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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

Activity Coefficient and Conductivity Measurements of High-charge (3-1, 1-3, 3-2) Electrolytes. I.[1a]

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Mean activity and osmotic coefficients have been determined at 25° for aqueous solutions of $Co(en)_3(NO_3)_3$, $Co(pn)_3(ClO_4)_3$, $K_3Co(CN)_6$ and $[Co(en)_3]_2(SO_4)_3$, by isopiestic comparison with potassium chloride solutions. At the concentrations required, these salts do not obey the simple laws for 3-1 or 3-2 types, requiring low values of $\mathring{a}$ to represent the data by means of the Debye–Hückel equation. The solubilities of $Co(en)_3(NO_3)_3 \cdot H_2O$ and $K_3Co(CN)_6$ were determined to be 0.2749 and 1.311 *m*, respectively. Conductivity measurements were made on solutions of the same four electrolytes. A decided deviation from the Onsager limiting law was observed. The limiting values obtained for the complex ions are in agreement with those found by previous workers.

Introduction

This paper is a continuation of a program of investigation of the properties of high-charge electrolytes in aqueous solution.[2,3] Four additional compounds, tris-(ethylenediamine)-cobalt(III) nitrate, tris-(propylenediamine)-cobalt(III) perchlorate, potassium hexacyanocobaltate(III) and tris-(ethylenediamine)-cobalt(III) sulfate, have been prepared and studied. The activity coefficients have been determined by isopiestic comparison with potassium chloride. In addition the contributions of high-order terms of the electrophoretic effect to conductivity were calculated as was done by Dye and Spedding[4] for the alkaline earth and rare earth salts.

Experimental

Materials.—Conductivity water was prepared by distillation from an alkaline permanganate solution using a glass-packed column. The water then was redistilled in a stream of purified nitrogen and was introduced into the conductivity cells without exposure to atmospheric CO_2.

Potassium hexacyanocobaltate(III) was prepared according to the procedure given in "Inorganic Syntheses"[5] and the product was purified by recrystallization three times from conductivity water or by repeated fractional precipitation with dioxane from conductivity water. The anhydrous form results with either method and was the form used in this work. Both procedures give identical results.

Tris-(propylenediamine)-cobalt(III) perchlorate was prepared by a quantitative metathesis reaction between $Co(pn)_3(Cl_3)$[6] and $AgClO_4$ in aqueous solution. The anhydrous propylenediamine used was made from 70% propylenediamine by the method of Rollinson and Bailar.[7] The $AgClO_4$ was prepared by treating an excess of Ag_2O, nitrate free, with 0.1 *M* $HClO_4$. The resulting $AgClO_4$ solution was separated from the excess Ag_2O by filtration, then diluted and analyzed by AgCl precipitation. An aqueous solution of the complex chloride then was titrated quantitatively with the standardized $AgClO_4$ solution, making sure no more than one or two drops excess were added. The AgCl was filtered off after digestion on a steam-bath for 1 hr. The resulting $Co(pn)_3(ClO_4)_3$ solution then was concentrated by evaporation and the $Co(pn)_3(ClO_4)_3 \cdot H_2O$ precipitated by addition of ethyl alcohol. The salt was recrystallized a minimum of three times from conductivity water and dried in a vacuum oven at 90° until the anhydrous form resulted.

Anal. Calcd. for $Co(pn)_3(ClO_4)_3$: Co, 10.17; N, 14.50; C, 18.65; H, 5.22. Found: Co, 10.14; N, 14.52; C, 18.52; H, 5.34.

Tris-(ethylenediamine)-cobalt(III) nitrate was prepared by a quantitative metathesis reaction between $Co(en)_3Cl_3$[8] and $AgNO_3$ in aqueous solution. The metathesis reaction was carried out as above. The $Co(en)_3(NO_3)_3$ was recovered by evaporation of the filtrate and was dried until the anhydrous form resulted.

Anal. Calcd. for $Co(en)_3(NO_3)_3$: Co, 13.85. Found: Co, 13.76.

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[1] (a) This research was supported by a research grant from The National Science Foundation. (b) To whom correspondence should be directed.

[2] C. H. Brubaker, Jr., THIS JOURNAL, **78**, 5762 (1956).

