 10^{-3}$, where 350 is the mobility of the ion (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 172), this amount was subtracted from the measured specific conductivities before calculation of the equivalent conductivities.

Trispropylenediaminocobalt(III) sulphate. 11.6 ml. of specially pure B.D.H. propylenediamine were diluted to 41 ml. with water, and poured into 17 ml. of water containing 5.3 g. of cobalt sulphate. Air was bubbled through vigorously for 5 hours. The solution was evaporated to 15 ml., and the salt precipitated by addition of 4 ml. of concentrated sulphuric acid and 40 ml. of ethyl alcohol. After cooling, the salt was filtered off. Initially, it formed an oil, but crystallised out after vigorous stirring. Methyl alcohol was used during the recrystallisations, and it caused the salt to settle out as a fine yellow powder. After several recrystallisations from water and alcohol, the salt was dried in a vacuum oven at 30–50° for 2 days. The concentrations of the stock solutions were found gravimetrically as sulphate, duplicates agreeing to within $\pm 0.03\%$. The pH of the strongest solution was 4.9, and solvent corrections were applied as in the previous case.

The results are given in Table I.

DISCUSSION.

From the conductivities of the chlorides, the limiting mobilities of the cations may be obtained with a high degree of accuracy. For this purpose Onsager's method of extrapolation

FIG. 1.
Onsager extrapolations for Λ° :
(a) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$; (b) $\text{Co en}_3\text{Cl}_3$; (c) $\text{Co pn}_3\text{Cl}_3$.

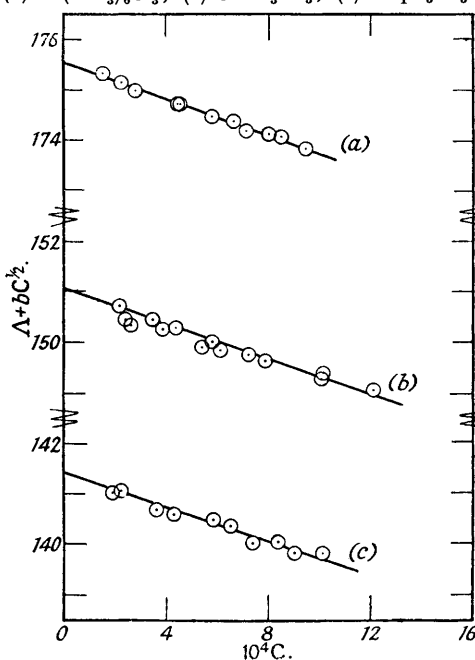
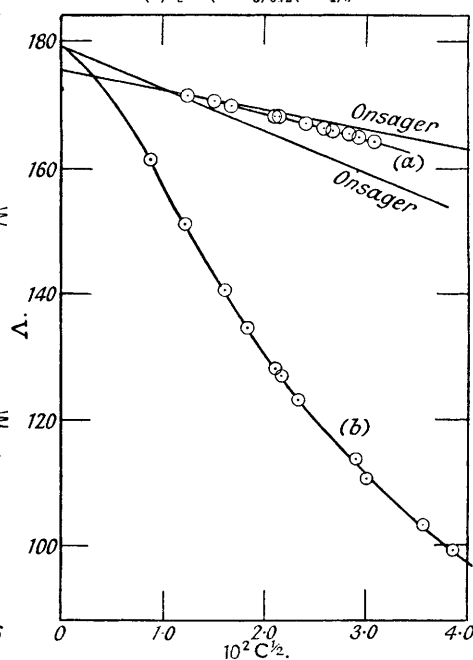


FIG. 2.
Conductivities of (a) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$;
(b) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$.



was used (*Physikal. Z.*, 1927, 28, 277). An approximate value of Λ° , the equivalent conductivity at zero concentration, is obtained in the usual manner, *i.e.*, by plotting Λ against $C^\frac{1}{2}$. From this the theoretical slope b is calculated by means of Onsager's conductivity equation, and then $\Lambda + bC^\frac{1}{2}$ is plotted against C . These sensitive plots are shown in Fig. 1, and Λ° , the limiting mobilities of the cations thereby obtained, are listed in Table II. The experimental conductivity curves, Λ being plotted against $C^\frac{1}{2}$, lie slightly below the theoretical line; this is illustrated in the case of hexamminocobalt(III) chloride in Fig. 2. This slight difference may be attributed to ion-pair formation between the cation and chloride ions. The dissociation constant corresponding to the equilibrium $\text{Co}(\text{NH}_3)_6^{3+} + \text{Cl}^- \rightleftharpoons \text{Co}(\text{NH}_3)_6\text{Cl}^{2+}$ has been calculated as follows. Let $(1 - \alpha)m$ represent the concentration of $\text{Co}(\text{NH}_3)_6^{3+}$ ions when the total molar concentration of salt is m . The concentration of $\text{Co}(\text{NH}_3)_6^{3+}$ is then αm , and the solution is treated as a mixture of (i) the 1:3-valent salt $[\text{Co}(\text{NH}_3)_6^{3+}, 3\text{Cl}^-]$ of molar concentration αm , for which the Onsager equation is $\Lambda_{31} = 175.55 - 221.5I^\frac{1}{2}$, where I is the actual ionic strength $= \frac{1}{2}\{\text{Cl}^- + 4[\text{Co}(\text{NH}_3)_6\text{Cl}^{2+}] + 9[\text{Co}(\text{NH}_3)_6^{3+}]\} = (1 + \alpha)C$, where C is the

