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Total Pressure Measurements for Lithium Chloride + Methanol + Ethanol at 303.15 K

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Total pressure for the ternary system lithium chloride + methanol + ethanol and constituent binaries was measured at 303.15 K. Measurements were performed as a function of salt concentration along different paths of virtually constant salt-free solvent composition. The results were reduced by Barker's method using an empirical expression for the Gibbs free energy of the liquid phase. The vapor-phase compositions for the two alcohols are calculated in a data reduction procedure. The vapor-phase mole fraction of ethanol increases on the addition of lithium chloride to the methanol + ethanol system, indicating a salting-out effect of lithium chloride on ethanol.

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1. Introduction

Total pressure for systems containing two or more alcohols and a salt is of interest since the vapor−liquid equilibrium behavior of solvent mixtures is influenced by the presence of salts. A change of relative volatilities of the solvent components compared to the salt-free system is generally observed by addition of salts, which in many cases results in a shifting or complete elimination of azeotropic points. Therefore, salts have been used as separating agents in extractive or azeotropic distillation for obtaining a better recovery of selective solvent (Furter, 1976). The availability of successful correlations and predictive models for the vapor−liquid equilibrium behavior is essential for the design of many separation processes utilizing the salt effect. However, the required experimental information for developing and testing correlations is limited. While many data exist for aqueous salt systems, far fewer are available for nonaqueous salt systems, especially for salts in methanol + ethanol liquid mixtures.

A previously published paper (Oh and Campbell, 1995) gives total pressure measurements for the mixed solvent−salt system copper(II) chloride + methanol + ethanol and constituent salt−solvent binaries at 303.15 K. In continuation of our work, total pressure measurements are reported here as a function of liquid-phase composition for lithium chloride + methanol + ethanol, lithium chloride + methanol, and lithium chloride + ethanol at 303.15 K. These results would be a contribution to the data base for systems comprised of a salt in two or more solvents.

2. Experimental Section

2.1. Chemicals. Methanol and lithium chloride used in this work were of 99.99+% HPLC grade and 99.99+%, respectively, from Aldrich Chemical Co. Ethanol was supplied by Aaper Alcohol & Chemical Co. and had a purity of 99.9+%, absolute 200 proof. All chemicals were used without further purification except degassing. Solvents were degassed following the procedure described by Bhethanabotla and Campbell (1991).

2.2. Apparatus and Procedure. The experimental apparatus is a modified version of that used for salt-free systems by Bhethanabotla and Campbell (1991). A detailed description of the apparatus and operating procedure has been given in an earlier publication (Oh and Campbell, 1995).

2.3. Data Reduction. Total pressure as a function of overall composition in the equilibrium cell was determined from the following experimental information: the mass of salt initially placed in the equilibrium cell, the volumes of solvent (or solvent mixture for the ternary runs) displaced from the piston injector to the equilibrium cell, and the pressure difference between the equilibrium and reference cells. The maximum uncertainty in the bath temperature is ±0.02 K, although the effect of this uncertainty is minimized by using the reference cell. The absolute uncertainty in pressure is estimated to be ±0.03 kPa. The estimated uncertainties in overall cell composition are 0.0005 or less in mole fraction for the binary salt + solvent mixtures. For the ternary runs, the uncertainty in overall composition within the equilibrium cell is slightly higher than 0.0005 in mole fraction, due to an additional uncertainty in the composition of the solvent + solvent mixtures (estimated to be 0.0002 in mole fraction).

Overall cell composition was then corrected into liquid-phase composition using Barker's method (Barker, 1953), which is an algorithm used in data reduction and is described in detail elsewhere (Oh and Campbell, 1995). An empirical expression of the excess Gibbs free energy of the liquid-phase is proposed, and the best set of parameters in the expression is determined by regressing pressure versus liquid-phase mole fraction such that the measured and calculated pressures are minimized. A nonlinear regression program based on Marquardt's method was used for parameter estimation. The vapor-phase compositions are also calculated in this step.

