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Isothermal Vapor−Liquid Equilibrium Data for the Acetone + Methanol + Lithium Nitrate System

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Isothermal vapor−liquid equilibrium data at (39.5, 55.0, and 70.6) °C have been measured for the system acetone (1) + methanol (2) + lithium nitrate (3) at constant salt molalities (0.000, 0.500, 1.00, 2.000, and 3.000) with the help of headspace gas chromatography. The data were compared with the predicted results using the LIQUAC model.

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1. Introduction

For the synthesis and design of industrial separation processes a reliable knowledge of the phase-equilibrium behavior for the system to be separated is required. While powerful models (g^E -models, equations of state, group contribution methods) are available for nonelectrolyte systems, the situation is worse for electrolyte systems. However, this information is required to describe the influence of electrolytes (salting in or salting out effects) on vapor−liquid equilibria, liquid−liquid equilibria, gas solubilities, salt solubilities to be able to simulate separation processes, such as salt distillation (Furter, 1977), crystallization processes, e.g., extractive crystallization of salts (Weingaertner et al., 1991), extraction processes, etc. This has been the incentive for the development of a database that now contains more than 1800 VLE data sets for electrolyte systems and a software package with the available thermodynamic models for the correlation and prediction of phase equilibria of electrolyte systems.

In continuation of our studies on the effect of salts on the vapor−liquid equilibrium behavior (Polka and Gmehling, 1994; Yan et al., 1997), isothermal vapor−liquid equilibrium data at three temperatures (39.5, 55.0, and 70.6 °C) are presented for acetone (1) + methanol (2) + lithium nitrate (3) at constant salt molalities (0.000, 0.500, 1.000, 2.000, and 3.000) with the objective to obtain the required data for the further development of thermodynamic models for electrolyte systems. The addition of lithium nitrate to this solvent mixture increases the amount of acetone present in the vapor phase. For all temperatures the azeotropic behavior disappears at higher salt concentration.

The present data of vapor−liquid equilibria were used to extend the parameter matrix of the LIQUAC model published by Li et al. (1994). At the same time the vapor−liquid equilibrium behavior for the same system at 100.0 kPa was predicted using the new parameters obtained in this work.

Table 1. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2) + Lithium Nitrate (3) at 39.5 °C

x'_1 [a]	y_1	Δy_1 [b]	$\ln(a_s/a_0)$ [c]	x'_1	y_1	Δy_1	$\ln(a_s/a_0)$
$m = 0.0$ mol·kg^{-1}				$m = 0.50$ mol·kg^{-1}			
0.1000	0.236	0.000		0.1000	0.246	0.014	0.055
0.1501	0.309	−0.001		0.1501	0.324	0.010	0.073
0.1998	0.366	−0.003		0.1998	0.387	0.007	0.090
0.2999	0.462	0.000		0.2999	0.492	0.004	0.118
0.3981	0.534	−0.002		0.3981	0.569	−0.002	0.141
0.5000	0.606	0.001		0.5000	0.641	−0.005	0.150
0.5999	0.665	−0.006		0.5999	0.707	−0.007	0.191
0.6998	0.731	−0.009		0.6998	0.772	−0.008	0.222
0.7994	0.807	−0.008		0.7994	0.839	−0.010	0.224
0.8481	0.848	−0.007		0.8481	0.877	−0.008	0.240
0.8900	0.885	−0.007		0.8900	0.907	−0.009	0.237
$m = 1.0$ mol·kg^{-1}				$m = 2.0$ mol·kg^{-1}			
0.1000	0.256	−0.015	0.107	0.1000	0.272	0.012	0.190
0.1501	0.342	0.016	0.151	0.1501	0.366	0.014	0.259
0.1998	0.411	0.015	0.189	0.1998	0.437	0.009	0.295
0.2999	0.516	0.007	0.216	0.2999	0.551	0.001	0.354
0.3981	0.589	−0.008	0.225	0.3981	0.640	−0.004	0.439
0.5000	0.664	−0.011	0.248	0.5000	0.716	−0.008	0.494
0.5999	0.739	−0.006	0.352	0.5999	0.782	−0.010	0.587
0.6998	0.800	−0.010	0.389	0.6998	0.842	−0.011	0.676
0.7994	0.864	−0.011	0.419	0.7994	0.898	−0.010	0.748
0.8481	0.898	−0.008	0.458	0.8481	0.923	−0.010	0.769
0.8900	0.925	−0.008	0.472	0.8900	0.944	−0.009	0.770
$m = 3.0$ mol·kg^{-1}							
0.1000	0.286	0.009	0.261	0.5000	0.749	−0.012	0.662
0.1501	0.385	0.009	0.337	0.5999	0.812	−0.014	0.778
0.1998	0.461	0.004	0.393	0.6998	0.867	−0.014	0.876
0.2999	0.583	−0.002	0.488	0.7994	0.915	−0.013	0.942
0.3981	0.675	−0.006	0.593	0.8481	0.940	−0.008	1.026
mean absolute deviation (Δy_1)						0.008	

