Isothermal Vapor−Liquid Equilibrium Data for the System Methanol + Toluene + Triphenylbenzylphosphonium Chloride

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Isothermal vapor−liquid equilibrium data for the system methanol + toluene + triphenylbenzylphosphonium chloride at five salt molalities {(0.100, 0.500, 1.000, 1.500, and 2.000) mol·kg^{-1}} have been measured with the help of headspace gas chromatography at (313.15 and 318.15) K. The experimental data were correlated using the electrolyte nonrandom two-liquid model. Several new interaction parameters for this model were obtained and are presented in this work.

Introduction

Organic salts are important and are usually used as intermediate chemicals, reaction catalysts, inhibitors to undesired reactions, supporting electrolytes, and surfactants. These salts are also used for separation processes to modify and improve distillation, evaporation, and pervaporation process performance as well as inorganic salts and ionic liquids. The electrolyte systems containing large organic ions (ammonium, borate, phosphonium, sulfonium, arsonium, and other organic salts and ionic liquids) continue to represent an important area of theoretical interest as well.[1] When the electrolyte species being studied contain apolar regions, such as hydrocarbon chains or aromatic structures, their properties of solution show interesting behavior which can be attributed to a complex balance between long-ranged Coulombic and short-ranged intermolecular forces and possibly conformational changes in the electrolyte. The organic salts provide a convenient model system in which to study the interplay of these forces. Correlation and prediction of the physical properties of these electrolyte systems have proven to be difficult due to the complexity of the molecular interactions. Some years ago, there were a number of experimental studies of the vapor−liquid equilibrium (VLE) behavior of ternary solutions consisting of salts with large organic ions in mixed solvent mixtures.[2−6]

The aims of this work are: (1) to determine the effect of triphenylbenzylphosphonium chloride on the VLE of the methanol + toluene system at {(313.15 and 318.15) K} and different constant salt concentrations {(0.100, 0.500, 1.000, 1.500, and 2.000) 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 + triphenylbenzylphosphonium chloride were found in the literature. This salt was not studied earlier in the ternary azeotrope systems. There is only one published paper[7] about VLE data for the salt + toluene + methanol system found in the literature. Aneke[7] has studied the methanol + toluene system saturated with sodium bromide.

This work is a continuation of our investigation on salts having large organic ions (ammonium and borate salts) to determine the VLE data in systems with these salts in mixed solvents.[2−4]

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) models[8−10] and electrolyte UNIFAC model of Kikic et al.[11] are usually used for the systems with salts having large organic ions or ionic liquids.[2−6,12] The experimental data presented in this work were correlated using the electrolyte NRTL model of Mock et al.[8]

Experimental Section

Materials. Methanol ($w \geq 99.8$ %, Fluka) and toluene ($w \geq 99.5$ %, Fluka) were stored above the molecular sieves (3 Å). Triphenylbenzylphosphonium chloride ($[(C_6H_5)_3C_6H_5CH_2P]^+Cl^-$) was obtained from Aldrich ($w \geq 99.0$ %).

Procedure. Mixtures consisting of methanol, toluene, and triphenylbenzylphosphonium chloride were prepared gravimetrically with an analytical balance (Ohaus Explorer Pro 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. The uncertainty of the measured temperature was 0.1 K.

The gas chromatograph was calibrated using a mixture 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 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 %).

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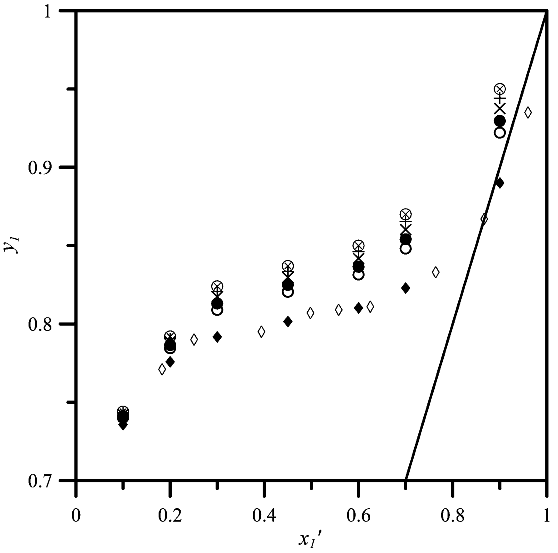

Figure 1. Vapor mole fraction (y_1) of methanol in the methanol (1) + toluene (2) + triphenylbenzylphosphonium chloride (3) system at 318.15 K: ◆, no salt (this work); ◇, no salt (Nagata[15]); ○, $m_3 = 0.100$ mol·kg^{-1}; ●, $m_3 = 0.500$ mol·kg^{-1}; ×, $m_3 = 1.000$ mol·kg^{-1}; +, $m_3 = 1.500$ mol·kg^{-1}; ⊗, $m_3 = 2.000$ mol·kg^{-1}. Liquid mole fraction of methanol (x'_1) is on a salt-free basis.

