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Measurement and Correlation of Isothermal Vapor−Liquid Equilibrium Data for the System Tetrahydrofuran + Methanol + Lithium Bromide

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The isothermal vapor−liquid equilibrium of the system tetrahydrofuran (1) + methanol (2) + lithium bromide (3) at three temperatures (30.2, 50.2, and 65.0) °C was investigated at constant salt molalities (0.00, 0.25, 0.50, 1.00, and 2.00 mol·kg^{-1}) with the help of the headspace gas chromatography (HSGC) technique. The experimental data were fitted using the extended UNIQUAC model, the electrolyte UNIFAC group-contribution model, and the LIQUAC model. The vapor−liquid equilibrium of the system tetrahydrofuran + methanol was considerably altered by the presence of salt; the azeotropic point was shifted to higher THF concentrations.

Introduction

The synthesis and design of industrial separation processes such as salt distillation,[1] crystallization processes (e.g., extractive crystallization of salts[2]), and the simulation of unit operations for electrolyte systems all require an accurate description of the phase equilibrium behavior of electrolyte systems. This has been the incentive to develop a database and thermodynamic models suitable for the correlation and prediction of phase equilibria of electrolyte systems.

The addition of a salt to a 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 concerning salt effects on phase equilibrium behavior have been stored in the Dortmund Data Bank. While much data exist for systems with water or alcohols, 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. No such difficulty exists for isothermal data, because we can neglect the pressure dependence of the activity coefficients at low or moderate pressures. The aim of this work is to measure the effect of lithium bromide on the vapor−liquid equilibrium behavior of the tetrahydrofuran + methanol system at three temperatures (30.2, 50.2, and 65.0 °C) and different constant salt concentrations (0.00, 0.25, 0.50, 1.00, and 2.00 mol·kg^{-1}), for which no data were found in the literature. The addition of lithium bromide to this solvent mixture increases the concentration of tetrahydrofuran 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 three models based on the local composition or group-contribution concept: the modified UNIQUAC model of Sander et al.[3] the modified UNIFAC model of Kikic et al.,[4] and the LIQUAC model of Li et al.[5]

Experimental Section

Materials. Tetrahydrofuran (99.5 mass %, Acros) and methanol (99.8+ mass %, Baker, HPLC Reagent) were dried with the help of molecular sieves. The purity was checked by gas chromatography. The purity was greater than 99.5 mass % (tetrahydrofuran) and 99.7 mass % (methanol). To remove the remaining moisture from lithium bromide, the salt (99.0+ mass %, Aldrich) was dried at 120 °C in a vacuum oven until a constant mass was reached.

Apparatus. All liquid mixtures consisting of tetrahydrofuran, methanol, and lithium bromide were prepared gravimetrically by using a Sartorius analytical balance with an accuracy of ±0.1 mg. For each experimental point, approximately 8 cm^3 of sample solution was put into the 22 cm^3 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 introduced into a 30-position rotating carrousel which was kept at a specified temperature 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 measurement of the vapor-phase composition, an aliquot of the vapor in the vial headspace was automatically transferred with a Perkin-Elmer F45 GLC headspace autosampler into a gas chromatograph (F22) where the analysis took place with the help of a thermal conductivity detector and an integrator [Hewlett-Packard 3390A]. For all separations, a 1.5 m stainless steel column filled with Porapalo Q 80−100 μm was used. The optimum operating conditions were as follows: injection temperature, 180 °C;

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Table 1. Vapor−Liquid Equilibrium Data for the System Tetrahydrofuran (1) + Methanol (2) + Lithium Bromide (3) at 30.2 °C

