

# Measurement and Correlation of Isothermal Vapor–Liquid Equilibrium Data for the System Acetone + Methanol + Lithium Bromide

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Isothermal vapor–liquid equilibrium data at three temperatures (39.5, 55.0, and 70.6) °C have been measured for the system acetone (1) + methanol (2) + lithium bromide (3) at constant salt molalities (0.500, 1.00, 2.00, 3.00 and 4.00 mol·kg<sup>-1</sup>) with the help of headspace gas chromatography. The experimental data were fitted using the electrolyte NRTL model (Mock et al., 1986), the extended UNIQUAC model (Sander et al., 1986), the electrolyte UNIFAC group-contribution model (Kikic et al., 1991) and the LIQUAC model (Li et al., 1994). The results of correlation were compared with the experimental data. Superior results were obtained for the LIQUAC model.

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## 1. Introduction

The synthesis and design of industrial separation processes such as salt distillation (Furter, 1977), crystallization processes, e.g., extractive crystallization of salts (Weingaertner et al., 1991), and the simulation of unit operations for electrolyte systems require an accurate description of the phase-equilibrium behavior of electrolyte systems. This has been the incentive to the development of a database and thermodynamic models suitable for the correlation and prediction of phase equilibria of electrolyte systems.

The addition of salt to solvent mixture influences the boiling point, the mutual solubility of the two liquid components, and the relative volatility of solvents or gases. Many experimental data (799 ternary data sets and 830 binary data sets) concerning salt effects on the phase equilibrium behavior have been stored in the Dortmund Data Bank (DDB). While many data exist for water and alcohol, much less data are available for salts in organic solvents or in mixed solvents, mainly because of the low solubility of salts in these solvents. Furthermore, most of the data are reported for isobaric, rather than isothermal, conditions. For systems of salts in solvent mixtures, the temperature for isobaric data may change drastically. Data correlation becomes complicated unless it is assumed that the model parameters are independent of temperature or unless an explicit temperature dependence is incorporated into the model used for the data correlation. No such difficulty exists for isothermal data, for it is an excellent assumption to neglect the pressure dependence of the activity coefficients at low or moderate pressures. The aim of this work is to study systematically the effect of lithium bromide on the vapor–liquid equilibrium behavior of the acetone + methanol system at three temperatures (39.5, 55.0, and 70.6 °C) and different constant salt concentrations (0.500, 1.00, 2.00, 3.00, and 4.00 mol·kg<sup>-1</sup>), for which

no data were found in the literature. The addition of lithium bromide to this solvent mixture increases the concentration of acetone in the vapor phase. At all temperatures the azeotropic behavior disappears at moderate salt concentrations.

Various predictive and correlative models were proposed in the past decade to calculate the phase-equilibrium behavior of the mixed-solvent electrolyte systems. The present experimental data were correlated using four models based on the local composition or group-contribution concept: the electrolyte NRTL model of Mock et al. (1986), the modified UNIQUAC model of Sander et al. (1986), the modified UNIFAC model of Kikic et al. (1991), and the LIQUAC model of Li et al. (1994). The new set of interaction parameters for each model was fitted using the experimental data measured in this work.

## 2. Experimental Section

**2.1. Materials.** Acetone (99.5 mass %, Scharlau) and methanol (99.8 mass %, Scharlau) were dried 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 bromide, 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 bromide were prepared directly by using a Sartorius analytical balance, the accuracy of which was ±0.1 mg. For each experimental point, approximately 8 cm<sup>3</sup> of sample solution was put into the 22 cm<sup>3</sup> sample vial. After the sample vials were tightly closed by means of a special aluminum lid, with a washer and a Teflon disk, they were kept at the desired temperature in a thermostatic bath controlled within ±0.1 °C. The measurements were started after the samples were kept at constant temperature at least for 12 h to ensure phase equilibrium.

