Liquid-Vapor Equilibrium of Aqueous Lithium Chloride, from 25° to 100°C and from 1.0 to 18.5 Molal, and Related Properties

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Vapor pressures of aqueous 1.0–18.5*m* lithium chloride were measured from 25° to 100°C. From these measurements, other precise vapor-pressure and freezing-point measurements, and calorimetric enthalpy and heat capacity data, a 25-parameter quintic equation in the molality was developed for the nonDebye-Hückel part of the osmotic coefficient. With a similar equation for sodium chloride, the isotonic ratios of sodium chloride and lithium chloride were calculated and compared with literature values. The lithium chloride equation was compared with measurements of vapor pressure, freezing-point depression, and the electromotive force of concentration cells. The agreement is generally good.

Recently, we reported static vapor-pressure measurements on aqueous sodium chloride (*21*) and synthetic seawater (*2*). The same apparatus with only minor changes was used to measure the vapor pressures of aqueous lithium chloride. The small size of the lithium ion relative to the sodium ion causes striking differences in the properties of the two chlorides in water. Lithium chloride is quite hygroscopic and has a molar solubility at 25°C more than three times greater than that of sodium chloride. The wide range of concentrations and water activities attainable with lithium chloride is one of the reasons it was chosen for study.

Apparatus

The apparatus and procedure are the same as those described (*21*) except for one modification to improve the degassing procedure. Previous work (*24*) showed that an effective method for degassing nonelectrolyte solutions is to expand off the vapor from the cell while the solution is stirred at a temperature near the maximum temperature at which measurements are to be made. To adapt our apparatus for this degassing method, a mercury, porous glass frit valve was added to one arm of the solvent transfer U tube (Figure 1). During degassing, vapor is allowed to escape from the cell by lowering the mercury in the U tube to the level of the glass frit. The rate at which vapor escapes can be controlled roughly by adjusting the surface area of the frit which is exposed. The mercury, glass frit valve eliminates possible contamination of the cell with helium from the right side of the solvent transfer U tube, which must be pressurized at temperatures much above 25°C.

Materials

Fisher reagent-grade lithium chloride was twice recrystallized from conductivity water and dried in a vacuum oven at 130°C. The solid was powdered and stored in the drying oven at 130°C until use. The purification and degassing of the water used in preparing solutions have been described (*21*).

Procedure

Finely powdered lithium chloride is added to the cell with a long-stemmed funnel through the ground glass joint G (Figure 1). This must be done quickly because the salt is extremely hygroscopic. The joint G is sealed with mercury, the cell is evacuated, and the system is pumped out for 24 hr at room temperature with a mercury diffusion pump. The salt is dissolved by distilling 6 ml of thoroughly degassed water from a reservoir with the cell cooled to about 10°C. The solution is heated with stirring to 75°C, and over a period of about 8 hr, the vapor is periodically expanded off through the valve F. Degassing is complete after about 0.5 ml of water has been collected in the degassing manifold. The measuring procedure, the analysis of the solution, and the reduction of the results are unchanged (*21*).

Results and Analytical Expression

The experimental quantities are the equilibrium temperature and pressure, the volume of the vapor space, and the total number of moles of each component. From these results and the equation of state of the vapor, the composition of the liquid and the molal osmotic coefficient ϕ are calculated (*21*).

As with sodium chloride (*21*), we express the quantity $\phi - 1$ by a modified Debye-Hückel term plus a power series in the molality. Parameters for cubic, quartic, and quintic equations in m have been calculated on the IBM 360 computer of the Southern Illinois University Computation Center. The quintic equation, which (when the temperature dependence of ϕ is considered) contains 25 parameters, is required for an adequate representation of all of the results. Of these parameters, five were determined from the calorimetric enthalpies at 25°C (*16*), five were determined from the calorimetric heat capacities at 25°C (*16*), and 15 were determined from our osmotic coefficients, and other results judged sufficiently accurate.

The following measurements of osmotic coefficients were used in determining the parameters of the equation: our vapor-pressure measurements (1.0–18.5*m*, 25–100°C) in Table II, those of Kangro and Groeneveld (*4, 10*) (2.2–18.4*m*, 20° and 25°C), those of Lindsay and Liu (*12*) (1*m*, 125–275°C), and the freezing-point measurements of Scatchard and Prentiss (*22*) (0.01–1.2*m*), Fawaz (*1*) (0.1–1.4*m*), and Momicchioli et al. (*15*) (0.01–3.9*m*). The value of the ion-size parameter a' was chosen as 1.5 and was assumed to be independent of temperature. We also tried using a value of 1.155 for a' derived by a nonlinear least-squares analysis of Scatchard and Prentiss' freezing points (*20*), but this resulted in a much poorer fit of both the calorimetric and free energy results.