$x_1'^{a}$	y_1	γ_1^{b}	γ_2^{b}	x_1'	y_1	γ_1	γ_2
$m = 0.00$ mol·kg^{-1}				$m = 0.25$ mol·kg^{-1}			
0.0509	0.1099	2.0475	1.0017	0.0509	0.1207	2.2185	0.9949
0.1008	0.1991	1.9227	1.0068	0.1008	0.2156	2.1141	0.9949
0.1500	0.2725	1.8074	1.0157	0.1500	0.2922	2.0019	0.9977
0.1737	0.2971	1.7579	1.0216	0.1737	0.3216	1.9484	1.0002
0.2997	0.4113	1.5184	1.0686	0.2997	0.4508	1.6901	1.0276
0.3985	0.4880	1.3726	1.1298	0.3985	0.5263	1.5246	1.0669
0.4960	0.5490	1.2541	1.2132	0.4960	0.5892	1.3915	1.1233
0.6001	0.6104	1.1578	1.3376	0.6001	0.6549	1.2787	1.2057
0.6986	0.6699	1.0887	1.5003	0.6986	0.7253	1.1959	1.3085
0.7994	0.7451	1.0392	1.7234	0.7994	0.7992	1.1323	1.4429
0.8492	0.7881	1.0225	1.8631	0.8492	0.8487	1.1080	1.5215
0.9014	0.9395	1.0097	2.0315	0.9014	0.8941	1.0873	1.6128
$m = 0.50$ mol·kg^{-1}				$m = 1.00$ mol·kg^{-1}			
0.0509	0.1283	2.3291	0.9855	0.0509	0.1407	2.4604	0.9591
0.1008	0.2273	2.2551	0.9816	0.1008	0.2488	2.4536	0.9488
0.1500	0.3040	2.1523	0.9799	0.1500	0.3387	2.3777	0.9397
0.1737	0.3354	2.1000	0.9800	0.1737	0.3728	2.3313	0.9359
0.2997	0.4679	1.8337	0.9921	0.2997	0.5175	2.0630	0.9242
0.3985	0.5473	1.6563	1.0158	0.3985	0.6057	1.8696	0.9249
0.4960	0.6185	1.5113	1.0523	0.4960	0.6827	1.7058	0.9339
0.6001	0.6882	1.3859	1.1067	0.6001	0.7538	1.5602	0.9524
0.6986	0.7602	1.2918	1.1740	0.6986	0.8233	1.4474	0.9781
0.7994	0.8307	1.2167	1.2606	0.7994	0.8947	1.3538	1.0128
0.8492	0.8823	1.1867	1.3104	0.8492	0.9303	1.3149	1.0330
0.9014	0.9200	1.1598	1.3678	0.9014	0.9554	1.2788	1.0565
$m = 2.00$ mol·kg^{-1}							
0.0509	0.1623	2.4943	0.8831	0.4960	0.7820	1.9244	0.7472
0.1008	0.2874	2.6072	0.8633	0.6001	0.8483	1.7548	0.7319
0.1500	0.3873	2.5905	0.8436	0.6986	0.9013	1.6197	0.7222
0.1737	0.4268	2.5603	0.8345	0.7994	0.9560	1.5047	0.7165
0.2997	0.6077	2.3153	0.7923	0.8492	0.9680	1.4558	0.7151
0.3985	0.7019	2.1088	0.7667	0.9014	0.9795	1.4097	0.7148

[a] Liquid-phase mole fraction on a salt-free basis. [b] Activity coefficients calculated with the LIQUAC model using the parameters given in Table 6.

Table 2. Vapor−Liquid Equilibrium Data for the System Tetrahydrofuran (1) + Methanol (2) + Lithium Bromide (3) at 50.2 °C[a]

