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Volumetric and Cryoscopic Measurements of Aqueous $[Co(en)_3]^{3+}$ near 273 K

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Osmotic coefficients of aqueous solutions of tris(ethylenediamine)cobalt(III) oxalate have been obtained from 0.000 to 0.010 mol·kg^{-1} by the freezing-point method. Apparent molar volumes have been determined by density measurements of aqueous solutions of tris(ethylenediamine)cobalt(III) perchlorate at 288 and 278 K in the range 0.000–0.060 mol·kg^{-1}. Partial molar volumes at infinite dilution for the complex cation at 288, 278, and 273 K are estimated.

Introduction

The volumetric properties of inorganic complexes in aqueous solution have been the subject of increasing interest in the last 20 years. By a suitable selection of ligands such factors as the size, structure, and electric charge distribution on the complex surface can be changed systematically. Nevertheless, it is difficult to find literature data at temperatures other than 298.15 K.

The cation $[Co(en)_3]^{3+}$ (en = 1,2-diaminoethane or ethylenediamine) is of great interest in aqueous solution by the combination of three factors: pronounced stability, high valency, and some hydrophobic character due to the presence of alkyl groups in the outer sphere of coordination. Nevertheless, for the 3:1 and 3:2 electrolytes, the available osmotic and activity coefficients apply mostly to salts with metallic cations which exhibit a very different behavior owing to a high charge-size ratio, responsible for an intense hydration.

We have previously devoted a considerable piece of work to the study of the aqueous solutions of this cation and other cobalt–amine-type compounds (*1–3*). In this paper we report the following: (a) the densities of dilute aqueous solutions of $[Co(en)_3](ClO_4)_3$ at 288.15 and 278.15 K as a continuation of our previous investigations at 298.15 K on this aqueous system (*3*); (b) osmotic coefficients of very dilute aqueous solutions of $[Co(en)_3]_2(C_2O_4)_3$ at approximately 273 K obtained by the freezing-point method.

The object of both sets of measurements is to continue our investigation about the interaction between the cation $[Co(en)_3]^{3+}$ and the water solvent molecules.

Experimental Section

Apparatus and Procedure. The experimental procedure and apparatus for the cryoscopic measurements have been previously described (*1, 2*).

We have used optical measurements for molality determinations of the equilibrium solutions carried out with a 1-cm-path-length cell at 466 nm where the aqueous ion $[Co(en)_3]^{3+}$ has a broad maximum (*4*).

The correlation between molality and absorbance measurements has been investigated for the aqueous solutions of tris(ethylenediamine)cobalt(III) oxalate. The equation $m = 0.0055754A - 3.4 \times 10^{-6}A^2$, where m is the molality (mol·kg^{-1}) and A the absorbance of the electrolyte solution, fits our seven experimental values with a standard deviation $\sigma(m) = 5.5 \times 10^{-6}$ in the molality range 0.0000–0.0068 mol·kg^{-1}.

The densities of the aqueous solutions of tris(ethylenediamine)cobalt(III) perchlorate were measured with a vibrating tube densimeter as previously reported (*3*). The temperature of the tube was kept within 1 mK, and the experimental densities were reproducible to within $\pm 5 \times 10^{-6}$ g·cm^{-3} in consecutive runs. The instrument was calibrated using water and air or nitrogen as standards.

Materials. Tris(ethylenediamine)cobalt(III) perchlorate and chloride were prepared by literature methods and recrystallized twice from purified water (*3, 5*). The crystals were then dissolved in water and reprecipitated by addition of pure ethyl alcohol (Fluka puriss) three times. The slightly soluble in water tris(ethylenediamine)cobalt(III) oxalate was prepared by precipitation of tris(ethylenediamine)cobalt(III) chloride with an aqueous solution of $Na_2C_2O_4$ (Carlo Erba RPE). All the salts were dried in a vacuum oven at 373 K to constant mass and analyzed as previously reported (*1*). The solutions were made up by weight of the dried salts from purified water (Millipore, Milli-Q).

We have been informed about some explosive behavior of the complex perchlorate, and very careful handling is recommended when it is being dried.

