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

Alexander V. Kurzin,* Andrey N. Evdokimov, Victorija B. Antipina, and Olesja S. Pavlova

Organic Chemistry Department, Faculty of Chemical Technology, Saint-Petersburg State Technological University of Plant Polymers, 4 Ivana Chernykh, Saint-Petersburg 198095, Russia

Isothermal vapor−liquid equilibrium data for the system acetonitrile + water + tetrapropylammonium bromide at four constant salt molalities [(0.200, 0.400, 0.800, and 1.000) mol·kg^{-1}] have been measured with the help of headspace gas chromatography at (298.15 and 323.15) K. The experimental data were correlated using two different electrolyte models: an electrolyte nonrandom two-liquid model and an electrolyte universal quasi-chemical functional-group activity coefficients model. Mean absolute deviations of vapor phase compositions for these models were 0.006 and 0.007, respectively.

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.

The electrolyte systems containing large organic ions (ammonium, borate, phosphonium, and other organic salts) continue to represent an important area of theoretical interest as well. The behavior of these systems has prompted investigations of the conductance, density, viscosity, vibrational spectroscopy, osmotic coefficient, and thermal diffusion of aqueous and mixed solvent solutions of these salts in an effort to probe the influence of molecular structure on the properties of their solutions.[1−6] The effect of the tetraalkylammonium salt on the thermodynamic behavior of the solvent is seen through the salt effect on the vapor−liquid equilibrium (VLE) of water + solution mixture.

This work is a continuation of our investigation on salts with large organic ions to determine the VLE data in systems with these salts in mixed solvents. The aim of this work is to determine the effect of tetrapropylammonium bromide on the VLE of the acetonitrile + water system at two temperatures [(298.15 and 323.15) K] and four different constant salt concentrations [(0.200, 0.400, 0.800, and 1.000) mol·kg^{-1}] with the help of headspace gas chromatography. No VLE data about ternary system acetonitrile + water + tetrapropylammonium bromide were found in the literature.

Several correlative and predictive models based on the local composition or group-contribution concept have been proposed to calculate the VLE of systems formed by mixed solvents and electrolytes. Only an electrolyte NRTL model of Mock et al.[7] and the NRTL model of Chen and co-workers[8,9] are used to describe the VLE behavior in systems with salts having large organic ions.[1,10−12] However, the solid−liquid equilibria data for the binary system tetrabutylammonium bromide + benzene[13] were correlated using the original UNIQUAC model[14] with the Pitzer−Debye−Huckel equation.[15]

The experimental data presented in this work were correlated using an electrolyte nonrandom two-liquid (NRTL) model of

* To whom correspondence should be addressed. E-mail: zakora@mail.ru.

Mock et al.[7] and an electrolyte universal quasi-chemical functional-group activity coefficients (UNIFAC) model of Kikic et al.[16] Several new interaction parameters for these models were obtained and are presented in this work.

Experimental Section

Materials. The acetonitrile (≥ 99.9 mass %, Fluka) was stored above the molecular sieves 3 Å. Double-distilled and deionized water was used. Tetra-*n*-propylammonium bromide (TPAB) (≥ 99.0 mass %, Fluka) was previously dried at 60 °C in a vacuum oven until a constant mass was reached.

Procedure. A mixture consisting of acetonitrile, water, and tetrapropylammonium bromide was prepared gravimetrically using a analytical balance with an uncertainty 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 6 h at the target temperature [(298.15 and 323.15) K]. The uncertainty of measured temperature was ± 0.1 K. The uncertainty of liquid composition was less than 1 %.

Analysis Method. Acetonitrile and water mole fractions (on salt-free basis) in the vapor (y_i) phase were analyzed by headspace gas chromatography method proposed by Takamatsu and Ohe.[17] 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) was used with a thermal conductivity detector (electric current was 80 mA), a 2.5 m glass column (Chromosorb W HP), and an integrator. The injector and chamber temperatures were 200 °C and 135 °C, respectively. The carrier gas was helium (purity = 99.9 %) flowing at 0.5 cm^3·s^{-1}.