[3] C. H. Brubaker, Jr., *ibid.*, **79**, 4274 (1957).

[4] J. L. Dye and F. H. Spedding, *ibid.*, **76**, 888 (1954).

[5] J. H. Bigelow, "Inorganic Syntheses," McGraw Hill Book Co., Inc., New York, N. Y., 1946, Vol. II, p. 225.

[6] I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, 68 (1951).

[7] C. L. Rollinson and J. C. Bailar, "Inorganic Syntheses," Vol. II, McGraw Hill Book Co., Inc., New York, N. Y., 1946, p. 197.

[8] J. B. Work, *ibid.*, p. 221.

TABLE I

ISOPIESTIC MOLALITIES AND OSMOTIC COEFFICIENTS OF ELECTROLYTES AT 25°

$Co(pn)_3(ClO_4)_3$			$Co(en)_3(NO_3)_3$		$K_3Co(CN)_6$		$[Co(en)_3]_2(SO_4)_3$	
$m_{av.}$	$\phi_{obsd.}$	$\phi_{calcd.}$	$m_{av.}$	$\phi_{obsd.}$	$m_{av.}$	$\phi_{obsd.}$	$m_{av.}$	$\phi_{obsd.}$
0.05747	0.6693	0.6778	0.03055	0.6918	0.03035	0.7479	0.08160	0.2613
.06898	.6603	.6633	.05267	.6789	.07393	.7075	.1453	.2417
.09056	.6424	.6418	.08776	.6468	.1508	.6926	.1489	.2379
.1117	.6270	.6259	.1266	.6241	.2730	.6819	.2407	.2027
.1336	.6098	.6099	.1349	.6098	.4571	.6768	.3504	.1705
.1548	.5984	.5973	.1574	.5952	.5828	.6768	.4580	.1705
.1659	.5894	.5910	.1853	.5795	.6775	.6804	.5004	.1681
.2027	.5719	.5718	.2587	.5410	.7309	.6857	.6190	.1641
.2243	.5629	.5616	.2612	.5408	.7667	.6876	.8993	.1862
.2503	.5523	.5498	.2749	.5361	.8172	.6918	1.003	.1993
.2578	.5464	.5466			.8497	.6924	1.064	.2043
.2612	.5498	.5450			.9507	.7007	1.252	.2259
					1.026	.7063	1.298	.2310
					1.082	.7116	1.429	.2499
					1.217	.7258	1.536	.2622
					1.223	.7305	1.800	.2979
					1.235	.7331	1.844	.3050
					1.306	.7421		
					1.311	.7425		

Tris-(ethylenediamine)-cobalt(III) sulfate was prepared from $Co(en)_3Cl_3$[8] and H_2SO_4 using the method described by Meyer and Grohler.[9] The compound could not be dried to the anhydrous form so stock solutions were prepared and the concentrations determined by gravimetric sulfate analysis as $BaSO_4$; duplicates agreed to within ±0.03%.

For all salts studied, the *p*H values of stock solutions were measured to insure the absence of hydrolysis. The solutions were found to be neutral.

Apparatus.—The experimental procedure and apparatus used for the isopiestic measurements have been previously described.[3] The temperature was 24.978 ±0.005°.

The resistance measurements were made with an a.c. bridge designed by Thompson and Rogers.[10] The oscillator used permitted resistance values to be taken at five frequencies over the range 400 to 4,000 cycles per sec. An oscilloscope was used to determine the balance point. Before each run the value of a standard resistance was checked to ensure that the bridge was functioning properly.

The cells were held at a constant temperature of 25.00 ±0.015° in an oil bath. Three cells were used to cover the concentration range. The two low concentration cells (cell constants about 0.3 cm.$^{-1}$ and 1.0 cm.$^{-1}$) were similar to the erlenmeyer type described by Daggett, Bair and Kraus.[11] A Leeds and Northrup type A conductance cell was sealed to a 500-ml. erlenmeyer flask with two stopcocks. One stopcock was attached to the cap and the other to an added side-arm. This permitted the introduction of carbon dioxide-free conductivity water directly from the distilling apparatus under a pressure of nitrogen. Also, a steady stream of nitrogen saturated with water vapor was permitted to flow through the cell when additions were made to the solution. The cell constants were determined using aqueous KCl. Runs with KCl were made in the same manner as with the samples and covered the same resistance range. At least five additions of KCl were made for each calibration.

