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

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Isothermal vapor−liquid equilibrium data for the system methanol + water + ammonium bromide at four salt molalities {(0.500, 1.000, 2.000, and 4.000) mol·kg^{-1}} have been measured with the help of headspace gas chromatography at (298.15 and 313.15) K. The experimental data were correlated using the electrolyte nonrandom two-liquid model and the extended universal quasichemical model.

Introduction

Phase equilibria for mixed solvent + electrolytes mixtures are of considerable importance in a variety of fields such as extractive distillation of salt-containing liquids, extractive crystallization, and liquid−liquid extraction for mixtures including salts.[1−3] No data about the ternary system methanol + water + ammonium bromide were found in the literature.[3−5]

The aim of this work is to determine the effect of ammonium bromide on the vapor−liquid equilibrium of the methanol + water system at two temperatures {(298.15 and 313.15) K} and different constant salt concentrations {(0.500, 1.000, 2.000, and 4.000) mol·kg^{-1}} with the help of headspace gas chromatography.

Several correlative and predictive models based on the local composition or the group contribution concept have been proposed to calculate the VLE of systems formed by mixed solvents and electrolytes. The experimental data presented in this work were correlated using the electrolyte nonrandom two-liquid (NRTL) model of Mock et al.[6] and the extended universal quasichemical (UNIQUAC) model of Sander et al.[7]

Experimental Section

Materials. Methanol (mass fraction 99.9 %) from Merck was stored above the molecular sieves 3A. The mass fraction of water content in the methanol was determined by a GC method and did not exceed 0.02 %. Double distilled water was used. Ammonium bromide (NH_4Br) was obtained from Fluka (mass fraction > 99.5 %).

Procedure. Mixtures consisting of methanol, water, and ammonium bromide were prepared gravimetrically with an analytical balance with an accuracy of ± 0.1 mg. For each experiment, about 8 cm^3 of sample was charged into the 30 cm^3 heated sample vial. After the vial was closed by means of a special lid equipped with a washer, it was brought to the required temperature in a thermostatic cell that was controlled to within ± 0.05 K of the desired temperature. The mixture was continuously agitated for 10 h at the target temperature (298.15 and 313.15) K. The uncertainty of liquid composition was less than 1 %.

Analysis Method. Water and methanol mole fractions (on salt-free basis) in the vapor (y_i) phase were analyzed by headspace gas chromatography method proposed by Takamatsu and Ohe.[8] To analyze the vapor phase, a gastight syringe (1 mL) was used. The sampling volume of headspace gas was about 0.2 mL. The syringe was held at the same temperature as the vial, which prevented partial condensation in the syringe and maintained an equilibrium in the vial. A gas chromatograph (Chrom-5, Laboratorni Pristroje, Czech Republic) was used with a thermal conductivity detector (electric current was 80 mA) and 1.5 m glass column (Separon CHN 0.125−0.200 mm) and an integrator. The injector and chamber temperatures were 220 °C and 105 °C, respectively. The carrier gas was helium (purity = 99.9 %) flowing at 0.5 cm^3·s^{-1}. Uncertainty of the measured temperature was 0.1 K.

Calibrations were necessary before the peak areas could be used to determine composition of the vapor phase. The gas chromatograph was calibrated using a mixture of methanol and water that was prepared gravimetrically by using an analytical balance with an accuracy of ± 0.1 mg. Because of negligible amounts in the vapor phase (small vapor volume, moderate pressure), it was reasonable to assume that the liquid phase composition is the same as the feed composition. To prepare the calibration samples for the vapor phase, various methanol and water mixtures were completely evaporated in a (1000 ± 0.1 cm^3) vessel and injected. To obtain the calibration equation, the required mass fractions and area fractions were correlated with a third-order polynomial by a least-squares method (mean deviation = 0.1 %). The average uncertainty in the measurement of the mole fraction is ± 0.005, which was obtained by comparing the known composition of the prepared liquid samples with the composition calculated from the calibration equation. The experimental setup is described in detail in our previously work.[9]

Results and Discussion

Vapor−liquid equilibrium data of methanol + water without the salt system are presented in Table 1. This system was studied earlier.[10−12] Our measured data were compared with published isothermal data at 298.15 K for the same system.[12] The comparison is shown in Figure 1. Good agreement was observed. In the system containing