Table 1. Experimental Vapor−Liquid Equilibrium Data for the System Methanol (1) + Toluene (2) + Triphenylbenzylphosphonium Chloride (3), Liquid Mole Fraction of Methanol on a Salt-Free Basis (x_1'), and Vapor Mole Fraction of Methanol (y_1)

	y_1			y_1	
x'_1	T/K = 313.15	T/K = 318.15	x'_1	T/K = 313.15	T/K = 318.15
	m_3/(mol·kg^{-1}) = 0.000			m_3/(mol·kg^{-1}) = 1.000	
0.200	0.786	0.776	0.200	0.795	0.789
0.300	0.791	0.792	0.300	0.815	0.817
0.450	0.811	0.802	0.450	0.840	0.830
0.600	0.820	0.810	0.600	0.851	0.842
0.700	0.828	0.823	0.700	0.870	0.860
0.900	0.896	0.935	0.900	0.917	0.938
	m_3/(mol·kg^{-1}) = 0.100			m_3/(mol·kg^{-1}) = 1.500	
0.200	0.792	0.784	0.200	0.796	0.790
0.300	0.807	0.809	0.300	0.818	0.821
0.450	0.830	0.820	0.450	0.844	0.834
0.600	0.841	0.832	0.600	0.855	0.846
0.700	0.856	0.848	0.700	0.876	0.865
0.900	0.910	0.922	0.900	0.920	0.944
	m_3/(mol·kg^{-1}) = 0.500			m_3/(mol·kg^{-1}) = 2.000	
0.200	0.793	0.786	0.200	0.797	0.792
0.300	0.811	0.813	0.300	0.821	0.824
0.450	0.835	0.825	0.450	0.847	0.837
0.600	0.846	0.842	0.600	0.859	0.850
0.700	0.863	0.860	0.700	0.881	0.870
0.900	0.914	0.938	0.900	0.923	0.950

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.

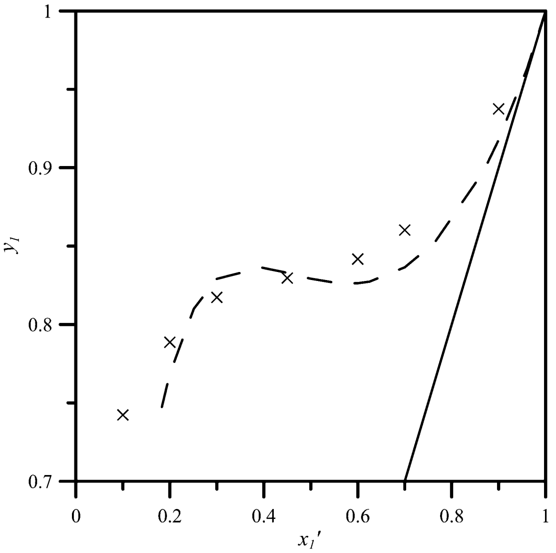

Figure 2. Experimental and calculated $x_1'-y_1$ diagrams for the methanol (1) + toluene (2) + triphenylbenzylphosphonium chloride (3) system at 318.15 K: ×, experimental $x_1'-y_1$ for $m_3 = 1.000$ mol·kg^{-1}; dashed line, calculated $x_1'-y_1$ for $m_3 = 1.000$ mol·kg^{-1}. Liquid mole fraction of methanol (x'_1) is on a salt-free basis.

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.[13] 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 °C and 120 °C, respectively. The carrier gas was argon (purity = 99.9 %) flowing at 0.5 cm^3·s^{-1}. The experimental setup is described in detail in our previous works.[2−4]

Results and Discussion

Vapor−liquid equilibrium data of methanol + toluene without the salt system are presented in Table 1. This system was studied earlier.[7,14−17] Our measured data are compared with published isothermal data at 318.15 K.[15] The comparison is shown in Figure 1. Good agreement was observed.

