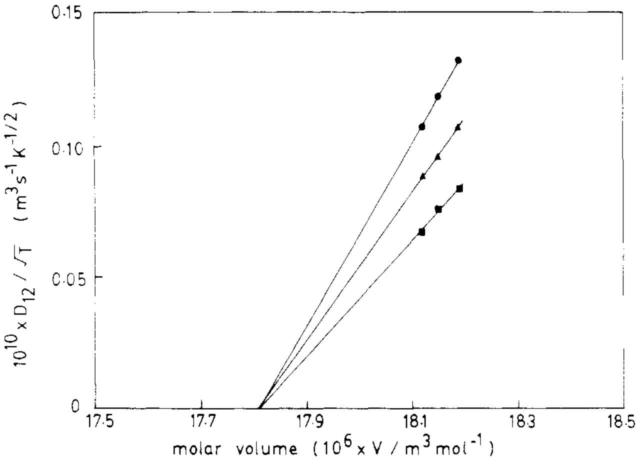

Figure 1. Free-volume relationship for mutual diffusion of several alcohols in water. Symbols: (●) methanol, (▲) ethanol, (■) 1-butanol.

Table II. Coefficients β and V_D for Methanol, Ethanol, and 1-Butanol

solute	$10^5\beta$, mol m^{-1} s^{-1} $K^{-1/2}$	$10^6 V_D$, m^3 mol^{-1}
methanol	0.3650	17.82
ethanol	0.2846	17.81
1-butanol	0.2235	17.82

Figure 1 illustrates the plots of $D_{12}/T^{1/2}$ for the alcohol/water systems. The linear relationship was demonstrated for all three systems studied. In Table II, the values of β and V_D obtained are listed. With the values of V_D obtained, the rigid-sphere diameter for the solvent can be calculated by means of the following equation:

$$V_D = bV_0 = BN\sigma_2^3 \qquad (5)$$

where N is the Avogadro constant, σ_2 is the hard-sphere diameter of the solvent molecules, and b is a constant used to account for the effects of correlated molecular motions in hard-sphere fluids (*16*, *17*). The constant b has been found to be 1.3509 from linear regression of the molecular dynamics simulation results of Easteal et al. (*18*). Subsequently, the molecular diameter of the solvent was calculated with eq 5 to be 0.314 nm.

By a development analogous to that for diffusion, Dymond (*19*) has shown that the viscosity of hard-sphere fluids can be represented by

$$T^{1/2}/\eta = \beta'(V - V_\eta) \qquad (6)$$

where η is the measured viscosity and V_η is the molar volume at which fluidity approaches zero. This quantity is analogous to V_D calculated from diffusion data and therefore can also be used to determine the molecular diameter of the solvent. Viscosity data from literature (*20*) were obtained. The values of V_η and σ_η were also determined by plotting $T^{1/2}/\eta$ versus V. The agreement between V_D and V_η was within 0.2%, and the diameters determined from both properties were in complete agreement.

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Osmotic Coefficients of Some Cobalt-Amine-Type Salts from Cryoscopic Measurements

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Osmotic coefficients of aqueous solutions of tris(ethylenediamine)cobalt(III) chloride, tris(ethylenediamine)cobalt(III) bromide, tris(ethylenediamine)cobalt(III) iodide, tris(ethylenediamine)cobalt(III) nitrate, and tris(ethylenediamine)cobalt(III) perchlorate have been measured from 0.000 to 0.025 mol·kg^{-1}. The freezing-point method was used for the determination of the osmotic coefficients. These results were fitted to semiempirical least-squares equations, and these equations were used to calculate the mean molal activity coefficients.

Introduction

The osmotic and activity coefficients of single and mixed electrolytes have been available in the literature for many years. A considerable number of aqueous solutions containing salts were investigated by Scatchard and his collaborators who developed the freezing-point method for the determination of the osmotic coefficients to a high degree of precision. The same method was used by Lange to investigate other systems at low solute concentrations, and more recently by Prue et al. and Lilley and Scott. A bibliography of these previous investigations is reported in ref 1.