The G^E model used in this work is similar to that used in the previous work (Oh and Campbell, 1995). For the salt-free binary mixture, the four-suffix Margules equation is used:

$$G^E/RT = x_2x_3\,(A_{32}x_2 + A_{23}x_3 - \alpha_{23}x_2x_3) \qquad (1)$$

For the lithium chloride (1) + methanol (2) binary, a three-suffix Margules equation is combined with the semiempirical formula proposed by Hála (1983):

$$G^E/RT = E_{12}x_1^{3/2}x_2 + x_1x_2(A_{21}x_1 + A_{12}x_2) \qquad (2)$$

The expression for the lithium chloride (1) + ethanol (3)[1] system is

$$G^E/RT = E_{13}x_1^{3/2}x_3 + x_1x_3(A_{31}x_1 + A_{13}x_3) \qquad (3)$$

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Table 1. Total Pressure as a Function of Liquid-Phase Mole Fraction x_i for Lithium Chloride (1) + Methanol (2) and Lithium Chloride (1) + Ethanol (3) at 303.15 K

LiCl + MeOH		LiCl + EtOH	
x_2[a]	P/kPa	x_3[a]	P/kPa
0.870 96	12.094	0.830 99	4.647
0.886 48	13.831	0.847 60	5.315
0.898 24	15.081	0.864 37	6.131
0.911 21	16.416	0.881 32	7.048
0.924 67	17.698	0.902 03	8.058
0.939 10	18.855	0.917 39	8.698
0.955 06	19.921	0.937 66	9.332
0.968 79	20.678	0.957 21	9.825
0.974 92	20.995	0.978 21	10.220
0.983 96	21.390	1.000 00	10.515[c]
1.000 00	21.959[b]		

[a] Mole fraction of solvent with no salt dissociation. [b] Saturated pressure of methanol. [c] Saturated pressure of ethanol.

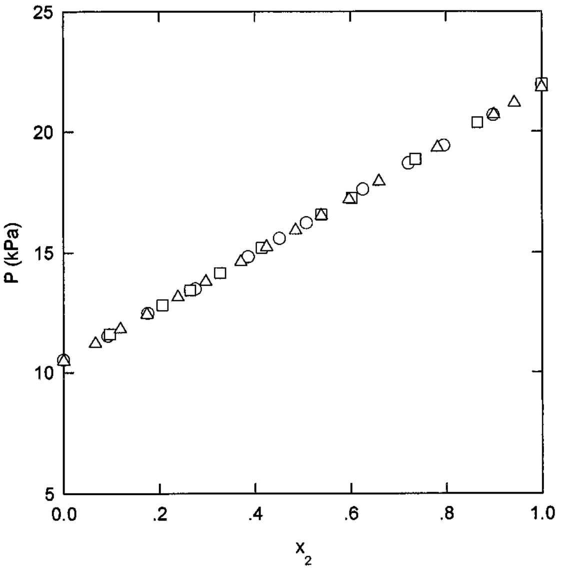

Figure 1. Total pressure for the methanol + ethanol system at 303.15 K: ○, this study; □, Oh and Campbell (1995); △, Zielkiewicz et al. (1990).

For the ternary system it was assumed that

$$G^E/RT = (G^E/RT)_{12} + (G^E/RT)_{13} + (G^E/RT)_{23} - Cx_1x_2x_3 \quad (4)$$

where $(G^E/RT)ij$ is the excess Gibbs function for the ij binary system and C is a single adjustable ternary parameter. Expressions for the activity coefficients γ_2 and γ_3 of methanol and ethanol, respectively, are obtained from eq 4 in the usual manner. Pressure and vapor-phase composition are calculated for a given liquid composition through

$$P = \gamma_2 x_2 P_2^{\text{sat}}/\Phi_2 + \gamma_3 x_3 P_3^{\text{sat}}/\Phi_3 \quad (5)$$

$$y_2 = \gamma_2 x_2 P_2^{\text{sat}}/\Phi_2 P \quad (6)$$

where

$$\Phi_j = (\phi_j/\phi_j^{\text{sat}}) \exp[-V_j^{\text{L}}(P - P_j^{\text{sat}})/RT] \quad (7)$$

In eq 7, ϕ_j is the fugacity coefficient of solvent component j in the vapor phase and ϕ_j^{sat} is the fugacity coefficient of pure solvent component j at the temperature of the mixture and its own pressure. Both are calculated using the two-term virial equation (pressure series). Second virial coefficients were calculated to be −1830, −2658, and −2200 cm^3 mol^{-1} for B_{22}, B_{33}, and B_{23}, respectively, using the method of Tsonopoulos (1974). Saturated liquid volumes V_j^{L} (40.97 and 58.97 cm^3 mol^{-1} for methanol and ethanol, respectively) for use in the Poytning correction term in eq 7 were obtained from Stephan and Hildwein (1987).