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 acetonitrile and water that was prepared gravimetrically by using an

Table 1. Experimental Vapor−Liquid Equilibrium Data for the System Acetonitrile (1) + Water (2) + Tetrapropylammonium Bromide (3), Liquid Mole Fraction of Acetonitrile on a Salt-Free Basis (x_1'), and Vapor Mole Fraction of Acetonitrile (y_1)

x_1'	y_1	x_1'	y_1	x_1'	y_1	x_1'	y_1
		$m_3 = 0.000$ mol·kg^{-1}; $T = 298.15$ K					
0.052	0.497	0.201	0.690	0.499	0.768	0.880	0.858
0.101	0.606	0.299	0.725	0.750	0.798	0.950	0.937
		$m_3 = 0.200$ mol·kg^{-1}; $T = 298.15$ K					
0.052	0.473	0.201	0.674	0.499	0.726	0.880	0.842
0.101	0.582	0.299	0.703	0.750	0.773	0.950	0.915
		$m_3 = 0.400$ mol·kg^{-1}; $T = 298.15$ K					
0.052	0.397	0.201	0.651	0.499	0.712	0.880	0.822
0.101	0.536	0.299	0.680	0.750	0.754	0.950	0.886
		$m_3 = 0.800$ mol·kg^{-1}; $T = 298.15$ K					
0.052	0.294	0.201	0.573	0.499	0.666	0.880	0.786
0.101	0.441	0.299	0.619	0.750	0.725	0.950	0.858
		$m_3 = 1.000$ mol·kg^{-1}; $T = 298.15$ K					
0.052	0.225	0.201	0.530	0.499	0.641	0.880	0.774
0.101	0.408	0.299	0.581	0.750	0.707	0.950	0.847
		$m_3 = 0.000$ mol·kg^{-1}; $T = 323.15$ K					
0.052	0.620	0.201	0.760	0.499	0.795	0.880	0.860
0.101	0.703	0.299	0.778	0.750	0.821	0.950	0.919
		$m_3 = 0.200$ mol·kg^{-1}; $T = 323.15$ K					
0.052	0.361	0.201	0.593	0.499	0.642	0.880	0.783
0.101	0.524	0.299	0.614	0.750	0.694	0.950	0.885
		$m_3 = 0.400$ mol·kg^{-1}; $T = 323.15$ K					
0.052	0.304	0.201	0.541	0.499	0.615	0.880	0.764
0.101	0.458	0.299	0.569	0.750	0.686	0.950	0.846
		$m_3 = 0.800$ mol·kg^{-1}; $T = 323.15$ K					
0.052	0.215	0.201	0.444	0.499	0.531	0.880	0.731
0.101	0.372	0.299	0.477	0.750	0.608	0.950	0.825
		$m_3 = 1.000$ mol·kg^{-1}; $T = 323.15$ K					
0.052	0.182	0.201	0.391	0.499	0.459	0.880	0.701
0.101	0.331	0.299	0.413	0.750	0.555	0.950	0.816

analytical balance with an uncertainty 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 acetonitrile 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 works.[11,12]

Results and Discussion

The experimental isothermal vapor−liquid equilibrium data for the system acetonitrile + water + tetrapropylammonium bromide are given in Table 1 and Figure 1. Only isothermal VLE data for the acetonitrile + water system were measured earlier.[12] The VLE data for the ternary system acetonitrile + water + tetrapropylammonium bromide were not studied earlier.

To describe the VLE behavior, the experimental data are correlated using the following two different electrolyte models.

Electrolyte NRTL Model of Mock et al.[7] 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.[7] The model parameters are specific for the solvent−solvent and solvent−salt pairs. For the system acetonitrile + water + tetrapropylammonium bromide,
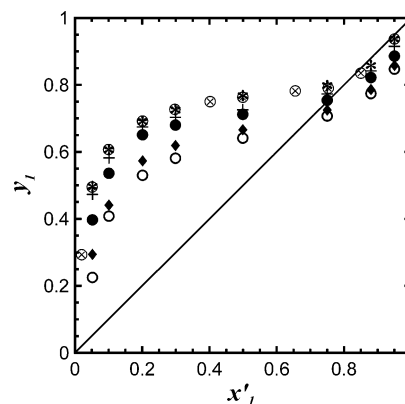

Figure 1. Vapor mole fraction (y_1) of acetonitrile in acetonitrile (1) + water (2) + tetrapropylammonium bromide (3) system at 298.15 K: ⊗, no salt (Kurzin et al.[12]); *, no salt (this work); +, $m_3 = 0.200$ mol·kg^{-1}; ●, $m_3 = 0.400$ mol·kg^{-1}; ◆, $m_3 = 0.800$ mol·kg^{-1}; ○, $m_3 = 1.000$ mol·kg^{-1}. Liquid mole fraction of acetonitrile (x'_1) on a salt-free basis.