The electrodes were lightly platinized. Cell resistances were linear functions of $(\text{frequency})^{-1/2}$ and were extrapolated to infinite frequency in the usual fashion. When the total variation of resistance with frequency was greater than 0.2%, the electrodes were cleaned with fuming nitric acid and replatinized, and the cell constant was redetermined.

The water was forced into the weighed empty cell by means of nitrogen pressure. The cell plus water then was weighed and placed in the thermostat to permit determination of solvent conductance (specific conductivity $\approx 0.6 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$). The resistance of the water and a standard resistance in parallel was recorded after repeated mixing. In the event of "drifting" resistance readings, the water was discarded and the cell was cleaned. After determination of the water resistance, successive portions of a stock solution were added. Blank runs involving the addition of water gave only the resistance changes to be expected due to differences in specific conductance of the two samples of water. A correction for this difference was made for all stock additions and amounted to less than 0.03%. Following each addition the contents of the cell were thoroughly mixed and the cell was placed back in the bath. The attainment of temperature equilibrium was indicated when successive resistance readings checked to within 0.01%. The resistance values were then recorded. The cell was removed from the bath and the contents remixed. Remixing of the solution was continued until successive readings checked to within 0.01%. For the higher concentrations the stock solutions were added directly to a Leeds and Northrup type B conductance cell (cell constant about 30 cm.$^{-1}$) after the cell had been rinsed several times with the solution. The resistances were recorded after equilibrium was reached and the procedure was repeated for new portions of the solution. That the solutions were stable was indicated by the lack of drift of resistance readings and the general reproducibility of the data.

Densities of solutions of the compounds also were measured in order to be able to convert molality data to volume concentration. They were determined at 25° with a pycnometer (Cenco #10669) and can be represented within experimental error up to about 0.03*m* by the equation

$$\rho = 0.9971 + Am \qquad (1)$$

The values of *A* for the various electrolytes are: $Co(en)_3(NO_3)_3$, 0.1945; $Co(pn)_3(ClO_4)_3$, 0.2558; $K_3Co(CN)_6$, 0.1862; $[Co(en)_3]_2(SO_4)_3$, 0.3740.

Results and Discussion

Activity Coefficients.—The experimental results are given in Table I as molalities of the isopiestic solutions and the corresponding osmotic coefficients, which were calculated from known values of potassium chloride solutions. The molalities of the saturated solutions of $Co(en)_3(NO_3)_3 \cdot H_2O$ and $K_3Co(CN)_6$ were found to be 0.2749 and 1.311 *m*, respectively. The conversion of the undissolved $Co(pn)_3(ClO_4)_3$ to the monohydrate in equilibrium with the saturated solution was slow and its solubility was not determined but is estimated to be about 0.27 *m*. The highest concentration em-

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(9) J. Meyer and K. Grohler, *Z. anorg. Chem.*, **155**, 91 (1926).

(10) H. B. Thompson and M. T. Rogers, *Rev. Sci. Instruments*, **27**, 1079 (1956).

(11) H. M. Daggett, E. J. Bair and C. A. Kraus, THIS JOURNAL, **73**, 799 (1951).