[a] Mole fraction on a salt-free basis: $x'_1 = n_1/(n_1 + n_2)$, where n_1, n_2 are the numbers of moles of solvents 1 and 2. [b] $y_1 = y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}$. [c] a is the relative volatility.

2. Experimental Section

2.1. Materials. Acetone (99.5 mass %, Scharlau) and methanol (99.8 mass %, Scharlau) were dehydrated with the help of molecular sieves. The purity was checked by gas chromatography. The purity was greater than 99.9 mass % (acetone) and 99.7 mass % (methanol). For removing the remaining moisture in the lithium nitrate, the salt (99.0+ mass %, Fluka) was dried at 120 °C in a vacuum oven until constant mass was reached.

2.2. Apparatus. All liquid mixtures consisting of acetone, methanol, and lithium nitrate were prepared directly by using a Sartorius analytical balance, the accuracy of which was ±0.1 mg. For each experimental point, approximately 8 cm^3 of sample solution was taken and put into the 22 cm^3 sample vial. After the sample vials were

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Table 2. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2) + Lithium Nitrate (3) at 55.0 °C

x'_1 [a]	y_1	Δy_1 [b]	$\ln(a_s/a_0)$ [c]	x'_1	y_1	Δy_1	$\ln(a_s/a_0)$
$m = 0.0$ mol·kg^{-1}				$m = 0.50$ mol·kg^{-1}			
0.1000	0.211	0.000		0.1000	0.220	0.014	0.051
0.1501	0.277	−0.004		0.1501	0.290	0.009	0.065
0.1998	0.331	−0.007		0.1998	0.351	0.006	0.086
0.2999	0.429	−0.002		0.2999	0.454	0.004	0.104
0.3981	0.506	0.000		0.3981	0.535	0.001	0.117
0.5000	0.573	−0.004		0.5000	0.607	−0.004	0.137
0.5999	0.639	−0.007		0.5999	0.679	−0.004	0.179
0.6998	0.708	−0.010		0.6998	0.750	−0.005	0.183
0.7994	0.792	−0.008		0.7994	0.823	−0.008	0.199
0.8481	0.836	−0.005		0.8481	0.862	−0.008	0.200
0.8900	0.874	−0.006		0.8900	0.897	−0.008	0.229
$m = 1.0$ mol·kg^{-1}				$m = 2.0$ mol·kg^{-1}			
0.1000	0.227	0.015	0.094	0.1000	0.239	0.011	0.162
0.1501	0.301	0.010	0.120	0.1501	0.325	0.012	0.230
0.1998	0.366	0.008	0.154	0.1998	0.387	0.001	0.242
0.2999	0.473	0.004	0.179	0.2999	0.511	0.005	0.331
0.3981	0.560	0.002	0.218	0.3981	0.605	0.003	0.401
0.5000	0.629	−0.010	0.234	0.5000	0.683	−0.004	0.471
0.5999	0.711	−0.002	0.327	0.5999	0.750	−0.011	0.529
0.6998	0.780	−0.005	0.381	0.6998	0.818	−0.011	0.618
0.7994	0.849	−0.008	0.389	0.7994	0.881	−0.011	0.665
0.8481	0.883	−0.009	0.394	0.8481	0.910	−0.011	0.678
0.8900	0.915	−0.008	0.431	0.8900	0.935	−0.009	0.720
$m = 3.0$ mol·kg^{-1}							
0.1000	0.248	0.006	0.210	0.5000	0.711	−0.013	0.606
0.1501	0.340	0.006	0.298	0.5999	0.782	−0.014	0.705
0.1998	0.416	0.005	0.363	0.6998	0.842	−0.017	0.791
0.2999	0.540	0.001	0.448	0.7994	0.897	−0.016	0.826
0.3981	0.634	−0.004	0.527	0.8481	0.926	−0.011	0.893
mean absolute deviation (Δy_1)						0.007	

