Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

A_{ij}, B_{ij}, etc	multicomponent adjustable parameters in eq 12 and 13
B_{ii}, B_{ij}	virial coefficients, eq 2
c'	total number of adjustable parameters corresponding to the binary mixtures in eq 13
c	total number of ternary parameters in eq 13
m	total number of data points which correspond to the system of the high order (ternary system in the present work)
N	number of components
P	total pressure, mmHg
P_i^0	vapor pressure of pure component i, mmHg
T	boiling temperature of a mixture
T_i^0	boiling temperature of pure component i
t	temperature, °C
x_i, y_i	mole fraction of component i in the liquid and vapor phases
α_i	coefficient, Antoine equation
β_i	coefficient, Antoine equation
γ_i	activity coefficient of component i
δ_i	coefficient, Antoine equation
σ^2	error variance, eq 14
Λ_{ij}	constant, Wilson equation

Subscripts and Superscripts

calcd	calculated
obsd	observed
max	maximum
min	minimum

Registry No. Methanol, 67-56-1; 2-propanol, 67-63-0; propyl bromide, 106-94-5.

Literature Cited

(1) Garber, Y. N.; Mironenko, V. F. *Zh. Prikl. Khim.* **1968**, *41*, 2022.
(2) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(3) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1946**, *40*, 345.
(4) Van Diemen, A. J. G.; Houtepen, C. J. M.; Stein, H. N. *J. Chem. Thermodyn.* **1974**, *6*, 805.
(5) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt, 1977; Vol. I, Part 2a.
(6) Kohoutova, J.; Suska, J.; Novak, J. P.; Pick, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 3210.
(7) TRC Tables, "Selected Values of Properties of Chemical Components"; Thermodynamics Research Center Data Project, College Station, TX, 1974.
(8) Boublikova, L.; Lu, B. C. Y. *J. Appl. Chem.* **1969**, *19*, 89.
(9) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1975**, *20*, 168.
(10) Van Ness, H. C.; Abbott, M. M. "Classical Thermodynamics of Nonelectrolyte Solutions"; McGraw-Hill: New York, 1982.
(11) Tsonopoulos, C. *AIChE J.* **1974**, *33*, 263.
(12) McDermott, C.; Ellis, S. R. M. *Chem. Eng. Sci.* **1965**, *20*, 293.
(13) Wisniak, J., Tamir, A. *J. Chem. Eng. Data* **1977**, *22*, 253.
(14) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(15) Tamir, A. *Chem. Eng. Sci.* **1981**, *36*, 1453.
(16) Tamir, A.; Wisniak, J. *Chem. Eng. Sci.* **1978**, *33*, 657.

Received for review June 25, 1984. Accepted Decemer 26, 1984.

Osmotic and Activity Coefficients of Some Cobaltammine Salts

Miguel A. Castellanos, Mercedes Cáceres, and Javier Núñez*
Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain

Osmotic coefficients of aqueous solutions of chloropentaaminecobalt(III) chloride, hexaamminecobalt(III) chloride, hexaamminecobalt(III) bromide, hexaamminecobalt(III) iodide, hexaamminecobalt(III) nitrate, hexaamminecobalt(III) perchlorate, aquopentaamminecobalt(III) chloride, and aquopentaamminecobalt(III) bromide have been measured from 0.00 to 0.04 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 (*1–8*) 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 (*9*, *10*) to investigate other systems at low solute concentrations, and more recently by Prue et al. (*11*, *12*) and Lilley and Scott (*13*). From the freezing point temperatures the osmotic and activity coefficients can be determined, and plots of data of this type result in families of curves which are useful in estimating the properties of the solutions.

The object of this work is to extend the above-mentioned studies and present experimental results on aqueous cobaltammine salts solutions in the molality range 0–0.04 mol kg^{-1}.

Experimental Section

Apparatus. The freezing point lowering determinations were carried out in an apparatus similar to that used by Prue (*11*), with the exception that the thermocouple was replaced by a HP 2801A quartz crystal thermometer with a resolution of 0.0001 °C coupled to a digital clock recorder. A diagram of the equipment is shown on Figure 1.

The thermometer probes were calibrated in the range of operating temperatures by determining the freezing point temperatures of KCl solutions and comparing with the existing literature values (*2–10*, *14–17*).

The probes were connected to an oscillator and its outputs were scanned and measured by the quartz thermometer.

The calibration process was done taking care to eliminate hysteresis effects. In this way two independent temperature runs were made: the first determining the freezing point temperatures of KCl solutions beginning with a high concentration and then diluting; the second beginning from a low molality and then increasing it to cover the experimental temperature range.

