

Effects of Lithium Nitrate on the Vapor–Liquid Equilibria of Methyl Acetate + Methanol and Ethyl Acetate + Ethanol

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Isobaric vapor–liquid equilibrium data for the system methyl acetate (1) + methanol (2) + lithium nitrate (3) and ethyl acetate (1) + ethanol (2) + lithium nitrate (3) at constant salt molalities have been measured with the help of a modified Scott ebulliometer at 101.3 kPa and temperatures between 53 °C and 83 °C. The measured data were correlated using the electrolyte model LIQUAC.

1. Introduction

A reliable knowledge of the phase equilibria of electrolyte systems is essential for the design and simulation of different chemical processes including wastewater treatment, extractive distillation, extractive and antisolvent crystallization of salts, and gas scrubbing. The quality of the description of the phase equilibrium behavior for electrolyte systems strongly depends on the thermodynamic model (g^E -model, equation of state (EOS), EOS + g^E mixing rules) and the quality of the parameters used.

To obtain reliable model parameters for predictive methods, a large database should be applied. The Dortmund Data Bank (DDB) formed the basis for various thermodynamic models developed in our research group. It is a steadily growing database, which contains more than 2500 vapor–liquid equilibrium (VLE) and 3000 salt solubility data sets for electrolyte systems. But for a large number of systems no VLE data are available.

The aim of this investigation is the methodical study of the effect of lithium nitrate on the vapor–liquid equilibrium of the azeotropic systems ethyl acetate + ethanol and methyl acetate + methanol. Up to now no VLE data were available for these systems. The measurements were carried out at 101.3 kPa and different constant salt concentrations using a modified Scott ebulliometer. In addition the experimental data were correlated using the local composition model LIQUAC.¹

2. Experimental Section

2.1. Materials. Methyl acetate (99.5 wt %), ethyl acetate (99.5 wt %), ethanol (99.5 wt %), and methanol (99.5 wt %) were purified by fractional distillation using a 1.0 m Vigreux column, dried, and stored over 3 Å molecular sieves. The water content was determined using the Karl Fischer method. Finally the water content of all liquid components was <100 ppm. Methyl acetate and ethyl acetate had a final purity of 99.8 wt %, ethanol had one of 99.9 wt %, and methanol had one of 99.7 wt % determined by gas chromatography (GC) using a thermal conductivity detector (TCD). Lithium nitrate (99.0+ wt %, Fluka) was dried at 90 °C in a vacuum oven until constant mass was reached.

2.2. Apparatus. The experimental apparatus used for the VLE measurements is schematically shown in Figure

1. The modified Scott ebulliometer is similar to the one used by Dallinga in 1993.² However, some modifications have been carried out: (1) A liquid sampling port (B1) and a vapor sampling port (B2) now allow the vapor-phase compositions to be determined analytically, whereby the volume of the vapor sampling port, which is filled with a small amount of the condensed vapor phase (approximately 0.5 cm³), is small compared with the volume of the liquid phase (approximately 300 cm³). (2) A vertically adjustable quartz thermometer (C) ensures that the equilibrium temperature can be measured accurately. (3) A primary pressure controller (L, Vacuubrand vacuum controller CVC 24) was used to keep the pressure constant with the help of a 50-L ballast tank in order to improve the temperature stability of the system (± 0.01 °C).

The total pressure was measured and controlled by a pressure controller consisting of an MKS 390 HA transducer sensor head (G), an MKS 250 controller, and an MKS 270 signal conditioner. Dry air in the 50-L ballast tank enters the system via an automatically controlled needle valve (H1). The system pressure is indicated on a digital display with a resolution of 10⁻² kPa and kept constant within $\pm 10^{-2}$ kPa during the complete measurement cycle.

A magnetic stirrer/heater (E, IKA-MAG RH) heats the content of the ebulliometer to the boiling point at the given pressure, takes care of a thorough mixing, and prevents the occurrence of bumping.