Table 2. Total Pressure as a Function of Liquid-Phase Mole Fractions x_2 and x_3 for Lithium Chloride (1) + Methanol (2) + Ethanol (3) at 303.15 K

x_2[a]	x_3[a]	P/kPa	x_2[a]	x_3[a]	P/kPa
0.076 92	0.752 83	4.790	0.430 90	0.417 23	7.257
0.078 79	0.767 00	5.454	0.438 69	0.425 52	8.413
0.080 09	0.783 65	6.389	0.445 66	0.432 44	9.529
0.081 79	0.798 34	7.338	0.453 45	0.440 27	10.786
0.083 18	0.815 23	8.350	0.461 75	0.448 41	12.023
0.084 79	0.832 15	9.230	0.470 61	0.456 69	13.120
0.086 79	0.849 70	9.968	0.479 37	0.465 06	14.063
0.088 76	0.868 14	10.581	0.488 57	0.473 76	14.884[b]
0.090 31	0.883 77	10.989[b]			
			0.535 76	0.321 75	8.463
0.147 03	0.686 29	5.415	0.543 12	0.325 67	9.404
0.149 82	0.699 43	6.188	0.552 76	0.331 53	10.809
0.152 23	0.713 76	7.172	0.561 08	0.336 85	12.052
0.155 53	0.725 66	8.072	0.575 70	0.345 29	13.795
0.158 19	0.742 69	9.155	0.581 32	0.348 60	14.344
0.161 48	0.757 25	10.035	0.592 00	0.354 38	15.312
0.164 66	0.773 17	10.795	0.602 98	0.360 72	16.174[b]
0.165 77	0.778 22	11.005[b]			
			0.618 85	0.241 01	9.498
0.231 70	0.609 00	5.877	0.629 40	0.244 52	10.789
0.235 18	0.618 69	6.608	0.638 74	0.248 13	11.990
0.239 58	0.630 64	7.654	0.650 15	0.252 70	13.304
0.242 85	0.640 13	8.511	0.660 13	0.256 53	14.366
0.246 69	0.649 25	9.341	0.671 07	0.260 44	15.413
0.253 24	0.667 93	10.765	0.683 28	0.264 95	16.433
0.258 48	0.681 73	11.642	0.695 77	0.269 36	17.292[b]
0.263 72	0.695 45	12.345			
0.269 58	0.709 65	12.965[b]	0.715 40	0.185 13	13.722
			0.717 74	0.185 87	13.982
0.325 17	0.518 75	6.464	0.729 32	0.189 12	15.171
0.331 14	0.527 81	7.427	0.741 73	0.192 15	16.282
0.336 53	0.537 10	8.466	0.754 52	0.195 09	17.245
0.343 26	0.547 78	9.738	0.767 74	0.198 23	18.101
0.349 41	0.558 12	10.877	0.778 58	0.200 77	18.695[b]
0.355 47	0.567 90	11.806			
0.362 90	0.579 15	12.756	0.791 09	0.089 69	12.692
0.370 01	0.590 57	13.537	0.803 48	0.091 07	14.132
0.377 40	0.601 52	14.177[b]	0.814 77	0.092 82	15.341
			0.827 95	0.093 77	16.522
0.382 49	0.464 94	6.854	0.842 01	0.095 62	17.676
0.387 68	0.472 41	7.711	0.854 63	0.096 68	18.534
0.394 85	0.481 71	8.975	0.867 55	0.098 26	19.314
0.402 19	0.489 75	10.155	0.880 57	0.099 52	19.963[b]
0.408 99	0.499 13	11.351			
0.417 12	0.508 62	12.469			
0.425 10	0.518 20	13.412			
0.433 54	0.528 02	14.236			
0.442 73	0.538 26	14.982[b]			

[a] Mole fraction of solvent with no salt dissociation. [b] Methanol + ethanol binary measurement.