72 The Conductivities of Some Complex Cobalt Chlorides and Sulphates.

equivalent concentration, and (ii) the 1:2-valent salt $[\text{Co}(\text{NH}_3)_6\text{Cl}^{2+}, 2\text{Cl}^-]$ of molar concentration $(1 - \alpha)m$, for which the Onsager equation is $\Lambda_{21} = 142.5 - 146.5I^{\frac{1}{2}}$. In this case, the mobility of the bivalent ion-pair is taken as two-thirds of that of the tervalent cation. The solvent-corrected specific conductivity of the solution is given by

$$\begin{aligned} 10^3\kappa &= 3\alpha m\Lambda_{\text{Co}(\text{NH}_3)_6^{3+}} + 2(1 - \alpha)m\Lambda_{\text{Co}(\text{NH}_3)_6\text{Cl}^{2+}} + (2 + \alpha)m\Lambda_{\text{Cl}^-} \\ &= 3\alpha m\Lambda_{31} + 2(1 - \alpha)m\Lambda_{21} \end{aligned}$$

Whence

$$\begin{aligned} \Lambda &= 10^3\kappa/3m = \alpha\Lambda_{31} + \frac{2}{3}(1 - \alpha)\Lambda_{21} \\ &= 94.94 - 97.7I^{\frac{1}{2}} + \alpha(80.6 - 123.8I^{\frac{1}{2}}) \end{aligned}$$

At first, α is assumed to be unity and the corresponding value of I is used in this equation, thereby giving a truer value to α with which to calculate a truer value of I , and so on, until constant figures are obtained. The dissociation constant results

$$K = \frac{\{\text{Cl}^-\}\{\text{Co}(\text{NH}_3)_6^{3+}\}}{\{\text{Co}(\text{NH}_3)_6\text{Cl}^{2+}\}} = \frac{(2 + \alpha)\alpha m f_1 f_2}{(1 - \alpha)f_3}$$

are given in Table I (i). The activity coefficients f_1 , f_2 , and f_3 have been calculated from the Debye-Huckel equation, $-\log f_i = 0.509z_i^2I^{\frac{1}{2}}$ where z_i is the ion valency. Exactly the same treatment has been applied to the other two chlorides, and the average results are 0.032 for $\text{Co}(\text{NH}_3)_6\text{Cl}^{2+}$, 0.019 for $\text{Co en}_3\text{Cl}^{2+}$, and 0.025 for $\text{Co pn}_3\text{Cl}^{2+}$. Since these are dependent on very slight differences between theory and practice, and are sensitive to very small changes in Λ° , we cannot expect these figures to do more than indicate the orders of the dissociation constants, but it is noteworthy that they are comparable with the values obtained with 1:3-valent salts where the anion is tervalent, namely, 0.068 for $\text{NaP}_3\text{O}_9'''$ (Davies and Monk, *J.*, 1949, 413), and 0.06 for $\text{KFe}(\text{CN})_6''$ and $\text{KCo}(\text{CN})_6''$ (James and Monk, *Trans. Faraday Soc.*, in the press).

The limiting cation mobilities obtained from the chlorides, together with 80.00 for the sulphate ion (Jenkins and Monk, *J. Amer. Chem. Soc.*, 1950, 72, 2695), have been used in discussing the conductivities of the sulphates. This method of obtaining Λ° is preferable to obtaining it by extrapolation of the sulphate conductivities, since this is a rather uncertain method with higher-valent electrolytes. In Fig. 2, where the conductivity curve for hexaminocobalt(III) sulphate is compared with the theoretical Onsager line for the fully ionised electrolyte, there is a large discrepancy, through strong association between the complex cation and the sulphate ions. This is also the case with the other two sulphates, and the dissociation constants of these, e.g., for the equilibrium $\text{Co}(\text{NH}_3)_6(\text{SO}_4)' \rightleftharpoons \text{Co}(\text{NH}_3)_6^{3+} + \text{SO}_4''$, have been obtained as follows. The three Onsager equations for the three types of ion are

$$\begin{aligned} \text{For } \text{Co}(\text{NH}_3)_6^{3+} \quad \Lambda_1^{\ddagger} &= 99.2 - 224.4I^{\frac{1}{2}} \\ \text{,, } \text{SO}_4'' \quad \Lambda_2^{\ddagger} &= 80.00 - 168.4I^{\frac{1}{2}} \\ \text{,, } \text{Co}(\text{NH}_3)_6(\text{SO}_4)' \quad \Lambda_3^{\ddagger} &= 33.07 - 74.8I^{\frac{1}{2}} \end{aligned}$$