All liquid mixtures, consisting of ethyl acetate + ethanol, methyl acetate + methanol, and lithium nitrate, were prepared gravimetrically with a Sartorius analytical balance with an accuracy of ± 0.1 mg. For each experimental point approximately 300 cm³ of the desired mixture were placed into the ebulliometer. The pressure had been set to 101.3 kPa, before the ebulliometer was heated and the steady-state boiling condition was observed. The equilibrium temperature was measured with the help of a Hewlett-Packard quartz thermometer (model 2804 A) with an accuracy of ± 0.01 °C. Thereafter, for each data point a sample of approximately 0.1 g was withdrawn through the vapor sampling port in order to determine the vapor-phase composition of the system.

2.3. Sample Analysis. The presence of the nonvolatile salt in the liquid phase precluded direct solvent analysis via gas chromatography (GC). Therefore, the liquid-phase composition was calculated by material balance. The vapor-phase composition was determined using a Hewlett-Pack-

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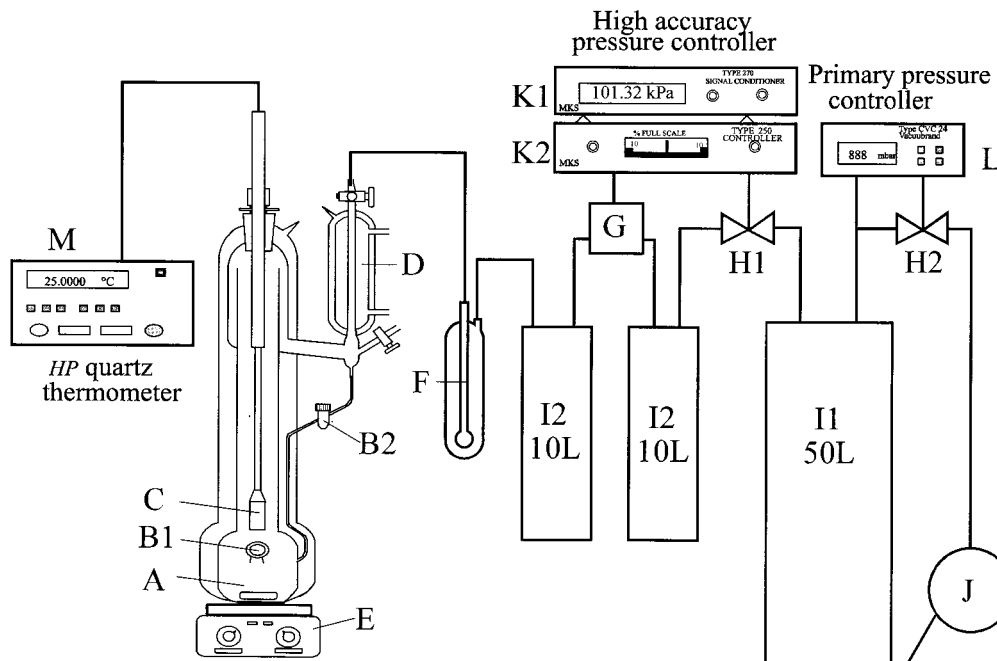


Figure 1. Schematic diagram of the experimental apparatus: A, ebullimeter; B, liquid and vapor sampling ports; C, quartz thermometer sensor; D, condenser; E, magnetic stirrer/heater (IKA-MAG RH); F, cold trap; G, pressure sensor head (MKS type 390 HA); H, needle valve; I, ballast tank; J, vacuum pump; K, high accuracy pressure controller (MKS pressure controller); L, primary pressure controller (Vacuubrand vacuum controller CVC 24); M, HP quartz thermometer (HP model 2804 A).