Our equation for the osmotic coefficients of a uniunivalent electrolyte is

$$\phi = 1 - SZ/a' + \sum_{j=1}^{\omega} D_j m^j \tag{1}$$

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The Debye functions S and Z are given by

$$S = 1.17284 - 6202.357 \frac{\tau}{T_s^2(1 + \tau/T_s)} + 54.42507 \ln (1 + \tau/T_s) - 0.1619930\, \tau + 8.596094 \times 10^{-5}(2\, T_s\tau + \tau^2) \quad (2)$$

and

$$Z = \{1 + x - 1/(1 + x) - 2 \ln (1 + x)\}/x^2 \quad (3)$$

where $\tau = T - T_s$, T is the absolute temperature, $T_s = 298.16\text{K}$, $x = a'I^{1/2}$, and I is the ionic strength measured in moles of solute per kilogram of solvent. The coefficients of the power series in m are given by

$$D_j = D_j^{(s)} - 0.2516103 \{(-D_j^{(0)} + T_sD_j^{(1)} - (1/2)T_s^2D_j^{(2)} + (1/6)T_s^3D_j^{(3)}) \frac{\tau}{T_s^2(1 + \tau/T_s)} + (D_j^{(1)} - T_sD_j^{(2)} + (1/2)T_s^2D_j^{(3)}) \ln (1 + \tau/T_s) + ((1/2)D_j^{(2)} - (1/2)T_sD_j^{(3)})\tau + (1/12)D_j^{(3)}(2\, T_s\tau + \tau^2)\} \quad (4)$$

The $D_j^{(i)}$ parameters for aqueous lithium chloride are given in Table I. The results of our measurements are given in Table II. The first column is the molality, the second is the Celsius temperature, the third is the osmotic coefficient, and the fourth is the experimental osmotic coefficient minus the value calculated by Equations 1-4 with the parameters of Table I. Table III gives values of the osmotic coefficient calculated for rounded temperatures and molalities, and Table IV gives the corresponding activity coefficients, calculated by Equation 12 of Ref. *21*. Table V gives the apparent molal enthalpy.

Isotonic ratios of lithium chloride and sodium chloride. An interesting test of the consistency of the results of our measurements on two different systems is the calculation of the isotonic or isopiestic ratio of sodium chloride and lithium chloride. The condition for isotonic equilibrium between a lithium chloride and a sodium chloride solution is the equality of the chemical potential or activity of water in the two solutions. In terms of the osmotic coefficients of the solutions, this condition is expressed

$$m_{\text{LiCl}}\phi_{\text{LiCl}} = m_{\text{NaCl}}\phi_{\text{NaCl}} \quad (5)$$

The equilibrium ratio $R = m_{\text{NaCl}}/m_{\text{LiCl}}$ is calculated by simultaneous solution of Equations 1-5 and 16 of Ref. *21*. The resulting equation, which is quite complicated, is solved manually by a method of successive approximations with the use of computer-printed tables of the osmotic coefficient of each salt at $0.1m$ intervals.

The results of our calculation of the isotonic ratio of lithium chloride and sodium chloride are shown in Figure 2. The ordinate δR is an arbitrary deviation function defined by

$$\delta R = R - 1 - 0.9539\, m_{\text{LiCl}} + 0.01375\, m^2_{\text{LiCl}} - 0.000959\, m^3_{\text{LiCl}} \quad (6)$$

The curve gives the results from our equations for lithium chloride and sodium chloride. The filled circles show the experimental results of Robinson (*18*) at 25°C. Except for the three most dilute solutions (the deviation for one of which, at 0.2080, is not shown), the agreement of the calculated and experimental values is excellent. Above $2m$ the calculated ratios appear to be about as accurate as the experimental ratios; below $2m$ the calculated ratios are probably considerably more accurate. Figure 2 also shows deviations for the isotonic measurements of Kirgintsev and Luk'yanov (*11*). Their values of R are evidently too large by about 0.005.

Osmotic coefficients near 25°C. Figure 3 shows the deviations from Equation 1 of our osmotic coefficients at 25°C and those of other workers at 20° and 25°C. The deviations of our measurements at other temperatures are given in the fourth column of Table II. Our results and those of Kangro and Groeneveld (*4, 10*) were included in the least-squares analysis to obtain the parameters of Equation 4; those of Gibson and Adams (*3*) (static method, 20.28°C) and Pearce and Nelson (*17*) (dynamic method, 25°C) were not. Even in the hands of skilled investigators, the dynamic vapor saturation method used by Pearce and Nelson is not capable of the precision of the static method. A likely cause for the large negative deviations of Gibson and Adams is incomplete degassing of the solutions.