0021-9568/85/1730-0344$01.50/0

Table I. Calculated and Experimental Mass Percentages of Co and NH_3 Found in the Cobaltammine Salts

	NH_3		Co	
salt	anal	calcd	anal	calcd
$Co(NH_3)_6Cl_3$ (*19*)	38.15	38.20	22.4	22.03
$Co(NH_3)_6Br_3$ (*19*)	25.2	25.49	14.8	14.70
$Co(NH_3)_6I_3$ (*20*)	18.6	18.86	10.6	10.89
$Co(NH_3)_6(NO_3)_3$ (*19*)	45.8	45.80	26.3	26.41
$Co(NH_3)_6(ClO_4)_3$ (*20, 21*)	22.0	22.24	12.8	12.83
$Co(H_2O(NH_3)_3)Cl_3$ (*20*)	31.9	31.72	21.5	21.95
$Co(H_2O(NH_3)_5Br_3$ (*20*)	20.8	21.19	14.7	14.67
$CoCl(NH)_5Cl_2$ (*22, 23*)	33.6	34.00	23.8	23.53

Special care has been taken to eliminate other sources of temperature fluctuations as effects of environmental temperature on the equipment or heat-transfer effects. In this way the oscillator and connecting wires were kept in a water-proof container surrounded by cracked ice inside the thermostat.

The achieved calibration accuracy is 0.0001 °C relative to the experimental temperature range −0.4–0 °C.

The concentration of the equilibrium solution was determined by means of a Metrohm-Herisau E 365 conductimeter using different thermostated inmersion cells to cover the experimental concentration range. Optical density measurements were also undertaken to determine the concentration of the equilibrium solutions by using a UV–vis Perkin-Elmer Coleman 55 spectrophotometer as described elsewhere (*18*).

Procedure. The Dewar vessels (VD) are set in position inside the thermostat and surrounded by cracked ice. The vessels are half filled with cracked ice of distilled water which is previously washed with distilled water.

The Dewar vessels are then covered with Teflon stoppers (TT) with Viton o-rings to ensure water tightness. The temperature probes (S) and sampling and air bubbling tube (TE) for stirring the solutions are screwed through the Teflon stoppers.

Once the vessels are in position the previously cooled solution of the electrolyte is introduced inside one of the vessels while the other is filled with cooled distilled water. The temperature measurement equipment permits independent readings in each vessel as well as differential readings. The vessel containing distilled water in equilibrium with ice is a check on the equipment.

Pure air at 0 °C is then bubbled through the Dewar flasks by means of tube TE for about 30 min. This method stirs the solution well, bringing it to a stationary temperature equilibrium within a short time and saturating the solution and the pure water with air. Longer bubbling times (3–6 h) yielded the same results. Temperature readings were taken when two consecutive passages of air gave the same temperature results and remained constant for at least 1 h. Once the equilibrium was attained a sample of the solution is withdrawn by means of the sampling tube TE, and its molality was determined from the electrical conductance or optical density in an external cell.

An equal volume of another cooled electrolyte solution is then added and the above process repeated to obtain new equilibrium conditions.

Materials. The salts used in this work were prepared by literature methods (*19–23*) and were recrystallized from conductivity water. The salts were vacuum-dried to constant mass.

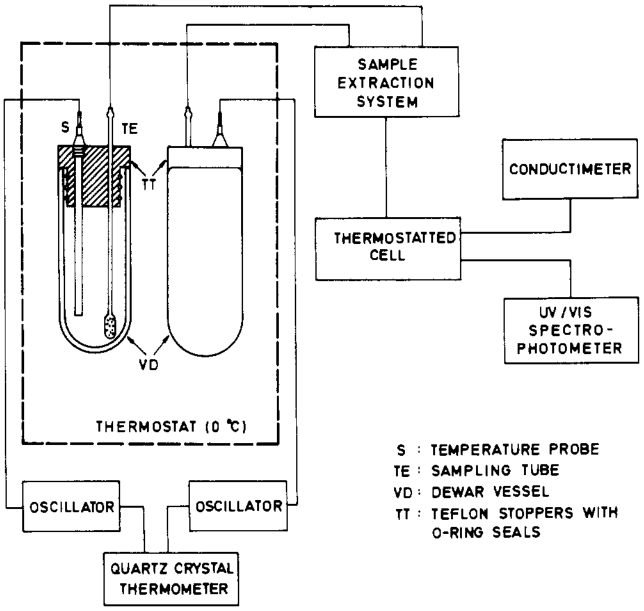

Figure 1. Schematic diagram of the freezing point apparatus.

The products were analyzed with the mass percentages given in Table I. Co was determined with a Perkin-Elmer 460 atomic absorption spectrophotometer. Occasional determinations of Co by decomposing a weighed quantity with sulfuric acid, evaporating to constant weight, and weighing the cobalt as cobaltous sulfate gave identical results within experimental error. NH_3 was determined with a Carlo Erba 1400 Automatic Nitrogen Analyser.

A Philips PW 1050/25 X-ray diffractometer was used to obtain the X-ray diffraction spectrums of powered samples of the hexaamminecobalt(III) salts which showed only a set of peaks that were identified as belonging to $Co(NH_3)_6^{3+}$.

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

Results and Discussion

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

$$\theta = \sum_i A_i m^i \qquad (1)$$

where m is the molality (mol.kg^{-1}) of the electrolyte solution. The coefficients of eq 1 and the standard deviations are given in Table II.