For the determination of the vapor-phase composition, samples of the vapor phase were automatically withdrawn using a Perkin-Elmer F45 GLC vapor analyzer and ana-

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**Table 1. Vapor–Liquid Equilibrium Data for the System Acetone (1) + Methanol (2) + Lithium Bromide (3) at 39.5 °C**

$x_1^a$	$y_1$	$\gamma_1^b$	$\gamma_2^b$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
$m = 0.500 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.000 \text{ mol}\cdot\text{kg}^{-1}$			
0.1000	0.251	1.8369	0.9920	0.1000	0.270	2.0218	0.9630
0.1501	0.330	1.7410	0.9923	0.1501	0.351	1.9131	0.9552
0.1998	0.397	1.6551	0.9947	0.1998	0.420	1.8156	0.9488
0.2999	0.498	1.5070	1.0057	0.2999	0.533	1.6466	0.9397
0.3981	0.577	1.3888	1.0239	0.3981	0.621	1.5105	0.9340
0.5000	0.656	1.2897	1.0488	0.5000	0.701	1.3945	0.9284
0.5999	0.723	1.2119	1.0764	0.5999	0.776	1.3012	0.9181
0.6998	0.795	1.1501	1.1000	0.6998	0.848	1.2246	0.8930
0.7994	0.861	1.1021	1.0995	0.7994	0.914	1.1620	0.8279
0.8481	0.900	1.0830	1.0727	0.8481	0.940	1.1357	0.7610
0.8900	0.931	1.0687	1.0138	0.8900	0.959	1.1151	0.6622
$m = 2.000 \text{ mol}\cdot\text{kg}^{-1}$				$m = 3.000 \text{ mol}\cdot\text{kg}^{-1}$			
0.1000	0.311	2.3445	0.8780	0.1000	0.357	2.5436	0.7721
0.1501	0.407	2.2060	0.8569	0.1501	0.459	2.3773	0.7429
0.1998	0.485	2.0821	0.8371	0.1998	0.553	2.2294	0.7151
0.2999	0.610	1.8670	0.7991	0.2999	0.680	1.9748	0.6615
0.3981	0.705	1.6931	0.7622	0.3981	0.779	1.7702	0.6094
0.5000	0.792	1.5434	0.7204	0.5000	0.857	1.5946	0.5526
0.5999	0.860	1.4210	0.6705	0.5999	0.909	1.4511	0.4892
0.6998	0.909	1.3180	0.6016	0.6998	0.941	1.3303	0.4098
0.7994	0.945	1.2311	0.4911	0.7994	0.961	1.2279	0.2986
0.8481	0.961	1.1934	0.4062	0.8481	0.969	1.1833	0.2237
0.8900	0.972	1.1633	0.3032	0.8900	0.973	1.1475	0.1443
$m = 4.000 \text{ mol}\cdot\text{kg}^{-1}$							
0.1000	0.389	2.5853	0.6584	0.5000	0.893	1.5462	0.4181
0.1501	0.504	2.4000	0.6255	0.5999	0.933	1.3930	0.3541
0.1998	0.575	2.2363	0.5943	0.6998	0.957	1.2645	0.2787
0.2999	0.733	1.9571	0.5347	0.7994	0.975	1.1562	0.1825
0.3981	0.827	1.7350	0.4781				

<sup>a</sup> Liquid-phase mole fraction on a salt-free basis. <sup>b</sup> Activity coefficients calculated by LIQUAC model using the parameters given in Table 7.

lyzed 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<sup>3</sup>·s<sup>-1</sup>. More details of the experimental setup have already 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 by mass and injected three times for each sample. The mole fractions and average area fractions were correlated using a fifth-order polynomial (mean deviation: 0.17% for mole fraction). The vapor-phase composition was determined with the help of the calibration curve. The average error in the measurement of the mole fraction is  $\pm 0.002$ , 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 reasonable to assume that the 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 composition via gas chromatography. The uncertainty of this assumption was  $\pm 0.002$  in mole fraction.