[a] Mole fraction on a salt-free basis: $x'_1 = n_1/(n_1 + n_2)$, where n_1, n_2 are the numbers of moles of solvents 1 and 2. [b] $\Delta y_1 = y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}$. [c] a is the relative volatility.

Table 3. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2) + Lithium Nitrate (3) at 70.6 °C

x'_1 [a]	y_1	Δy_1 [b]	$\ln(a_s/a_0)$ [c]	x'_1	y_1	Δy_1	$\ln(a_s/a_0)$
$m = 0.0$ mol·kg^{-1}				$m = 0.50$ mol·kg^{-1}			
0.1000	0.194	0.004		0.1000	0.202	0.019	0.046
0.1501	0.255	−0.001		0.1501	0.267	0.015	0.062
0.1998	0.309	−0.002		0.1998	0.326	0.014	0.075
0.2999	0.400	−0.002		0.2999	0.422	0.008	0.090
0.3981	0.476	0.000		0.3981	0.504	0.005	0.113
0.5000	0.547	0.000		0.5000	0.577	−0.001	0.122
0.5999	0.616	−0.001		0.5999	0.647	−0.006	0.133
0.6998	0.698	0.007		0.6998	0.729	−0.001	0.153
0.7994	0.777	0.003		0.7994	0.810	−0.002	0.204
0.8481	0.817	−0.004		0.8481	0.847	−0.008	0.211
0.8900	0.861	−0.003		0.8900	0.885	−0.008	0.221
$m = 1.0$ mol·kg^{-1}				$m = 2.0$ mol·kg^{-1}			
0.1000	0.208	0.020	0.087	0.1000	0.216	0.016	0.130
0.1501	0.277	0.016	0.112	0.1501	0.296	0.017	0.206
0.1998	0.336	0.012	0.121	0.1998	0.363	0.015	0.238
0.2999	0.437	0.006	0.149	0.2999	0.460	−0.005	0.244
0.3981	0.523	0.002	0.188	0.3981	0.555	−0.007	0.319
0.5000	0.596	−0.008	0.200	0.5000	0.632	−0.018	0.351
0.5999	0.673	−0.009	0.248	0.5999	0.716	−0.013	0.452
0.6998	0.754	−0.005	0.283	0.6998	0.794	−0.010	0.508
0.7994	0.831	−0.007	0.347	0.7994	0.861	−0.013	0.575
0.8481	0.869	−0.008	0.391	0.8481	0.895	−0.012	0.641
0.8900	0.903	−0.009	0.416	0.8900	0.924	−0.011	0.682
$m = 3.0$ mol·kg^{-1}							
0.1000	0.225	0.012	0.183	0.5000	0.673	−0.014	0.532
0.1501	0.304	0.007	0.245	0.5999	0.746	−0.019	0.602
0.1998	0.378	0.008	0.305	0.6998	0.821	−0.014	0.683
0.2999	0.490	−0.005	0.366	0.7994	0.883	−0.015	0.779
0.3981	0.593	−0.004	0.471	0.8481	0.913	−0.013	0.846
mean absolute deviation (Δy_1)						0.008	

[a] Mole fraction on a salt-free basis: $x'_1 = n_1/(n_1 + n_2)$, where n_1, n_2 are the numbers of moles of solvents 1 and 2. [b] $\Delta y_1 = y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}$. [c] a is the relative volatility.

