Table V. Estimated Mixture Critical Points Using the
Peng-Robinson Equation of State with the Binary Interaction
Parameter Determined from Our Data

	$x^c_{CO_2}$	critical press., MPa
CO_2-*n*-butane at 37.7 °C	0.925	72.25
CO_2-1-butene at 37.7 °C	0.940	73.75
CO_2-1-butene at 45.0 °C	0.887	75.07

where N_i is the mole number of species *i*. Thus, while the species fugacity involves an integral over volume, a differentiation with respect to mole number (or mole fraction) is required. Therefore, the species fugacities, and thus the phase equilibrium predictions, are much more sensitive to the mixing rule and the binary interaction parameter used than they are to the equation of state in predicting specific volumes or densities. Consequently, it is not surprising that all the equations of state considered here yield similar phase equilibrium predictions.

Finally, for enhanced oil recovery or supercritical extraction processes, it would be useful to have estimates of the critical points of each of the mixtures studied. Rather than trying to establish the critical mixture compositions and pressures for the temperatures of our data sets by extrapolation, we have used the Peng–Robinson equation of state with the previously determined binary interaction parameters, and the critical point calculational method of Michelsen and Heidemann (*7*, *8*), even though cubic equations of state are not especially accurate in the critical region. The results appear in Table V.

Glossary

a, *b*, *c*	equation of state constants
$\bar{f}_i$	species fugacity
k_{ij}	binary interaction coefficient
N	number of moles
P	pressure
R	gas constant
T	temperature
v	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Literature Cited

(1) Besserer, G. J.; Robinson, D. B. *Can. J. Chem. Eng.* **1971**, *26*, 651.
(2) Nagahama, K.; Konishi, H.; Hoshino, D.; Hirata, M. *J. Chem. Eng. Jpn.* **1974**, *7*, 323.
(3) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(4) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
(5) Patel, N. C.; Teja, A. S. *Chem. Eng. Sci.* **1982**, *37*, 463.
(6) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969; p 89.
(7) Heidemann, R. A.; Khalil, A. M. *AIChE J.* **1980**, *26*, 769.
(8) Michelsen, M. L.; Heidemann, R. A. *AIChE J.* **1981**, *27*, 521.

Enthalpy of Dilution of Aqueous Solutions of Na₂SO₄, K₂SO₄, and MgSO₄ at 373.15 and 423.65 K and of MgCl₂ at 373.15, 423.65, and 472.95 K

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The enthalpies of dilution of aqueous solutions of MgCl₂, Na₂SO₄, and MgSO₄ have been measured at temperatures of 373.15 and 423.65 K. In addition, MgCl₂ has also been measured at 472.95 K. These measurements, together with literature data at lower temperatures, have been used to calculate reliable values of the relative apparent molar enthalpy, L_ϕ, the difference in osmotic coefficient on going from 298.15 K to *T*, $\phi(T) - \phi(298.15 \text{ K})$, and the logarithm of the ratio of activity coefficients at *T* and 298.15 K, $\ln[\gamma(T)/\gamma(298.15 \text{ K})]$ for both aqueous MgCl₂ and Na₂SO₄. The results are in reasonable agreement with other data from the literature.

Introduction

The measurements reported here are part of a continuing investigation of the thermodynamic properties of aqueous salt solutions at high temperatures using flow calorimetry (*1*, *2*). This paper represents enthalpy of dilution data for several

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electrolytes containing divalent ions. From these data and previous room-temperature measurements, the osmotic and activity coefficients of MgCl₂ and Na₂SO₄ have been calculated up to 473 and 423 K, respectively.

Experimental Section

Calorimeter. The flow calorimeter used in these experiments and its method of operation have been described in detail elsewhere (*2*, *3*). The accuracy of the calorimeter is approximately 1% and the temperatures of experiments are accurate to about 0.3 K. The pressures were kept constant at 0.1–0.3 MPa greater than the water vapor pressure at the experimental temperature.