TABLE II

MEAN ACTIVITY COEFFICIENTS AND SMOOTHED OSMOTIC COEFFICIENTS OF ELECTROLYTES AT 25°

	$Co(en)_3(NO_3)_3$		$Co(pn)_3(ClO_4)_3$		$K_3Co(CN)_6$		$[Co(en)_3]_2(CO_4)_3$	
m	$\gamma\pm$	ϕ	$\gamma\pm$	ϕ	$\gamma\pm$	ϕ	$\gamma\pm$	ϕ
0.01	0.505	0.7980	0.513	0.7967	0.522	0.9126	0.152	0.4787
.03	.357	.7185	.368	.7156	.385	.7487	.0654	.3418
.05	.296	.6832	.305	.6787	.323	.7116	.0440	.2943
.07	.258	.6592	.266	.6563	.293	.7089	.0339	.2761
.10	.222	.6338	.228	.6351	.260	.6968	.0256	.2569
.15	.184	.5995	.189	.6003	.228	.6902	.0186	.2393
.20	.158	.5709	.163	.5740	.207	.6838	.0146	.2219
.25	.140	.5465	.145	.5527	.193	.6830	.0120	.2040
.2612			.141	.5498[a]				
.2749	.133	.5361[a]						
.30					.181	.6801	.0102	.1872
.50					.153	.6758	.00648	.1685
.75					.135	.6887	.00462	.1686
1.00					.127	.7055	.00381	.2100
1.20					.123	.7284	.00337	.2291
1.30					.122	.7424	.00320	.2385
1.311					.122	.7425[a]		
1.50							.00294	.2625
1.75							.00272	.2962
1.844							.00265	.3047

[a] Saturated solutions.

ployed for the $[Co(en)_3]_2(SO_4)_3$ was limited by the amount which could be weighed conveniently into the dishes.

Calculation of the osmotic coefficients by the method of Scatchard and Prentiss[12] was attempted in all cases. $Co(pn)_3(ClO_4)_3$ was the only salt, however, for which the method was able to reproduce the experimental data with sufficient accuracy over a concentration range large enough to warrant its use. A comparison of the observed and calculated osmotic coefficients for $Co(pn)_3(ClO_4)_3$ is given in Table II.

The activity coefficient of the perchlorate was then calculated.[3,13] The deviations were smallest for $\mathring{a} = 3.83$ and $B = 0.971$.

In the other cases, the activity coefficients were determined by graphical integration of the equation

$$\ln \gamma_{\pm} = -(1 - \phi) - 2 \int_0^m \left(\frac{1 - \phi}{m^{1/2}}\right) dm^{1/2} \quad (2)$$

The extension of the function $(1 - \phi)/m^{1/2}$ *vs.* $m^{1/2}$ to infinite dilution was carried out with the aid of the Debye–Hückel equation and required that the parameter $\mathring{a}$ have the values: $Co(en)_3(NO_3)_3$, 3.23; $Co(pn)_3(ClO_4)_3$, 3.16 (from equation 2, *i.e.*, $B = 0$), $K_3Co(CN)_6$, 4.01; $[Co(en)_3]_2(SO_4)_3$, 3.43.

It was found in both the present study and that previously reported[3] that while the value of the $\mathring{a}$ parameter is sensitive to the method of extrapolation, the activity coefficients calculated by the two methods differ by only about 1%.

Table II gives the mean activity and osmotic coefficients for solutions of the salts studied. The logarithms of the activity coefficients given in Table II are plotted in Fig. 1, along with the values obtained for $Co(en)_3Cl_3$.[3] The activity coefficients of the $Co(en)_3(NO_3)_3$, $Co(pn)_3(ClO_4)_3$ and $Co(en)_3Cl_3$ are all within about 2% of each other and are represented by a single curve up to approximately 0.09 *m*. Data such as these would seem to indicate the feasibility of estimating the activity coefficients of other complexes of similar size and charge type.

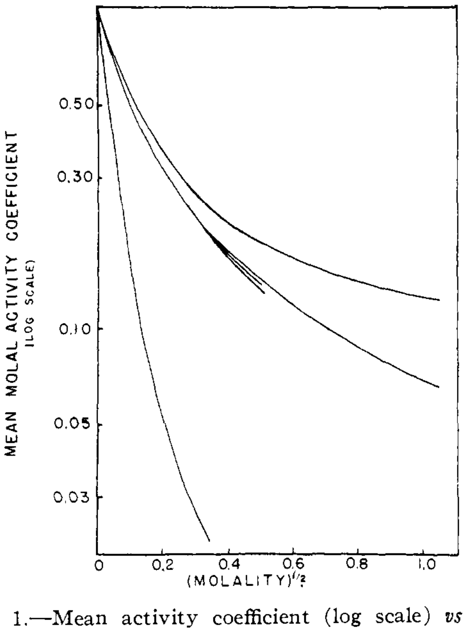

Fig. 1.—Mean activity coefficient (log scale) *vs.* $\sqrt{m}$. Left to right: $[Co(en)_3]_2(SO_4)_3$; $Co(en)_3(NO_3)_3$; $Co(pn)_3(ClO_4)_3$; $Co(en)_3Cl_3$; $K_3Co(CN)_6$.