The object of this work is to continue our investigations on cobalt-amine salts (*1*) and present experimental results on

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Table I. Coefficients c_i and standard deviation $\sigma(m)$ for Equation 1

electrolyte	$10^6 c_0$	$10^2 c_1$	$10^4 c_2$	$10^4 c_3$	$10^5 \sigma$
$[Co(en)_3]Cl_3$	1.474	1.1314	1.8328	0	4.4
$[Co(en)_3]Br_3$	0.295	1.1532	1.4245	1.063	1.5
$[Co(en)_3](NO_3)_3$	8.600	1.1264	1.3469	0	2.2
$[Co(en)_3](ClO_4)_3$	0	1.1395	0.3876	0.815	0.8

Table II. Coefficients a_i and Standard Deviation $\sigma(\theta)$ for Equation 2

electrolyte	a_1	a_2	a_3	a_4	$10^4 \sigma$
$[Co(en)_3]Cl_3$	-0.03322	8.5573	-28.3257	74.8602	1.0
$[Co(en)_3]Br_3$	0.01397	6.6354	-9.8527	8.0303	1.4
$[Co(en)_3]I_3$	0.02726	6.8784	-16.7298	38.5672	1.3
$[Co(en)_3](NO_3)_3$	0.00422	7.2549	-22.1889	53.5017	3.2
$[Co(en)_3](ClO_4)_3$	0.03038	6.2084	-5.7392	-0.9525	1.6

aqueous tris(ethylenediamine)cobalt(III) salt solutions in the molality range 0–0.025 mol·kg^{-1}.

Experimental Section

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

We have used optical density measurements for molality determinations of the equilibrium solutions carried out with a 1-cm path-length cell at 466 nm where the tris(ethylenediamine) cobalt(III) ion ($[Co(en)_3]^{3+}$) has a broad maximum (*2*).

Correlations between molality and absorbance measurements have been investigated in all cases and are reported by polynomials of the type

$$m = \sum_i c_i A^i \tag{1}$$

where m is the molality (mol·kg^{-1}) and A the absorbance of the electrolyte solution. The differences for the different salts are generally very small and negligible between $[Co(en)_3]Cl_3$ and $[Co(en)_3]I_3$. The coefficients of eq 1 and the standard deviations are given in Table I.

Materials. The salts used in this work were prepared by literature methods (*2–6*) and recrystallized from conductivity water. The salts were vacuum-dried to constant mass.

The products were analyzed as previously (*1*). Deviations from calculated to found mass percentages were lower than 1% in every case.

Conductivity water (triply distilled) was used throughout. Cracked ice for experiments was also prepared from conductivity water.

Results

The experimental results obtained from the freezing temperature depressions θ for the solutions investigated were fitted to polynomials of the form

$$\theta = \sum_{i=1} a_i m^{i/2} \tag{2}$$

where m is the molality of the electrolyte solution. The coefficients of eq 2 and the standard deviations are given in Table II.

The experimental freezing-point depressions are plotted against the molality in Figure 1.

Osmotic coefficients ϕ of the solutions at their freezing-point temperatures were calculated from (*7*)

$$\phi = \frac{\theta(1 + b\theta)}{\nu \lambda m} \tag{3}$$

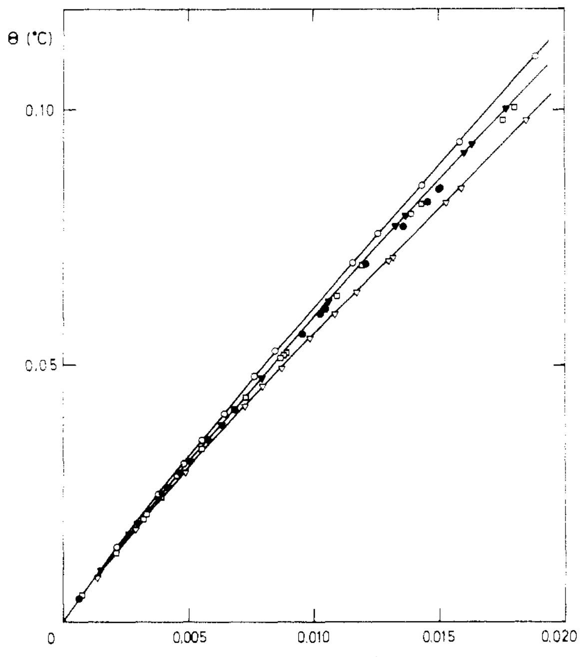

Figure 1. Experimental freezing-point depressions for aqueous solutions of tris(ethylenediamine)cobalt(III) salts as a function of the molality: ○, $[Co(en)_3]Cl_3$; □, $[Co(en)_3]Br_3$; ●, $[Co(en)_3]I_3$; ▽, $[Co(en)_3](NO_3)_3$; ▼, $[Co(en)_3](ClO_4)_3$.