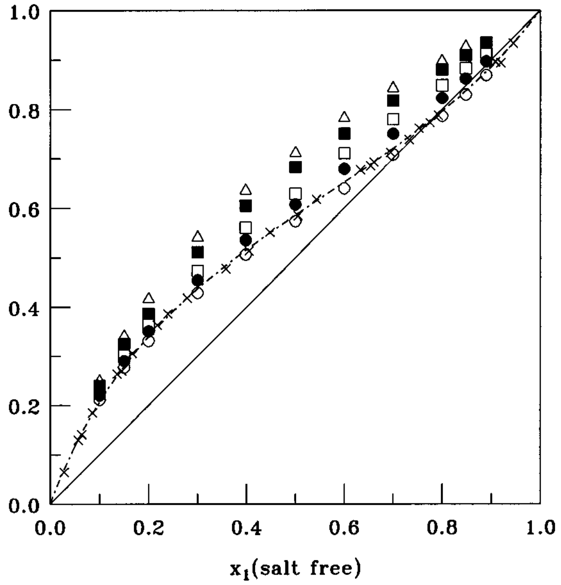

Figure 1. $x-y$ vapor−liquid equilibrium diagram for the system acetone (1) + methanol (2) + LiNO$_3$ at 55.0 °C: ○, $m = 0.0$; ●, $m = 0.5$; □, $m = 1.0$; ■, $m = 2.0$; △, $m = 3.0$; − - −, ($m = 0.0$) mol·kg^{-1} calculated by the UNIQUAC model (parameters taken from Gmehling et al. (1977)); ×, $m = 0.0$ mol·kg^{-1}, 55.0 °C (Freshwater and Pike, 1967).

tightly closed by means of a special aluminum lid, with a washer and a Teflon disk, they were brought to the desired temperature in the thermostatic bath controlled within ±0.1 °C. The experimental temperature was measured using a thermometer with 0.02 K accuracy. The composition measurements were performed after the samples were kept at a constant temperature at least for 12 h to ensure phase equilibrium.

For the determination of the vapor-phase composition, the vapor was automatically withdrawn using a Perkin-Elmer F45 GLC vapor analyzer and analyzed by a F22 gas chromatograph with the help of a thermal conductivity detector and an integrator [Hewlett-Packard 3390A]. For the separation in all cases a 1.2 m stainless steel column filled with Porapak Q 80/100 was used. The optimum operating conditions were the following: injection temperature, 210 °C; oven temperature, 190 °C; detector temperature, 210 °C; carrier gas, helium (purity 99.9%) with a flow rate of 0.41 cm^3·s^{-1}. More details of the experimental setup have been described before (Weidlich and Gmehling, 1985).

Calibration was necessary before the peak areas could be used to determine the vapor-phase composition. To obtain the calibration curve, various acetone + methanol mixtures were prepared and injected. The mole fractions and area fractions were correlated using a fourth-order polynomial. With the help of the calibration curve, the vapor-phase compositions were determined. The average error of the mole fraction is ±0.002, which was obtained by comparing the known composition of the made-up liquid samples with the composition calculated from the calibration curve.