Osmotic coefficients ϕ were calculated from

$$\theta(1 + b\theta) = \phi\nu\lambda m \qquad (2)$$

where λ is the cryoscopic constant (1.860 K mol^{-1} kg) (*16*), m

Table II. Coefficients A_i and Standard Deviation $\sigma(\theta)$ Corresponding to Eq 1, Relating θ with m

electrolyte	$10^5 A_0$	A_1	A_2	A_3	A_4	$10^5 \sigma(\theta)$
$CoCl(NH_3)_5Cl_2$	0.885 88	5.457 44	−69.4539	2873.37		5
$Co(NH_3)_6Cl_3$	2.093 76	6.573 38	−88.1033	2637.19	−31 565.1	10
$Co(NH_3)_6Br_3$	0.302 36	6.552 17	−124.1419	7182.83	−169 904.3	7
$Co(NH_3)_6I_3$	−0.493 15	6.755 33	−171.7758	9740.12		3
$Co(NH_3)_6(NO_3)_3$	0.744 98	6.441 72	−68.0514	1284.74		9
$Co(NH_3)_6(ClO_4)_3$	0.999 06	7.142 02	−334.9067	26 550.72		4
$Co(NH_3)_5H_2OCl_3$	1.071 29	6.358 48	−77.0860	2290.29	−28 224.1	7
$Co(NH_3)_5H_2OBr_3$	0.228 08	6.772 61	−184.0690	6885.23		6

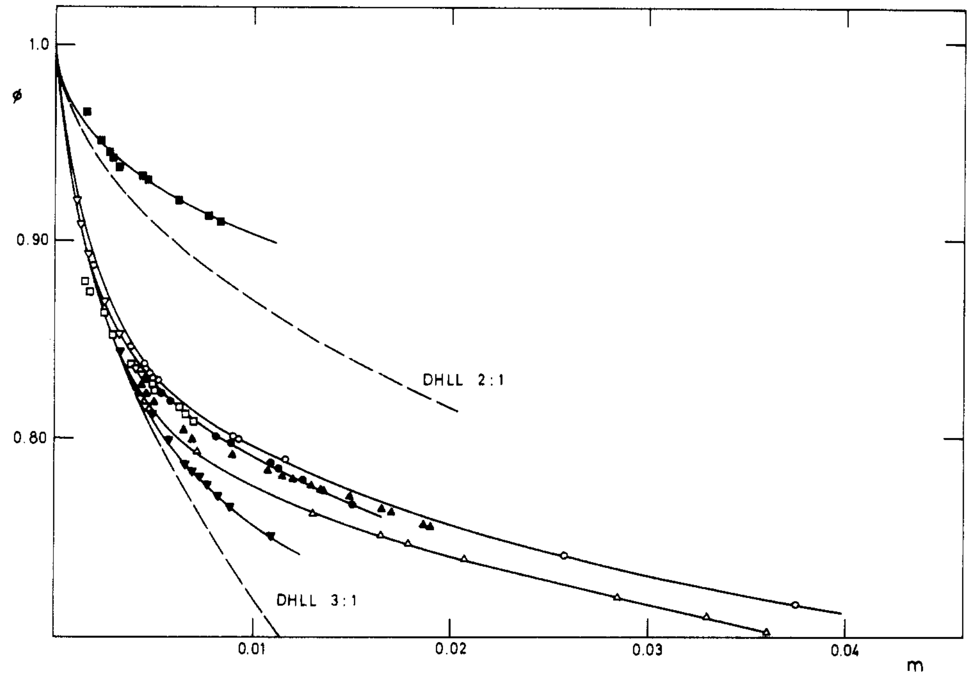

Figure 2. Experimental osmotic coefficients for aqueous solutions of amminecobalt(III) salts at their freezing temperature as a function of the molality. The dashed curves correspond to the Debye–Hückel limiting law (DHLL): ○, $Co(NH_3)_6Cl_3$; ■, $Co(Cl(NH_3)_5)Cl_2$; ▲, $Co(NH_3)_6Br_3$; □, $Co(NH_3)_6I_3$; ●, $Co(NH_3)_6(NO_3)_3$; ▽, $Co(NH_3)_6(ClO_4)_3$; △, $Co(H_2O(NH_3)_5)Cl_3$; ▼, $Co(H_2O(NH_3)_5)Br_3$.

is the molality of the solute, b is a calculable factor (4.9×10^{-4} K^{-1}), and υ is the number of ions per molecule of salt.

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

The osmotic coefficients were fitted to an extended Hamer and Wu (*17*, *24–27*) equation of the form

$$\phi = 1 + \frac{|Z_+Z_-|A_m}{B_0^3 I}| - (1 + B_0 I^{1/2})2 \ln (1 + B_0 I^{1/2}) + 1/(1 + B_0 I^{1/2})\,| + \sum_{i=1} \frac{i}{i+1} B_i m^i \quad (3)$$

where Z_+ and Z_- are the ion charges, I is the ionic strength, A_m is the Debye–Hückel constant (1.129 38 $kg^{1/2}$ $mol^{-1/2}$) (*28*), and B_i are constants. The values obtained by least squares for the coefficients in eq 3 are given in Table IV together with the standard deviation.

