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Activity Coefficients of Electrolytes of High Charge: Tris-(ethylenediamine)-platinum-(IV) Perchlorate and Tris-(ethylenediamine)-cobalt (III) Chloride

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Activity and osmotic coefficients of aqueous solutions of $Pt(en)_3(ClO_4)_4$ and $Co(en)_3Cl_3$ have been determined at 25° by isopiestic comparison with KCl solutions. Measurements have been made on solutions varying from about 0.05 *m* to saturation. The solubilities of $Pt(en)_3(ClO_4)_4$ and $Co(en)_3Cl_3$ were found to be 0.2229 and 1.110 *m*, respectively. The platinum complex appears to be a strong 4-1 electrolyte, but the cobalt compound does not behave as a typical 3-1 salt.

As part of a program of investigation of the properties of solutions of electrolytes of high charge,[1,2] two additional compounds, tris-(ethylenediamine)-platinum(IV) perchlorate and tris-(ethylenediamine)-cobalt(III) chloride, which showed some promise of serving as representative electrolytes of high charge and large size, have been prepared and studied. The first seems to qualify as a 4–1 electrolyte, perhaps stronger than potassium octacyanomolybdate(IV),[2] but the cobalt complex is very different in behavior from other 3–1 chlorides.[3] Osmotic coefficients of these salts were determined by isopiestic comparison with potassium chloride solutions at 25° and activity coefficients have been derived from the osmotic coefficients.[4]

Experimental

The experimental procedure and apparatus were the same as in the previous work,[2] with the exception that the gold plated sample containers have been replaced with platinum ones. The temperature was 24.953 ± 0.005°.

Tris-(ethylenediamine)-platinum(IV) perchlorate was prepared by a quantitative metathesis reaction between $Pt(en)_3Cl_4$[2] and $AgClO_4$ in aqueous solution. An excess of freshly prepared, nitrate free, Ag_2O was treated with 0.1 *M* $HClO_4$ and the resulting 0.1 *M* $AgClO_4$ solution was separated from the excess Ag_2O by filtration. From this a 0.0580 *M* solution was prepared.

2.1127 g. of $Pt(en)_3Cl_4$ in 25 ml. of water was titrated with the $AgClO_4$ solution and care was taken that only a drop or two excess $AgClO_4$ was used. The silver chloride was filtered off after being digested on a steam-bath for one hour and the $Pt(en)_3(ClO_4)_4$ was recovered by evaporation. This product was dried in an oven at 70° and was weighed. 3.1532 g. of $Pt(en)_3(ClO_4)_4$ was obtained; the theoretical yield would be 3.159 g.

The $Pt(en)_3(ClO_4)_4$ was then recrystallized from water three times and was dried at 70° and stored over barium oxide. This salt occurs as a hydrate in equilibrium with water at room temperature, but much water is lost on standing in air and the compound can be completely dehydrated at 70° or by drying over barium oxide. The exact degree of hydration was not determined, but there are probably $2H_2O$ or $2.5H_2O$ (compare $Pt(en)_3(NO_3)_4 \cdot 2H_2O$[5] and $Pt(en)_3Cl_4 \cdot 2.5H_2O$).[6] The anhydrous material does not absorb moisture from the air readily and was the form weighed in these experiments.

$Co(en)_3Cl_3$ was prepared according to the method in "Inorganic Syntheses"[7] and the product was purified by recrystallizing three times from water. The trihydrate is prepared by this process, but the water is removed by drying in an oven at 100° and the anhydrous salt can be weighed conveniently.

Results and Discussion

The notation employed in this section is that used in reference 4. In Table I are given the experimental molalities and osmotic coefficients for $Pt(en)_3(ClO_4)_4$ and $Co(en)_3Cl_3$. The concentrations of the saturated solutions were found to be 0.2229 and 1.110 *m*, respectively. Of course the hydrated forms of the two salts are in equilibrium with these solutions, although the samples were prepared from the anhydrous compounds.