In the case of $[Co(en)_3]_2(SO_4)_3$ the extrapolation is somewhat uncertain, but the results are of the same order of magnitude as for other 3–2 electrolytes.[14]

Conductivity.—The experimental conductance data and standard deviations from smooth curves are given in Table III.

From the experimental results given in Table III, except for the data on $[Co(en)_3]_2(SO_4)_3$, the values

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(12) G. Scatchard and S. S. Prentiss, THIS JOURNAL, **55**, 4355 (1933).

(13) R. P. Smith, *ibid.*, **61**, 500 (1939).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 566.

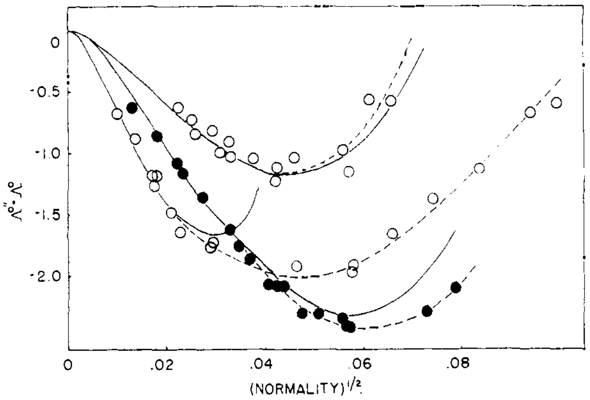

Fig. 2.—($\Lambda_0'' - \Lambda_0$) *vs.* $\sqrt{N}$. Left to right: $Co(pn)_3(ClO_4)_3$; $Co(en)_3(NO_3)_3$; $K_3Co(CN)_6$. Solid lines calculated by equation 3.

of $\Lambda^{0''}$, Λ^0, A and B in the expression

$$\Lambda^{0''} \equiv \Lambda + S N^{1/2} = \Lambda^0 + AN \log N + BN \quad (3)$$

were calculated as described in the paper which follows.[15] This Owen method of extrapolation[16] fits the data below the minimum in the $\Lambda^{0''}$ curve as shown by the solid lines in Fig. 2. The values of A, B and Λ^0 required are given in Table IV. From the limiting conductivities of the nitrate, perchlorate, potassium and sulfate ions,[17,18] the limiting conductivities of the complex cobaltic ions can be obtained and compared with the literature values.[6,19] The results are given in Table V.

Table III

Equivalent Conductances of Electrolytes at 25°

$Co(en)_3(NO_3)_3$			$Co(pn)_3(ClO_4)_3$		
$N \times 10^3$	Run no.	Λ	$N \times 10^3$	Run no.	Λ
0.17248	1	141.87	0.098169	1	129.05
.32775	2	140.23	.18140	1	127.88
.50332	1	138.78	.29019	1	126.61
.55665	3	138.36	.30363	2	126.44
.79662	1	136.99	.31845	1	126.40
1.0990	2	135.18	.43880	1	125.26
1.2053	1	134.60	.51138	2	124.74
1.2057	3	134.60	0.84051	1	122.78
1.3817	4	133.80	0.86718	2	122.69
1.6524	3	132.61	2.1662	2	117.86
1.8254	2	132.01	3.3393	3	114.75
1.8907	1	131.79	3.3528	2	114.78
2.2708	3	130.28	4.3566	2	112.77
2.6028	2	129.42	5.5635	2	110.79
3.1044	3	128.05	7.0419	3	108.49
3.2343	4	127.66	8.8596	3	106.18
3.2964	2	127.49	19.289	3	98.637
5.3353	4	123.15	27.267	3	94.587
6.2610	5	121.65			
9.9483	5	117.20			
29.627	5	102.19			
78.432	5	88.285			
211.58	5	74.213			
288.89	5	69.812			