The curve in Figure 3 shows the deviations of the values tabulated by Robinson and Stokes (*19*). These values have not been corrected for nonideality of water vapor, which would lower the osmotic coefficient of lithi-

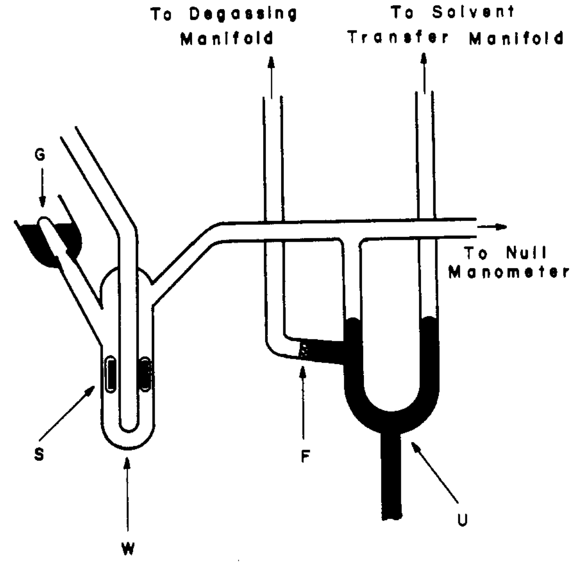

Figure 1. Vapor-pressure cell and degassing valve

G, ground glass stopper; S, stirrer; W, thermopile well; F, fritted glass disc; U, seal

Table I. Parameters of Equation 4

$D_1^{(s)} = 9.947194 \times 10^{-2}$
$D_2^{(s)} = 8.226815 \times 10^{-3}$
$D_3^{(s)} = 2.238653 \times 10^{-4}$
$D_4^{(s)} = -7.046113 \times 10^{-5}$
$D_5^{(s)} = 1.982918 \times 10^{-6}$

$D_1^{(0)} = 5.328557 \times 10^{1}$
$D_2^{(0)} = 3.126828 \times 10^{1}$
$D_3^{(0)} = -3.094298$
$D_4^{(0)} = 2.368127 \times 10^{-1}$
$D_5^{(0)} = -7.457059 \times 10^{-3}$

$D_1^{(1)} = 1.764393$
$D_2^{(1)} = -3.632635 \times 10^{-1}$
$D_3^{(1)} = 6.336939 \times 10^{-2}$
$D_4^{(1)} = -4.792288 \times 10^{-3}$
$D_5^{(1)} = 1.201533 \times 10^{-4}$

$D_1^{(2)} = -1.945510 \times 10^{-2}$
$D_2^{(2)} = 5.074271 \times 10^{-3}$
$D_3^{(2)} = 8.763426 \times 10^{-4}$
$D_4^{(2)} = -1.314343 \times 10^{-4}$
$D_5^{(2)} = 4.821150 \times 10^{-6}$

$D_1^{(3)} = 9.832480 \times 10^{-4}$
$D_2^{(3)} = -5.225767 \times 10^{-4}$
$D_3^{(2)} = 2.689426 \times 10^{-5}$
$D_4^{(2)} = 1.467403 \times 10^{-6}$
$D_5^{(2)} = -1.252579 \times 10^{-7}$

um chloride by as much as 0.0026 at 25°C. Up to about 5*m*, Robinson and Stokes' values are based on the isotonic ratios of lithium chloride and sodium chloride (*18*). Above 5*m* they used isotonic comparisons of lithium chloride with sulfuric acid. It seems likely that some of the "bump" in their deviation curve at 5*m* is due to the change of isotonic standards. Despite the number of attempts to obtain precise water activities for sulfuric acid solutions (*6–8, 25, 26*), the uncertainty in the osmotic coefficients in concentrated solutions (molality > 11) is 0.2–0.3%. The deviations of about 0.01 in the curve between 14 and 18.5*m* may reflect this uncertainty in the osmotic coefficients of sulfuric acid.