TABLE I

ISOPIESTIC MOLALITIES, OBSERVED AND CALCULATED OSMOTIC COEFFICIENTS OF $Pt(en)_3(ClO_4)_4$ AND $Co(en)_3Cl_3$

$Pt(en)_3(ClO_4)_4$			$Co(en)_3Cl_3$		
m_{av}	ϕ_{obsd}	ϕ_{calcd}	m_{av}	ϕ_{obsd}	ϕ_{calcd}
0.03390	0.8260	0.8279	0.05351	0.6705	0.6734
.04411	.8178	.8178	.07027	.6524	.6524
.06586	.8070	.8015	.1069	.6219	.6214
.08594	.7860	.7854	.1102	.6141	.6192
.09715	.7751	.7754	.2244	.5654	.5666
.1470	.7338	.7339	.3497	.5318	.5318
.2229[a]	.6792	.6792	.5055	.4995	.4994
			.5086	.5064	
			.7635	.4864	
			.9930	.4685	
			1.110[a]	.4833	

[a] Saturated solutions.

It was found that the osmotic coefficients of both salts, up to about 0.25 *m* could be calculated (Table I) very well from

$$(1 - \phi)_{\text{calc}} = 0.7676 S_m(\text{f})\sigma_m\sqrt{m} + {}^1/_2 Bm - (\Delta\phi)_{\text{smoothed}} \quad (1)$$

where

$$\Delta\phi = 0.7676 S_m(\text{f})\sigma_m\sqrt{m} + {}^1/_2 Bm - (1 - \phi)_{\text{obs}}$$

The smoothed values are obtained by the method discussed by Scatchard and Prentiss[8] in treating freezing point data. The $\Delta\phi$ are smallest (*ca.* 1% or less) when, for $Pt(en)_3(ClO_4)_4$, $\mathring{a}$ = 11.5 and B = 2.06 and for $Co(en)_3Cl_3$, $\mathring{a}$ = 3.42 and B = 0.610. We notice that the sign of the linear term is positive and that the $\mathring{a}$ for $Co(en)_3Cl_3$ is much too small. This only serves to emphasize the empirical nature of equation 1. The chief virtues of this equation are that, besides giving good agreement with observed osmotic coefficients, it approaches the limiting value with the theoretical limiting slope. In the case of $Co(en)_3Cl_3$, above 0.25 *m* the $\Delta\phi$ become large and so calculated values are not

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(1) This program is supported by a research grant from The National Science Foundation.

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

(3) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, pp. 474, 487.

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Ch. 9, 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

(5) F. M. Jäger, *Z. Krist.*, **58**, 172 (1923).

(6) J. Lifschitz and E. Rosenbohm, *Z. physik. Chem.*, **97**, 1 (1921).

(7) J. B. Work, "Inorganic Syntheses," Vol. II, ed. by W. C. Fernelius, McGraw-Hill Book Co., New York, N. Y., 1946, p. 221.

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

given at higher concentrations (it appears that a negative term in m^2 would have to be added to equation 1 to keep $\Delta\phi$ small at the higher concentrations).

We notice that $\mathring{a}$ for the platinum compound (11.5) is somewhat greater than the 8–10 Å. we might expect, if we consider the crystal radii[5] of $Pt(en)_3^{+4}$ and ClO_4^-, but perhaps it is not unreasonably large. Thus, this compound may represent a strong 4–1 electrolyte.

If equation 1 is used in treating the data for $K_4Mo(CN)_8$ instead of the simple form previously employed,[2] $\mathring{a}$ can be increased only from 4.33 to about 4.85 and the activity coefficients are changed by less than 1%. It appears, then, that the much larger $\mathring{a}$ for the platinum salt is not wholly a result of using a different extrapolation than was used for $K_4Mo(CN)_8$.

It is certain that $Co(en)_3Cl_3$ is not strong and perhaps should not even be considered a 3–1 electrolyte. The osmotic coefficients do not resemble those of other 3–1 chlorides at similar concentrations.[3] It is not surprising that this is not a strong electrolyte for conductance measurements[9] also suggest incomplete dissociation.