Run no.	$L_{H_2O} \times 10^6$	Cell const.	Run no.	$L_{H_2O} \times 10^6$	Cell const.
1	0.548	0.3146	1	0.778	1.0367
2	.629	1.0323	2	0.775	1.0367
3	.815	1.0323	3	[a]	30.00
4	.661	1.0365			
5	[a]	30.00			
RMS deviation 0.039 conductance unit			RMS deviation 0.060 conductance unit		

$K_3Co(CN)_6$			$[Co(en)_3]_2(SO_4)_3$		
$N \times 10^3$	Run no.	Λ	$N \times 10^3$	Run no.	Λ
0.51600	2	164.81	0.23889	1	136.05
.66384	2	163.76	0.81565	1	108.82
.67491	1	163.58	1.4727	1	94.901
.86460	2	162.55	2.3912	1	84.133
.97386	3	161.79	3.8719	1	74.356
1.0824	2	161.37	5.6155	1	67.467
1.1288	1	161.01	6.0890	2	65.566
1.4242	2	159.73	6.6255	1	64.628
1.7722	1	158.17	14.898	2	51.560
1.8225	3	158.10	26.707	2	44.161
2.1315	2	157.09	44.457	2	38.577
3.1473	2	154.06	153.10	2	27.920
3.2655	4	153.55	337.91	2	23.130
3.7839	4	152.79			
4.3572	2	151.36			
6.4080	2	148.34			
12.663	4	141.93			
19.294	4	135.38			
28.882	4	130.24			
119.36	4	113.30			
210.09	4	107.40			
299.27	4	103.91			

Run no.	$L_{H_2O} \times 10^6$	Cell const.	Run no.	$L_{H_2O} \times 10^6$	Cell const.
1	0.710	1.0323	1	1.071	1.0367
2	.497	1.0365	2	[a]	30.00
3	.748	0.2500			
4	[a]	30.00			
RMS deviation 0.067 conductance unit			RMS deviation not determined		

[a] Variable; measurements made on separate solutions; water conductance measured for each stock.

Table IV

Parameters of the Owen Equation at 25°

Electrolyte	A	B	Λ^0
$Co(en)_3(NO_3)_3$	1586	3,248	146.14
$Co(pn)_3(ClO_4)_3$	4679	12,400	132.42
$K_3Co(CN)_6$	1293	2,914	172.50

Table V

Limiting Equivalent Conductivities at 25°

Ion	This work	Lit. value
$Co(en)_3^{+3}$	74.68	74.7[6]
$Co(pn)_3^{+3}$	65.06	65.06[6]
$Co(CN)_6^{-6}$	99.00	98.9[17]

The larger mobility of the $Co(CN)_6^{-3}$ and $Co(en)_3^{+3}$ ions compared with those of the rare earth trivalent ions would seem to indicate that with the former the first layer of water molecules is replaced by the cyanide or ethylenediamine group, respectively, and water molecules do not appear to attach themselves to these foreign groups as readily as to other water molecules. With large spherical ions one would expect solvation effects to be much smaller owing to the lower charge

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[15] K. O. Groves, J. L. Dye and C. H. Brubaker, Jr., This Journal, **82**, 4445 (1960).

[16] B. B. Owen, *ibid.*, **61**, 1939 (1939).

[17] Reference 14, p. 231, Table (6-8-2).

[18] R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Butterworth Scientific Publications, London, 1955, p. 452.

[19] J. C. James and C. B. Monk, *Trans. Faraday Soc.*, **46**, 1041 (1950).

densities on the surfaces, which would lead to a higher mobility.

The method of Dye and Spedding[4] was applied to the data for the 3-1 and 1-3 electrolytes. It was possible to fit the data up to 4 to 16 × 10^{-4} *N*. The $\mathring{a}$ values required are: $Co(en)_3(NO_3)_3$, 3.23; $Co(pn)_3(ClO_4)_3$, 3.47; $K_3Co(CN)_6$, 3.80. These values are too small but are of the same order of magnitude as those required to fit activity data. It is apparent that in both cases all of the inadequacies of present theory are being absorbed by the single parameter $\mathring{a}$, and it is not surprising that the "adjusted ionic size" is not its actual size. However, this calculation serves to emphasize the fact that these higher terms are *not* negligible.