Results and Discussion

Osmotic Coefficients of Aqueous $[Co(en)_3]_2(C_2O_4)_3$. Osmotic coefficients ϕ of the solutions at their freezing-point temperatures were calculated from (*6*)

$$\phi = [\theta(1 + b\theta)]/\nu\lambda m \qquad (1)$$

where λ is the cryoscopic constant of water (1.860 K·mol^{-1}·kg), m is the molality of the solute, b is a calculable factor of very little importance in the dilute range (4.9×10^{-4} K^{-1}), and ν is the number of ions per molecule of salt.

In Table 1 we give the experimental freezing-point depressions together with osmotic coefficients for the system $[Co(en)_3]_2(C_2O_4)_3$ + water. Also shown in Table 1 are the osmotic coefficients calculated at 273.15 K from the extended equation of Debye–Hückel:

$$\phi = 1 - \frac{|z_+z_-|A_m}{(Ba)^3 I}[-(1 + BaI^{1/2}) + 2\ln(1 + BaI^{1/2}) + 1/(1 + BaI^{1/2})] \qquad (2)$$

where z_+ and z_- are the ion charges, I is the molal ionic strength, A_m is the molal Debye–Hückel limiting law slope at 273.15 K (1.1293 kg$^{1/2}$·mol$^{-1/2}$), B is a calculable factor (0.3246 Å^{-1}·kg$^{1/2}$·mol$^{-1/2}$ at 273.15 K), and a is an interaction parameter related to the distance of closest approach of the ions (*6–8*).

Figure 1 gives a plot of ϕ against m where our experimental results are compared to those obtained from eq 2 with an interaction parameter a = 6.75 Å.

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Table 1. Experimental Freezing Point Depression θ and Osmotic Coefficients ϕ and Calculated Osmotic Coefficients ϕ_{DH} from Eq 2 of $[Co(en)_3]_2(C_2O_4)_3$

$10^3m/(mol \cdot kg^{-1})$	θ/K	ϕ	ϕ_{DH}[a]
0.000	0.0000	1.000	1.000
1.165	0.0093	0.858	0.849
1.990	0.0150	0.811	0.815
2.296	0.0173	0.810	0.805
2.648	0.0199	0.808	0.796
3.071	0.0227	0.795	0.786
3.790	0.0272	0.772	0.772
5.099	0.0354	0.747	0.750
5.444	0.0379	0.749	0.746
6.062	0.0416	0.738	0.738
7.131	0.0481	0.725	0.728
7.354	0.0496	0.725	0.725
7.710	0.0519	0.724	0.722
9.296	0.0611	0.707	0.709

[a] Eq 2 (a = 6.75 Å).

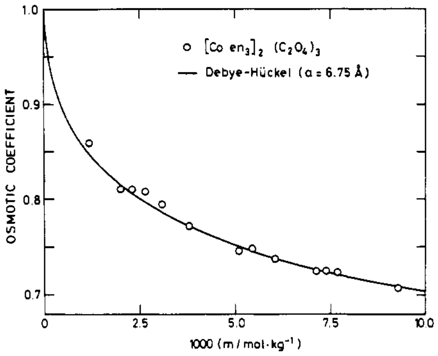

Figure 1. Experimental osmotic coefficients for aqueous solutions of tris(ethylenediamine)cobalt(III) oxalate at their freezing temperature as a function of the molality, ○; calculated from eq 2 with a = 6.75 Å, —.

Table 2. Experimental Densities and Apparent Molar Volumes at 288.15 and 278.15 K of Aqueous $[Co(en)_3](ClO_4)_3$

$10^3m/(mol \cdot kg^{-1})$	10^6-$(d - d_0)$	$V_\phi/(cm^3 \cdot mol^{-1})$	$10^3m/(mol \cdot kg^{-1})$	10^6-$(d - d_0)$	$V_\phi/(cm^3 \cdot mol^{-1})$
		T = 288.15 K, d_0 = 0.999 100 g·cm^{-3}			
4.440	123	260.2	30.640	831	264.2
4.923	136	260.9	35.702	967	264.2
13.108	359	262.7	42.678	1150	265.1
14.732	404	262.3	47.200	1273	264.5
23.738	646	263.7	58.530	1572	264.8
		T = 278.15 K, d_0 = 0.999 964 g·cm^{-3}			
8.249	233	254.5	29.540	827	255.5
11.655	331	252.7	39.017	1082	257.5
17.408	492	253.7	41.660	1160	256.2
19.250	541	255.2	45.780	1273	256.2
21.290	600	254.2			

Densities of Aqueous $[Co(en)_3](ClO_4)_3$. The apparent molar volumes of the solute, V_ϕ (cm^3·mol^{-1}), were calculated from the experimental solution densities using

$$V_\phi = M/d - 1000(d - d_0)/md_0d \qquad (3)$$

where m is the molality, M is the molar mass of the solute, d is the density of the solution, and d_0 is the density of pure water, taken as 0.999 100 g·cm^{-3} at 288.15 K and 0.999 964 g·cm^{-3} at 278.15 K (*9*).