Solutions. All solutions were prepared from Fisher certified reagent salts. The purities listed by the manufacturer (in mass %) were as follows: MgCl₂, 99.98%; Na₂SO₄, 99.99%; K₂SO₄, 99.9%; and MgSO₄, 99.95%. Stock solutions were prepared for each salt and analyzed gravimetrically by using silver nitrate for the MgCl₂ solution and barium nitrate for the other solutions. All determinations were accurate to ±0.1%. The stock dilutions were diluted either by weighing or volumetrically (±0.1%). As a check on the volumetric dilutions, the concentration after

Table I. Enthalpies of Dilution, $\Delta_{dil}H$, of Aqueous Salt Solutions at Various Temperatures

m_i/ (mol kg⁻¹)	m_f/ (mol kg⁻¹)	N^a	$-\Delta_{dil}H^b$/ (J mol⁻¹)	σ_e^c/ (J mol⁻¹)	Δ^d/ (J mol⁻¹)
(A) MgCl₂; T = 373.15 K					
3.609	1.722	1	9278	10	0
1.722	0.8440	1	4750	5	-7
0.8440	0.4183	1	2922	3	31
0.4183	0.2083	3	2076	4	-46
0.2083	0.1040	4	1620	33	-8
0.1040	0.0519	10	1356	61	12
0.0519	0.02595	10	1092	74	55
0.02595	0.01297	8	922	27	11
0.01297	0.00649	3	704	150	27
0.00649	0.00324	3	563	300	-3
0.00324	0.00162	3	488	375	-70
(B) MgCl₂; T = 423.65 K					
5.428	2.518	2	18225	40	-6
3.861	1.834	1	13326	30	41
2.782	1.343	1	10062	30	-86
2.041	0.9960	2	7919	16	26
1.290	0.6360	1	5838	15	88
0.8160	0.4050	1	4547	10	-15
0.5365	0.2668	2	3748	2	-70
0.2994	0.1492	1	3027	5	-69
0.1629	0.0813	1	2517	5	8
0.0901	0.04500	1	2134	15	74
0.05080	0.02538	1	1844	20	72
0.02967	0.01483	1	1601	30	41
0.01750	0.00875	1	1220	50	163
0.01031	0.00516	1	1201	100	-60
(C) MgCl₂; T = 472.95 K					
5.428	2.518	5	23010	20	0
2.862	1.381	1	14040	20	-1
1.532	0.7530	1	9371	10	4
0.8392	0.4159	1	7148	10	5
0.4620	0.2300	1	5748	10	-32
0.2554	0.1274	1	4835	10	-9
0.1416	0.07070	1	4146	10	67
0.07860	0.03927	1	3609	10	69
0.04390	0.02196	1	3140	20	13
0.02456	0.01228	1	2690	50	-46
0.01380	0.00690	1	2500	100	-333
0.00765ᵉ	0.00382	1	2630	150	-895
(D) Na₂SO₄; T = 373.15 K					
1.393	0.6843	2	1851	3	2
0.6843	0.3397	2	1650	14	-8
0.3397	0.1693	6	1576	37	-8
0.1693	0.08455	6	1454	20	45
0.08455	0.04225	10	1303	35	43
0.04225	0.02112	10	1135	31	-2
0.02112	0.01056	10	1090	106	-183
0.01056	0.00528	3	772	92	-72
0.00528	0.00264	3	622	230	-95
(E) Na₂SO₄; T = 423.65 K					
2.141	1.039	2	5186	30	4
1.579	0.7740	1	5201	30	-74
1.158	0.5707	2	4199	35	216
0.7230	0.3590	1	3661	40	-170
0.5060	0.2515	1	3365	40	-135
0.3603	0.1795	1	3147	40	-38
0.2599	0.1296	1	2968	40	55
0.1746	0.0872	1	2739	30	150
0.1206	0.06020	1	2584	30	141