Table 1. Vapor–Liquid Equilibrium Data of the Ethyl Acetate (1) + Ethanol (2) System at 101.3 kPa

liquid phase		vapor phase		temperature	
x_1	y_1	Δy_1^a	$t/^\circ\text{C}$	$\Delta t^b/^\circ\text{C}$	
0.0000	0.0000		78.30		
0.0749	0.1513	0.0026	75.97	-0.16	
0.1502	0.2452	-0.0087	74.28	-0.34	
0.2498	0.3720	0.0181	73.09	-0.24	
0.3495	0.4432	0.0142	72.33	-0.23	
0.4502	0.5003	0.0083	71.94	-0.20	
0.5474	0.5489	0.0005	71.81	-0.20	
0.6498	0.6063	-0.0037	71.99	-0.16	
0.7394	0.6537	-0.0181	72.45	-0.12	
0.8502	0.7727	0.0017	73.67	-0.01	
0.9497	0.9066	0.0032	75.62	-0.04	
1.0000	1.0000		77.01		
Mean deviation		0.0079		0.17	

^a $\Delta y_1 = y_{1,\text{exp}} - y_{1,\text{calc}}$; calculated values using the UNIQUAC equation (parameters taken from Gmehling et al.⁵). ^b $\Delta t = t_{\text{exp}} - t_{\text{calc}}$; calculated values using the UNIQUAC equation (parameters taken from Gmehling et al.⁵).

ard (model 6890) gas chromatograph including a thermal conductivity detector (TCD) that was connected to a computer with HP ChemStation software. A 30 m glass capillary column (stationary phase HP 19091-133) was used at the following conditions: inlet temperature, 100 °C; oven temperature, 100 to 120 °C; detector temperature, 250 °C. Helium was used as carrier gas, which passed through the column at a flow rate of 1.3 cm³·min⁻¹. The calibration was carried out by injection of ethyl acetate + ethanol and methyl acetate + methanol mixtures of known composition prepared gravimetrically. The accuracy of the measured mole fraction was within ± 0.001 , which was confirmed by comparing the known composition of the made-up sample with the composition measured by GC.

Knowing the vapor-phase volume of the ebullimeter, it is simple to calculate the total amount of each component in the vapor phase according to the vapor-phase composition measured by GC. Then the liquid-phase composition can be estimated by subtracting the amount in the vapor

Table 2. Vapor–Liquid Equilibrium Data of the Methyl Acetate (1) + Methanol (2) System at 101.3 kPa

liquid phase		vapor phase		temperature	
x_1	y_1	Δy_1^a	$t/^\circ\text{C}$	$\Delta t^b/^\circ\text{C}$	
0.0000	0.0000		64.45		
0.1004	0.2612	0.0000	59.67	-0.50	
0.2006	0.3788	0.0120	56.95	-0.47	
0.3014	0.4671	-0.0030	55.38	-0.54	
0.4037	0.5344	0.0014	54.36	-0.57	
0.4996	0.5740	0.0068	53.85	-0.65	
0.5965	0.6272	-0.0022	53.48	-0.64	
0.7000	0.6866	0.0037	53.47	-0.73	
0.8001	0.7482	0.0073	53.82	-0.74	
0.8998	0.8446	0.0010	54.76	-0.75	
1.0000	1.0000	0.0014	56.74	-0.80	
Mean deviation		0.0043		0.67	

^a $\Delta y_1 = y_{1,\text{exp}} - y_{1,\text{calc}}$; calculated values using the UNIQUAC equation (parameters taken from Gmehling et al.⁵). ^b $\Delta t = t_{\text{exp}} - t_{\text{calc}}$; calculated values using the UNIQUAC equation (parameters taken from Gmehling et al.⁵).

phase and the condensed mass in the vapor sampling port (B2) from the known composition of the made-up samples. To validate the experimental method, experiments for the binary systems ethyl acetate + ethanol and methyl acetate + methanol without salt were also performed whereby the liquid-phase composition was estimated by material balance and compared to that analyzed by gas chromatography. The uncertainty was found to be within ± 0.0012 in mole fraction.