**Table 2. Vapor–Liquid Equilibrium Data for the System Acetone (1) + Methanol (2) + Lithium Bromide (3) at 55.0 °C<sup>a</sup>**

$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
$m = 0.500 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.000 \text{ mol}\cdot\text{kg}^{-1}$			
0.1000	0.222	1.7947	0.9938	0.1000	0.233	1.9701	0.9675
0.1501	0.292	1.7024	0.9944	0.1501	0.311	1.8656	0.9603
0.1998	0.353	1.6200	0.9971	0.1998	0.377	1.7721	0.9547
0.2999	0.457	1.4783	1.0086	0.2999	0.489	1.6107	0.9470
0.3981	0.543	1.3659	1.0270	0.3981	0.583	1.4814	0.9425
0.5000	0.620	1.2721	1.0519	0.5000	0.671	1.3717	0.9381
0.5999	0.695	1.1988	1.0789	0.5999	0.750	1.2840	0.9288
0.6998	0.774	1.1410	1.1013	0.6998	0.829	1.2124	0.9041
0.7994	0.847	1.0965	1.0989	0.7994	0.889	1.1542	0.8385
0.8481	0.892	1.0788	1.0712	0.8481	0.923	1.1299	0.7709
0.8900	0.921	1.0656	1.0115	0.8900	0.950	1.1109	0.6710
$m = 2.000 \text{ mol}\cdot\text{kg}^{-1}$				$m = 3.000 \text{ mol}\cdot\text{kg}^{-1}$			
0.1000	0.270	2.2797	0.8884	0.1000	0.309	2.4739	0.7872
0.1501	0.363	2.1467	0.8683	0.1501	0.414	2.3141	0.7588
0.1998	0.440	2.0279	0.8495	0.1998	0.503	2.1722	0.7318
0.2999	0.569	1.8226	0.8134	0.2999	0.641	1.9287	0.6796
0.3981	0.670	1.6572	0.7781	0.3981	0.747	1.7336	0.6287
0.5000	0.761	1.5156	0.7378	0.5000	0.830	1.5666	0.5725
0.5999	0.836	1.4001	0.6889	0.5999	0.890	1.4306	0.5088
0.6998	0.896	1.3034	0.6199	0.6998	0.932	1.3163	0.4280
0.7994	0.937	1.2220	0.5076	0.7994	0.956	1.2196	0.3133
0.8481	0.947	1.1869	0.4205	0.8481	0.963	1.1775	0.2355
0.8900	0.960	1.1587	0.3147	0.8900	0.969	1.1438	0.1526
$m = 4.000 \text{ mol}\cdot\text{kg}^{-1}$							
0.1000	0.346	2.5181	0.6761	0.5000	0.869	1.5213	0.4373
0.1501	0.462	2.3396	0.6437	0.5999	0.916	1.3751	0.3720
0.1998	0.535	2.1821	0.6129	0.6998	0.946	1.2528	0.2943
0.2999	0.699	1.9142	0.5540	0.7994	0.969	1.1497	0.1938
0.3981	0.798	1.7017	0.4976				

<sup>a</sup> See footnotes *a*, *b* in Table 1.

### 3. Results

**3.1. Experimental Data.** Isothermal vapor–liquid equilibrium data for the system acetone (1) + methanol (2) + lithium bromide (3) have been measured at three temperatures (39.5, 55.0, and 70.6 °C) and various salt concentrations ( $m = 0.5, 1.0, 2.0, 3.0,$  and  $4.0 \text{ mol}\cdot\text{kg}^{-1}$ ). The experimental results are given in Tables 1–3. As a typical example, experimental data from Table 3 are plotted in the form of an  $x$ – $y$  diagram (Figure 1). From this figure, it can be seen that the addition of lithium bromide to the system acetone + methanol increases the amount of acetone in the vapor phase and shifts the azeotrope to the acetone-rich region, whereby the azeotropic point at all temperatures disappears at salt concentrations above  $0.5 \text{ mol}\cdot\text{kg}^{-1}$ .

**3.2. Calculation of VLE for Salt-Containing Systems.** To describe the observed VLE behavior, the experimental data are correlated using the following four models.

