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Vapor−Liquid Equilibrium Data for the System Methanol + Toluene + Tetrabutylammonium Tetraphenylborate

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Isothermal vapor−liquid equilibrium data for the system methanol + toluene + tetrabutylammonium tetraphenylborate at four salt molalities, (0.100, 0.200, 0.300, and 0.500) mol·kg^{-1}, have been measured with the help of headspace gas chromatography at 318.15 K. The experimental data were correlated using the electrolyte nonrandom two-liquid model.

Introduction

Organic salts are important and are usually used as intermediate chemicals, reaction catalysts, inhibitors to undesired reactions, supporting electrolytes, and surfactants.[1,2] These salts are also used for separation processes to modify and improve distillation, evaporation, and pervaporation process performance as well as inorganic salts, alkali, hydroxides, and ionic liquids. The electrolyte systems containing salts with large organic ions (ammonium, borate, phosphonium, sulfonium, arsonium, pyridinium, pyrrolidynium, imidazolium, and others), betaines, and ionic liquids continue to represent an important area of theoretical interest as well. Some years ago, there were a number of experimental studies of the vapor−liquid equilibrium (VLE) behavior of binary and ternary solutions consisting of salts with large organic ions.[3–12]

The aims of this work are: (1) to determine the effect of tetrabutylammonium tetraphenylborate on the VLE of the methanol + toluene system at 318.15 K and different salt concentrations, (0.100, 0.200, 0.300, and 0.500) mol·kg^{-1}, with the help of headspace gas chromatography, and (2) to achieve breaking an existing azeotrope in this system. No VLE data for the ternary system methanol + toluene + tetrabutylammonium tetraphenylborate were found in the literature. This salt was not studied earlier in the azeotrope systems. Only triphenylbenzylphosphonium chloride and sodium bromide were studied in the ternary electrolyte + methanol + toluene systems.[8,13]

This work is a continuation of our investigation on salts having large organic ions (ammonium, borate, phosphonium, and pyridinium salts) to determine the VLE data in systems with these salts in mixed solvents.[5–9,12]

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. The electrolyte nonrandom two-liquid (NRTL) model of Mock et al.[14] is usually used for correlation and prediction of VLE in the systems with salts having different large organic ions or ionic liquids.[5–9,15–17] The experimental data presented in this work were correlated using the electrolyte NRTL model of Mock et al.[14]

Experimental Section

Materials. Methanol ($w \geq 99.8$ %, Merck) and toluene ($w \geq 99.5$ %, Vekton) were stored above the molecular sieves (3Å). Tetrabutylammonium tetraphenylborate $[(n\text{-}C_4H_9)_4N^+B^-(C_6H_5)_4]$ was obtained from Aldrich ($w \geq 99.0$ %) and previously dried in a vacuum oven until a constant mass was reached (mp = (236 to 237) °C).

Procedure. Mixtures consisting of methanol, toluene, and tetrabutylammonium tetraphenylborate were prepared gravimetrically with an 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 7 h at the target temperature. The uncertainty of the measured temperature was 0.01 K.

The combined standard uncertainties of the measured mole fraction in the vapor phase and mole fraction of solvents (on a salt-free basis) were 0.001.

Analysis Method. Methanol and toluene mole fractions (on a salt-free basis) in the vapor (y_i) phase were analyzed by the headspace gas chromatography method proposed by Takamatsu and Ohe.[18] 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 2.5 m glass column (15 % Apiezon L on Chromaton N-AW) and an integrator. The injector and chamber temperatures were (160 and 120) °C, respectively. The carrier gas was argon (purity = 99.9 %) flowing at 0.5 cm^3·s^{-1}.

The gas chromatograph was calibrated using the mixtures of methanol and toluene that were prepared gravimetrically by using an 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 methanol and toluene mixtures were completely evaporated in a (1000 ± 0.1) cm^3 vessel and

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Table 1. Experimental Vapor−Liquid Equilibrium Data for the System Methanol (1) + Toluene (2) + Tetrabutylammonium Tetraphenylborate (3) at T = 318.15 K, Vapor Mole Fraction of Methanol y_1 As a Function of Liquid Mole Fraction of Methanol on a Salt-Free Basis x'_1, and Salt Molality m_3

x'_1	y_1
$m_3/(\text{mol}\cdot\text{kg}^{-1}) = 0.000$	
0.200	0.775
0.300	0.792
0.450	0.802
0.600	0.810
0.700	0.823
0.900	0.934
$m_3/(\text{mol}\cdot\text{kg}^{-1}) = 0.100$	
0.200	0.776
0.300	0.795
0.450	0.805
0.600	0.814
0.700	0.828
0.900	0.896
$m_3/(\text{mol}\cdot\text{kg}^{-1}) = 0.200$	
0.200	0.778
0.300	0.799
0.450	0.809
0.600	0.818
0.700	0.833
0.900	0.903
$m_3/(\text{mol}\cdot\text{kg}^{-1}) = 0.300$	
0.200	0.780
0.300	0.802
0.450	0.813
0.600	0.822
0.700	0.838
0.900	0.909
$m_3/(\text{mol}\cdot\text{kg}^{-1}) = 0.500$	
0.200	0.784
0.300	0.811
0.450	0.821
0.600	0.831
0.700	0.848
0.900	0.922