x_1'	y_1	γ_1	γ_2	x_1'	y_1	γ_1	γ_2
$m = 0.00$ mol·kg^{-1}				$m = 0.25$ mol·kg^{-1}			
0.0509	0.0989	2.0016	1.0018	0.0509	0.1016	2.1754	0.9954
0.1008	0.1756	1.8779	1.0069	0.1008	0.1851	2.0653	0.9957
0.1500	0.2355	1.7647	1.0159	0.1500	0.2505	1.9525	0.9989
0.1737	0.2647	1.7143	1.0218	0.1737	0.2787	1.8996	1.0016
0.2997	0.3815	1.4853	1.0289	0.2997	0.4069	1.6485	1.0297
0.3985	0.4484	1.3482	1.0674	0.3985	0.4767	1.4903	1.0691
0.4960	0.5142	1.2353	1.2074	0.4960	0.5437	1.3646	1.1246
0.6001	0.5784	1.1447	1.3240	0.6001	0.6192	1.2590	1.2044
0.6986	0.6504	1.0808	1.4705	0.6986	0.6980	1.1824	1.3022
0.7994	0.7331	1.0355	1.6745	0.7994	0.7860	1.1242	1.4279
0.8492	0.7830	1.0200	1.7980	0.8492	0.8295	1.1022	1.5002
0.9014	0.8391	1.0069	1.9438	0.9014	0.8838	1.0835	1.5832
$m = 0.50$ mol·kg^{-1}				$m = 1.00$ mol·kg^{-1}			
0.0509	0.1122	2.2921	0.9870	0.0509	0.1203	2.4410	0.9636
0.1008	0.1983	2.2052	0.9837	0.1008	0.2140	2.4076	0.9544
0.1500	0.2642	2.0989	0.9827	0.1500	0.2864	2.3219	0.9465
0.1737	0.2928	2.0463	0.9832	0.1737	0.3180	2.2735	0.9434
0.2997	0.4236	1.7857	0.9972	0.2997	0.4668	2.0073	0.9354
0.3985	0.5047	1.6158	1.0223	0.3985	0.5569	1.8213	0.9392
0.4960	0.5832	1.4786	1.0597	0.4960	0.6339	1.6661	0.9513
0.6001	0.6556	1.3613	1.1144	0.6001	0.7220	1.5299	0.9731
0.6986	0.7342	1.2743	1.1810	0.6986	0.8095	1.4255	1.0018
0.7994	0.8270	1.2056	1.2650	0.7994	0.8798	1.3399	1.0392
0.8492	0.8653	1.1785	1.3125	0.8492	0.9139	1.3047	1.0605
0.9014	0.9085	1.1545	1.3666	0.9014	0.9409	1.2723	1.0849
$m = 2.00$ mol·kg^{-1}							
0.0509	0.1399	2.5178	0.8945	0.4960	0.7450	1.8833	0.7764
0.1008	0.2503	2.5839	0.8763	0.6001	0.8292	1.7237	0.7655
0.1500	0.3430	2.5464	0.8586	0.6986	0.8894	1.5979	0.7599
0.1737	0.3807	2.5108	0.8504	0.7994	0.9328	1.4917	0.7584
0.2997	0.5558	2.2595	0.8134	0.8492	0.9514	1.4469	0.7591
0.3985	0.6541	2.0590	0.7919	0.9014	0.9679	1.4048	0.7608

[a] See footnotes *a* and *b* in Table 1.

oven temperature, 130 °C; detector temperature, 130 °C; carrier gas, helium (purity 99.9%) at a flow rate of 0.40 cm^3·s^{-1}. Details of the experimental setup have been described previously.[6]

Calibration was necessary before the peak areas could be used to determine vapor-phase compositions. To obtain the calibration curve, various tetrahydrofuran + methanol mixtures were prepared by mass and injected in triplicate for each sample. The mole fractions and average area fractions were correlated using a fifth-order polynomial (mean deviation: 0.15% for mole fraction). The vapor-phase composition was determined with the help of the calibration curve. The average uncertainty in the measurement of the mole fraction is ±0.0018, which was obtained by comparing the known composition of the made-up liquid samples with the composition calculated from the calibration curve.

Results

Experimental Data. Isothermal vapor−liquid equilibrium data for the system tetrahydrofuran (1) + methanol (2) + lithium bromide (3) have been measured at three temperatures (30.2, 50.2, and 65.0 °C) and various salt concentrations (m = 0.00, 0.25, 0.50, 1.0, and 2.0 mol·kg^{-1}). The experimental results are given in Tables 1−3.

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

Extended UNIQUAC Model of Sander et al.[3] Sander et al. 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,

$$a_{im} = a_{im}{}^{*} + \theta_i \sum_{j \neq i} \delta_{ij,m} \theta_j \tag{1}$$

$$a_{mi} = a_{mi}{}^{*} + \theta_i \sum_{j \neq i} \delta_{ij,m} \theta_j \tag{2}$$