Because of the negligible amounts evaporated (small vapor volume, moderate pressure), it was assumed that liquid-phase composition is identical with the feed composition. To validate the assumption, salt-free experiments for the acetone + methanol system were performed. In equilibrium, the liquid composition was calculated by material balance and compared to the analysis of the liquid com-

Table 4. Binary Interaction Parameters, Volume, and Surface Area Parameters for the LIQUAC Model (Li et al. 1994)

i	*j*	a_{ij}	a_{ji}	b_{ij}	c_{ij}	r_i	q_i
acetone	methanol	223.8	−54.2				
acetone	Li^+	1555.0	1163.0	3.065	1.256		
acetone	NO_3^-	−249.05(f)	194.04(f)	1.9774(f)	−1.9451(f)		
methanol	Li^+	298.6	−634.80	5.760	1.117		
methanol	NO_3^-	−681.752(f)	116.950(f)	−2.9287(f)	−1.3017(f)		
Li^+	NO_3^-	405.70	442.5	0.1331	−0.2879		
acetone						2.574	2.336
methanol						1.431	1.432
Li^+						1.000	1.000
NO_3^-						1.000	1.000

[a] (f) means that these interaction parameters have been fitted in this work.

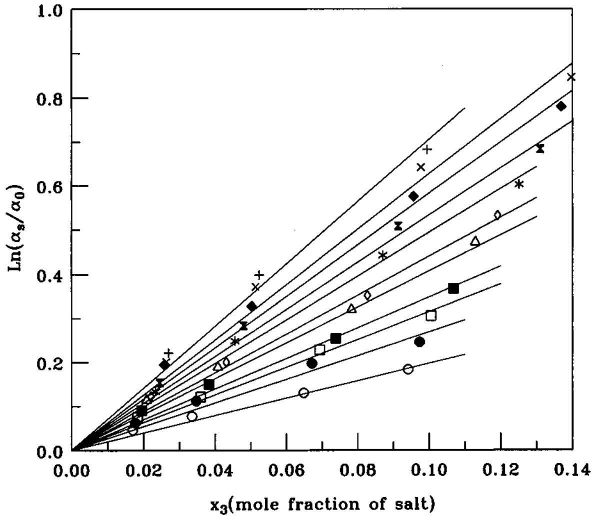

Figure 2. Salt effects of lithium nitrate on the acetone (1) + methanol (2) system at different compositions (70.5 °C): x_1' (○) 0.1000; (●) 0.1501; (□) 0.1998; (■) 0.2999; (△) 0.3981; (◇) 0.5000; (*) 0.5999; (filled ⧗) 0.6998; (◆) 0.7994; (×) 0.8481; (+) 0.8900.

position via gas chromatography. The uncertainty of this assumption was ±0.002 in mole fraction.

3.Results and Discussion

3.1. Experimental Data. Isothermal vapor−liquid equilibrium data for the system acetone (1) + methanol (2) + lithium nitrate (3) have been measured at three temperatures (39.5, 55.0, and 70.6 °C) and various salt concentrations ($m = 0.5$, 1.0, 2.0, and 3.0 mol·kg^{-1}). To confirm the reliability of the experimental vapor-phase equilibrium data, also the salt-free system acetone (1) + methanol (2) was measured at three temperatures. The experimental results are given in Tables1−3. The experimental data for the salt-free acetone + methanol system were compared with the results calculated by the UNIQUAC model (parameters taken from Gmehling et al. (1977)). The observed mean absolute deviations in mole fraction was 0.004 (39.5 °C), 0.005 (55.0 °C), and 0.002 (70.6 °C). Thermodynamic consistency of the experimental data was examined with the help of the Redlich−Kister area test. The area deviations found are 5.8% (39.5 °C), 6.4% (55.0 °C), and 0.2% (70.6 °C), respectively. This means that the VLE data measured for the system acetone (1) + methanol (2) can be considered as thermodynamic consistent. All VLE data at 55.0 °C on the salt-free bases are shown in Figure 1. Furthermore the data for the binary system acetone (1) + methanol (2) are compared with the results reported by Freshwater and Pike (1967). It can be seen that good agreement with our data is obtained. From Figure 1 the salt effect on the vapor−liquid equilibrium of the acetone + methanol system with lithium nitrate can be judged. The presence of lithium nitrate increases the acetone mole fraction in the vapor phase, whereby the azeotropic point disappears at salt concentrations above 0.5 mol·kg^{-1}.

