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Isothermal Vapor−Liquid Equilibrium Data for the System Methanol + Benzene + Sodium Tetraphenylborate

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Isothermal vapor−liquid equilibrium data for the system methanol + benzene + sodium tetraphenylborate at five salt molalities [(0.05, 0.10, 0.15, 0.20, and 0.25) mol·kg^{-1}] have been measured with the help of headspace gas chromatography at (298 and 308) K. The experimental data were correlated using the electrolyte nonrandom two-liquid model.

Introduction

The synthesis and design of industrial processes such as extractive distillation, extractive crystallization of salts, gas scrubbing, wastewater treatment, and others require an accurate description of the phase equilibrium behavior of electrolyte systems.[1] Electrolyte systems containing large organic ions continue to represent an important area of theoretical interest as well.

The aim of this work is to determine the effect of sodium tetraphenylborate on the vapor−liquid equilibrium of the methanol + benzene system at two temperatures [(298 and 308) K] and different constant salt concentrations [(0.05, 0.10, 0.15, 0.20, and 0.25) mol·kg^{-1}] with the help of headspace gas chromatography.

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 experimental data presented in this work were correlated using the electrolyte nonrandom two-liquid (NRTL) model of Mock et al.[2] This model is used for the systems with salts having large organic ions.[3,4] Several new interaction parameters for the electrolyte NRTL model of Mock et al.[2] were obtained and are presented in this work.

Experimental Section

Materials**.** Methanol (≥ 99.9 mass fraction %, Fluka) and benzene (≥ 99.5 mass fraction %, Fluka) were stored above the 3 Å molecular sieves. Sodium tetraphenylborate ($NaB(C_6H_5)_4$) was obtained from Merck (≥ 99.0 mass fraction %).

Procedure. Mixtures consisting of methanol, benzene, and sodium tetraphenylborate were prepared gravimetrically with an analytical balance with an accuracy of ± 0.1 mg. For each experiment, about 10 cm^3 of sample was charged into the 20 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 and 308) K].

Analysis Method. Methanol and benzene mole fractions (on salt-free basis) in the vapor (y_i) phase were analyzed by headspace gas chromatography method proposed by Takamatsu and Ohe.[5] To analyze the vapor phase, a gas syringe (1 mL) was used. A gas chromatograph (Chrom-5, Laboratorni Pristroje, Czech Republic) 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 150 °C and 110 °C, respectively. The carrier gas was argon (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 methanol and benzene 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 benzene 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 ± 0.002, which was obtained by comparing the known composition of the prepared liquid samples with the composition calculated from the calibration equation. Uncertainty of temperature was 0.1 K.

Results and Discussion

Vapor−liquid equilibrium data of methanol + benzene without the salt system is presented in Table 1. The observed data were compared with published data for the same system.[6−8] The comparison is shown in Figure 1. Good agreement was observed for the vapor−liquid equilibria of the methanol + benzene system. In the system containing salt, the measurement results are presented in Table 1 and Figure 1.

To describe the observed VLE behavior, the experimental data are correlated using the electrolyte NRTL model of Mock et al.[2] The electrolyte NRTL model used to correlate the VLE data is an extension of Chen model (for single-solvent electrolyte systems) to mixed-solvent electrolyte

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Table 1. Experimental Vapor−Liquid Equilibrium Data for the System Methanol (1) + Benzene (2) + Sodium Tetraphenylborate (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	x_1'	y_1
$m = 0.000$ mol·kg^{-1}; $T = 298$ K		$m = 0.000$ mol·kg^{-1}; $T = 308$ K	
0.3000	0.5509	0.3000	0.5219
0.4508	0.5711	0.4508	0.5467
0.6505	0.5996	0.6505	0.5923
0.8009	0.6325	0.8009	0.6510
0.9507	0.8419	0.9507	0.8217
$m = 0.050$ mol·kg^{-1}; $T = 298$ K		$m = 0.050$ mol·kg^{-1}; $T = 308$ K	
0.3000	0.5345	0.3000	0.5234
0.4508	0.5619	0.4508	0.5422
0.6505	0.5901	0.6505	0.5660
0.8009	0.6123	0.8009	0.6031
0.9507	0.8212	0.9507	0.7767
$m = 0.100$ mol·kg^{-1}; $T = 298$ K		$m = 0.100$ mol·kg^{-1}; $T = 308$ K	
0.3000	0.5235	0.3000	0.5187
0.4508	0.5514	0.4508	0.5374
0.6505	0.5825	0.6505	0.5580
0.8009	0.6009	0.8009	0.5972
0.9507	0.8177	0.9507	0.7691
$m = 0.150$ mol·kg^{-1}; $T = 298$ K		$m = 0.150$ mol·kg^{-1}; $T = 308$ K	
0.3000	0.5178	0.3000	0.5093
0.4508	0.5456	0.4508	0.5301
0.6505	0.5742	0.6505	0.5466
0.8009	0.5926	0.8009	0.5910
0.9507	0.8013	0.9507	0.7608
$m = 0.200$ mol·kg^{-1}; $T = 298$ K		$m = 0.200$ mol·kg^{-1}; $T = 308$ K	
0.3000	0.5064	0.3000	0.4978
0.4508	0.5381	0.4508	0.5234
0.6505	0.5675	0.6505	0.5390
0.8009	0.5866	0.8009	0.5860
0.9507	0.7968	0.9507	0.7557
$m = 0.250$ mol·kg^{-1}; $T = 298$ K		$m = 0.250$ mol·kg^{-1}; $T = 308$ K	
0.3000	0.4972	0.3000	0.4867
0.4508	0.5374	0.4508	0.5177
0.6505	0.5658	0.6505	0.5305
0.8009	0.5849	0.8009	0.5790
0.9507	0.7880	0.9507	0.7489