2.4. Consistency of the Experimental Data. To confirm the reliability of the experimental VLE data, all experimental data for the salt free system ethyl acetate (1) + ethanol (2) and methyl acetate (1) + methanol (2) were measured twice at 101.3 kPa. The mean values of the experimental data obtained are given in Tables 1 and 2 and shown in Figures 2 and 3. They were also compared with published data^{3,4} and the smoothed values calculated by the UNIQUAC equation (parameters taken from the literature⁵). The mean deviation between experimental and

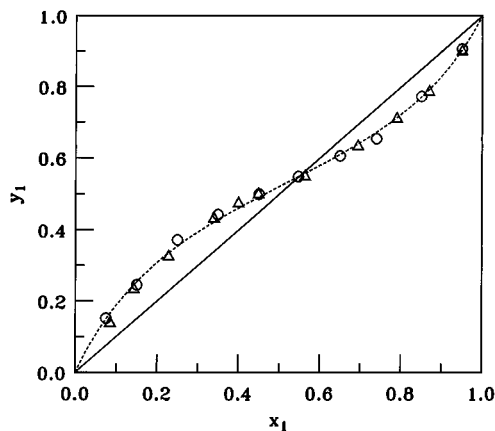


Figure 2. Vapor-liquid equilibrium diagram for the system ethyl acetate (1) + ethanol (2) at 101.3 kPa: \circ , this work; Δ , van Zandijcke et al.;³ dashed line, calculated by the UNIQUAC model.⁵

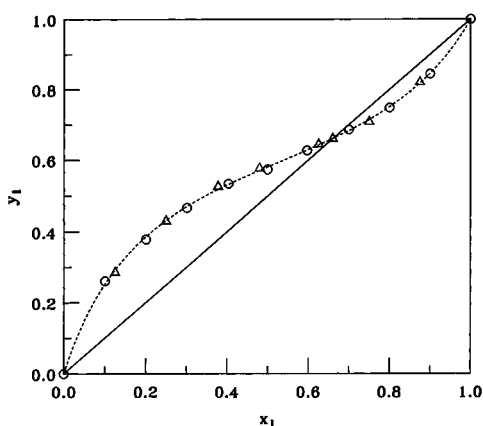


Figure 3. Vapor-liquid equilibrium diagram for the system methyl acetate (1) + methanol (2) at 101.3 kPa: \circ , this work; Δ , Vasileva et al.;⁴ dashed line, calculated by the UNIQUAC model.⁵

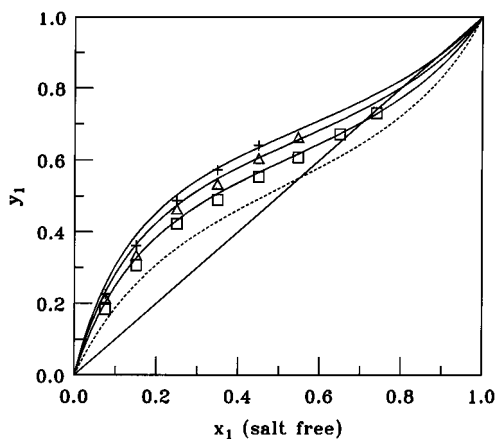


Figure 4. Vapor-liquid equilibrium diagram for the system ethyl acetate (1) + ethanol (2) + lithium nitrate (3) at 101.3 kPa: \square , $x_3 = 0.05$; Δ , $x_3 = 0.10$; $+$, $x_3 = 0.15$; continuous line, calculated by the LIQUAC model;¹ dashed line, calculated by the UNIQUAC model⁵ ($x_3 = 0$).

smoothed values for the ethyl acetate (methyl acetate) + ethanol (methanol) system was 0.008 (0.004) in the vapor-phase mole fraction and 0.17 (0.67) °C in the temperature. The thermodynamic consistency of the experimental data was checked with the Redlich-Kister area test.⁶ The average area deviation was 0.1%. Accordingly, it can be deduced that reliable and thermodynamically consistent