3.2. Calculation of VLE for Salt Containing Systems. To describe the observed VLE behavior, the experimental data are correlated using the LIQUAC model proposed by Li et al. (1994), which is based on an expression of the excess Gibbs energy, consisting of three terms:

$$G^E = G^E_{LR} + G^E_{MR} + G^E_{SR} \tag{1}$$

The G^E_{LR} term represents the long-range (LR) interaction contribution caused by the Coulomb electrostatic forces, which can be expressed using the extended Debye−Hückel theory. The G^E_{MR} term, which accounts for the middle-range (MR) interactions, represents the ion−dipole effects. The middle-range contribution is described by the Pitzer model, but it is a little different from the Pitzer model in that the ion−solvent interaction parameters are introdued into this model, but three species interaction parameters are ignored in the LIQUAC model. The G^E_{SR} term expresses the contribution of the short-range (SR) interactions to the excess Gibbs energy and is described with the help of the UNIQUAC equation.

The LIQUAC model is suitable for the description of both single and mixed solvent systems and was successfully applied also at high electrolyte concentration (Polka et al., 1994). The model includes only binary interaction parameters, which are associated with the solvent−solvent, solvent−ion, and ion−ion pairs. For a system with two solvents and one salt, 22 parameters are needed: 12 UNIQUAC parameters (a_{ij}) and 10 middle-range interaction parameters (b_{ij} and c_{ij}). Fortunately a large number of parameters have already been published (Li et al., 1994). Therefore in this work parameters were directly taken from the published parameter matrix, shown in Table 4. The remaining parameters were fitted to the new experimental data with the help of the Simplex−Nelder−Mead method (Nelder and Mead, 1965) using the following objective function

$$F(a_{ij}, a_{ji}, b_{ij}, c_{ij}) = \sum_{nt}\sum_{np} g_y (y_{\mathrm{exp}} - y_{\mathrm{calc}})^2 = \min \tag{2}$$

where y represents vapor-phase mole fraction and g_y the weighting factor. *nt* and *np* are the number of data sets in the database and the number of data points for each data set. The subscripts, exp and calc, denote experimental data and calculated values. The vapor-phase composition,

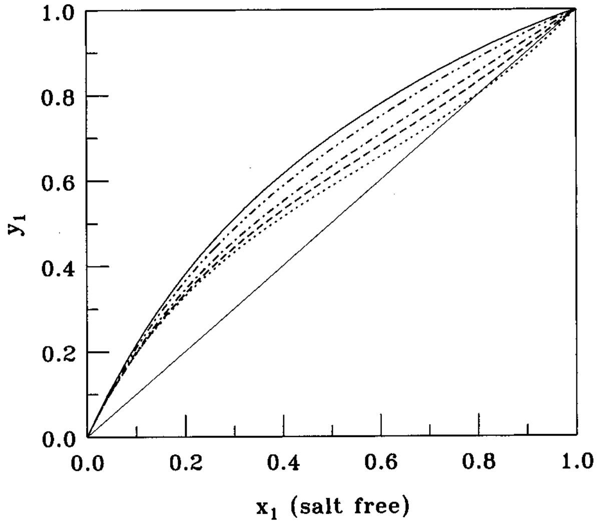

Figure 3. Predicted $x-y$ diagram at 100.0 kPa for different $LiNO_3$ concentrations: ···, $m = 0.05$; - - -, $m = 0.5$; —·—·, $m = 1.0$; —··—, $m = 2.0$; —, $m = 3.0$ mol·kg^{-1}.