systems.[2] The model parameters are specific for the solvent−solvent and solvent−salt pairs. For the system methanol + benzene + sodium tetraphenylborate, six energy parameters (Δg_{ij}, Δg_{ji}) and three nonrandomness factors (α_{ij}) are required. Binary solvent−solvent parameters were directly taken from published data.[9] The nonrandomness factors ($\alpha_{\mathrm{STPB,methanol}}$ and $\alpha_{\mathrm{STPB,benzene}}$) were set to 0.1 and 1.0, respectively. The remaining model parameters were fitted to the experimental data by minimization of the following objective function *F* using the Simplex−Nelder−Mead method:[10]

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

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.

The binary model parameters are expressed by[2]:

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

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

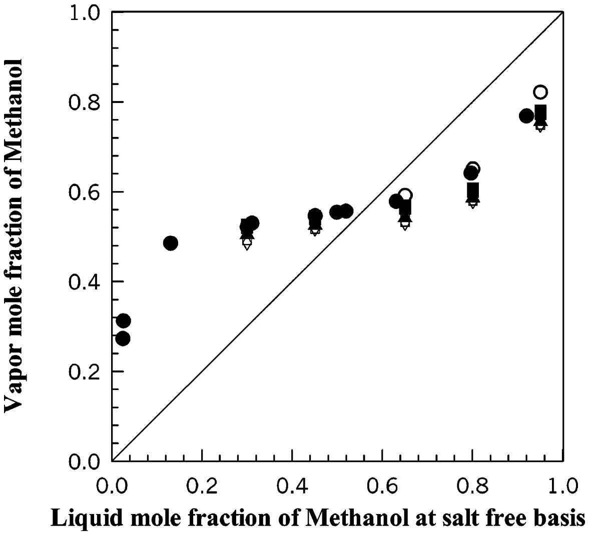

Figure 1. Vapor mole fraction (*y*) of methanol in methanol + benzene + sodium tetraphenylborate system at 308 K: ●, no salt (this work); ○, no salt (Scatchard et al.[6]); ■, $m = 0.050$ mol·kg^{-1}; ♦, $m = 0.100$ mol·kg^{-1}; ▲, $m = 0.150$ mol·kg^{-1}; □, $m = 0.200$ mol·kg^{-1}; ◇, $m = 0.250$ mol·kg^{-1}.

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	benzene	0.47	5160.49	3038.17
methanol	$NaB(C_6H_5)_4$	0.1	5068.64 (f)[b]	−655.94(f)
benzene	$NaB(C_6H_5)_4$	1.0	1294.65 (f)	−767.91(f)

[a] Ref 2. [b] (f) means that these interaction parameters have been fitted in this work.

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

The vapor-phase composition can be calculated by solving iteratively the equilibrium condition:

$$y_iP = x_i\gamma_iP_i^{\mathrm{s}}\Phi_i \quad (4)$$

where

$$P = x_1\gamma_1P_1^{\mathrm{s}}\Phi_1 + x_2\gamma_2P_2^{\mathrm{s}}\Phi_2 \quad (5)$$

$$\Phi_i = \varphi_i^{\mathrm{s}}PF_i/\varphi_i^{\mathrm{v}} \quad (6)$$

The saturation vapor pressure of pure solvent *i* (P_i^{s}) at system temperature was calculated with the published Antoine constants.[9] 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 PF_i is 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 PF_i is approximately equal to 1 at atmosphere pressure, and so Φ_i is equal to 1.

Conclusion

The VLE behavior of the system methanol + benzene + sodium tetraphenylborate has been investigated at (298 and 308) K at five different salt concentrations [(0.05, 0.10, 0.15, 0.20, and 0.25) mol·kg^{-1}] with the help of headspace gas chromatography. The electrolyte NRTL model was used to correlate the VLE behavior of methanol + benzene +

sodium tetraphenylborate system. This model represents the experimental data with the required accuracy ($|\Delta y_1|_{\mathrm{av}} = 0.006$).

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