m_i/ (mol kg⁻¹)	m_f/ (mol kg⁻¹)	N^a	$-\Delta_{dil}H^b$/ (J mol⁻¹)	σ_e^c/ (J mol⁻¹)	Δ^d/ (J mol⁻¹)
0.0849	0.04240	1	2418	30	110
0.06000	0.03000	1	2213	30	96
0.04320	0.02157	1	2105	30	-5
0.03135	0.01567	2	1976	20	-88
0.02122	0.01061	1	1815	30	-172
0.01467	0.00734	1	1454	30	-29
0.01040	0.00520	2	1455	60	-213
(F) K₂SO₄; T = 373.15 K					
0.6553	0.3234	2	1450	1	
0.3234	0.1607	3	1381	6	
0.1607	0.0801	4	1289	44	
0.0801	0.04000	7	1158	24	
0.04000	0.01999	10	1022	35	
0.01999	0.01000	10	902	56	
0.01000	0.00500	3	682	85	
0.00500	0.00250	3	560	73	
(G) K₂SO₄; T = 423.65 K					
0.6553	0.3233	2	3166	1	
0.4696	0.2326	1	2971	3	
0.4345	0.2155	2	2926	2	
0.3448	0.1714	2	2812	3	
0.2416	0.1202	1	2652	5	
0.2295	0.1143	2	2643	10	
0.1277	0.06370	1	2382	20	
0.06580	0.03290	1	2158	50	
0.03645	0.01821	1	1928	50	
0.02172	0.01085	1	1649	100	
0.01408	0.00704	2	1369	80	
(H) MgSO₄; T = 373.15 K					
1.988	0.983	1	3702	3	
0.983	0.490	1	2700	3	
0.490	0.2448	4	2244	22	
0.2448	0.1224	8	1928	18	
0.1224	0.0612	10	1744	8	
0.0612	0.0306	12	1681	15	
0.0306	0.0153	13	1685	54	
0.0153	0.00765	15	1724	58	
0.00765	0.00382	11	1737	145	
0.00832	0.00191	3	1749	318	
0.00191	0.000955	3	1590	500	
(I) MgSO₄; T = 423.65 K					
2.712	1.332	1	6178	6	
1.841	0.912	1	4944	5	
1.280	0.637	1	4254	4	
0.907	0.4524	1	3824	4	
0.6507	0.3249	1	3506	4	
0.4778	0.2388	1	3262	3	
0.3508	0.1753	2	3057	2	
0.2263	0.1131	1	2837	3	
0.1495	0.0747	1	2656	3	
0.1007	0.0503	1	2583	3	
0.0690	0.0345	1	2493	6	
0.03422	0.01711	2	2654	20	
0.02165	0.01082	1	2732	30	
0.01351	0.00676	1	2852	30	
0.00853	0.00426	1	2985	90	
0.00546	0.00273	2	3151	120	
0.002832	0.001416	1	2197	240	
0.00345	0.00172	1	3590	150	
0.00223	0.00112	4	2159	300	

^{a} N is the number of duplicate experiments. ^{b} $\Delta_{dil}H$ is the average experimental enthalpy of dilution. ^{c} σ_e is the error of $\Delta_{dil}H$ estimated from the scatter of the N points and the calorimetric behavior. ^{d} Δ is $\Delta_{dil}H$(calcd by eq 1) minus $\Delta_{dil}H$(exptl). ^{e} These experiments were not included in the least-squares fit because deviations from the fit were greater than 2σ.

a whole series of dilutions was checked to within 0.2%. All masses were corrected for buoyancy.

Results and Data Treatment

The results of the measurements are presented in Table I. This table gives the initial molality of the solution, m_i, the final molality of the solution, m_f, and observed and calculated enthalpies of dilution, $\Delta_{dil}H$. At many concentrations, repeated experiments were run and Table I gives the average result plus σ_e, an estimate of the accuracy of the average taking into account the scatter of the points, and the behavior of the calorimeter at the time of measurement.