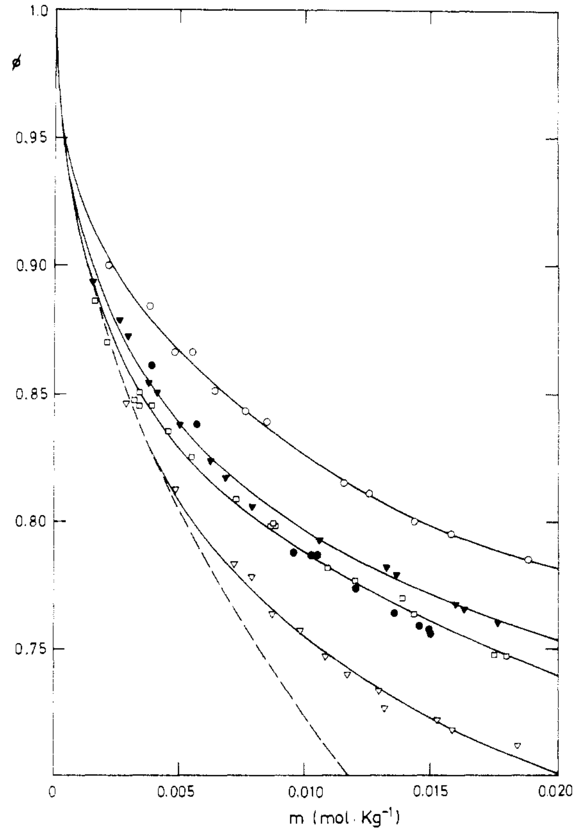

Figure 2. Experimental osmotic coefficients for aqueous solutions of tris(ethylenediamine)cobalt(III) salts at their freezing temperature as a function of the molality. The dashed curve correspond to 3–1 electrolyte Debye–Hückel limiting law (DHLL): ○, $[Co(en)_3]Cl_3$; □, $[Co(en)_3]Br_3$; ●, $[Co(en)_3]I_3$; ▽, $[Co(en)_3](NO_3)_3$; ▼, $[Co(en)_3](ClO_4)_3$.

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 (4.9 × 10^{-4} K^{-1}), and ν is the number of ions per molecule of salt.

The experimental freezing-point depressions together with the osmotic coefficients are given in Table III.

Table III. Experimental Freezing-Point Depression (θ) and Osmotic Coefficients (ϕ)

10^3m	θ	$10^5\delta\theta$	ϕ	$10^3\delta\phi$	10^3m	θ	$10^5\delta\theta$	ϕ	$10^3\delta\phi$
				$[Co(en)_3]Cl_3$					
0.000	0.0000	0	1.000	0	8.439	0.0527	-1.6	0.839	-1.9
2.153	0.0143	-0.2	0.900	3.6	11.534	0.0700	0	0.816	0.5
3.755	0.0247	-0.7	0.884	-3.6	12.563	0.0758	-0.9	0.811	-0.5
4.763	0.0307	1.5	0.866	3.1	14.312	0.0852	1.3	0.800	1.5
5.497	0.0354	-1	0.866	-4.2	15.845	0.0937	0	0.795	-0.2
6.395	0.0405	1.4	0.851	2.6	18.930	0.1105	-0.3	0.785	-0.5
7.606	0.0477	0.3	0.843	0.5					
				$[Co(en)_3]Br_3$					
0.000	0.0000	0	1.000	0	8.706	0.0517	-0.2	0.798	-2
0.749	0.0053	-1.4	0.951	-27.5	8.729	0.0519	-1	0.799	-3.2
1.532	0.0101	0.4	0.886	6.5	8.833	0.0524	-0.3	0.797	-2
2.118	0.0137	0.7	0.869	7	10.919	0.0635	1.3	0.782	1.5
3.175	0.0200	1.7	0.847	7.5	11.994	0.0693	0.3	0.777	1
3.324	0.0209	1.6	0.845	6.4	13.876	0.0795	-3.j	0.770	-1.8
3.404	0.0218	-2.6	0.850	0.2	14.331	0.0814	1.1	0.764	2.7
3.898	0.0245	-0.4	0.845	-2.4	17.609	0.0979	2.6	0.747	3.2
4.540	0.0282	0.2	0.835	-1.3	18.059	0.1004	0.1	0.747	0.9
5.492	0.0337	0	0.825	-2.2	20.580	0.1130	-1.o	0.738	-2.8
7.282	0.0438	1.5	0.809	-2.1					
				$[Co(en)_3]I_3$					
0.000	0.0000	0	1.000	0	10.437	0.0611	-1.6	0.787	-2.6
3.904	0.0250	0.6	0.861	-0.3	12.071	0.0695	-0.4	0.774	-1.5
5.693	0.0355	-2.2	0.838	-3.6	13.572	0.0771	0.8	0.764	-0.3
6.821	0.0414	1.4	0.816	4.2	14.548	0.0822	-0.4	0.759	0.2
9.530	0.0559	2.5	0.788	4	14.972	0.0844	-0.8	0.758	-0.5
10.262	0.0601	-0.8	0.787	-1.2	15.007	0.0844	0.9	0.756	1.4
				$[Co(en)_3](NO_3)_3$					
0.000	0.0000	0	1.000	0	10.831	0.0602	0.8	0.747	1.2
1.306	0.0086	0.7	0.885	7.6	11.684	0.0643	2	0.740	2.7
2.878	0.0181	0.2	0.845	0.8	12.943	0.0708	-1.3	0.735	-0.8
4.831	0.0292	-0.6	0.812	-2.6	13.152	0.0711	5.9	0.727	6.5
7.193	0.0419	-1.3	0.783	-3.1	15.263	0.0820	-1.3	0.722	-0.8
7.914	0.0458	-2.8	0.778	-5.3	15.867	0.0848	-0.3	0.718	0
8.704	0.0494	1.7	0.763	2.2	18.516	0.0981	-7.6	0.712	-5.7
9.818	0.0553	-0.8	0.757	-1.1	20.520	0.1063	4.8	0.696	2.6
				$[Co(en)_3](ClO_4)_3$					
0.000	0.0000	0	1.000	0	6.846	0.0416	1.2	0.817	2.6
1.482	0.0098	2.4	0.893	9.2	7.908	0.0474	3	0.806	5
2.601	0.0170	-0.7	0.879	-3.4	10.568	0.0623	0.9	0.793	0.3
2.944	0.0191	-1	0.872	-3.5	13.256	0.0771	-2.3	0.782	-2.7
3.745	0.0238	-0.	0.854	1	13.670	0.0792	-1.3	0.779	-1.6
4.111	0.0260	-0.6	0.850	-0.2	16.002	0.0913	0.3	0.767	0.3
4.593	0.0291	-3.3	0.852	-8.3	16.349	0.0931	0.3	0.765	0.5
5.017	0.0312	0.4	0.838	0.6	17.709	0.1001	0.6	0.760	0.7
6.270	0.0384	0.5	0.823	1.5					