In the system containing salt, the measurement results are presented in Table 1 and Figure 1. The addition of triphenylbenzylphosphonium chloride 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 minimal salt concentration ($m_3 = 0.1$ mol·kg^{-1}). This triphenylbenzylphosphonium chloride concentration is lower than that obtained when a saturated solution of sodium bromide was used.[7]

To describe the observed VLE behavior, the experimental data are correlated using the electrolyte NRTL model of Mock et al.[8] For the system methanol + toluene + triphenylbenzylphosphonium chloride, six energy parameters (Δg_{ij}, Δg_{ji}) and three nonrandomness factors (α_{ij}) are required. Binary solvent−solvent parameters were taken from published data.[17] 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[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 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.

The binary model parameters are expressed by[8]

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

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

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	1633.12(f)[c]	3422.45(f)
toluene	salt[b]	0.1	892.21(f)	212.76(f)

[a] Ref 8. [b] Triphenylbenzylphosphonium chloride. [c] (f) means that these interaction parameters have been fitted in this work.

Table 3. Mean Absolute Deviation (δy) and Standard Deviation (σy) between Experimental and Calculated Values of the Vapor-Phase Mole Fractions

m_3	δy^a		σy^b	
mol·kg^{-1}	T/K = 313.15	T/K = 318.15	T/K = 313.15	T/K = 318.15
0.100	0.009	0.009	0.008	0.008
0.500	0.008	0.008	0.008	0.008
1.000	0.009	0.008	0.008	0.009
1.500	0.008	0.007	0.008	0.008
2.000	0.007	0.008	0.009	0.008

[a] $\delta y = (1/N)\ \Sigma|y_{\text{exptl}} - y_{\text{calcd}}|$. [b] $\sigma y = [1/(N-1)][\Sigma(y_{\text{exptl}} - y_{\text{calcd}})^2]^{1/2}$.

Table 4. Average Absolute Deviations of Vapor-Phase Compositions of the Ternary Systems with Salt Having Large Organic Ions or Ionic Liquids for the Electrolyte NRTL Models

system	δy^a
acetonitrile + water + tetrapropylammonium bromide[b]	0.006
1,4-dioxane + water + tetrabutylammonium nitrate[c]	0.005
acetonitrile + water + tetrabutylammonium bromide[c]	0.006
methanol + benzene + sodium tetraphenylborate[d]	0.006
1-propanol + water + tetrapropylammonium bromide[e]	0.006[h]
2-propanol + water + tetrapropylammonium bromide[e]	0.006[h]
1-propanol + water + tetrabutylammonium bromide[e]	0.006[h]
2-propanol + water + tetrabutylammonium bromide[e]	0.006[h]
methanol + toluene + triphenylbenzylphosphonium chloride[f]	0.008
acetone + methanol + 1−ethyl−3−methylimidazolium trifluoromethanesulfonate[g]	0.008

[a] $\delta y = (1/N)\ \Sigma|y_{\text{exptl}} - y_{\text{calcd}}|$. [b] Ref 4. [c] Ref 2. [d] Ref 3. [e] Ref 5. [f] This work. [g] Ref 12. [h] Calculated from ref 5 data.

The expressions for the activity coefficients of solvents were directly taken from the electrolyte NRTL model of Mock et al.[8] The NRTL energy parameters and nonrandomness factors are given in Table 2.

The ability of the model to reproduce the vapor−liquid equilibrium for this system can be seen in Figure 2 where the calculated and experimental vapor−liquid equilibrium of the methanol + toluene + triphenylbenzylphosphonium chloride ternary system is plotted on $x'_1 - y_1$ diagrams for $m_3 = 1.000$ mol·kg^{-1}. This figure and the mean absolute deviations from Table 3 reveal that the proposed model successfully fits the experimental data, and only for the lower triphenylbenzylphosphonium chloride concentrations, small differences can be appreciated. Mean absolute deviation and standard deviation between experimental and calculated values of the vapor-phase mole fractions are presented in Table 3.

Conclusion

The VLE behavior of the system methanol + toluene + triphenylbenzylphosphonium chloride has been investigated at {(313.15 and 318.15) K} at five different salt concentrations {(0.100, 0.500, 1.000, 1.500, and 2.000) mol·kg^{-1}} with the help of headspace gas chromatography. This salt is effective in breaking the azeotrope. The electrolyte NRTL model was used to correlate the VLE behavior of the studied system. The model represented the experimental data with the required accuracy for the studied system as well as other ternary mixed-solvent systems with salts having large organic ions or ionic liquids (Table 4). Therefore, this model is suitable to predict the VLE in the presence of these electrolytes.

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