Table II. Least-Squares Polynomial Coefficients for Each Salt in Eq 2

T/K	S_{D-H}/(kJ mol⁻³/² kg¹/²)	B_1/(kJ mol⁻² kg²)	B_2/(kJ mol⁻⁵/² kg³/²)	B_3/(kJ mol⁻³ kg²)	B_4/(kJ mol⁻⁷/² kg⁵/²)	B_5/(kJ mol⁻⁴ kg³)	m_{max}[a]/(mol kg⁻¹)	σ[b]/(kJ mol⁻¹)
			MgCl₂					
373.15	28.698	−40.560 07	42.434 37	−20.756 58	3.966 448	0	3.6	0.042
423.65	49.580	−75.169 84	87.687 01	−55.080 06	17.915 49	−2.322 46	5.4	0.088
472.95	83.948	−124.990 2	147.903 7	−99.746 11	35.311 76	−4.982 81	5.4	0.143
			Na₂SO₄					
373.15	28.698	−33.889 11	23.102 43	−6.226 22	0	0	1.4	0.093
423.65	49.580	−48.930 75	23.193 52	0	0	−1.264 71	2.1	0.139

[a] m_{max} is the maximum molality covered by the data. [b] σ is the standard error of a single point in the fit.

Table III. Relative Apparent Molar Enthalpies (L_ϕ), Changes in Osmotic Coefficient $(\phi(T) - \phi(298.15\ K))$, and Changes in Activity Coefficient $(\ln [\gamma(T)/\gamma(298.15\ K)])$ for Aqueous Solutions

m/(mol kg⁻¹)	L_ϕ/(kJ mol⁻¹)			$\phi(T) - \phi(298.15\ K)$			$\ln [\gamma(T)/\gamma(298.15\ K)]$		
T/K	373.15	423.15	473.15	373.15	423.15	473.15	373.15	423.15	473.15
				(A) MgCl₂					
0.10	6.17	10.38	17.87	−0.0362	−0.0706	−0.1168	−0.140	−0.276	−0.459
0.20	7.76	13.01	22.42	−0.0437	−0.0845	−0.1389	−0.175	−0.344	−0.570
0.30	8.85	14.80	25.47	−0.0511	−0.0979	−0.1594	−0.202	−0.394	−0.650
0.40	9.74	16.24	27.87	−0.0589	−0.1122	−0.1806	−0.225	−0.438	−0.720
0.50	10.53	17.49	29.90	−0.0672	−0.1270	−0.2022	−0.248	−0.479	−0.784
0.60	11.25	18.62	31.70	−0.0757	−0.1420	−0.2239	−0.269	−0.519	−0.845
0.70	11.93	19.67	33.32	−0.0841	−0.1569	−0.2452	−0.290	−0.557	−0.902
0.80	12.57	20.66	34.82	−0.0924	−0.1716	−0.2659	−0.310	−0.594	−0.957
0.90	13.19	21.60	36.21	−0.1006	−0.1858	−0.2861	−0.330	−0.629	−1.010
1.00	13.78	22.50	37.52	−0.1085	−0.1997	−0.3056	−0.348	−0.663	−1.060
1.50	16.49	26.53	43.19	−0.1468	−0.2646	−0.3973	−0.438	−0.821	−1.294
				(B) Na₂SO₄					
0.10	6.35	11.47		−0.0195	−0.0587		−0.106	−0.257	
0.20	7.87	14.39		−0.0123	−0.0546		−0.110	−0.292	
0.30	8.79	16.19		−0.0058	−0.0491		−0.107	−0.308	
0.40	9.44	17.50		−0.0003	−0.0447		−0.103	−0.317	
0.50	9.96	18.56		0.0044	−0.0418		−0.097	−0.324	
0.60	10.39	19.48		0.0086	−0.0400		−0.092	−0.329	
0.70	10.77	20.30		0.0126	−0.0390		−0.086	−0.334	
0.80	11.10	21.07		0.0165	−0.0384		−0.081	−0.339	
0.90	11.41	21.79		0.0204	−0.0380		−0.074	−0.343	
1.00	11.68	22.49		0.0244	−0.0374		−0.068	−0.346	

The experimental data for each temperature in Table II were fitted by using a least-squares technique for the equation

$$\Delta_{dil}H = L_\phi(m_f) - L_\phi(m_i) \qquad (1)$$

where the relative apparent molar enthalpy at a molality m, $L_\phi(m)$, is given by

$$L_\phi(m) = S_{D-H}(T)m^{1/2} + \sum_{i=1}^{n} B_i\, m^{(i+1)/2} \qquad (2)$$

where $S_{D-H}(T)$ is the Debye–Hückel limiting slope (taken from the compilation by Helgeson and Kirkham (4)) at the experimental temperature. The results of the least-squares fit are presented in Tables I and II. No corrections were made for changes in the pressure of the experiments with temperature, since these effects are negligible at these pressures.