Table II. Osmotic Coefficients of Lithium Chloride Solutions

m, mol kg^{-1}	t, °C	ϕ	$\phi - \phi_{calcd}$
1.0208	25.0	1.0198	0.0025
1.0209	37.5	1.0125	0.0005
1.0212	50.0	1.0109	0.0047
1.0215	62.5	0.9921	−0.0078
1.0218	75.0	0.9875	−0.0057
1.0227	87.5	0.9864	0.0002
1.0238	100.0	0.9740	−0.0047
2.197	25.0	1.1685	−0.0001
2.197	37.5	1.1580	0.0003
2.198	50.0	1.1493	0.0028
2.198	62.5	1.1323	−0.0023
2.199	75.0	1.1226	0.0000
2.201	87.5	1.1118	0.0013
2.202	100.0	1.0942	−0.0040
3.940	25.0	1.4350	0.0019
3.940	37.5	1.4131	0.0017
3.942	62.5	1.3696	0.0025
3.944	75.0	1.3435	−0.0016
3.946	87.5	1.3196	−0.0038
3.950	100.0	1.3148	0.0123
6.369	25.0	1.8464	−0.0047
6.370	37.5	1.8107	0.0007
6.371	50.0	1.7683	−0.0005
6.372	62.5	1.7265	−0.0010
6.375	75.0	1.6847	−0.0022
6.379	87.5	1.6448	−0.0026
6.384	100.0	1.6043	−0.0056
7.407	25.0	2.0259	−0.0087
7.408	37.5	1.9772	−0.0066
7.409	50.0	1.9248	−0.0083
7.411	62.5	1.8772	−0.0054
7.414	75.0	1.8275	−0.0052
7.418	87.5	1.7834	−0.0007
7.424	100.0	1.7375	−0.0003
8.492	25.0	2.2159	−0.0057
8.493	37.5	2.1575	−0.0025
8.494	50.0	2.0958	−0.0028
8.495	62.5	2.0392	0.0017
8.498	75.0	1.9770	−0.0002
8.502	87.5	1.9206	0.0021
8.508	100.0	1.8681	0.0056
11.536	25.0	2.6630	−0.0105
11.537	37.5	2.5760	−0.0022
11.542	62.5	2.3930	0.0001
11.546	75.0	2.3070	0.0045
11.533	87.5	2.2150	0.0016
11.562	100.0	2.1280	−0.0033
18.542	25.0	3.0540	−0.0013
18.544	37.5	2.9110	−0.0153
18.548	50.0	2.7840	−0.0131
18.551	62.5	2.6590	−0.0078
18.559	75.0	2.5420	0.0025
18.570	87.5	2.4300	0.0072
18.585	100.0	2.3240	−0.0033

For sulfuric acid solutions more concentrated than 11*m*, the isotonic measurements rely on the static vapor-pressure results of Shankman and Gordon (*25*). However, these authors reported only two values for the water activity between 12 and 18*m*, which corresponds isotonically to 13–20*m* lithium chloride. Moreover, neither we nor Groeneveld (*4, 10*) made any measurements on lithium chloride between 14.5 and 18.5*m*. Thus, in the range of water activities between 0.2 and 0.1, a gap exists in the available data both for lithium chloride and sulfuric acid. Until more data become available, we must conclude that the osmotic coefficients of aqueous lithium chloride are known only to within 0.01 or 0.02 for concentrations greater than 14*m*.

Freezing points. Osmotic coefficients were calculated from the freezing-point measurements of Scatchard and Prentiss (*22*), Fawaz (*1*), and Momicchioli et al. (*15*) by equation A1 of Scatchard et al. (*23*). Figure 4 shows the deviations from Equation 1 of these values, all of which were included in the least-squares analysis. The agreement with the values of Scatchard and Prentiss is excellent. The deviations for Fawaz's measurements, except for the most concentrated solution, are consistent with the precision of ±0.15% in his determination of the molality and ±0.001°C in the freezing-point depression. The deviations of Momicchioli et al. (*15*) vary systematically with concentration, but the differences from the values of