The final column in Table III gives the difference between the experimental osmotic coefficients and those calculated from eq 3 with the parameters given in Table IV.

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

It can be seen that chloropentaamminecobalt(III) chloride shows greater osmotic coefficients than the other cobalt(III) electrolytes as expected from a 2:1 electrolyte compared to a 3:1 electrolyte. It can be also seen that aquopentaamminecobalt(III) salt solutions show smaller osmotic coefficients than hexaamminecobalt(III) solutions. This behavior can be related with the contraction effect found when a NH_3 is substituted by a H_2O group in the coordination sphere. Previous works (*29–31*) have shown that the ionic size of an aquopentaamminecobalt(III) ion is smaller than that of an hexaamminecobalt(III) ion. This different ionic size is in agreement with the observed relative position of the experimental curves of the osmotic coefficients. The effect of the size of the anions is also shown; for a given cation the osmotic coefficients increase as the hydrophilic character of the anion increases. Figure 2 shows how chlorides have larger osmotic coefficients than bromides at equal molality due to the larger hydration number (*32*) of Cl^-.

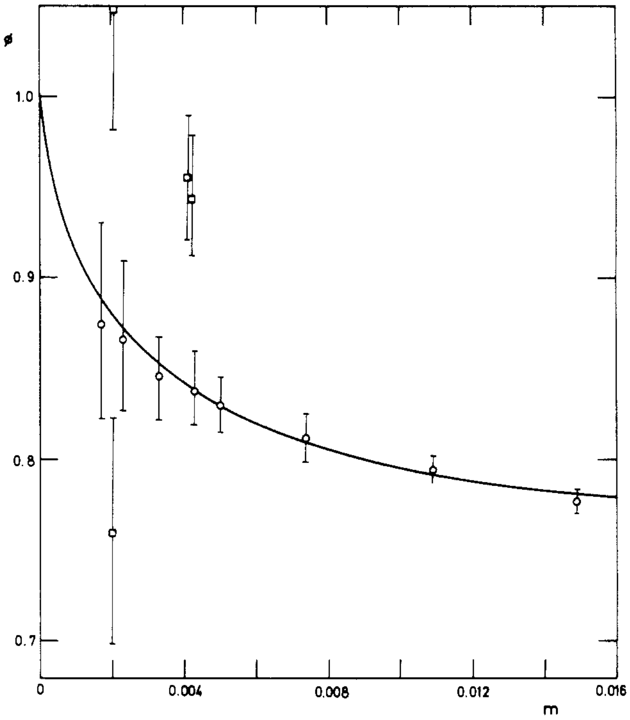

Figure 3. Experimental osmotic coefficients of $Co(NH_3)_6Cl_3$ solutions as a function of the molality: (—) this work, (○) Harkins et al., (□) Werner and Herty.

Figure 3 gives a plot of ϕ against m where our results for $Co(NH_3)_6Cl_3$ (solid line) are compared to those obtained by Harkins et al. (*23*) and Werner and Herty (*33*) which were recalculated with λ = 1.860 K mol^{-1} kg. The agreement between our results and those of Harkins is good within experimental error. The observed differences between Werner and Herty's results and the other two sets of results are probably due to the method of measurement of the freezing temperature used by these authors.