y_i, is calculated using following simplified equations

$$P = x_1\gamma_1 P_1^{s} + x_2\gamma_2 P_2^{s} \tag{3}$$

$$y_i = x_i\gamma_i P_i^{s}/P \tag{4}$$

where x_i is liquid-phase mole fraction of the solvent i based on the assumption of total dissociation of the salt. The saturation vapor pressure was calculated by the Antoine equation using Antoine constants from literature (Gmehling et al., 1977). The activity coefficient of the solvent i was calculated by LIQUAC model. The fitted interaction parameters are listed in Table 4, together with the published parameters (Li et al., 1994). The mean absolute deviations between experimental and calculated vapor-phase mole fractions are listed in Tables 1−3. The calculated vapor-phase mole fractions show satisfactory agreement with the experimental values.

The salt effect on the VLE can be judged more easily from the ratio of the relative volatilities (Johnson and Furter, 1960)

$$\ln\left(\frac{a_s}{a_0}\right) = \ln\frac{[(y_1/x_1')/(y_2/x_2')]_s}{[(y_1/x_1)/(y_2/x_2)]_0} = kx_3 \tag{5}$$

where the subscripts s and 0 denote the salt-containing and salt-free systems, respectively. k is a salt effect parameter, which depends on the system and the solvent composition. x_3 is the mole fraction of the salt. The values of $\ln(a_s/a_0)$ are listed in Tables 1−3. As a typical example, Figure 2 shows $\ln(a_s/a_0)$ as a function of x_3. From this figure it can be seen that the salt effect parameter, k, increases with increasing acetone concentration. When the solvent composition is fixed, the salt effect is proportional to the salt concentration.

In Figure 3 the predicted $x-y$ behavior at 100.0 kPa using the parameters given in Table 4 is shown. In the acetone + methanol + lithium nitrate system, the azeotropic point disappears at a salt molality higher than 0.5 mol·kg^{-1}.

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Literature Cited

Freshwater, D. C.; Pike, K. A. Vapor−Liquid Equilibrium Data for Systems of Acetone−Methanol−Isopropanol. *J. Chem. Eng. Data* **1967**, *12*, 179.

Furter, W. F. Salt Effect in Distillation: A Literature Review II. *Can. J. Chem. Eng.* **1977**, *55*, 229.

Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt, 1977; Vol. I, Part 2a.

Johnson, A.; Furter, W. Salt Effect in VLE. Part 2. *Can. J. Chem. Eng.* **1960**, *38*, 78.

Li, J. D.; Polka, H.-M.; Gmehling, J. A g^E Model for Single and Mixed Solvent Electrolyte Systems: 1. Model and Results for Strong Electrolytes. *Fluid Phase Equilib.* **1994**, *94*, 89.

Nelder, J. A.; Mead, R. A. A Simplex Method for Function Minimization. *Comput. J.* **1965**, *7*, 308.

Polka, H.-M.; Gmehling, J. Effect of Calcium Nitrate on the Vapor−Liquid Equilibria of Ethanol + Water and 2-Propanol + Water. *J. Chem Eng. Data* **1994**, *39*, 621.

Polka, H.-M.; Li, J. D.; Gmehling, J. A g^E Model for Single and Mixed Solvent Electrolyte Systems: 2. Results and Comparison with Other Models. *Fluid Phase Equilib.* **1994**, *94*, 115.

Weidlich, U.; Gmehling, J. Extension of UNIFAC by Headspace Gas Chromatography. *J. Chem. Eng. Data* **1985**, *30*, 95.

Weingaertner, D. A.; Lynn, S.; Hanson, D. N. Extractive Crystallization of Salts from Concentrated Aqueous Solution. *Ind. Eng. Chem. Res.* **1991**, *30*, 490.

Yan, W. D.; Rose, Chr.; Gmehling, J. Isothermal Vapor−Liquid Equilibrium Data for the Ethanol + Ethyl Acetate + Sodium Iodide System at Five Temperatures. *J. Chem. Eng. Data* **1997**, *42*, 603.

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