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

For a system with two solvents and one salt, 14 parameters are needed: two solvent−solvent, two ion−ion, eight ion−solvent, and two salt−solvent interaction parameters. The two binary solvent−solvent interaction parameters have been obtained directly from Gmehling et al.[7] For the tetrahydrofuran + methanol + lithium bromide system, eight interaction parameters were taken from the literature.[3,8] The remaining model parameters were determined by minimization of the following objective function F using the Simplex−Nelder−Mead method,[9]

$$F(a_{i,m}, a_{m,i}) = \sum_{nt} \sum_{np} [y_{i,1}(\text{exp}) - y_{i,1}(\text{calc})]^2 = \min \tag{3}$$

where y represents the vapor-phase mole fraction. nt and

Table 3. Vapor−Liquid Equilibrium Data for the System Tetrahydrofuran (1) + Methanol (2) + Lithium Bromide (3) at 65.0 °C[a]

x_1'	y_1	γ_1	γ_2	x_1'	y_1	γ_1	γ_2
$m = 0.00$ mol·kg^{-1}				$m = 0.25$ mol·kg^{-1}			
0.0509	0.0858	1.9678	1.0016	0.0509	0.0909	2.1430	0.9957
0.1008	0.1498	1.8454	1.0069	0.1008	0.1652	2.0302	0.9962
0.1500	0.2068	1.7342	1.0159	0.1500	0.2247	1.9178	0.9996
0.1737	0.2291	1.6848	1.0212	0.1737	0.2507	1.8656	1.0024
0.2997	0.3427	1.4625	1.0676	0.2997	0.3732	1.6204	1.0308
0.3985	0.4148	1.3271	1.1241	0.3985	0.4489	1.4677	1.0699
0.4960	0.4796	1.2221	1.2052	0.4960	0.5182	1.3471	1.1244
0.6001	0.5441	1.1361	1.3139	0.6001	0.5998	1.2465	1.2019
0.6986	0.6141	1.0799	1.4517	0.6986	0.6730	1.1740	1.2960
0.7994	0.7039	1.0331	1.6411	0.7994	0.7704	1.1193	1.4153
0.8492	0.7574	1.0186	1.7542	0.8492	0.8188	1.0987	1.4832
0.9014	0.8162	1.0081	1.8840	0.9014	0.8702	1.0814	1.5605
$m = 0.50$ mol·kg^{-1}				$m = 1.00$ mol·kg^{-1}			
0.0509	0.0987	2.2634	0.9879	0.0509	0.1082	2.4231	0.9662
0.1008	0.1760	2.1694	0.9849	0.1008	0.1925	2.3741	0.9576
0.1500	0.2405	2.0616	0.9844	0.1500	0.2700	2.2830	0.9505
0.1737	0.2702	2.0092	0.9851	0.1737	0.2979	2.2336	0.9478
0.2997	0.3877	1.7536	1.0001	0.2997	0.4386	1.9701	0.9419
0.3985	0.4725	1.5893	1.0258	0.3985	0.5374	1.7897	0.9475
0.4960	0.5489	1.4576	1.0635	0.4960	0.6153	1.6406	0.9613
0.6001	0.6233	1.3459	1.1178	0.6001	0.7066	1.5108	0.9847
0.6986	0.7081	1.2635	1.1831	0.6986	0.7910	1.4121	1.0147
0.7994	0.8036	1.1991	1.2645	0.7994	0.8706	1.3317	1.0530
0.8492	0.8533	1.1738	1.3101	0.8492	0.9039	1.2989	1.0745
0.9014	0.8936	1.1515	1.3614	0.9014	0.9346	1.2689	1.0990
$m = 2.00$ mol·kg^{-1}							
0.0509	0.1238	2.5272	0.9013	0.4960	0.7135	1.8565	0.7942
0.1008	0.2269	2.5646	0.8841	0.6001	0.7888	1.7039	0.7860
0.1500	0.3146	2.5146	0.8675	0.6986	0.8565	1.5844	0.7828
0.1737	0.3536	2.4758	0.8599	0.7994	0.9175	1.4843	0.7837
0.2997	0.5194	2.2218	0.8261	0.8492	0.9414	1.4422	0.7856
0.3985	0.6252	2.0260	0.8072	0.9014	0.9615	1.4030	0.7886

[a] See footnotes *a* and *b* in Table 1.

np are the number of data sets and the number of data points for each data set. The subscripts, exp and calc, denote experimental data and calculated values. The vapor-phase mole fraction y_i and total pressure P are calculated for a given liquid-phase composition through solving the following equilibrium condition iteratively:

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

where

$$P = x_1 \gamma_1 P_1^s \Phi_1 + x_2 \gamma_2 P_2^s \Phi_2 \tag{5}$$

$$\Phi_i = \varphi_i^s (Poy)_i / \varphi_i^v \tag{6}$$

and x_i is the liquid-phase mole fraction of solvent i based on the assumption of total dissociation of the salt. The saturation vapor pressure of pure solvent i, P_i^s, at the system temperature was calculated by the Antoine equation using constants from the literature (Gmehling et al.[7]). In eq 6, ϕ_i^v is the fugacity coefficient of solvent i in the vapor phase, ϕ_i^s is the fugacity coefficient of pure solvent i at the system temperature, and $(Poy)_i$ is the Poynting term. ϕ_i^s is approximately equal to ϕ_i^v, and Poy_i is approximately equal to one at atmospheric pressure, so Φ_i is equal to one, respectively. The activity coefficient of the solvent γ_i was calculated by eq 41 of Sander et al.[3] All the required parameters are given in Table 4.

Electrolyte UNIFAC Group-Contribution Model of Kikic et al.[4] The first electrolyte model based on the group-contribution method was published by Kikic et al.[4] This model combines a modified Debye−Hückel term according to the McMillan−Mayer solution theory as described by Cardoso and O'Connell[10] with the original UNIFAC group-contribution method for short-range physical interactions (Fredenslund et al.[11]) with concentration independent group interaction parameters.

Table 4. 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 (Sander et al.[3])[a]

	CH_3OH	THF	Li^+	Br^-
		a_{ij}*		
CH_3OH	0.0	−77.12	−803.6	−233.5
THF	316.90	0.0	385.19(f)	1340.05(f)
Li^+	-635.5	454.56(f)	0.0	281.10
Br^-	1034.0	-38.94(f)	852.23	0.0
		r_i and q_i		
r_i	1.4311	2.9415	1.000	1.2331
q_i	1.4322	2.7200	1.000	1.1510
		$\delta ij,m$		
Li^+-Br^-	-312.56	-362.35(f)		

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

For a system with three solvent groups and two ions, there are 20 UNIFAC group interaction parameters. The six group interaction parameters between solvent groups are the same as those published by Hansen et al.[12] Ten parameters between solvent group and ion or between ions were taken from the literature.[4] In this work only four 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 5.

LIQUAC Model of Li et al.[5] The LIQUAC model for the excess Gibbs energy was presented by Li et al.[5] to describe the behavior for both single and mixed solvent electrolyte systems.[13] 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. Therefore, in this work 18 parameters were directly taken from the literature[5,8]. The remaining 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 6. As suggested by Li et al.,[5] the volume and surface area parameters for the ions were set arbitrarily to 1.0.

Discussion

The experimental VLE data for the tetrahydrofuran + methanol system without salt at 30.2 °C are presented in Figure 1 as an $x-y$ diagram. The main objective for the study of the VLE for this system without salt was to validate the HSGC technique to study the VLE of binary mixtures before studying the effect of salt on the VLE of binary mixtures. This was done by comparing the results obtained using this technique with published results for the given system under the same conditions. Comparison of the results obtained with those calculated by the

Table 5. 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.[4])[a]

	a_{ij}				
	CH_2	CH_3OH	CH_2O(THF)	Li^+	Br^-
CH_2	0.0	697.2	476.4	6434.4	−673.87
CH_3OH	16.51	0.0	−128.6	−71.347	−1295.35
CH_2O(THF)	83.36	238.4	0.0	−686.425(f)	−69.449(f)
Li^+	4651.5	−798.23	1006.84(f)	0.0	23277.0
Br^-	3106.4	15164.3	596.20(f)	24.1	0.0

	R_i and Q_i				
	CH_2	CH_3OH	CH_2O(THF)	Li^+	Br^-
R_i	0.6744	1.4311	0.9183	1.0	1.2331
Q_i	0.5400	1.4320	1.1000	1.0	1.1510

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

Table 6. Binary Interaction Parameters, Relative van der Waals Volume Parameters, and Surface Area Parameters for the LIQUAC Model (Li et al.[5])[a]

i	j	a_{ij}	a_{ji}	b_{ij}	c_{ij}	r_i	q_i
CH_3OH	THF	−77.12	316.9				
CH_3OH	Li^+	298.6	−634.80	5.760	1.117		
CH_3OH	Br^-	−92.80	−62.15	−8.2110	−1.2630		
THF	Li^+	−355.01	957.98	−0.0148	2.8380		
THF	Br^-	934.79(f)	105.92(f)	−5.3795(f)	−2.6303(f)		
Li^+	Br^-	−812.40	−51.08	0.4646	−0.4535		
CH_3OH						1.431	1.432
THF						2.942	2.720
Li^+						1.000	1.000
Br^-						1.000	1.000

[a] Units: a_{ij} is in kelvin. b_{ij} and c_{ij} are in moles per kilogram. (f) means that these interaction parameters have been fitted in this work.