In view of the manner of calculating the osmotic coefficients and of the smallness of $\Delta\phi$, the activity coefficients of $Pt(en)_3(ClO_4)_4$ and of $Co(en)_3Cl_3$ (up to $m = 0.25$) were calculated by the method Smith[10] employed for sodium chloride solutions at the boiling points.

$$\ln \gamma\pm = -\frac{2.303 S_m(\mathrm{f})\sqrt{m}}{1 + A'_m\sqrt{m}} - Bm + \int_0^m \frac{\Delta\phi}{m}\,\mathrm{d}m + \Delta\phi \tag{2}$$

Since $\Delta\phi$ becomes large for $Co(en)_3Cl_3$ at concentrations above 0.25 m, the values of ln $\gamma\pm$ from $m = 0.25$ to $m = 1.110$ were determined by graphical integration of

$$\ln \gamma\pm = -(1 - \phi) - 2\int_{0.25}^{m} \frac{(1 - \phi)}{\sqrt{m}}\,\mathrm{d}\sqrt{m} - 1.4862 \tag{3}$$

where 1.4862 is twice the calculated (from 2) value of the integral from $m = 0$ to $m = 0.25$.

In Table II are given the smoothed values of the osmotic and activity coefficients for solutions of $Pt(en)_3(ClO_4)_4$ and $Co(en)_3Cl_3$. Those for $Pt(en)_3(ClO_4)_4$ differ considerably from those for $K_4Fe(CN)_6$[3] and $K_4Mo(CN)_8$,[2] but that may be due to its being a stronger electrolyte. Not only is $\mathring{a}$ large, but isopiestic molalities of KCl and $Pt(en)_3(ClO_4)_4$ are nearly in a ratio of 5:2 (*i.e.*, at equilibrium, $\nu_1 m_1 \cong \nu_2 m_2$). This is not true in the case of $K_4Mo(CN)_8$.

TABLE II

SMOOTHED ACTIVITY AND OSMOTIC COEFFICIENTS FOR $Co(en)_3Cl_3$ AND $Pt(en)_3(ClO_4)_4$ AT 25°

	$Co(en)_3Cl_3$		$Pt(en)_3(ClO_4)$	
m	$\gamma\pm$	ϕ	$\gamma\pm$	ϕ
0.01	0.508	0.7993	0.502	0.8463
.025	.384	.7326	.426	.8301
.050	.295	.6802	.372	.8147
.075	.264	.6513	.339	.7960
.10	.221	.6266	.308	.7770
.15	.188	.5975	.270	.7395
.2229	.156	.5660	.227[a]	.6785
.2500	.148	.5580		
.50	.101	.5003		
.75	.0805	.4774		
1.00	.0691	.4687		
1.110	.0659[a]	.4833		

[a] Saturated solutions.

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[CONTRIBUTION OF THE RICHARDSON CHEMISTRY LABORATORIES OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XIV. The Stability of the Complexes Formed between the Nickel(II) Ion and Tetraethylenepentamine

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The basicity constants of tetraethylenepentamine and the formation constants of the complex ions formed between nickel (II) and tetraethylenepentamine were measured by the method of Schwarzenbach. The formation constant of the complex was also measured by the method of Bjerrum. The complex ions $NiHtetren^{+3}$ and $Nitetren^{+2}$ were found to be present in aqueous solution having log K values of 12.6 ± 0.1 and 17.6 ± 0.1, respectively, at 25°.

Introduction

The stability of complexes of various metal ions of the transition series with members of the polyethyleneamine series has been the subject of considerable investigation. Bjerrum[1] developed a method for determining the stability constants for the formation of metal amine complexes in aqueous solution which is based upon the stepwise formation of the complex ion. Jonassen, *et al.*,[2–4] extending the equations derived by Bjerrum measured the dissociation constants of diethylenetriamine and triethylenetetramine and also the formation constants of the complexes formed between these ligands and the nickel(II) ion.

Schwarzenbach[5] has pointed out that "hydrogen complexes" (complexes formed by adding one or more protons to the polyamine(s) coördinated to the metal ion) also must be considered in addition to the simple MZ_x type, where Z is the polyamine and x equals 1,2,3,. . .n. Schwarzenbach developed a method for determining these complexes from a study of neutralization curves, and studied the complexes of nickel(II) with all of the members of

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[1] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[2] H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm and R. M. Rogan, THIS JOURNAL, **72**, 2430 (1950).

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[5] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).