Table III. Osmotic Coefficients at Rounded Temperatures and Molalities

m, mol kg^{-1}	°C				
	0	25	50	75	100
0.1	0.9443	0.9418	0.9379	0.9331	0.9276
0.2	0.9441	0.9409	0.9359	0.9298	0.9227
0.3	0.9496	0.9458	0.9400	0.9329	0.9247
0.4	0.9575	0.9532	0.9466	0.9387	0.9294
0.5	0.9668	0.9619	0.9547	0.9458	0.9357
0.6	0.9769	0.9715	0.9635	0.9539	0.9428
0.7	0.9877	0.9818	0.9730	0.9626	0.9507
0.8	0.9990	0.9925	0.9830	0.9717	0.9589
0.9	1.0108	1.0035	0.9933	0.9812	0.9676
1.0	1.0228	1.0149	1.0039	0.9910	0.9766
1.2	1.0479	1.0385	1.0259	1.0113	0.9952
1.4	1.0741	1.0631	1.0487	1.0324	1.0146
1.5	1.0876	1.0757	1.0604	1.0432	1.0245
1.6	1.1013	1.0885	1.0722	1.0541	1.0346
1.8	1.1293	1.1146	1.0965	1.0764	1.0553
2.0	1.1582	1.1415	1.1213	1.0993	1.0764
2.5	1.2339	1.2115	1.1859	1.1587	1.1311
3.0	1.3140	1.2853	1.2538	1.2210	1.1884
3.5	1.3982	1.3626	1.3274	1.2857	1.2477
4.0	1.4860	1.4429	1.3982	1.3527	1.3087
4.5	1.5768	1.5259	1.4739	1.4213	1.3710
5.0	1.6704	1.6110	1.5513	1.4913	1.4342
5.5	1.7660	1.6978	1.6301	1.5622	1.4978
6.0	1.8632	1.7858	1.7096	1.6335	1.5614
7.0	2.0601	1.9629	1.8688	1.7752	1.6864
8.0	2.2565	2.1378	2.0244	1.9121	1.8055
9.0	2.4477	2.3059	2.1721	2.0402	1.9149
10.0	2.6293	2.4629	2.3077	2.1557	2.0115
11.0	2.7970	2.6048	2.4277	2.2555	2.0929
12.0	2.9471	2.7284	2.5294	2.3374	2.1575
13.0	3.0761	2.8813	2.6111	2.4005	2.2053
14.0	3.1819	2.9124	2.6729	2.4453	2.2374
15.0	3.2626	2.9719	2.7162	2.4743	2.2571
16.0	3.3180	3.0117	2.7447	2.4919	2.2695
17.0	3.3487	3.0355	2.7642	2.5049	2.2819
18.0	3.3569	3.0492	2.7831	2.5228	2.3044

Scatchard and Prentiss near 1*m* suggest that the accuracy of the measurements is not nearly as good as their precision.

Electromotive force. MacInnes and Beattie (*14*) and Harned (*5*) measured at 25°C the electromotive force of concentration cells without liquid junction. In these studies silver, silver chloride, and lithium amalgam electrodes were used. The latter were troublesome, particularly at high lithium chloride concentrations. The most direct comparison of our equation with their results is the calculation of the potentials of their cells from the activity coefficients of Table IV. Figure 5 shows this comparison. The ordinate is the observed potential minus the value calculated with the Nernst equation, and the abscissa is the square root of the molality. Deviations for the measurements of MacInnes and Beattie are shown by unbroken lines joining the square roots of the molalities of the two solutions in the concentration cell. Because one of the solutions in Harned's cells was always 0.1*m*, a deviation for his work is shown as a circle whose abscissa is the square root of the molality of the other solution in the cell.

Up to 2*m* the agreement of the observed and calculated potentials for Harned's measurements is excellent. Above 2*m* the deviations increase rapidly and reach nearly 3 mV for 4*m* lithium chloride. These deviations are probably caused by a decomposition of the lithium amalgam, which is accelerated by high lithium chloride concentrations. The same conclusion applies to the most concentrated solution studied by MacInnes and Beattie. From 0.03 to 1.00*m* the agreement of their potentials with the calculated values is fair. By comparison of their results with those for concentration cells with liquid junction, MacInnes and Beattie recognized that the potentials for the most dilute solutions were too low. This was attributed to the presence of a small amount of dissolved oxygen in the solutions.

MacInnes and Beattie (*14*) also measured the potentials of concentration cells with liquid junction. The potentials obtained from such cells are often used in conjunction with measurements of the cation transference number to obtain activity coefficients. For comparison of our equation with these measurements, we have calculated the cell potentials from the reported molalities, the transference numbers of lithium ion, and activity coefficients, given by Equation 12 of Ref. *21*.

For a uniunivalent electrolyte the expression for the cell potential E in a concentration cell with liquid junction at 25°C is

$$E = -0.051377 \int_{\mathrm{I}}^{\mathrm{II}} t_{+}(1/m + \partial \ln \gamma_{\pm}/\partial m)dm \qquad (7)$$