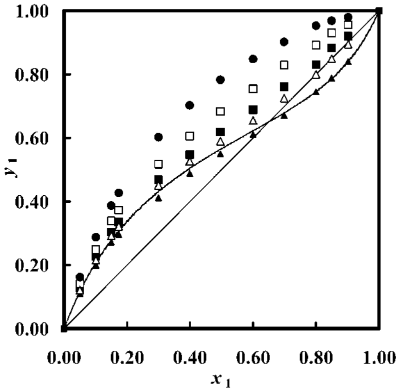

Figure 1. $x-y$ vapor−liquid equilibrium diagram for the system tetrahydrofuran (1) + methanol (2) + LiBr (3) at 30.2 °C: ▲, m = 0.0 mol·kg^{-1}; △, m = 0.25 mol·kg^{-1}; ■, m = 0.5 mol·kg^{-1}; □, m = 1.0 mol·kg^{-1}; ●, m = 2.0 mol·kg^{-1}; - - - (m = 0.0 mol·kg^{-1}), calculated by the UNIQUAC model (parameters taken from ref 7).

Table 7. Mean Absolute Deviations of Vapor-Phase Composition for the Different Electrolyte Models

		Δy^a		
t/°C	no. of data points	UNIQUAC[3]	UNIFAC[4]	LIQUAC[5]
30.2	60	0.0053	0.0064	0.0052
50.2	60	0.0076	0.0089	0.0060
65.0	60	0.0107	0.0101	0.0059
	avg dev	0.0070	0.0085	0.0057

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

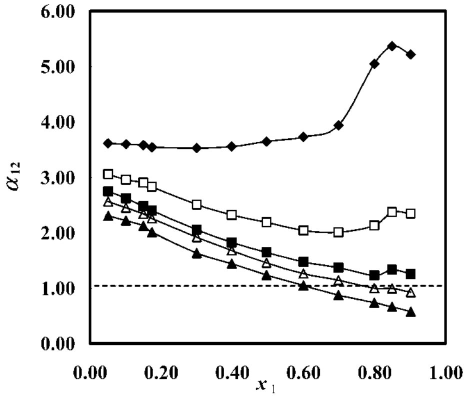

Figure 2. Relative volatility of the tetrahydrofuran (1) + methanol (2) system at different concentrations of lithium bromide at 30.2 °C: ▲, m = 0.00 mol·kg^{-1}; △, m = 0.25 mol·kg^{-1}; ■, m = 0.50 mol·kg^{-1}; □, m = 1.00 mol·kg^{-1}; ◆, m = 2.00 mol·kg^{-1}.

UNIQUAC model (parameters taken from ref 7), as shown in Figure 1, showed good agreement. This proved the validation of using the HSGC technique to study the effect of salt on the VLE of binary mixtures.

The experimental VLE data for the tetrahydrofuran + methanol system in the presence of lithium bromide at 30.2 °C are plotted in Figure 1. From this figure, it can be seen that the addition of lithium bromide to the system tetrahydrofuran + methanol increases the amount of tetrahydrofuran in the vapor phase and shifts the azeotropic point to the tetrahydrofuran-rich region, whereby the azeotropic point does not occur at high concentrations of salt.

The interaction parameters fitted for each model are listed in Tables 4−6 together with the parameters taken from the literature. The mean absolute deviations in vapor-phase mole fraction for the three models are listed in Table 7. 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.

The relative volatility, defined as,

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \tag{7}$$

was calculated for the tetrahydrofuran (1) + methanol (2) system with salt and without salt to identify the presence of any azeotropic points, where the relative volatility equals unity. The effects of lithium bromide on the relative volatility of the tetrahydrofuran (1) + methanol (2) system at different concentrations of lithium bromide at 30.2 °C are shown in Figure 2. Figure 2 shows that above 0.5 mol·kg^{-1} azeotropic behavior is eliminated.

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