The experimental densities and apparent molar volumes of dilute solutions of $[Co(en)_3](ClO_4)_3$ are shown in Table 2.

The apparent molar volumes obtained at 288.15 and 278.15 K are given in Figure 2. Following Redlich and Meyer (*10*), we have plotted the quantity $V_\phi - S_vm^{1/2}$ *vs* m to obtain $V_\phi°$, the apparent molar volume at infinite dilution or partial molar volume of the solute at infinite dilution. S_v is a calculable coefficient; for 3:1 electrolytes S_v = 22.49 at 278.15 K and 24.94 at 288.15 K (*11*). The infinite dilution values were obtained by least-squares extrapolation of $V_\phi - S_vm^{1/2}$.

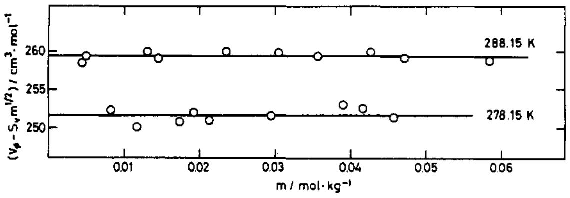

Figure 2. Experimental $V_\phi - S_vm^{1/2}$ *vs* molality for tris(ethylenediamine)cobalt(III) perchlorate in water at 288.15 and 278.15 K, and horizontal extrapolation at infinite dilution.

Table 3. Variation of Apparent Molar Volume at Infinite Dilution $V_\phi°$ with Temperature, Estimated Cationic Volume V^{3+} at 273.15 K, and Cationic Radius r_v for Aqueous $[Co(en)_3](ClO_4)_3$

$V_\phi°/(cm^3 \cdot mol^{-1})$					
298.15 K[a]	288.15 K	278.15 K	273.15 K[b]	V^{3+}	r_v/Å
265.7 ± 0.8	259.4 ± 0.5	251.6 ± 0.9	247.1	109.7	3.52

[a] Taken from ref 3. [b] Estimated from a quadratic extrapolation.

The change of $V_\phi°$ with temperature is shown in Table 3. The value at 298.15 K are taken from ref 3 and the corresponding value at 273.15 K has been calculated with a quadratic extrapolation. Also shown in Table 3 are the cationic volume V^{3+} at 273.15 K and the cationic radius r_v (Å) ($V^{3+} = 2.52r_v^3$). V^{3+} has been obtained by subtracting the contribution of the perchlorate anions on the assumption that the limiting partial molar volume for H^+ is −5.1 cm^3·mol^{-1} (*12*).

It should be emphasized that dilute aqueous solutions exhibit an anomalous density maximum near 277 K, and then the extrapolated value at 273.15 K is only of limited confidence (*13*).

Conclusions

We have measured the density of dilute aqueous solutions of $[Co(en)_3](ClO_4)_3$ at 288.15 and 278.15 K and obtained the apparent molar volumes of solute at infinite dilution. We have calculated the molar volume of the complex cation by subtracting the contribution of the perchlorate anions. An estimation of the molar volume of aqueous $[Co(en)_3]^{3+}$ at 273.15 K has been obtained with a quadratic extrapolation of these results and our previous value at 298.15 K (*3*). This yields a cationic radius of 3.52 Å at 273.15 K.

We have also measured the osmotic coefficient of very dilute aqueous solutions of $[Co(en)_3]_2(C_2O_4)_3$. The extended theory of Debye–Hückel, with a large, but not very unrealistic, parameter of interaction a = 6.75 Å, fits our results very well. Two features are surprising: (a) The theory is usually unsuccessful when applied to highly charged electrolytes. (b) The large parameter of interaction suggests that ion-pairing is unimportant when other 3:2 systems, especially with a sulfate anion, show the opposite trend.

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