Table 3. Values of Parameters Appearing in Excess Gibbs Free Energy Expression for Lithium Chloride (1) + Methanol (2) + Ethanol (3) at 303.15 K

A_{23}[a]	−0.0333	A_{32}[a]	−0.0326
α_{23}[a]	−0.0969	C	24.1060
A_{12}	−12.7672	A_{21}	−23.8986
A_{13}	−10.6172	A_{31}	−20.7177
E_{12}	−2.2236	E_{13}	3.7619

[a] Parameters supplied to the extended fit.

An extended fit to pressure was employed as recommended by Oh and Campbell (1992). For the methanol + ethanol system, binary parameters A_{23}, A_{32}, and α_{23} are obtained from an unweighted fit to the methanol−ethanol binary total pressure data. These salt-free parameters are then used as inputs in the extended data reduction procedure in which ternary data and binary data for its

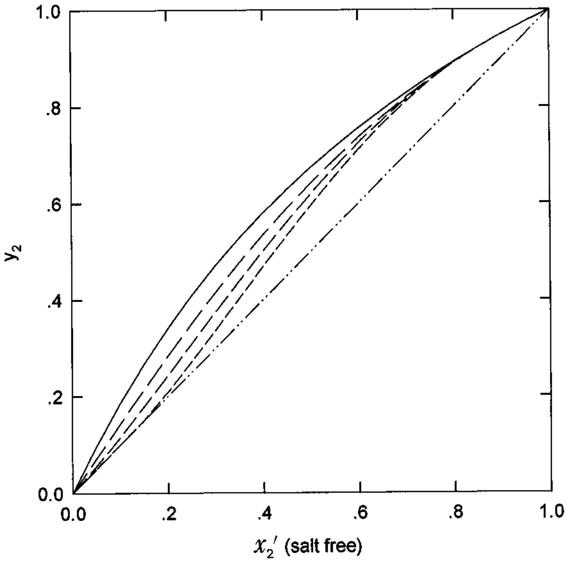

Figure 2. Calculated vapor-phase mole fraction y_2 vs liquid-phase mole fraction (on a salt-free basis) x_2' for lithium chloride (1) + methanol (2) + ethanol (3) at 303.15 K. The solid line is for $x_1 = 0$, the long dashed line is for $x_1 = 0.05$, the middle dashed line is for $x_1 = 0.10$, and the short dashed line is for $x_1 = 0.15$.

two-constituent salt + solvent systems are regressed simultaneously to obtain the salt–solvent binary parameters A_{12}, A_{21}, A_{13}, A_{31}, E_{12}, and E_{13} and a single adjustable ternary parameter C. Data were weighted by the maximum likelihood principle as described by Oh (1993). For the system examined here the assumption of complete salt dissociation yields slightly better deviations in pressure. However, analytical mole fractions calculated on the assumption of no salt dissociation are reported here.

3. Results

Total pressure as a function of liquid-phase composition is reported for lithium chloride + methanol + ethanol, lithium chloride + methanol, and lithium chloride + ethanol at 303.15 K. Total pressures for lithium chloride (1) + methanol (2) and lithium chloride (1) + ethanol (3) binary systems are given in Table 1. As shown in Table 1, the saturated vapor pressures of methanol and ethanol at 303.15 K were measured to be 21.959 and 10.515 kPa, respectively, which are in good agreement with the values of 21.861 and 10.462 kPa reported by Ambrose and Sparke (1970). Experimental results for the ternary system lithium chloride (1) + methanol (2) + ethanol (3) at 303.15 K, along with those for the methanol + ethanol system, are given in Table 2. Results for the methanol + ethanol system are compared to those measured by Zielkiewicz et al. (1990) in Figure 1, and they are in good agreement. Given in the Table 3 are the parameters obtained from the data reduction procedure. The resulting average deviation between the measured and calculated pressures is 0.068 kPa.

As mentioned earlier, vapor-phase mole fractions are calculated as part of the data reduction procedure. To demonstrate the salt effect of lithium chloride on vapor–liquid equilibria of the methanol (2) + ethanol (3) system at 303.15 K, the calculated vapor-phase mole fraction of methanol is plotted in Figure 2 as a function of salt-free liquid phase mole fraction $x_2' = x_2/(x_2 + x_3)$ for several different salt mole fractions x_1's. As shown in Figure 2, the vapor-phase mole fraction of methanol is decreased upon addition of lithium chloride to the methanol (2) + ethanol (3) system, indicating that methanol is salted-in and ethanol is salted-out for this system.

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