Table IV. Coefficients B_i and Standard Deviation $\sigma(\phi)$ Corresponding to Equation 4

electrolyte	B_1	B_2	B_3	B_4	$10^3\sigma$
$[Co(en)_3]Cl_3$	19.3165	-98.9736	-111.0507	1969.0484	0.8
$[Co(en)_3]Br_3$	-8.2283	291.2918	-1709.1000	2741.4659	7.3
$[Co(en)_3]I_3$	18.1914	-216.1254	1028.3597	-399.0876	0.9
$[Co(en)_3](NO_3)_3$	-16.6365	394.2905	-2549.9633	5824.2169	3.8
$[Co(en)_3](ClO_4)_3$	3.9003	55.4777	-181.9696	-337.2763	3.9

The osmotic coefficients were fitted to an equation of the form

$$\phi = 1 - \frac{|z_+z_-|A_m}{3} I^{1/2} + \sum_{i=1} B_i m^{(i+1)/2} \tag{4}$$

where z_+ and z_- are the ions' charges, I is the ionic strength, A_m is the Debye-Hückel constant at 0 °C (1.12938 $kg^{1/2} \cdot mol^{-1/2}$) (*8*), and B_i are constants. The values obtained by least-squares for the coefficients in eq 4 are given in Table IV together with the standard deviations. We have used this equation because it gives satisfactory results when fitting the experimental data and it is easier to handle than others we have used in preceding papers (*1*).

The columns $\delta\theta$ and $\delta\phi$ in Table III give the difference between the experimental freezing-point depressions and osmotic coefficients and those calculated from eq 2 and 4.

The experimental osmotic coefficients are plotted against the molality in Figure 2.

The osmotic coefficients can be used in the calculation of the mean molal activity coefficients of the electrolytes. Applications of the Gibbs-Duhem equation gives

$$\ln \gamma_\pm = \phi - 1 - \int_0^m (1 - \phi)\, d \ln m \tag{5}$$

where $\gamma_\pm$ is the mean molal activity coefficient.

These integrations are most conveniently performed with analytic representations for the osmotic coefficients.

Substitution of eq 4 into eq 5 and integrating yields

$$\ln \gamma_\pm = -|z_+z_-|A_m I^{1/2} + \sum_{i=1} \frac{i+3}{i+1} B_i m^{(i+1)/2} \tag{6}$$

where the symbols have the same meaning as in eq 4 and the B_i coefficients are reported in Table IV.