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

m	θ	$10^5\ \delta\theta$	ϕ	$10^3\ \delta\phi$
		$CoCl(NH_3)_5Cl_2$		
0.000 00	0.0000	0.9	1.0000	
0.001 53	0.0083	-9	0.9665	-3
0.002 29	0.0122	-2	0.9514	-0.4
0.002 74	0.0145	0	0.9453	-0.8
0.002 77	0.0146	5	0.9419	3
0.003 03	0.0159	9	0.9379	4
0.004 41	0.0230	-3	0.9340	-3
0.004 55	0.0237	-3	0.9333	-3
0.006 21	0.0319	0.9	0.9197	2
0.007 71	0.0393	-3	0.9129	0.5
0.008 23	0.0418	2	0.9098	-0.7
		$Co(NH_3)_6Cl_3$		
0.000 00	0.0000	2	1.0000	
0.001 97	0.0129	-25	0.8801	3
0.003 78	0.0238	-5	0.8463	0.4
0.004 49	0.0280	-1	0.8382	-2
0.004 71	0.0292	9	0.8333	0.5
0.005 14	0.0317	11	0.8296	-0.7
0.009 02	0.0538	7	0.8017	-1
0.009 32	0.0555	3	0.8004	-1
0.011 53	0.0677	-12	0.7892	2
0.025 69	0.1417	0.9	0.7414	-0.1
0.037 55	0.1995	-0.1	0.7142	0
		$Co(NH_3)_6Br_3$		
0.000 00	0.0000	0.3	1.0000	
0.004 27	0.0263	-8	0.8279	-0.2
0.004 51	0.0276	1	0.8226	2
0.004 97	0.0303	-2	0.8194	-0.5
0.006 46	0.0387	9	0.804	0.3
0.006 93	0.0414	5	0.8030	-1
0.008 88	0.0524	-3	0.7931	-1
0.010 70	0.0625	-3	0.7851	-0.2
0.011 46	0.0667	-3	0.7822	0.2
0.011 87	0.0690	-7	0.7809	0.1
0.012 72	0.0735	9	0.7767	1
0.013 44	0.0775	3	0.7751	0.6
0.013 59	0.0783	5	0.7744	0.9
0.014 83	0.0852	-12	-0.7719	-1
0.016 55	0.0943	-5	0.7657	-1
0.017 04	0.0967	12	0.7628	-0.1
0.018 76	0.1056	1	0.7565	0.5
0.018 85	0.1061	-4	0.7566	0.1
		$Co(NH_3)_6I_3$		
0.000 00	0.0000	-0.5	1.0000	
0.001 36	0.0089	-1	0.8796	6
0.001 54	0.0100	3	0.8728	6
0.002 32	0.0149	-3	0.8632	-6
0.002 84	0.0180	2	0.8519	-4
0.003 95	0.0246	-0.1	0.8371	-2
0.004 20	0.0261	-4	0.8353	-2
0.004 86	0.0299	-1	0.8269	1
0.004 99	0.0306	4	0.8242	3
0.00567	0.0345	5	0.8178	4
0.00633	0.0384	-6	0.8154	0.1
0.00655	0.0396	1	0.8126	0.1
0.007 00	0.0422	0.6	0.8084	-2
		$Co(NH_3)_6(NO_3)_3$		
0.000 00	0.0000	0.7	1.0000	
0.004 63	0.0286	-9	0.8303	7
0.005 24	0.0321	-2	0.8234	2
0.005 74	0.0350	-2	0.8189	-5
0.008 13	0.0484	17	0.8002	1
0.008 78	0.0521	9	0.7976	-8
0.010 87	0.0637	-6	-0.7877	-5
0.011 31	0.0661	-8	0.7850	3
0.012 49	0.0724	-5	0.7791	11
0.014 96	0.0854	5	0.7673	-4
		$Co(NH_3)_6(ClO_4)_3$		
0.000 00	0.0000	1	1.0000	
0.000 71	0.0050	-5	0.9412	-8
0.001 05	0.0072	-3	0.9217	-3
0.001 27	0.0086	-0.5	0.9102	-0.6
0.001 28	0.0087	-4	0.9093	0.3
0.001 61	0.0107	5	0.8933	4
0.001 86	0.0122	10	0.8816	7
0.002 53	0.0164	-3	0.8689	-0.4
0.003 16	0.0201	-3	0.8539	-2
0.003 18	0.0202	-1	0.8533	-2
0.003 91	0.0244	0.2	0.8375	-0.4
0.004 33	0.0268	1	0.8319	-0.6
0.004 85	0.0298	0	0.8259	1
		$Co(H_2O(NH_3)_5)Cl_3$		
0.000 00	0.0000	1	1.0000	
0.004 71	0.0286	-12	0.8162	4
0.007 11	0.0420	7	0.7940	-2
0.012 98	0.0737	6	0.7619	-3
0.016 44	0.0918	2	0.7506	-0.3
0.017 92	0.0995	-3	0.7473	0
0.020 74	0.1140	-6	0.7388	3
0.028 39	0.1525	0.9	0.7218	0.7
0.032 96	0.1745	4	0.7132	-3
0.035 98	0.1884	-3	0.7037	2
		$Co(H_2O(NH_3)_5)Br_3$		
0.000 00	0.0000	2	1.0000	
0.001 17	0.0078	-11	0.8977	6
0.003 32	0.0207	5	0.8454	-4
0.003 53	0.0220	-6	0.8377	-1
0.004 67	0.0283	4	0.8145	0.6
0.004 41	0.0269	0	0.8199	-0.3
0.005 65	0.0336	5	0.7993	0.5
0.006 53	0.0383	2	0.7863	2
0.006 85	0.0399	9	0.7829	1
0.007 28	0.0423	-7	0.7810	-1
0.007 62	0.0440	-1	0.7755	0.4
0.007 73	0.0446	-2	0.7751	-0.4
0.008 18	0.0469	-2	0.7706	-0.2
0.008 78	0.0500	-4	0.7649	0.2
0.010 85	0.0606	3	0.7507	-0.1