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Table 1. Experimental Vapor−Liquid Equilibrium Data for the System Methanol (1) + Water (2) + Ammonium Bromide (3), Liquid Mole Fraction of Methanol on a Salt-Free Basis (x'_1), and Vapor Mole Fraction of Methanol (y_1)

x_1'	y_1
$m_3 = 0.000$ mol·kg^{-1}; $T = 298.15$ K	
0.150	0.598
0.301	0.732
0.500	0.820
0.701	0.912
0.901	0.974
$m_3 = 0.500$ mol·kg^{-1}; $T = 298.15$ K	
0.150	0.609
0.301	0.738
0.500	0.834
0.701	0.918
0.901	0.976
$m_3 = 1.000$ mol·kg^{-1}; $T = 298.15$ K	
0.150	0.618
0.301	0.746
0.500	0.862
0.701	0.929
0.901	0.978
$m_3 = 2.000$ mol·kg^{-1}; $T = 298.15$ K	
0.150	0.633
0.301	0.772
0.500	0.871
0.701	0.935
0.901	0.983
$m_3 = 4.000$ mol·kg^{-1}; $T = 298.15$ K	
0.150	0.682
0.301	0.801
0.500	0.887
0.701	0.950
0.901	0.991
$m_3 = 0.000$ mol·kg^{-1}; $T = 313.15$ K	
0.150	0.573
0.301	0.714
0.500	0.828
0.701	0.903
0.901	0.970
$m_3 = 0.500$ mol·kg^{-1}; $T = 313.15$ K	
0.150	0.588
0.301	0.727
0.500	0.841
0.701	0.917
0.901	0.979
$m_3 = 1.000$ mol·kg^{-1}; $T = 313.15$ K	
0.150	0.593
0.301	0.734
0.500	0.848
0.701	0.921
0.901	0.982
$m_3 = 2.000$ mol·kg^{-1}; $T = 313.15$ K	
0.150	0.603
0.301	0.750
0.500	0.855
0.701	0.929
0.901	0.985
$m_3 = 4.000$ mol·kg^{-1}; $T = 313.15$ K	
0.150	0.622
0.301	0.781
0.500	0.888
0.701	0.946
0.901	0.998

salt, the measurement results are presented in Table 1 and Figure 1.

Calculation of VLE for the Studied System. To describe the observed VLE behavior, the experimental data are correlated using two electrolyte models: an electrolyte NRTL model of Mock et al.[6] and an extended UNIQUAC model of Sander et al.[7] The electrolyte NRTL model of Mock et al.[6] and the extended UNIQUAC model of Nicolaisen et al.[13] and Thomsen et al.[14] were earlier used to calculate (for correlation and prediction) the vapor−liquid, liquid−liquid, and solid−liquid equilibria data of ternary water + solvent (or solvent + solvent) + inorganic ammonium salt systems.[6,15−18]

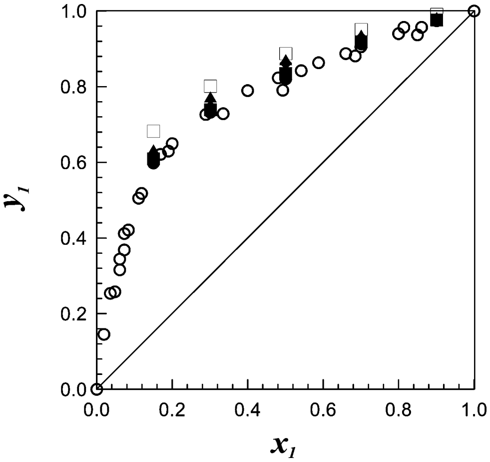

Figure 1. Vapor mole fraction (y_1) of methanol in methanol (1) + water (2) + ammonium bromide (3) system at 298.15 K: ●, no salt (this work); ○, no salt (Yang and Lee[12] collected data); ■, m = 0.500 mol·kg^{-1}; ◆, m = 1.000 mol·kg^{-1}; ▲, m = 2.000 mol·kg^{-1}; □, m = 4.000 mol·kg^{-1}. x_1 is on a salt-free basis.

(a) Electrolyte NRTL Model of Mock et al.[6] 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.[6] The model parameters are specific for the solvent + solvent and solvent + salt pairs. For the system methanol + water + ammonium bromide, six energy parameters (Δg_{ij}, Δg_{ji}) and three nonrandomness factors (α_{ij}) are required. All model parameters for this system were directly taken from published data.[6,17,19]

The vapor phase composition was calculated by solving iteratively the equilibrium condition:

$$y_iP = x_i\gamma_iP_i^{\mathrm{s}}\Phi_i \tag{1}$$

where

$$P = x_1\gamma_1P_1^{\mathrm{s}}\Phi_1 + x_2\gamma_2P_2^{\mathrm{s}}\Phi_2 \tag{2}$$

$$\Phi_i = \varphi_i^{\mathrm{s}}F_i/\varphi_i^{\mathrm{v}} \tag{3}$$

The saturation vapor pressure of pure solvent i (P_i^{s}), at system temperature was calculated with the published Antoine constants.[19] 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 saturation pressure, and F_i is the Poynting factor. x_i is the liquid-phase mole fraction of solvent i based on the assumption of total dissociation of salt. φ_i^{s} is approximately equal to φ_i^{v}, and F_i is approximately equal to one at atmosphere pressure and, so Φ_i is equal to 1.