Table 3. Vapor-Liquid Equilibrium Data for the Ethyl Acetate (1) + Ethanol (2) + Lithium Nitrate (3) System at 101.3 kPa

x_1^a	y_1^b	$t/^\circ\text{C}$	α_{12}^d	x_1'	y_1	$t/^\circ\text{C}$	α_{12}
$x_3 = 0.005$							
0.0749	0.1591	76.07	2.337	0.0749	0.1622	76.18	2.391
0.1502	0.2612	74.47	2.000	0.1502	0.2651	74.54	2.041
0.2498	0.3808	73.16	1.847	0.2498	0.3894	73.23	1.915
0.3495	0.4457	72.39	1.497	0.3495	0.4517	72.47	1.533
0.4502	0.5010	72.04	1.226	0.4502	0.5095	72.12	1.269
0.5474	0.5561	71.85	1.036	0.5474	0.5634	72.01	1.067
0.6498	0.6115	72.10	0.848	0.6498	0.6231	72.30	0.891
0.7394	0.6621	72.67	0.691	0.7394	0.6725	72.82	0.724
0.8502	0.7764	73.89	0.612	0.8502	0.7851	74.09	0.644
0.9497	0.9129	75.78	0.555				
$x_3 = 0.02$							
0.0749	0.1713	76.39	2.553	0.0749	0.1731	76.63	2.586
0.1502	0.2712	74.69	2.105	0.1502	0.2853	74.87	2.259
0.2498	0.3921	73.28	1.937	0.2498	0.4075	73.35	2.065
0.3495	0.4647	72.50	1.616	0.3495	0.4708	72.59	1.656
0.4502	0.5211	72.31	1.329	0.4502	0.5325	72.44	1.391
0.5474	0.5737	72.18	1.113	0.5474	0.5857	72.31	1.169
0.6498	0.6316	72.50	0.924	0.6498	0.6447	72.71	0.978
0.7394	0.6876	73.13	0.776	0.7394	0.7012	73.41	0.827
$x_3 = 0.04$							
0.0749	0.1830	76.91	2.767	0.0749	0.1831	77.22	2.768
0.1502	0.2901	74.92	2.312	0.1502	0.3056	75.33	2.490
0.2498	0.4100	73.70	2.087	0.2498	0.4232	73.48	2.203
0.3495	0.4831	72.68	1.740	0.3495	0.4893	72.87	1.783
0.4502	0.5440	72.59	1.457	0.4502	0.5534	72.72	1.513
0.5474	0.5970	72.66	1.225	0.5474	0.6072	72.69	1.278
0.6498	0.6574	72.88	1.034	0.6498	0.6717	73.13	1.103
0.7394	0.7192	73.64	0.903	0.7394	0.7299	73.88	0.952
$x_3 = 0.075$							
0.0749	0.1921	77.84	2.937	0.0749	0.2087	79.33	3.258
0.1502	0.3126	76.04	2.573	0.1502	0.3289	77.05	2.773
0.2498	0.4351	74.25	2.313	0.2498	0.4584	74.78	2.542
0.3495	0.5143	73.05	1.971	0.3495	0.5283	73.92	2.085
0.4502	0.5767	73.20	1.664	0.4502	0.5993	73.78	1.827
0.5474	0.6299	73.12	1.407	0.5474	0.6582	73.81	1.592
0.6498	0.6991	73.68	1.252				
0.7394	0.7406	74.05	1.006				
$x_3 = 0.125$							
0.0749	0.2098	80.46	3.279	0.0749	0.2251	82.61	3.588
0.1502	0.3398	77.86	2.912	0.1502	0.3612	79.66	3.199
0.2498	0.4722	75.51	2.687	0.2498	0.4875	77.25	2.857
0.3495	0.5469	74.62	2.247	0.3495	0.5722	75.46	2.489
0.4502	0.6236	74.61	2.023	0.4502	0.6408	75.45	2.179
0.5474	0.6779	74.32	1.740				
$x_3 = 0.15$							

^a Salt free liquid-phase mole fraction. ^b Vapor-phase mole fraction. ^c System temperature (°C). ^d Relative volatility $\alpha_{12} = (y_1/x_1)/(y_2/x_2)$.