Table IV. Coefficients B_i and Standard Deviation $\sigma(\phi)$ Corresponding to Eq 3

electrolyte	B_0	B_1	B_2	B_3	B_4	$10^3\ \sigma(\phi)$
$CoCl(NH_3)_5Cl_2$	7.1776	-18.0710	466.1			3
$Co(NH_3)_6Cl_3$	0.1624	-0.5845	1487.9	-59 815.2	742 654.1	2
$Co(NH_3)_6Br_3$	0.0812	-12.4106	3325.8	-171 203.4	3075 427.3	1.5
$Co(NH_3)_6I_3$	11.8673	-151.3194	22419.2	-1414 569.9		7.7
$Co(NH_3)_6(NO_3)_3$	0.1299	-2.6761	1648.6	-55 577.8		0.8
$Co(NH_3)_6(ClO_4)_3$	12.0169	-105.1966	-8707.1	-260 325.6		4.4
$Co(H_2O(NH_3)_5)Cl_3$	0.1462	-5.636	1357.1	-42 878.9	453 991.4	2.9
$Co(H_2O(NH_3)_5)Br_3$	2.2735	-41.3370	2127.3	-51 665.1		4

Our ϕ results for $CoCl(NH_3)_5Cl_2$ are compared to those of Harkins et al. (*23*) in Figure 4. It can be also seen that the agreement between both sets of data is good within experimental error.

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

$$\ln \gamma_{\pm} = \phi - 1 - \int_0^m (1 - \phi)\, d \ln m \qquad (4)$$

Table V. Osmotic Coefficients and Activity Coefficients at Even Molalities, at the Temperature of the Freezing Point of the Solutions

m	ϕ	γ
	$CoCl(NH_3)_5Cl_2$	
0.001	0.9664	0.8990
0.002	0.9536	0.8635
0.003	0.9436	0.8374
0.004	0.9351	0.8160
0.005	0.9278	0.7978
0.006	0.9215	0.7819
0.007	0.9159	0.7679
0.008	0.9111	0.7555
	$Co(NH_3)_6Cl_3$	
0.001	0.9148	0.7723
0.002	0.8826	0.6974
0.003	0.8601	0.6474
0.004	0.8434	0.6101
0.005	0.8305	0.5807
0.006	0.8203	0.5568
0.007	0.8122	0.5369
0.008	0.8058	0.5200
0.009	0.8007	0.5055
0.01	0.7965	0.4928
0.02	0.7668	0.4117
0.03	0.7205	0.3546
0.04	0.7321	0.3305
	$Co(NH_3)_6Br_3$	
0.004	0.8314	0.5916
0.005	0.8184	0.5615
0.006	0.8086	0.5375
0.007	0.8013	0.5178
0.008	0.7956	0.5012
0.009	0.7911	0.4869
0.01	0.7873	0.4744
0.02	0.7540	0.3918
	$Co(NH_3)_6I_3$	
0.001	0.9053	0.7635
0.002	0.8649	0.6774
0.003	0.8435	0.6247
0.004	0.8332	0.5652
0.005	0.8277	0.5651
0.006	0.8203	0.5433
0.007	0.8045	0.5197
	$Co(NH_3)_6(NO_3)_3$	
0.001	0.9135	0.7703
0.002	0.8803	0.6940
0.003	0.8572	0.6430
0.004	0.8398	0.6050
0.005	0.8264	0.5752
0.006	0.8159	0.5510
0.007	0.8077	0.5308
0.008	0.8011	0.5137
0.009	0.7956	0.4989
0.01	0.7909	0.4859
0.02	0.7132	0.3822
	$Co(NH_3)_6(ClO_4)_3$	
0.001	0.9214	0.7924
0.002	0.8832	0.7133
0.003	0.8556	0.6582
0.004	0.8366	0.6178
0.005	0.8247	0.5878
	$Co(H_2O(NH_3)_5)Cl_3$	
0.001	0.9121	0.7681
0.002	0.8769	0.6897
0.003	0.8517	0.6366
0.004	0.8321	0.5965
0.005	0.8164	0.5646
0.006	0.8035	0.5384
0.007	0.7930	0.5165
0.008	0.7844	0.4978
0.009	0.7773	0.4816
0.01	0.7714	0.4676
0.02	0.7431	0.3839
0.03	0.7179	0.3358
0.04	0.7078	0.3057
	$Co(H_2O(NH_3)_5)Br_3$	
0.001	0.9122	0.7691
0.002	0.8757	0.6895
0.003	0.8486	0.6347
0.004	0.8270	0.5928
0.005	0.8094	0.5593
0.006	0.7947	0.5317
0.007	0.7825	0.5084
0.008	0.7723	0.4884
0.009	0.7635	0.4711
0.01	0.7560	0.4559

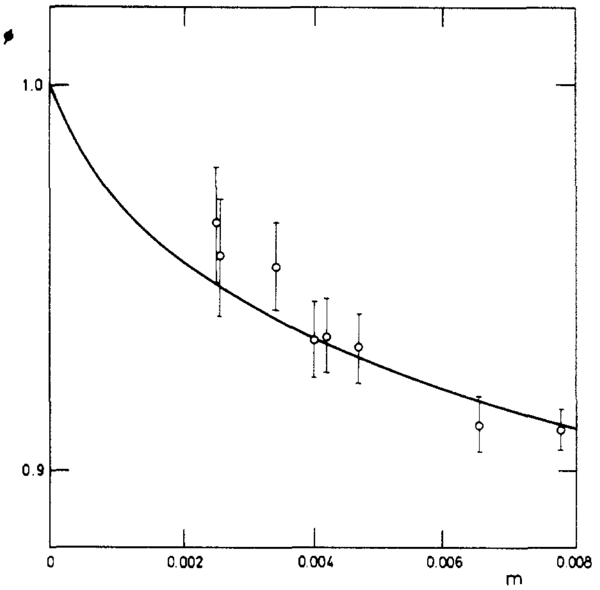

Figure 4. Experimental osmotic coefficients of $Co(Cl(NH_3)_5Cl_2$ solutions as a function of the molality: (—) this work, (O) Harkins et al.