Table IV. Activity Coefficients[a] at Rounded Temperatures and Molalities

m, mol kg^{-1}	°C				
	0	25	50	75	100
0.1	0.9034	0.8995	0.8936	0.9331	0.8783
0.2	0.8863	0.8812	0.8735	0.9298	0.8534
0.3	0.8792	0.8733	0.8643	0.9329	0.8408
0.4	0.8768	0.8701	0.8601	0.9387	0.8337
0.5	0.8772	0.8698	0.8588	0.9458	0.8298
0.6	0.8793	0.8713	0.8594	0.9539	0.8281
0.7	0.8828	0.8742	0.8613	0.9626	0.8279
0.8	0.8873	0.8781	0.8644	0.9717	0.8289
0.9	0.8927	0.8828	0.8682	0.8508	0.8308
1.0	0.8987	0.8881	0.8728	0.8544	0.8334
1.2	0.9123	0.9005	0.8835	0.8633	0.8404
1.4	0.9278	0.9145	0.8959	0.8739	0.8491
1.5	0.9360	0.9221	0.9026	0.8797	0.8540
1.6	0.9446	0.9299	0.9096	0.8858	0.8592
1.8	0.9627	0.9464	0.9244	0.8988	0.8704
2.0	0.9818	0.9639	0.9401	0.9128	0.8826
2.5	1.0335	1.0113	0.9567	0.9510	0.9163
3.0	1.0899	1.0629	1.0297	0.9929	0.9538
3.5	1.1502	1.1181	1.0798	1.0379	0.9940
4.0	1.2138	1.1763	1.1326	1.0855	1.0366
4.5	1.2804	1.2370	1.1878	1.1350	1.0810
5.0	1.3495	1.3000	1.2448	1.1863	1.1269
5.5	1.4208	1.3647	1.3034	1.2389	1.1738
6.0	1.4937	1.4309	1.3632	1.2924	1.2214
7.0	1.6434	1.5662	1.4851	1.4010	1.3174
8.0	1.7958	1.7030	1.6075	1.5093	1.4123
9.0	1.9479	1.8385	1.7278	1.6148	1.5038
10.0	2.0972	1.9700	1.8434	1.7152	1.5898
11.0	2.2409	2.0951	1.9522	1.8085	1.6688
12.0	2.3768	2.2118	2.0522	1.8931	1.7394
13.0	2.5029	2.3184	2.1424	1.9681	1.8012
14.0	2.6173	2.4139	2.2221	2.0334	1.8546
15.0	2.7191	2.4980	2.2917	2.0898	1.9005
16.0	2.8073	2.5711	2.3526	2.1390	1.9413
17.0	2.8822	2.6348	2.4073	2.1841	1.9803
18.0	2.9442	2.6914	2.4595	2.2294	2.0221

[a] Quantity tabulated is $1 + \log_{10} \gamma_{\pm}$.

Table V. Apparent Molal Enthalpies[a] at Rounded Temperatures and Molalities

m, mol kg^{-1}	°C				
	0	25	50	75	100
0.1	51	118	177	241	320
0.2	66	155	234	318	424
0.3	76	182	275	374	498
0.4	84	203	308	419	558
0.5	92	222	336	457	610
0.6	98	239	362	492	656
0.7	105	255	386	524	698
0.8	111	270	408	554	737
0.9	118	285	429	582	774
1.0	124	299	450	609	805
1.2	138	326	488	660	874
1.4	152	352	526	708	934
1.5	159	366	544	731	963
1.6	166	379	562	754	991
1.8	182	405	598	798	1046
2.0	198	432	633	842	1098
2.5	243	499	721	949	1224
3.0	293	569	810	1055	1344
3.5	349	642	901	1161	1461
4.0	409	718	994	1269	1578
4.5	474	798	1090	1379	1696
5.0	544	880	1188	1492	1815
5.5	618	965	1289	1608	1936
6.0	695	1053	1394	1726	2060
7.0	862	1238	1611	1974	2319
8.0	1042	1434	1840	2234	2591
9.0	1236	1641	2080	2507	2877
10.0	1443	1860	2330	2790	3175
11.0	1663	2088	2590	3083	3482
12.0	1894	2325	2857	3382	3793
13.0	2137	2569	3129	3685	4105
14.0	2388	2818	3405	3989	4412
15.0	2645	3069	3681	4291	4709
16.0	2906	3318	3954	4587	4990
17.0	3164	3558	4219	4874	5248
18.0	3414	3782	4472	5149	5479

[a] Quantity tabulated is Φ_L, cal mol^{-1}.

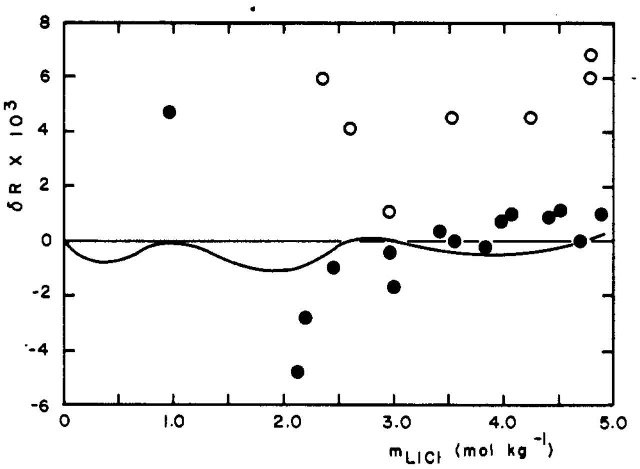

Figure 2. Sodium chloride, lithium chloride isotonic ratio deviations

Filled circles, Robinson (*18*); open circles, Kirgintsev and Luk'yanov (*11*); curve calculated from lithium chloride and sodium chloride equations