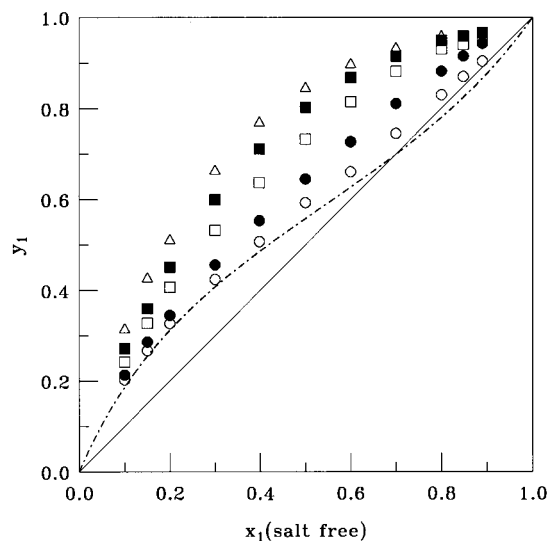
**3.2.1. The Electrolyte NRTL Model of Mock et al. (1986).** The electrolyte NRTL model used to correlate the VLE data is an extension of the Chen model for single solvent electrolyte systems to mixed-solvent electrolyte systems neglecting the long-range interaction contribution term (Mock et al., 1986). The two fundamental assumptions for the local composition of an electrolyte solution are (1) strong repulsion of ions of the same sign, so that the local composition of cations (anions) around a central cation (anion) is zero, and (2) local electroneutrality, which means that the sum of the charges of cations and anions around a central molecule is zero.

The model parameters are specific for the solvent–solvent and solvent–salt pairs. For a system with two solvents,  $m_1$  and  $m_2$ , and one salt, ca, 6 energy parameters ( $\Delta g_{m_1, m_2}$ ,  $\Delta g_{m_2, m_1}$ ,  $\Delta g_{m_1, ca}$ ,  $\Delta g_{ca, m_1}$ ,  $\Delta g_{m_2, ca}$  and  $\Delta g_{ca, m_2}$ ) and

**Table 3. Vapor–Liquid Equilibrium Data for the System Acetone (1) + Methanol (2) + Lithium Bromide (3) at 70.6 °C<sup>a</sup>**

$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
$m = 0.500 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.000 \text{ mol}\cdot\text{kg}^{-1}$			
0.1000	0.222	1.7561	0.9953	0.1000	0.233	1.9230	0.9714
0.1501	0.292	1.6672	0.9961	0.1501	0.311	1.8226	0.9647
0.1998	0.353	1.5881	0.9991	0.1998	0.377	1.7329	0.9596
0.2999	0.457	1.4526	1.0109	0.2999	0.489	1.5787	0.9530
0.3981	0.543	1.3456	1.0293	0.3981	0.583	1.4556	0.9495
0.5000	0.620	1.2566	1.0538	0.5000	0.671	1.3517	0.9459
0.5999	0.695	1.1874	1.0800	0.5999	0.750	1.2690	0.9371
0.6998	0.774	1.1332	1.1010	0.6998	0.829	1.2018	0.9125
0.7994	0.847	1.0916	1.0968	0.7994	0.889	1.1475	0.8464
0.8481	0.892	1.0753	1.0681	0.8481	0.923	1.1250	0.7782
0.8900	0.921	1.0630	1.0078	0.8900	0.950	1.1073	0.6775
$m = 2.000 \text{ mol}\cdot\text{kg}^{-1}$				$m = 3.000 \text{ mol}\cdot\text{kg}^{-1}$			
0.1000	0.270	2.2208	0.8972	0.1000	0.309	2.4102	0.8000
0.1501	0.363	2.0930	0.8780	0.1501	0.414	2.2563	0.7724
0.1998	0.440	1.9791	0.8599	0.1998	0.503	2.1202	0.7462
0.2999	0.569	1.7828	0.8255	0.2999	0.641	1.8869	0.6953
0.3981	0.670	1.6253	0.7917	0.3981	0.747	1.7006	0.6453
0.5000	0.761	1.4909	0.7526	0.5000	0.830	1.5416	0.5897
0.5999	0.836	1.3817	0.7044	0.5999	0.890	1.4124	0.5260
0.6998	0.896	1.2906	0.6353	0.6998	0.932	1.3039	0.4440
0.7994	0.937	1.2141	0.5215	0.7994	0.956	1.2124	0.3263
0.8481	0.947	1.1812	0.4327	0.8481	0.963	1.1726	0.2459
0.8900	0.960	1.1548	0.3245	0.8900	0.969	1.1406	0.1601
$m = 4.000 \text{ mol}\cdot\text{kg}^{-1}$							
0.1000	0.346	2.4559	0.6915	0.5000	0.869	1.4987	0.4543
0.1501	0.462	2.2839	0.6595	0.5999	0.916	1.3591	0.3881
0.1998	0.535	2.1323	0.6292	0.6998	0.946	1.2423	0.3083
0.2999	0.699	1.8750	0.5709	0.7994	0.969	1.1440	0.2042
0.3981	0.798	1.6713	0.5148				