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

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

Substitution of eq 3 into eq 4 and integration yields

$$\ln \gamma_\pm = \frac{-|Z_+Z_-|A_m I^{1/2}}{1 + B_0 I^{1/2}} + \sum_{i=1} B_i m^i \quad (5)$$

where the symbols have the same meaning as in eq 3. Table V contains values of ϕ and $\gamma_\pm$ at the temperature of the freezing point of the solutions, calculated with eq 3 and 5 at various even molalities.

Registry No. $CoCl(NH_3)_5Cl_2$, 13859-51-3; $Co(NH_3)_6Cl_3$, 10534-89-1; $Co(NH_3)_6Br_3$, 10534-85-7; $Co(NH_3)_6I_3$, 13841-85-5; $Co(NH_3)_6(NO_3)_3$, 10534-86-8; $Co(NH_3)_6(ClO_4)_3$, 13820-83-2; $Co(NH_3)_5H_2OCl_3$, 13820-80-9; $Co(NH_3)_5H_2OBr_3$, 14404-37-6.

Literature Cited

(1) Scatchard, G.; Jones, P. T.; Prentiss, S. S. *J. Am. Chem. Soc.* **1932**, *54*, 2690.
(2) Scatchard, G.; Jones, P. T.; Prentiss, S. S. *J. Am. Chem. Soc.* **1934**, *56*, 805.
(3) Scatchard, G.; Prentiss, S. S. *J. Am. Chem. Soc.* **1932**, *54*, 2926.
(4) Scatchard, G.; Prentiss, S. S. *J. Am. Chem. Soc.* **1933**, *55*, 4355.
(5) Scatchard, G.; Prentiss, S. S. *J. Am. Chem. Soc.* **1934**, *56*, 807.
(6) Scatchard, G.; Prentiss, S. S. *J. Am. Chem. Soc.* **1934**, *56*, 1486.
(7) Scatchard, G.; Prentiss, S. S. *J. Am. Chem. Soc.* **1934**, *56*, 2314.
(8) Scatchard, G.; Prentiss, S. S. *J. Am. Chem. Soc.* **1934**, *56*, 2320.
(9) Lange, J. *Z. Phys. Chem.* (*Frankfurt am Main*) **1934**, *168A*, 147.
(10) Lange, J. *Z. Phys. Chem.* (*Frankfurt/Main*) **1936**, *177A*, 193.

J. Chem. Eng. Data 1985, 30, 349-352 349

(11) Brown, P. G. M.; Prue, J. E. *Proc. Soc. London, Ser. A* **1955**, *A232*, 320.
(12) Prue, J. E.; Cavanagh, K.; Scott, V. E. *J. Chem. Thermodyn.* **1974**, *6*, 93.
(13) Lilley, T. H.; Scott, R. P. *J. Chem. Thermodyn.* **1974**, *6*, 1015.
(14) Adams, L. H. *J. Am. Chem. Soc.* **1915**, *37*, 481.
(15) Brown, P. G. M. Doctoral Thesis, University of Reading, England, 1954.
(16) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworths: London, 1959.
(17) Hamer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.
(18) Arsuaga, J. M.; Castellanos, M. A.; Núñez, J. *J. Chem. Thermodyn.* **1982**, *14*, 555.
(19) Bjerrum, J.; Reynolds, J. P. *Inorg. Synth.* **1946**, *2*, 217.
(20) Gmelin-Kraut's "Handbuch der Anorganischem Chemie"; Carl Winter's Universitatsbuchhandlung: Heildelberg, West Germany, 1909; Vol. V.
(21) Pascal, P. "Nouveau Traite de Chemie Minerale"; Masson: Paris, 1959; Vol. XVIII.
(22) Schelessinger, G. G. *Inorg. Synth.* **1960**, *6*, 182.
(23) Harkins, W. D.; Hall, R. E.; Roberts, W. A. *J. Am. Chem. Soc.* **1918**, *38*, 2643.
(24) Wu, Y. C.; Hamer, W. J. "Osmotic Coefficients and Mean Activity Coefficients of a Series of Uni-Bivalent Electrolytes in Aqueous Solutions at 25 °C"; *Natl. Bur. Stand.* [*Tech.-Rep.*] *NBSIR* (*U.S.*) **1969**, NBSIR 10052, part XIV, 83.
(25) Staples, B.; Nutall, R. L. *J. Phys. Chem. Ref. Data* **1977**, *6*, 385.
(26) Goldberg, R. N.; Nutall, R. L. *J. Phys. Chem. Ref. Data* **1978**, *7*, 263.
(27) Staples, B. R.; Nutall, R. L. "Computer Programs for the Evaluation of Activity and Osmotic Coefficients"; U.S. Government Printing Office: Washington DC 20234, 1978; N.B.S. Tech. Note 928.
(28) Clarke, E. C. W.; Glew, D. N. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1911.
(29) Biltz, W. *Z. Anorg. Chem.* **1927**, *164*, 240.
(30) Clark, G. L.; Quick, A. J.; Harkins, W. D. *J. Am. Chem. Soc.* **1920**, *42*, 2483.
(31) Ephraim, F.; Schutz, O. *Helv. Chim. Acta* **1926**, *9*, 629.
(32) Bockris, J. O'M. *Q. Rev., Chem. Soc.* **1949**, *3*, 173.
(33) Werner, A.; Herty, Ch. *Z. Phys. Chem.* (*Leipzig*) **1901**, *38*, 331.