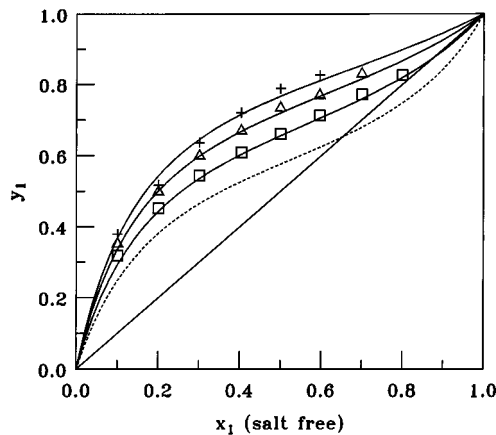


Figure 5. Vapor-liquid equilibrium diagram for the system methyl acetate (1) + methanol (2) + lithium nitrate (3) at 101.3 kPa: \square , $x_3 = 0.05$; Δ , $x_3 = 0.10$; $+$, $x_3 = 0.15$; continuous line, calculated by the LIQUAC model;¹ dashed line, calculated by the UNIQUAC model⁵ ($x_3 = 0$).

vapor-liquid equilibrium data can be measured with the experimental apparatus described in section 2.2.

Table 4. Vapor–Liquid Equilibrium Data for the Methyl Acetate (1) + Methanol (2) + Lithium Nitrate (3) System at 101.3 kPa

x_1^a	y_1^b	$t/^\circ\text{C}$	α_{12}^d	x_1'	y_1	$t/^\circ\text{C}$	α_{12}
$x_3 = 0.005$				$x_3 = 0.01$			
0.1004	0.2712	59.71	3.334	0.1004	0.2752	59.78	3.402
0.2006	0.3825	56.94	2.468	0.2006	0.3916	56.94	2.565
0.3014	0.4712	55.39	2.065	0.3014	0.4821	55.40	2.158
0.4037	0.5448	54.38	1.768	0.4037	0.5525	54.38	1.824
0.4996	0.5875	53.84	1.427	0.4996	0.6021	53.86	1.516
0.5965	0.6347	53.60	1.175	0.5965	0.6513	53.68	1.263
0.7000	0.6924	53.64	0.965	0.7000	0.7023	53.76	1.011
0.8001	0.7513	54.13	0.755	0.8001	0.7665	54.19	0.820
0.8998	0.8488	54.97	0.625	0.8998	0.8559	55.16	0.661
$x_3 = 0.02$				$x_3 = 0.03$			
0.1004	0.2881	59.95	3.626	0.1004	0.2945	60.17	3.740
0.2006	0.4124	57.00	2.797	0.2006	0.4288	57.04	2.992
0.3014	0.4856	55.40	2.188	0.3014	0.5145	55.44	2.456
0.4037	0.5702	54.42	1.960	0.4037	0.5802	54.47	2.041
0.4996	0.6116	54.01	1.577	0.4996	0.6312	54.15	1.714
0.5965	0.6637	53.83	1.335	0.5965	0.6779	53.99	1.424
0.7000	0.7181	53.96	1.092	0.7000	0.7362	54.18	1.196
0.8001	0.7811	54.47	0.892	0.8001	0.7939	54.69	0.962
0.8998	0.8700	55.43	0.745	0.8998	0.8828	55.66	0.839
$x_3 = 0.04$				$x_3 = 0.05$			
0.1004	0.3111	60.36	4.046	0.1004	0.3192	60.66	4.201
0.2006	0.4347	57.23	3.064	0.2006	0.4520	57.39	3.287
0.3014	0.5292	55.55	2.605	0.3014	0.5437	55.73	2.762
0.4037	0.5981	54.58	2.198	0.4037	0.6091	54.72	2.302
0.4996	0.6466	54.27	1.833	0.4996	0.6604	54.39	1.948
0.5965	0.6955	54.16	1.545	0.5965	0.7123	54.35	1.675
0.7000	0.7504	54.38	1.288	0.7000	0.7712	54.59	1.445
0.8001	0.8107	54.93	1.070	0.8001	0.8262	55.14	1.188
$x_3 = 0.075$				$x_3 = 0.1$			
0.1004	0.3339	61.91	4.492	0.1004	0.3513	63.52	4.852
0.2006	0.4737	58.07	3.587	0.2006	0.4980	59.07	3.953
0.3014	0.5666	56.32	3.030	0.3014	0.5987	57.24	3.458
0.4037	0.6411	55.15	2.639	0.4037	0.6688	55.80	2.983
0.4996	0.6969	54.93	2.303	0.4996	0.7325	55.51	2.743
0.5965	0.7442	54.81	1.968	0.5965	0.7683	55.33	2.243
0.7000	0.7931	55.07	1.643	0.7000	0.8297	55.56	2.088
0.8001	0.8508	55.57	1.425				
$x_3 = 0.125$				$x_3 = 0.15$			
0.1004	0.3682	65.38	5.222	0.1004	0.3793	67.66	5.475
0.2006	0.5024	60.38	4.023	0.2006	0.5174	62.07	4.272
0.3014	0.6198	58.40	3.779	0.3014	0.6360	60.01	4.050
0.4037	0.6965	56.63	3.390	0.4037	0.7201	57.65	3.800
0.4996	0.7624	56.27	3.214	0.4996	0.7873	57.25	3.707
0.5965	0.8024	55.88	2.747	0.5965	0.8264	56.56	3.220
0.7000	0.8510	56.00	2.448				