<sup>a</sup> See footnotes *a*, *b* in Table 1.



**Figure 1.**  $x$ - $y$  vapor–liquid equilibrium diagram for the system acetone (1) + methanol (2) + LiBr at 70.6 °C: ○,  $m = 0.5$ ; ●,  $m = 1.0$ ; □,  $m = 2.0$ ; ■,  $m = 3.0$ ; △,  $m = 4.0 \text{ mol}\cdot\text{kg}^{-1}$ ; --- ( $m = 0.0 \text{ mol}\cdot\text{kg}^{-1}$ ) calculated by the UNIQUAC model (parameters taken from Gmehling et al. (1977)).

3 nonrandomness factors ( $\alpha_{m1,m2}$ ,  $\alpha_{ca,m1}$ , and  $\alpha_{ca,m2}$ ) are required. The binary parameter  $\tau_{ij}$  is expressed by:

$$\tau_{ij} = \Delta g_{ij}/RT \quad (1a)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (1b)$$

To minimize the number of parameters to be fitted, the binary solvent–solvent parameters ( $\Delta g_{m1,m2}$ ,  $\Delta g_{m2,m1}$ , and

**Table 4. Energy Parameters ( $\Delta g_{ij}$  and  $\Delta g_{ji}$ , J·mol<sup>-1</sup>) and Nonrandomness Factors ( $\alpha_{ij}$ ) for the Electrolyte NRTL Model**

$i$	$j$	$\alpha_{ij}$	$\Delta g_{ij}$	$\Delta g_{ji}$
CH <sub>3</sub> OH	CH <sub>3</sub> COCH <sub>3</sub>	0.2987	1819.29	151.86
CH <sub>3</sub> OH	LiBr	0.2	-7096.39 (f)	-2129.52 (f)
CH <sub>3</sub> COCH <sub>3</sub>	LiBr	0.1670 (f) <sup>a</sup>	3644.94 (f)	1091.52 (f)

<sup>a</sup> (f) means that these interaction parameters have been fitted in this work.

$\alpha_{m1,m2}$ ) were directly taken from the literature (Gmehling et al., 1977). Moreover, as pointed out by Mock et al. (1986), the nonrandomness factor for the salted-in solvent and salt was set arbitrarily to 0.2. The remaining five parameters for the binary pairs acetone + lithium bromide and methanol + lithium bromide were determined by minimization of the following objective function  $F$  using the Simplex-Nelder–Mead method (Nelder and Mead, 1965)

$$F(\Delta g_{i,p}, \Delta g_{j,p}, \alpha_{i,j}) = \sum_{nt} \sum_{np} [y_{i,1}(\text{exp}) - y_{i,1}(\text{calc})]^2 = \min \quad (2)$$

where  $y$  represents the vapor-phase mole fraction.  $nt$  and  $np$  are the number of data sets and the number of data points for each data set. The terms exp and calc denote experimental data and calculated values. The vapor-phase compositions were calculated assuming ideal behavior of the vapor phase by solving the following equilibrium condition iteratively

$$y_i = x_i \gamma_i P_i^s / P \quad (3)$$

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  $P_i^s$  is calculated by the Antoine equation using Antoine constants from literature (Gmehling et al., 1977). The activity coefficient of the solvent  $i$  was calculated by eq 6 of Mock et al. (1986). The NRTL parameters and the nonrandomness factors are given in Table 4.