Table 2. Energy Parameters and Nonrandomness Factors for the Electrolyte NRTL Model[a]

i	j	α_{ij}	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}
acetonitrile	water	0.2858	1528.665	5538.057
acetonitrile	TPAB	0.05	4121.515(f)[b]	−1256.115(f)
water	TPAB	0.2	5873.216	−2757.497

[a] Ref 7. [b] (f) means that these interaction parameters have been fitted in this work. Other parameters were calculated from ones published in refs 1 and 7.

six energy parameters (Δg_{ij}, Δg_{ji}) and three nonrandomness factors (α_{ij}) are required. Some model parameters were calculated from published data.[1,7] The nonrandomness factors ($\alpha_{\text{TPAB,water}}$ and $\alpha_{\text{TPAB,acetonitrile}}$) were set arbitrarily to 0.2 and 0.05, respectively, as pointed out by Mock et al.[7] The remaining model parameters were fitted to the experimental data by minimization of the following objective function F using the Simplex−Nelder−Mead method:[18]

$$F(\Delta g_{ij}, \Delta g_{ji}, \alpha_{ij}) = \sum_{nt} \sum_{np} (y_{i,1(\text{exptl})} - y_{i,1(\text{calcd})})^2 = \min \quad (1)$$

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 model binary energy parameters (τ_{ij} and G_{ij}) were calculated as described by Mock et al.:[7]

$$\tau_{ij} = \Delta g_{ij}/RT \quad (2)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (3)$$

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

Electrolyte UNIFAC Model of Kikic et al.[16] Kikic et al.[16] presented a model for the calculation of salt effects on the VLE. This model combines a modified Debye−Huckel term according to the McMillan−Mayer solution theory as described by Cardoso and O'Connell[19] with the original UNIFAC group-contribution method.[20]

For the studied system, 32 model energy and geometrically parameters are needed. Some parameters were taken from the published data.[16,21,22] The remaining group interaction parameters were fitted to the experimental data with the help of the Simplex−Nelder−Mead method mentioned above.

Table 3. UNIFAC Group Interaction Parameters a_{ij}, Subgroup Volume Parameters R_i, and Surface Area Parameters Q_i for the Electrolyte UNIFAC Model[a]

			α_{ij}		
	H_2O	CCN	$(C)_3N$	CH_2	Br^-
H_2O	0.0	112.60	304.00	300.00	−1058.60
CCN	242.80	0.0	−253.10	24.82	541.87(f)[b]
$(C)_3N$	−598.80	−354.10	0.0	−83.98	−736.17(f)
CH_2	1318.00	597.00	206.60	0.0	−673.80
Br^-	−372.50	−2877.78 (f)	498.45(f)	3106.40	0.0

			R_i and Q_i		
	H_2O	CH_3CN	CH_2N	CH_3	CH_2	Br^-
R_i	0.92	1.8701	0.9597	0.9011	0.9597	1.2331
Q_i	1.40	1.7240	0.6320	0.8480	0.6320	1.1510

[a] Ref 16. [b] (f) means that these interaction parameters have been fitted in this work. Other parameters were taken from refs 16, 21, and 22.

Table 4. Mean Absolute Deviations of Vapor Phase Composition of Acetonitrile for the Electrolyte NRTL Model and Electrolyte UNIFAC Model

		$|\Delta y_1|$[a]	
T/K	data points	NRTL	UNIFAC
298.15	32	0.006	0.007
323.15	32	0.006	0.007
avg deviation		0.006	0.007

[a] $|\Delta y_1| = 1/n\sum_1^n |y_{1,i}(\text{exptl}) - y_{1,i}(\text{calcd})|$, where n represents the number of data points.

All UNIFAC group interaction parameters a_{ij}, subgroup volume parameters R_i, and surface area parameters Q_i for studied system are given in Table 3.

Conclusion

The VLE behavior of the system acetonitrile + water + tetrapropylammonium bromide has been investigated at [(298.15 and 323.15) K] at four different salt concentrations [(0.200, 0.400, 0.800, and 1.000) mol·kg⁻¹]. The electrolyte NRTL model and the modified UNIFAC group-contribution model were used for the correlation of the VLE behavior of the acetonitrile + water + tetrapropylammonium bromide system. These models represent the experimental data with required accuracy, which is represented in Table 4, but superior results are obtained for the NRTL model.

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