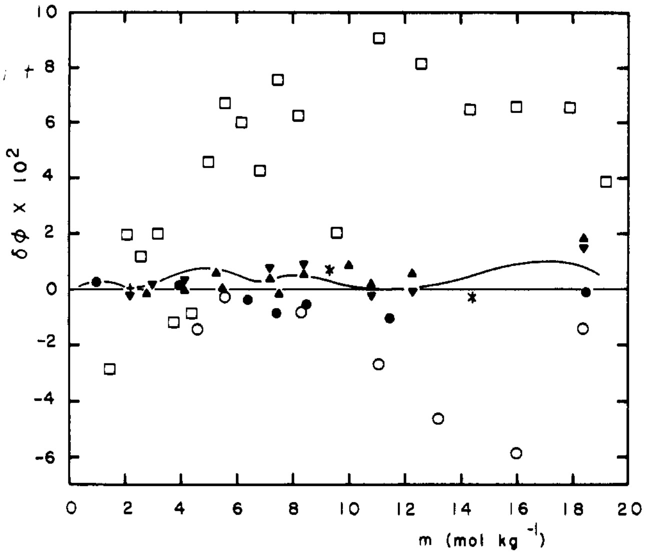

Figure 3. Deviations of osmotic coefficients from Equation 1 at 20° and 25°C

Filled circles, this work (25°C); triangles with points up, Kangro and Groeneveld (*10*) (20°C); triangles with points down, Kangro and Groeneveld (*10*) (25°C); *, nearly coincident points of Kangro and Groeneveld (*10*) (20° and 25°C); +, nearly coincident points of this work (25°C) and Kangro and Groeneveld (*10*) (20°C); squares, Pearce and Nelson (*17*) (25°C); open circles, Gibson and Adams (*3*) (20.28°C)

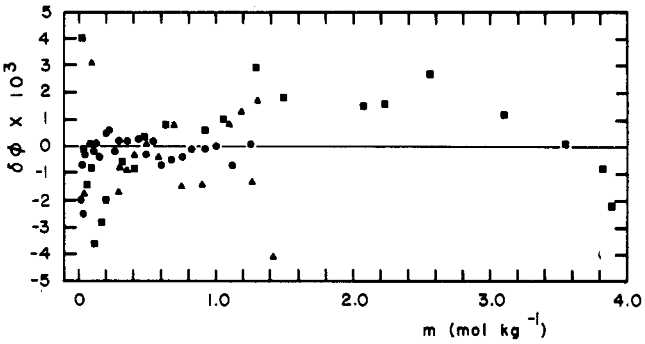

Figure 4. Osmotic coefficient deviations at freezing points of solutions

Circles, Scatchard and Prentiss (*22*); triangles, Fawaz (*1*); squares, Momicchioli et al. (*15*)

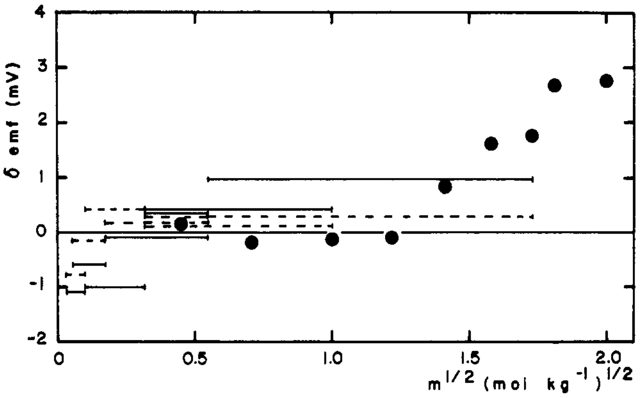

Figure 5. Electromotive force deviations at 25°C

Broken lines, MacInnes and Beattie (*14*), cells with liquid junction; unbroken lines, MacInnes and Beattie (*14*), cells without liquid junction; circles, Harned (*5*), cells without liquid junction

where t_+ is the transference number of the cation, and the limits of integration are the molalities of the cell compartments I and II. From the work of Longsworth (*13*) and Jones and Bradshaw (*9*), the lithium ion transference numbers over the concentration range of MacInnes and Beattie's measurements (0.01–3.0m) may be expressed by the relationship

$$t_+ = t_0/\{1 + t_0(t_1 m^{1/2} + t_2 m)\} \tag{8}$$

where $t_0 = 0.3364$, $t_1 = 0.53891$, and $t_2 = -0.015847$. For the quantity $\partial \ln \gamma_\pm/\partial m$, our equation gives

$$\partial \ln \gamma_\pm/\partial m = -S/\{2\, m^{1/2}\,(1 + a' m^{1/2})\} + 2\,D_1 + 3\,D_2 m + 4\,D_3 m^2 + 5\,D_4 m^3 + 6\,D_5 m^4 \tag{9}$$

and at 25°C, $S = 1.17495$, and $D_i = D_i^{(s)}$. Equations 8 and 9 were inserted into Equation 7, and the integral was computed numerically by Simpson's rule on the IBM 360 computer.