**3.2.2. Extended UNIQUAC Model of Sander et al. (1986).** Sander et al. (1986) presented an extension of the UNIQUAC equation to mixed solvent with salts. The activity coefficient of a solvent is calculated by the sum of a long-range interaction given by a simplified Debye–Hückel equation for mixed solvent and a short-range interaction contribution given by an extended UNIQUAC equation with concentration dependent parameters between an ion  $i$  and the solvent  $m$

$$a_{im} = a_{im}^* + \theta_i \sum_{j \neq i} \delta_{ij,m} \theta_j \quad (4)$$

$$a_{mi} = a_{mi}^* + \theta_i \sum_{j \neq i} \delta_{ij,m} \theta_j \quad (5)$$

where  $a_{im}^*$ ,  $a_{mi}^*$  represent reference interaction parameters,  $\delta_{ij,m}$  is a parameter, and the summation is over all ionic species except  $i$ .  $\theta_i$  represents the surface area fraction of ion  $i$ .

For a system with two solvents and one salt, 14 parameters are needed: 2 solvent–solvent, 2 ion–ion, 8 ion–solvent, and 2 salt–solvent interaction parameters. The binary solvent–solvent interaction parameters have been obtained directly from Gmehling et al. (1977). For the acetone + methanol + lithium bromide system, a few interaction parameters were taken from literature (Sander

**Table 5. UNIQUAC Reference Interaction Parameters  $a_{ij}^*$  (K), Concentration Dependent Parameters  $\delta_{ij,m}$ , Relative van der Waals Volume Parameters  $r_i$ , and Surface Area Parameters  $q_i$  for the Extended UNIQUAC Model of Sander et al. (1986)**

	CH <sub>3</sub> OH	CH <sub>3</sub> COCH <sub>3</sub>	Li <sup>+</sup>	Br <sup>-</sup>
		$a_{ij}^*$		
CH <sub>3</sub> OH	0.0	-54.2	-803.6	-233.5
CH <sub>3</sub> COCH <sub>3</sub>	223.8	0.0	292.52 (f)	973.44 (f)
Li <sup>+</sup>	-635.5	228.56 (f)	0.0	281.10 (f)
Br <sup>-</sup>	1034.0	-85.99 (f)	852.23 (f)	0.0
		$r_i$ and $q_i$		
$r_i$	1.4311	2.5735	1.0	1.2331
$q_i$	1.4322	2.3360	1.0	1.1510
		$\delta_{ij,m}$		
Li <sup>+</sup> -Br <sup>-</sup>	-312.56 (f) <sup>a</sup>	-218.67 (f)		

<sup>a</sup> (f) means that these interaction parameters have been fitted in this work.

**Table 6. UNIFAC Group Interaction Parameters  $a_{ij}$  (K), Subgroup Volume Parameters  $R_i$  and Surface Area Parameters  $Q_i$  for the Electrolyte UNIFAC Model (Kikic et al., 1991)**

	CH <sub>2</sub>	CH <sub>3</sub> OH	CH <sub>2</sub> CO	Li <sup>+</sup>	Br <sup>-</sup>
			$a_{ij}$		
CH <sub>2</sub>	0.0	697.2	476.4	6434.4	-673.87
CH <sub>3</sub> OH	16.51	0.0	23.39	-71.347	-1295.35
CH <sub>2</sub> CO	26.76	108.7	0.0	-261.153 (f)	384.28 (f)
Li <sup>+</sup>	4651.5	-798.23	542.838 (f) <sup>a</sup>	0.0	23277
Br <sup>-</sup>	3106.4	15164.3	-284.742 (f)	24.1	0.0
			$R_i$ and $Q_i$		
$R_i$	0.9011	1.4311	1.6724	1.0	1.2331
$Q_i$	0.8480	1.4320	1.4880	1.0	1.1510

<sup>a</sup> (f) means that these interaction parameters have been fitted in this work.

et al., 1986). The remaining 8 model parameters were fitted to the experimental data. All the required parameters are given in Table 5.