^{a-d} See footnotes *a–d* in Table 3.

3. Results and Discussion

3.1. Experimental Data. Isobaric vapor–liquid equilibrium data for the systems ethyl acetate + ethanol and methyl acetate + methanol were measured at 101.3 kPa

Table 5. Binary Interaction Parameters, Relative van der Waals Volume Parameters, and Surface Area Parameters^a for the LIQUAC Model¹

<i>i</i>	<i>j</i>	a_{ij}	a_{ji}	b_{ij}	c_{ij}	r_i	q_i
CH ₃ OH	CH ₃ COOCH ₃	-37.750	311.70				
C ₂ H ₅ OH	CH ₃ COOC ₂ H ₅	-58.670	230.14				
CH ₃ OH	Li ⁺	298.600	-634.80	5.7600	1.1170		
CH ₃ OH	NO ₃ ⁻	-497.760 ^b	590.170 ^b	-5.6119 ^b	-1.0075 ^b		
CH ₃ COOCH ₃	Li ⁺	685.219 ^b	562.262 ^b	0.1635 ^b	0.3259 ^b		
CH ₃ COOCH ₃	NO ₃ ⁻	-404.372 ^b	576.882 ^b	0.1707 ^b	-0.2803 ^b		
C ₂ H ₅ OH	Li ⁺	-374.760 ^b	2158.600 ^b	3.9232 ^b	0.7325 ^b		
C ₂ H ₅ OH	NO ₃ ⁻	-37.620	-3.430	-3.5370	-1.0920		
CH ₃ COOC ₂ H ₅	Li ⁺	-286.481 ^b	232.732 ^b	2.7421 ^b	0.3966 ^b		
CH ₃ COOC ₂ H ₅	NO ₃ ⁻	122.281 ^b	407.916 ^b	-1.9334 ^b	-0.0783 ^b		
Li ⁺	NO ₃ ⁻	405.70	442.50	0.1331	-0.2879		
CH ₃ OH						1.431	1.432
CH ₃ COOCH ₃						2.804	2.576
C ₂ H ₅ OH						2.106	1.972
CH ₃ COOC ₂ H ₅						3.749	3.116
Li ⁺						1.000	1.000
NO ₃ ⁻						1.000	1.000

^a Units: a_{ij} is in K. b_{ij} and c_{ij} are in mol·kg⁻¹. ^b These interaction parameters have been fitted in this work.