Association "constants" were calculated as described in the paper which follows.[15] The value of the association constant required to fit the data varied considerably with concentration, indicating that ion-pair formation alone is unable to account for the conductance behavior. Typically, a tenfold concentration decrease from 3 × 10^{-3} *N* to 3 × 10^{-4} N required a 100% or more increase in the association constant. This undoubtedly is due to lack of knowledge of the conductance to be expected for a completely ionized unsymmetrical electrolyte.

While current theory is inadequate, it is hoped that data such as these for a number of different unsymmetrical electrolytes will serve as a guide for the development of a satisfactory theory for dilute solutions of high-charge salts.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

Activity Coefficients and Conductances of High-charge (4-1, 1-4, 1-2) Electrolytes. II.[1a]

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RECEIVED AUGUST 27, 1959

Mean activity and osmotic coefficients of aqueous solutions of $Pt(pn)_3Cl_4$, $[NMe_4]_4Mo(CN)_8$, $K_4W(CN)_8$ and $K_2Pt(CN)_4$ were determined at 25° by isopiestic comparison with aqueous KCl solutions. The Debye–Hückel equation plus a linear term in concentration fit the data at low concentrations. Conductivity measurements were made with solutions of the four electrolytes and decided deviations from the Onsager limiting law were observed. The behavior of these unsymmetrical electrolytes and relationship to present theory is discussed.

The present work is a continuation of a program of investigation of the properties of solutions of high-charge electrolytes. Previously we have described the studies of a number of 4-1, 1-4, 3-1, 1-3 and 3-2 electrolytes.[2,3]

The compounds investigated in this work were tris-(1,2-diaminopropane)-platinum(IV) chloride monohydrate, tetramethylammonium octacyanomolybdate(IV) dihydrate, potassium octacyanotungstate(IV) dihydrate and potassium tetracyanoplatinate(II). Activity coefficients have been determined by the isopiestic method[2] and conductances were measured in line with our attempts to systematize the behavior of unsymmetrical electrolytes and to compare the results with existing theoretical treatments.

Experimental

Materials.—Conductivity water was prepared as described in the preceding paper.[4]

Potassium tetracyanoplatinate (II), $K_2Pt(CN)_4$, was prepared by the method of Knop and Schedermann.[5] Purification was effected by fractional crystallization. The product thus obtained was the colorless $K_2Pt(CN)_4 \cdot 3H_2O$. The yellow anhydrous salt was obtained by drying the hydrated salt in an oven overnight at 100°. The anhydrous salt was kept desiccated during storage since it slowly becomes hydrated in the air. However, hydration is not rapid, and the salt can be weighed in the air.

Tris-(1,2-diaminopropane)-platinum(IV) chloride monohydrate, $Pt(pn)_3Cl_4 \cdot H_2O$, was prepared by the method of Smirnoff.[6] The crude chloride was purified by fractional crystallization. Later, quantities of this salt were purified by precipitation as the oxalate, recrystallization in this form and reconversion to the chloride by reaction with calcium chloride as described by Dwyer and Garvan.[7] This latter method was found to be a much more efficient procedure.

Tetramethylammonium octacyanomolybdate(IV) dihydrate, $[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$, was prepared by a quantitative metathesis reaction between $Ag_4[Mo(CN)_8] \cdot 2H_2O$ and $N(Me)_4Br$. $Ag_4[Mo(CN)_8] \cdot 2H_2O$ was prepared from $K_4[Mo(CN)_8] \cdot 2H_2O$ by precipitation with silver nitrate. $K_4[Mo(CN)_8) \cdot 2H_2O$ was prepared and purified according to the directions given by Furman and Miller.[8] All of the above octacyanomolybdate salts were air dried.

Potassium octacyanotungstate(IV) dihydrate, $K_4W(CN)_8 \cdot 2H_2O$, was prepared and purified by the method of Olsson.[9]

The *p*H values of the solutions were determined and assured the absence of appreciable hydrolysis. Solutions were freshly prepared before each conductance run, and the lack of any time-dependence indicated stability of the solutions.

Apparatus.—The apparatus and experimental procedure used for the isopiestic measurements have been previously described.[2,10]

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