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 experimental setup is described in detail in our previous works.[6–9]

Results and Discussion

Vapor−liquid equilibrium data for the methanol + toluene + tetrabutylammonium tetraphenylborate system are presented in Table 1 and Figure 1. The measured data were compared with published isothermal data without the salt at 318.15 K.[8,19] The comparison is also shown in Figure 1.

The addition of tetrabutylammonium tetraphenylborate in the methanol + toluene system results in an increase of the methanol mole fraction in the vapor phase. The azeotrope of the mixed solvent system disappears at salt concentration m_3 = 0.3 mol·kg^{-1}.

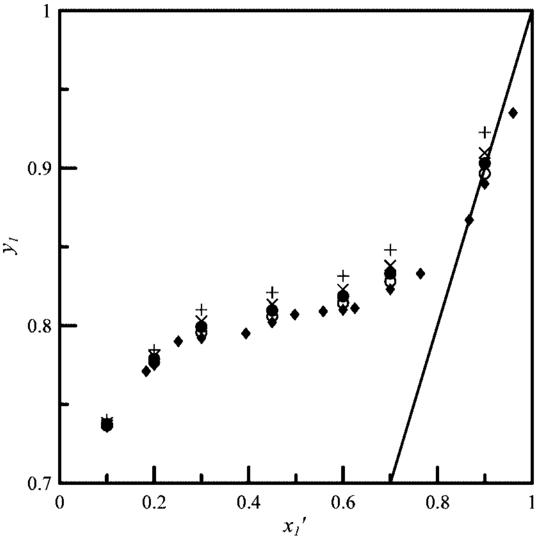

Figure 1. Vapor mole fraction (y_1) of methanol in the methanol (1) + toluene (2) + tetrabutylammonium tetraphenylborate (3) system at T = 318.15 K: ◆, no salt (Nagata[19] and Kurzin et al.[8]); ○, m_3 = 0.100 mol·kg^{-1}; ●, m_3 = 0.200 mol·kg^{-1}; ×, m_3 = 0.300 mol·kg^{-1}; +, m_3 = 0.500 mol·kg^{-1}. The liquid mole fraction of methanol x'_1 is on a salt-free basis. The solid line is to identify the azeotropic behavior.

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	toluene	0.4749	3380.8926	4666.501
methanol	salt[b]	0.1	1870.07(f)[c]	2860.43(f)
toluene	salt[b]	0.1	969.14(f)	116.25(f)

[a] Ref 14. [b] Tetrabutylammonium tetraphenylborate. [c] (f) means that these interaction parameters have been fitted in this work.

To describe the observed VLE behavior, the experimental data are correlated using the electrolyte NRTL model of Mock et al.[14] For the system methanol + toluene + tetrabutylammonium tetraphenylborate, six energy parameters (Δg_{ij}, Δg_{ji}) and three nonrandomness factors (α_{ij}) are required. Binary solvent−solvent parameters were taken from published data.[20] The nonrandomness factors ($\alpha_{\text{salt,methanol}}$ and $\alpha_{\text{salt,toluene}}$) were set to 0.1. The remaining model parameters were fitted to the experimental data by minimization of the following objective function F using the Simplex−Nelder−Mead method[21]

$$F(\Delta g_{ij}, \Delta g_{ji}, \alpha_{ij}) = \underset{\text{ntnp}}{\sum\sum}(y_{i,1(\text{exptl})} - y_{i,1(\text{calcd})})^2 = \min \qquad (1)$$

where y represents the vapor phase mole fraction, and 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. We used published[22] vapor pressures for pure methanol and toluene at 318.15 K of 44.53 kPa and 9.96 kPa, respectively.

The binary model parameters are expressed by[14]

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

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

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

Mean absolute deviation and standard deviation between experimental and calculated values of the vapor phase mole fractions are 0.009 and 0.008, respectively.

Conclusion

The VLE behavior of the system methanol + toluene + tetrabutylammonium tetraphenylborate has been investigated at 318.15 K at four different salt concentrations, (0.100, 0.200, 0.300, and 0.500) mol·kg^{-1}, with the help of headspace gas chromatography. This salt is effective in breaking the azeotrope. The electrolyte NRTL model was used for correlation of the

VLE behavior of the studied system. The model represented the experimental data with the required accuracy.

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