Table 6. Mean Absolute Deviations of Vapor-Phase Composition and Boiling Point for the LIQUAC Model at Different Salt Concentrations

	x_3	Δy	$\Delta t/^\circ\text{C}$
Ethyl Acetate (1) + Ethanol (2) + LiNO ₃ (3)			
	0.005	0.0063	0.17
	0.010	0.0063	0.18
	0.020	0.0093	0.23
	0.030	0.0108	0.34
	0.040	0.0113	0.45
	0.050	0.0115	0.55
	0.075	0.0160	0.74
	0.100	0.0170	0.78
	0.125	0.0191	1.02
	0.150	0.0167	1.09
Abs. deviation		0.0124	0.55
Methyl Acetate (1) + Methanol (2) + LiNO ₃ (3)			
	0.005	0.0055	0.62
	0.010	0.0070	0.58
	0.020	0.0076	0.49
	0.030	0.0074	0.44
	0.040	0.0086	0.47
	0.050	0.0099	0.46
	0.075	0.0058	0.48
	0.100	0.0069	0.62
	0.125	0.0125	0.82
	0.150	0.0149	1.04
Abs. deviation		0.0086	0.60

and various lithium nitrate concentrations. The experimental results are given in Tables 3 and 4. In Figures 4 and 5, these experimental data are plotted in the form of an x – y diagram on a salt-free basis. From these figures it can be seen that the addition of lithium nitrate to both systems increases the amount of the ester in the vapor phase, and therefore, the volatility α_{12} also enlarges with the addition of salt. So a salting-out effect of the ester occurs in both cases and the azeotropic point shifts to higher ester compositions.

3.2. Calculation of VLE for the Systems Containing Lithium Nitrate. To describe the observed vapor–liquid equilibrium behavior, the experimental data were correlated using the electrolyte LIQUAC model.

3.2.1. LIQUAC Model. The electrolyte model LIQUAC¹ allows the behavior for both single and mixed solvent electrolyte systems to be described.⁷ It consists of three contributions: (1) a Debye–Hückel term to consider long-range electrostatic interactions, (2) the UNIQUAC equation to describe the short-range interactions between all species, and (3) a middle-range contribution to include all indirect effects of the charge interactions.

For a system with two solvents and one salt, 12 short-range interaction parameters (a_{ij}) and 10 middle-range interaction parameters (b_{ij} and c_{ij}) are required. A large number of parameters have already been published.¹ Therefore, in this work 16 parameters were directly taken from the parameter matrix published. The remaining 24 interaction parameters were fitted to the new experimental data with the help of the Simplex–Nelder–Mead method using the following objective function.⁸

$$F = \sum_{nt} \sum_{np} \omega_y (Y_{i,1(\text{exp})} - Y_{i,1(\text{calc})})^2 + \sum_{nt} \sum_{np} \omega_T (T_{i(\text{exp})} - T_{i(\text{calc})})^2 \quad (1)$$

where ω is a weighting factor for data set type y , T . As suggested by Li et al. in 1994,¹ the relative volumes and surface areas for the ions were arbitrarily set to 1.0.

For the LIQUAC model the new interaction parameters, the relative volumes, and the surface areas are listed in Table 5 together with the parameters directly taken from the literature.^{1,9} Mean absolute deviations in vapor-phase mole fraction and boiling points for the model are listed in Table 6. The deviations between experimental and calculated data increase with rising salt concentration. Generally it can be seen that the model is able to present the experimental data with a high accuracy.

List of Symbols

Latin Symbols

a_{ij} = interaction parameter of the UNIQUAC equation (short range)

b_{ij} , c_{ij} = binary virial interaction parameters (middle range)

F = objective function

i, j = components of the system

nt = number of data set types

np = number of data points

q_i = relative van der Waals surface area of component i

r_i = relative van der Waals volume of component i

t = temperature in °C

T = absolute temperature in K

x_i = mole fraction of component i in the liquid phase

y_i = mole fraction of component i in the vapor phase

Greek Symbols

α_{ij} = relative volatility of component i with respect to component j

ω = weighting factor

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