The deviations of MacInnes and Beattie's potentials of cells with liquid junction from the values calculated by Equation 7 are shown by the broken lines in Figure 5. The agreement is much better than for the cells without liquid junction. This is to be expected because the cells without liquid junction lack the troublesome lithium amalgam electrode. The average deviation for the cells with liquid junction is 0.31 mV for all solutions and 0.23 mV if the 0.001–0.01m cell is omitted.

Acknowledgment

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Equilibrium-Phase Properties of *i*-Butane–Carbon Dioxide System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the *i*-butane–carbon dioxide system at 100°, 160°, 220°, and 250°F from the vapor pressure of *i*-butane to pressures in the critical region. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The equilibrium-phase densities were calculated from the measured phase composition and refractive index data by use of the Lorentz-Lorenz molar refractivity relationship.

Current methods for predicting the phase behavior and other thermodynamic properties of multicomponent systems of industrial interest usually require interaction parameters for each of the possible binary pairs which can be formed from the components in the mixture. As part of a general program to provide data of this type for systems of interest to the petroleum and natural gas industry, we studied the behavior of the *i*-butane–carbon dioxide binary because measurements on this system had not previously been reported in the literature.

The study included an experimental determination of the compositions and the refractive indices of the coexisting equilibrium phases at temperatures of 100°, 160°, 220°, and 250°F and at pressures from the vapor pressure of *i*-butane to the critical region of the system. The refractive index measurements were used to calculate the phase densities by use of the Lorentz-Lorenz molar average refractivity.

The mixtures of *i*-butane and carbon dioxide were confined between two pistons in a glass-windowed stainless-steel cell which has been described in detail by Besserer and Robinson (*1*). The hydraulic fluid preheating coils were not long enough for operations at temperatures above 200°F. Consequently, this fluid was initially passed through a coil immersed in a 200°F bath before entering the preheat coils in the shroud. The large temperature difference between the oil in the pump and the oil in the cell caused a small change in the working volume of the cell when the pistons were being moved simultaneously up or down. This situation was remedied by connecting a 10-cc displacement pump to one of the oil lines.

The temperature was measured with an iron-constantan thermocouple sheathed in 316 stainless steel with its reference junction in an ice bath and its measuring junction in the cell contents. The thermocouple was calibrated at the triple point and steam point of water. The cell temperature was controlled to within ±0.1°F of the set operating temperature.

The pressure was measured with a 0–1500-psi pressure transducer calibrated at atmospheric pressure and the vapor pressure of carbon dioxide at 20°C. The maximum combined nonlinearity and hysteresis of the transducer was ±3 psi. The pressure in the cell was easily maintained constant to 0.2 psi by manual adjustments.

The refractive indices of the phases were determined by measuring the minimum deviation angle of a beam of monochromatic light at a wavelength of 6328 Å which was passed through a prism of the fluid as described in the earlier paper (*1*).

Analytical

Samples of the equilibrium liquid and vapor phases were expanded to a pressure of 0.2 atm through micrometering valves into an evacuated line connected to the gas chromatograph gas sampling valve. The pressure in the line was measured with a differential pressure transducer. Two samples of each phase were taken, and triplicate chromatographs were run on each sample. The average size of each sample corresponded to about 0.2% depletion of the average load. For each point the six analyses (three from each of the two samples) were generally repeatable to within ±0.2 mol %, and the accuracy is judged to be within ±0.3 mol %.

The gas chromatograph was a Hewlett-Packard Model 700 equipped with a thermal conductivity cell detector. The detector was maintained at 200°C with a filament current of 150 mA. Helium was passed through the column at a rate of 25 cc/min. The column was ⅛ in. in diameter and 6-ft long and was packed with 10% UC-W98 oil on 80–100-mesh silica. The oven temperature was 20°C.

The chromatograph was calibrated with pure components, and the response was linear with sample size for the 1-cc sample loop at pressures up to 0.3 atm. To convert from area fraction to mole fraction, the area of the carbon dioxide peak was multiplied by 1.665, and the area of the *i*-butane peak by 1.000.

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