Registry No. $[Co(en)_3]Cl_3$, 13408-73-6; $[Co(en)_3]Br_3$, 13963-67-2; $[Co(en)_3]I_3$, 15375-81-2; $[Co(en)_3](NO_3)_3$, 6865-68-5; $[Co(en)_3](ClO_4)_3$, 14977-29-8.

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Vapor–Liquid Equilibria for the System Ammonia + Water up to the Critical Region

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Bubble points, dew points, and critical points were measured in the system ammonia + water for several mixtures of constant overall composition by direct observation. Bubble points were determined for 6 different mixtures, varying in composition from 18.9 to 80.0 mol % ammonia over a temperature range of 389.4–613.5 K and a pressure range of 1.29–21.52 MPa. Dew points were measured for 15 compositions between 19.4 and 90.0 mol % ammonia over a temperature range of 373.2–453.2 K and a pressure range of 0.14–9.70 MPa. Results have been compared with those of Müller et al., Rizvi and Heidemann, and Gillespie et al. It is concluded that at lower temperatures and pressures the four sources of reference data present a unique and consistent picture of vapor–liquid equilibria in the system ammonia + water. At temperatures above 473 K, significant deviations exist.

Introduction

Ammonia and water participate in many industrial processes. One might think of the manufacturing of urea where ammonia and carbon dioxide react to an aqueous solution of urea. Thermodynamic modeling of such a process requires information on the phase equilibria of the relevant (sub)systems.

When this investigation was started, reliable data for the system ammonia + water were scarce if not absent. For example, Tsiklis (*1*) investigated the global phase behavior over a wide pressure and temperature range, but the accuracy of the data is insufficient for plant design. On the other hand, accurate data could be found in the literature but then the experimental range appeared to be very limited, see, for example, Guillevic et al. (*2*) and Pawlikowski et al. (*3*). More recently, Müller et al. (*4*), Rizvi and Heidemann (*5*), and Gillespie et al. (*6*) published data over a broad temperature and pressure range. Rizvi and Heidemann (*5*) and Gillespie et al. (*6*), in particular, present data almost up to the critical point of water. Gillespie et al. (*6*) in comparing their data with those of Rizvi report in some cases an average deviation of 24.0% in the relative volatility. In view of the great significance of reliable data for the system ammonia + water as a key industrial system, we have undertaken an independent study on the vapor–liquid equilibria of this system over the full concentration range.

In this paper, a description of the experimental procedure is given first, after which the bubble point and dew point measurements in the system ammonia + water are presented. Finally, the results are compared with those in the literature.

Experimental Procedure

Equipment. The bubble point measurements were carried out in a stainless steel optical high-pressure cell for use with pressures up to 200 MPa and temperatures up to 673 K, which is described in detail by de Loos et al. (*7*). The cell is heated externally with two electric heating mantles, controlled by electronic regulators. The temperature was measured with a platinum resistance thermometer to an accuracy of +0.02 K; it was maintained constant better than ±0.1 K. A dead-weight pressure gauge was used to measure the pressure and to keep it constant. Bubble points could be measured within ±0.01 MPa.

The dew point measurements were performed in an apparatus for use with pressures up to 20 MPa and temperatures up to 473 K. This so called Cailletet apparatus is described earlier by de Loos et al. (*8*). The glass capillary tube that contains the mixture is kept at the desired temperature by a thermostat with circulating oil. The temperature was measured to an accuracy within ±0.01 K by using a platinum resistance thermometer; it was maintained constant better than ±0.05 K. The pressure was measured and kept constant with a dead-weight pressure gauge. Dew points could be measured within ±0.01 MPa.

Method. In the case of the bubble point measurements, mixtures were prepared by weighing a certain quantity of water in the top of a glass measuring vessel. The top of this measuring vessel is constructed of sapphire because water and ammonia corrode glass and even quartz at high temperatures and pressures. Besides the water, the measuring vessel also contained a nickel stirrer, which stirred the mixture during the experiments by means of a magnetic stirrer device of the high-pressure cell. The water was degassed by repeatedly melting and freezing the water in vacuum, after which a volumetrically determined amount of ammonia, at a well-known pressure and temperature, was pressed into the measuring vessel by mercury and condensed in the top of the vessel by means of liquid nitrogen. The mercury acted not only as a sealing liquid but also as a pressure-transmitting fluid between the mixture and the pressurizing fluid (silicon oil: Dow Corning 200 fluid 5CS) used in the high-pressure cell.

Then, the measuring vessel was placed between the windows of the high-pressure cell, after which the mixture was pressurized. At a constant temperature, variation of the pressure allowed one to determine visually that point at which

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