**3.2.3. Electrolyte UNIFAC Group-Contribution Model of Kikic et al. (1991).** The first electrolyte model based on the group-contribution method was published by Kikic et al. (1991). This model combines a modified

Debye-Hückel term according to the McMillan-Mayer solution theory as described by Cardoso and O'Connell (1987) with the original UNIFAC group-contribution method for short-range physical interactions (Fredenslund et al., 1977) with concentration-independent group-interaction parameters.

For a system with three solvent groups and two ions, there are 20 UNIFAC group-interaction parameters. The group-interaction parameters between solvent groups are the same as those published by Hansen et al. (1991). A few parameters between solvent groups and ions or between ions were taken from literature (Kikic et al., 1991). In this work only 4 group-interaction parameters were fitted. The fitted UNIFAC group-interaction parameters  $a_{ij}$ , the subgroup volume parameters  $R_i$ , and the surface area parameters  $Q_i$  are listed in Table 6.

**3.2.4. LIQUAC Model of Li et al. (1994).** The LIQUAC model for the excess Gibbs energy was presented by Li et al. (1994) to describe the behavior for both single- and mixed-solvent electrolyte systems (Polka et al., 1994). This model consists of three contributions: (1) a Debye-Hückel term to account for long-range electrostatic interactions, (2) the UNIQUAC equation for the description of 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 been published (Li et al., 1994). Therefore, in this work 14 parameters were directly taken from the published parameter matrix. The remaining 8 interaction parameters were fitted to the new experimental data with the help of the Simplex-Nelder-Mead method mentioned above. The interaction parameters with the volume and surface area parameters are given in Table 7. As suggested by Li et al. (1994), the relative volume and surface area parameters for the ions were set arbitrarily to 1.0.

**Table 7. Binary Interaction Parameters, Relative van der Waals Volume Parameters, and Surface Area Parameters for the LIQUAC Model (Li et al., 1994)<sup>a</sup>**

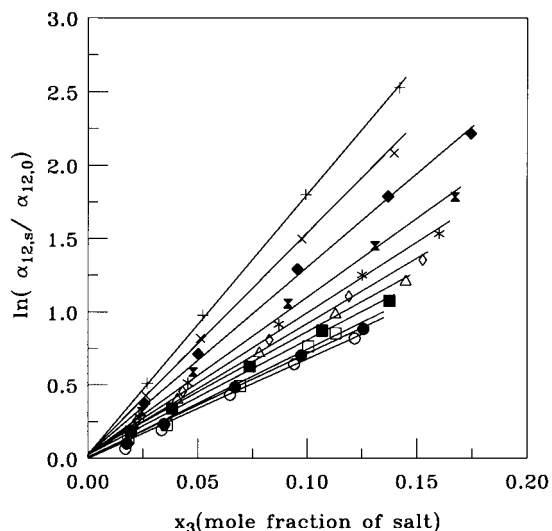
$i$	$j$	$a_{ij}$	$a_{ji}$	$b_{ij}$	$c_{ij}$	$r_i$	$q_i$
CH <sub>3</sub> OH	CH <sub>3</sub> COCH <sub>3</sub>	-54.2	223.8				
CH <sub>3</sub> OH	Li <sup>+</sup>	298.6	-634.80	5.760	1.117		
CH <sub>3</sub> OH	Br <sup>-</sup>	-2135.63(f)	2100.55(f)	-3.1242(f)	-1.1601 (f)		
CH <sub>3</sub> COCH <sub>3</sub>	Li <sup>+</sup>	1555.0	1163.0	3.065	1.256		
CH <sub>3</sub> COCH <sub>3</sub>	Br <sup>-</sup>	839.18(f)	-65.94(f)	1.8119(f)	-1.6488 (f)		
Li <sup>+</sup>	Br <sup>-</sup>	-812.40	-51.08	0.4646	-0.4535		
CH <sub>3</sub> OH						1.431	1.432
CH <sub>3</sub> COCH <sub>3</sub>						2.574	2.336
Li <sup>+</sup>						1.000	1.000
Br <sup>-</sup>						1.000	1.000

<sup>a</sup> Units:  $a_{ij}$  is K;  $b_{ij}$  and  $c_{ij}$  are mol·kg<sup>-1</sup>. <sup>b</sup> (f) means that these interaction parameters have been fitted in this work.