The limiting mobility of the ion-pair is taken as one-third of that of the tervalent cation. The total ionic strength is given by

$$I = \frac{1}{2}\{9[\text{Co}(\text{NH}_3)_6^{3+}] + 4[\text{SO}_4''] + [\text{Co}(\text{NH}_3)_6(\text{SO}_4)']\}$$

and if we let x be the concentration of the ion-pair at a total molar concentration m , then $I = 15m - 6x = 2.5C - 6x$. The observed conductivity, Λ , is related to the calculated conductivity by

$$6\Lambda m = 3(2m - x)\Lambda_1^{\ddagger} + 2(3m - x)\Lambda_2^{\ddagger} + x\Lambda_3^{\ddagger}$$

i.e.,

$$\Lambda_1^{\ddagger} + \Lambda_2^{\ddagger} - \Lambda = (x/C)(3\Lambda_1^{\ddagger} + 2\Lambda_2^{\ddagger} + \Lambda_3^{\ddagger})$$

From this, and from the ionic-strength relation, by approximating until constant x and I values are derived, the dissociation constant

$$K = \frac{\{\text{Co}(\text{NH}_3)_6^{3+}\}\{\text{SO}_4''\}}{\{\text{Co}(\text{NH}_3)_6(\text{SO}_4)'\}} = \frac{(2m - x)(3m - x)f_1 f_2}{x f_3}$$

has been obtained; the activity coefficients were calculated as in the previous case. The results are given in the tables, and the average values are: $\text{Co}(\text{NH}_3)_6(\text{SO}_4)' = 2.77 \times 10^{-4}$, $\text{Co en}_3(\text{SO}_4)' = 3.55 \times 10^{-4}$, and $\text{Co pn}_3(\text{SO}_4)' = 1.75 \times 10^{-3}$. The trend in these as the

size of the cobalt cation increases is in the expected direction. LaSO_4^+ , where we have a similar type of association, has a dissociation constant of the same order as these, namely 2.4×10^{-4} (Jenkins and Monk, *loc. cit.*).

In Table II, the variation in the limiting mobilities of the complex cobaltic cations also follows the expected trend; *i.e.*, as the size increases, the mobility becomes less. Inserting these results in equation (2), we obtain the ionic radii a given in Table II. By applying the same treatment to the data for the chloride ion (Harned and Owen, *loc. cit.*) and sulphate, the radii of the anions are obtained also. Addition of these cation and sulphate ionic radii gives the size of the ion pair, which may be compared with those derived from Bjerrum's equation (1).

TABLE II.

Ion.	Λ_i° .	a (A.).	Ion-pair.	Radii of ion-pairs (A.).	
				Eqn. (1).	Eqn. (2).
$\text{Co}(\text{NH}_3)_6^{+++}$	99.2	2.77	$\text{Co}(\text{NH}_3)_6(\text{SO}_4)^+$	2.56	5.06
$\text{Co}(\text{en})_3^{+++}$	74.7	3.68	$\text{Co}(\text{en})_3(\text{SO}_4)^+$	4.28	5.97
$\text{Co}(\text{pn})_3^{+++}$	65.06	4.23	$\text{Co}(\text{pn})_3(\text{SO}_4)^+$	5.76	6.52
Cl^-	76.34	1.20	—	—	—
SO_4^{--}	80.00	2.29	—	—	—

Although the sizes of the ion pairs are of the right order, it is only in the last case that the two methods give comparable results. Even with the use of Stokes's law, however, which gives the larger radii, it is probable that the calculations are on the small side, since the radius of the unhydrated chloride ion is 1.81 A. (Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1939, Chap. 10) whereas our calculations for the hydrated ion give 1.20 A. It is possible that with cases where both ions forming the ion-pair are large and symmetrical, truer results might be obtained. A pointer in this direction is provided by the case of lanthanum ferricyanide (Davies and James, *Proc. Roy. Soc.*, 1948, *A*, 195, 116), which has a dissociation constant of 1.83×10^{-4} at 25°, corresponding to a "Bjerrum distance" of 7.20 A. From the mobilities of the lanthanum and ferricyanide ions (Harned and Owen, *loc. cit.*), Stokes's law gives 6.67 A.

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