The model binary energy parameters (τ_{ij}, G_{ij}) were calculated as described by Mock et al.:[6]

$$\tau_{ij} = \Delta g_{ij}/RT \tag{4}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{5}$$

The NRTL energy parameters and nonrandomness factors are given in Table 2.

Table 2. Energy Parameters (Δg_{ij} and Δg_{ji}) and Nonrandomness Factors (α_{ij}) for the Electrolyte NRTL Model[a]

i	j	α_{ij}	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}
methanol	water	0.2994	−1063.76	3541.41
methanol	NH_4Br	1.0	6543.21	−2624.37
water	NH_4Br	1.0	6541.12	−762.29

[a] Ref 6.

Table 3. UNIQUAC Reference Interaction Parameters (a_{ij}*), Concentration-Dependent Parameters ($\delta_{ij,m}$), Volume Parameters (r_i), and Surface Area Parameters (q_i) for the Extended UNIQUAC Model[a]

	methanol	water	NH_4^+	Br^-
		a_{ij}*/K		
methanol	0.0	−164.8	620.3(f)[b]	−326.0
water	256.6	0.0	173.0(f)	9.4
NH_4^+	875.8(f)	−278.4(f)	0.0	345.1(f)
Br^-	−108.8	−168.0	389.0(f)	0.0
		r_i and q_i		
r_i	1.4311	0.92	0.476	1.2331
q_i	1.4322	1.40	0.610	1.1510
		$\delta_{ij,m}$		
$NH_4^+-Br^-$	6874.0(f)	2561.1(f)		

[a] Ref 7. [b] (f) means that these interaction parameters have been fitted in this work.

(b) Extended UNIQUAC Model of Sander et al.[7] Sander et al.[7] presented a model for the calculation of salt effects on the vapor−liquid equilibrium. The model combines a Debye−Huckel term with a modified UNIQUAC term. To ensure a rigorous expression for a Debye−Huckel term, Macedo et al.[20] modified the Debye−Huckel term of Sander's model according to the McMillan−Mayer solution theory.[21]

The interaction parameters between an ion i and a solvent m (a_{im}, and a_{mi}) are considered to be dependent on concentration in the same way as proposed by Sander et al.:[7]

$$a_{im} = a^*_{im} + \theta_i \sum_{j\neq i} \delta_{ij,m}\theta_j \tag{6}$$

$$a_{mi} = a^*_{im} + \theta_i \sum_{j\neq i} \delta_{ij,m}\theta_j \tag{7}$$

where a_{im}* and a_{mi}* represent reference interaction parameters, $\delta_{ij,m}$ is a parameter, the summation is over all ionic species except i, and θ_i represents the surface fraction of ion i. The volume and surface area parameters, r_i and q_i, are given in Table 3.

For this system, 14 energy parameters are needed: 2 water + methanol interaction parameters, 2 ion + ion interaction parameters, 4 ion + methanol interaction parameters, 4 ion + water interaction parameters, and 1 salt + methanol, 1 salt + water interaction parameters. A few a_{ij}* interaction parameters were available in the literature.[7,20] The remaining model parameters were fitted with the presented and published[17] experimental data by minimization of the following objective function (F) using the Simplex−Nelder−Mead method:[22]

$$F(a_{ij}, a_{ji}, \delta_{ij,m}) = \sum_{nt}\sum_{np}(y_{i,1(\text{exptl})} - y_{i,1(\text{calcd})})^2 = \min \tag{8}$$

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, respectively. The subscripts exptl and calcd denote experimental data and calculated values, respectively. All UNIQUAC parameters for studied system are given in Table 3.

Table 4. Mean Absolute Deviations of Vapor Phase Compositions for the Electrolyte NRTL Model and the Extended UNIQUAC Model

		$\|\Delta y\|$[a]	
T/K	data points	NRTL	UNIQUAC
298.15	20	0.007	0.006
313.15	20	0.007	0.006
avg deviation		0.007	0.006

[a] $|\Delta y| = 1/n\sum_1^n|y_{i,1}(\text{exptl}) - y_{i,1}(\text{calcd})|$, where n represents the number of data points.

Conclusion

The VLE behavior of the system methanol + water + ammonium bromide has been investigated at {(298.15 and 313.15) K} at four different salt concentrations {(0.500, 1.000, 2.000, and 4.000) mol·kg^{-1}}. The relative volatility of methanol increased with the salt concentration in this system. The VLE behavior can be described with help of the electrolyte NRTL model and the extended UNIQUAC model. These models represent the experimental data with the required accuracy, which are presented in Table 4, but superior results are obtained for the UNIQUAC model.

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