The present measurements, together with the relative apparent molar enthalpies at 298.15 K, were used to calculate changes in both osmotic and activity coefficients with temperature at constant molality. For MgCl₂, the relative apparent molar enthalpies were taken from Snipes, Manley, and Ensor (5), and for Na₂SO₄ from Thompson, Smith, and Wood (6). The results for K₂SO₄ were not fitted this way because of a lack of data at 298.15 K, and the MgSO₄ were not fitted because the strong association present in this salt did not allow accurate extrapolation of the heat of dilution data to infinite dilution using eq 2.

Standard thermodynamic manipulations give the equation for calculating the change in osmotic coefficient

$$\phi(T_2) - \phi(T_1) = (m^{1/2}/2\nu R) \int_{T_1}^{T_2} (\partial L_\phi/\partial m^{1/2})\, d(1/T) \qquad (3)$$

$$\ln [\gamma(T_2)/\gamma(T_1)] = [1/(\nu R)] \int_{T_1}^{T_2} [L_\phi + (\mu^{1/2}/2)(\partial L_\phi/\partial m^{1/2})]\, d(1/T) \qquad (4)$$

In order to tabulate values of L_ϕ, $\phi(T) - \phi(298.15\ K)$, and $\ln [\gamma(T)/\gamma(298.15\ K)]$ at round values of molality and temperature, we used the least-squares fit at each temperature to calculate values of L_ϕ and $\partial L_\phi/\partial m^{1/2}$ at round molalities. A cubic spline routine was then used to interpolate L_ϕ at round values of temperature and to integrate eq 3 and 4 to give values of $\phi(T) - \phi(298.15\ K)$ and $\ln [\gamma(T)/\gamma(298.15\ K)]$. The results are presented in Tables II and III. (More extensive tables are given in ref 3.)

Discussion

By combining the present calculations of the change in osmotic coefficient with the osmotic coefficients at 298.15 K of Goldberg and Nuttall (7), we can compare our results with other measurements of osmotic coefficients at high temperatures. A comparison of the results for MgCl₂ is given in Figure 1. The difference between the present calculations and the results of Holmes, Baes, and Mesmer (8) varies from −0.013 at 0.3 mol kg⁻¹ to +0.035 at 1 mol kg⁻¹. These differences are a little
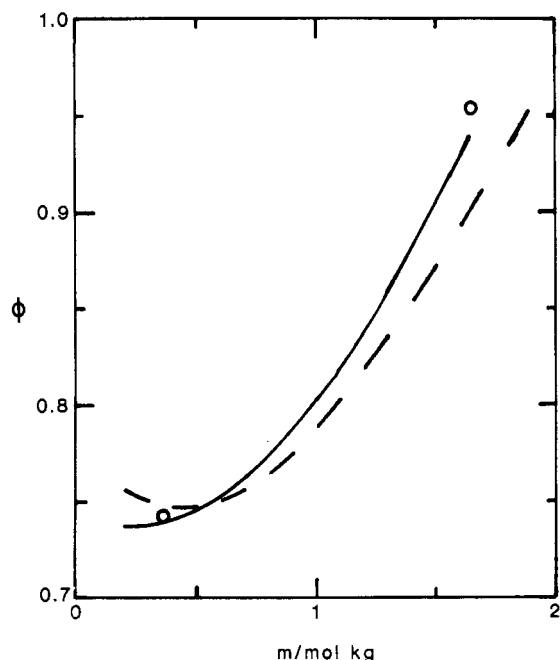
Figure 1. Osmotic coefficient of aqueous $MgCl_2$ at 473.15 K vs. molality: (—) present results; (– – –) Holmes, Baes, and Mesmer (8); (O) Liu and Lindsay (9).

larger than what is expected from the accuracy of the present calorimetric technique. Similar comparisons on alkali-metal halides normally gave agreement to better than 0.01 in osmotic coefficient at 473.15 K (2). The present results agree quite well with the measurements of Lindsay and Liu (9).