Received for review June 7, 1984. Accepted January 22, 1985.

Thermodynamic Properties of Dilute Solutions of C_2–C_6 *n*-Alkanoic Acids in Sulfolane

Liliana Jannelli* and Michele Pansini

Thermodynamics Section, The Institute of Chemistry, Faculty of Engineering, The University of Naples, Naples, Italy

Partial molar volumes, $\bar{v}_2$, of the first five members of the *n*-alkanoic acid series in dilute sulfolane solutions were measured at 303.16 K. Cryoscopic measurements were also carried out on propionic acid–sulfolane solutions in equilibrium with disordered crystal I. Both sets of experimental data suggest that interactions between the dissolved acid and sulfolane are of limited importance. Cryoscopic measurements further indicate that the dissolved acid does not dimerize or dissociate in these solutions. A partition of the acid between the disordered crystal I and liquid sulfolane solutions is suggested, however, and the partition coefficient is calculated from the cryoscopic measurements. Experimental data on volumes are analyzed in the light of current theories based on group contribution models and the COOH group contribution is calculated.

Introduction

Previously (*1*, *2*) we reported the results of some density measurements carried out on C_2–C_5 normal and branched alkanenitriles, in the pure state and in aqueous and nonaqueous solutions, with the aim of deriving the CN group contribution. On that occasion we illustrated a method for calculating the void volume of molecules, responsible for interactions of any kind, and proposed some criteria for evaluating the extent of solute–solute and solute–solvent interactions.

We provide herewith a new contribution for testing the adequacy of theory, by determining the partial molar volumes, $\bar{v}_2$, of C_2–C_6 *n*-alkanoic acids in dilute sulfolane solutions. This study allows us to calculate the COOH group contribution directly, as the dissolved acid neither dissociates nor dimerizes in sulfolane (the dissociation is indeed a feature of protic solvents, the association to molecular pairs of apolar solvents); sulfolane (*3*) is an aprotic solvent with a moderately high dielectric constant. With the aim of supporting the above statement, cryoscopic measurements are carried out on propionic acid-sulfolane solutions in equilibrium with disordered crystal I.

Experimental Section

Materials. Sulfolane kindly supplied by Shell Italia was carefully purified and dried as previously reported (*4*).

Carlo Erba RPE *n*-alkanoic acids were purified as recommended by Vogel (*5*). Acetic acid was partially frozen—about one-half was discarded as unfrozen liquid—and then fractionally distilled from potassium permanganate. Propionic, butyric, valeric, and caproic acids were repeatedly distilled over anhydrous sodium sulfate and then over potassium permanganate.

Physical properties of the purified materials are in good agreement with the most reliable literature data (*6–9*).

Solutions were prepared by weight (reduced to mass) in a drybox. Compositions are stated as molality of acid, *m*; the acids are indicated as component 2. Densities ($d_{1,2}$) are given in units of g·cm^{-3} and volumes (ϕ_2 and $\bar{v}_2$) in cm^3·mol^{-1}.

Apparatus. Densities were measured at 303.16 K with a DMA 60 vibrating-tube digital precision densimeter (Anton Paar, Austria). The apparatus and the temperature-controlling equipment were described elsewhere (*10*). The maximum error in density did not exceed 1 × 10^{-5} g·cm^{-3}. For each system densities were measured at different compositions ranging from 0.001 to 0.028 *m*.

Cryoscopic measurements on solutions were carried out by using the cryoscopic apparatus described elsewhere (*11*). Temperatures were measured with a NBS certified platinum resistance thermometer assembled with a G2 Model Müller bridge. The precision in temperature was 0.001 K. Both cooling and heating curves were taken; in the case of cooling curves the initial freezing points were determined by extrapolation across the undercooling region. Agreement between the initial freezing temperature and the final melting temperature of each solution was usually within 0.005 K.

Results

Densities. Experimental values of density $d_{1,2}^{303.16K}$ and molalities, *m*, of selected dilute C_2–C_6 *n*-alkanoic acid–sulfolane

0021-9568/85/1730-0349$01.50/0