**Table 8. Mean Absolute Deviations of Vapor-Phase Composition for the Different Electrolyte Models**

$t/^\circ\text{C}$	data points	$\Delta y^a$			
		NRTL (Mock, 1986)	UNIQUAC (Sander, 1986)	UNIFAC (Kikic, 1991)	LIQUAC (Li et al., 1994)
39.5	53	0.0085	0.010	0.013	0.006
55.0	53	0.0098	0.011	0.014	0.008
70.6	53	0.0096	0.011	0.013	0.007
	average deviation	0.009	0.011	0.014	0.007

<sup>a</sup>  $\Delta y = (1/N) \sum_i^N |y_{i,1}(\text{exp}) - y_{i,1}(\text{calc})|$  where  $N$  represents the number of data points.



**Figure 2.** Salt effects of lithium bromide on the acetone (1) + methanol (2) system at different liquid-phase mole fractions on a salt-free basis at 39.5 °C: ○,  $x_1 = 0.1000$ ; ●,  $x_1 = 0.1501$ ; □,  $x_1 = 0.1998$ ; ■,  $x_1 = 0.2999$ ; △,  $x_1 = 0.3981$ ; ◇,  $x_1 = 0.5000$ ; \*,  $x_1 = 0.5999$ ; x,  $x_1 = 0.6998$ ; ◆,  $x_1 = 0.7994$ ; ×,  $x_1 = 0.8481$ ; +,  $x_1 = 0.8900$ .

#### 4. Discussion

The new sets of interaction parameters fitted for each model are listed in Tables 4–7 together with the parameters taken from literature directly. The mean absolute deviations in vapor-phase mole fraction for the four models are listed in Table 8. It can be seen that all models represent the experimental data with very good accuracy, but superior correlation results were obtained using the LIQUAC model (Li et al., 1994). Moreover, it should be mentioned that the temperature-independent parameters  $\Delta g_{ij}$  instead of the interaction parameters  $\tau_{ij}$  (see eq 1) were fitted for the electrolyte NRTL model of Mock et al. (1986) in this work.

The salt effect on the VLE behavior can be judged using the equation (Johnson and Furter, 1960) for the ratio of relative volatilities  $\alpha_{12} = (y_1/x_1)/(y_2/x_2)$

$$\ln(\alpha_{12,s}/\alpha_{12,0}) = kx_3 \quad (6)$$

where the subscripts s and 0 denote the salt-containing and salt-free systems, respectively.  $x_3$  is the mole fraction of the salt. The coefficient  $k$  depends on the system and the solvent composition. The value and sign of  $k$  indicate the affinity of the salt for particular solvents. For example, if  $k > 0$  in eq 6, solvent 1 (acetone in this work) will be salted-

out because of less affinity to the salt. If  $k < 0$ , solvent 1 will be salted-in because of higher affinity to the salt.

If the phase-equilibrium condition eq 3 is used, eq 6 can be written as

$$\ln \frac{\alpha_{12,s}}{\alpha_{12,0}} = \ln \frac{(\gamma_1/\gamma_2)_s}{(\gamma_1/\gamma_2)_0} = kx_3 \quad (7)$$

where the activity coefficients of the solvents in the salt-free system can be calculated using the UNIQUAC model with the interaction parameters taken from Gmehling et al. (1977). The activity coefficients of solvents for the salt-containing systems in Tables 1–3 were calculated using the LIQUAC model using the parameters given in Table 7. As a typical example, Figure 2 shows  $\ln(\alpha_{12,s}/\alpha_{12,0})$  as a function of  $x_3$  at 39.5 °C. 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.

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