The present results for Na_2SO_4 can be compared with the measurements of the heat capacity of aqueous Na_2SO_4 of Rogers and Pitzer (10). From their measurements of heat capacity as a function of temperature and molality, Rogers and Pitzer calculated the relative apparent molar enthalpy, and this can be compared with the present results. The results are in fair agreement at 423.15 K and 1 mol kg^{-1}. Rogers and Pitzer find $L_\phi = 24.68$ kJ mol^{-1}, compared with the present result of 22.49 kJ mol^{-1}. Similarly, at 0.1 mol kg^{-1}, the results are 11.67 and 11.47 kJ mol^{-1}. (A series of measurements on aqueous

Na_2SO_4 at 472.95 K (3) are not reported here because there appears to have been an error in these measurements. The relative molar enthalpies at 472.95 K do not follow a smooth trend with temperature, they do not agree with the results of Rogers and Pitzer, and they do not agree with a check measurement made in this laboratory at 448.41 K and 17.7 MPa of the heat capacity of a 0.9985 mol kg^{-1} Na_2SO_4 solution; $C_{p,\phi} = +2.2$ J mol^{-1} K^{-1}. This result is in agreement with the result of Rogers and Pitzer, considering the difference in pressure, and does not agree with our measurements at 472.95 K.) Using the same osmotic coefficients at 298.15 K used by Rogers and Pitzer, we can calculate the osmotic coefficients at 423.15 K and compare with their values. Our results at 0.1, 0.5, and 1.0 mol kg^{-1} are 0.734, 0.648, and 0.604, whereas Rogers and Pitzer get 0.728, 0.630, and 0.597, respectively. This is reasonable agreement.

Literature Cited

(1) Messikomer, E. E.; Wood, R. H. *J. Chem. Thermodyn.* **1975**, *7*, 119.
(2) Mayrath, J. E.; Wood, R. H. *J. Chem. Thermodyn.* **1982**, *14*, 15, 563.
(3) Mayrath, J. E. Ph.D. Dissertation, University of Delaware, Newark, DE, May 1980.
(4) Helgeson, H. C.; Kirkham, D. H. *Am. J. Sci.* **1974**, *274*, 1199.
(5) Snipes, H. P.; Manly, C.; Ensor, D. D. *J. Chem. Eng. Data* **1975**, *20*, 287.
(6) Thompson, P. T.; Smith, D. E.; Wood, R. H. *J. Chem. Eng. Data* **1974**, *19*, 386.
(7) Goldberg, R. N.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1978**, *1*, 263.
(8) Holmes, H. F.; Baes, C. F., Jr.; Mesmer, R. W. *J. Chem. Thermodyn.* **1978**, *10*, 983.
(9) Lindsay, W. T., Jr.; Liu, C. T. Office of Saline Water Research and Development Progress Reports, No. 347, 1968, and No. 722, 1971. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. Catalog Nos. 1 1.88:347 and 1 1.88:722.
(10) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem.* **1981**, *85*, 2886.

Solubility of Carbon Monoxide in Alcohols

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The solubility of carbon monoxide in various alcohols at pressures up to 4000 kPa has been measured by using a chromatographic technique to analyze equilibrated gas-in-liquid mixtures from a pressure vessel. Typical dilute-solution behavior was observed with the data fitting a Henry's law relationship. Values of carbon monoxide solubility in methanol, ethanol, 1- and 2-propanol, 2-methyl-1-propanol, 2-methyl-2-propanol, and 1- and 2-butanol are reported at 298 and 323 K.

Introduction

The solubility of carbon monoxide in various alcohols has been determined as part of a study of the base-catalyzed formation of formate esters (1).

$$ROH + CO = HCOOR \qquad (1)$$

It has been suggested that the kinetics of these reactions may be controlled by the solubility of the gas in the different alcohols (2, 3) and, in order to test this hypothesis, it is necessary to measure solubilities. The data obtained are also of interest in