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Vapor−Liquid Equilibrium of the Acetic Acid + Octane Binary System at 323.15 K and 343.15 K

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In this work $P-T-x-y$ vapor liquid equilibrium data were obtained for the acetic acid + octane mixture at two temperatures, 323.15 and 343.15 K. This mixture is very nonideal due to the association of acetic acid, and the data could only be correlated with sufficient accuracy by using two recently proposed activity coefficient models that include association in both the liquid and vapor phases.

Introduction

Association due to hydrogen bonding in both the vapor and liquid phases complicates the correlation and prediction of the phase equilibrium of mixtures. Recently, several new models were proposed for the representation of the vapor−liquid equilibrium (VLE) of associating mixtures (Fu and Sandler, 1995; Fu et al., 1995, 1996). To test these and other models, experimental data are needed for mixtures containing a highly associating compound. The acetic acid + octane binary mixture is such a system due to the strongly associating nature of the acid, and no isothermal data are available for this system in the 323.15 to 343.15 K temperature range. For this system isobaric data at higher temperatures were reported earlier (Wichterle et al., 1993; TRC Data Base, 1996).

This mixture is very nonideal, with a low-boiling azeotrope, and almost exhibits a liquid−liquid phase split at the azeotropic pressure. Several equation of state and activity coefficient models were considered for the correlation of the data. Among the models considered, only those that explicitly account for association in both the vapor and liquid phases were capable of representing the behavior of this system with acceptable accuracy.

Experimental Measurements

Materials. Both acetic acid and octane were obtained from Aldrich Chemical Corp.; the acid had a reported purity of more than 99.8%, and octane was 99% pure. Octane was dried with molecular sieves, and both chemicals were tested by gas chromatography using a flame ionization detector (FID); they are found to be 99.9% pure by mass. In addition, as a further check of purity, we measured the pure component vapor pressures of both substances and obtained good agreement with the literature data (Vargaftik, 1975; Boublik et al., 1973; TRC Thermodynamic Tables, 1990). The pure component vapor pressure data are reported in Table 1, and a comparison of our measured vapor pressure of acetic acid with the literature data is shown in Figure 1. For this we first fit three parameters of the Antoine equation

$$P\ (\mathrm{kPa}) = \exp\left[\mathrm{A} - \frac{B}{T(\mathrm{K}) - C}\right] \qquad (1)$$

to the pure component saturation pressure data measured here to obtain values of equation constants as $A = 14.614$, $B = 3290.4$, and $C = 61.58$. Next, we computed the deviations of individual data points of several previous measurements from eq 1. Most of the data points are in agreement with one another within 0.05 kPa, though there is a negative bias in the present data with respect to previously measured data at temperatures above 335 K.

Table 1. Vapor Pressure of Octane and Acetic Acid

T/K	*P*/kPa	*T*/K	*P*/kPa
	Octane		
310.13	3.470	336.67	12.178
312.85	4.000	339.19	13.555
318.07	5.212	343.41	16.120
322.65	6.505	346.52	18.219
326.75	7.863	349.54	20.455
329.47	8.893	352.31	22.740
333.78	10.757		
	Acetic Acid		
309.75	3.877	332.66	11.920
309.80	3.882	332.72	11.940
313.07	4.640	336.10	13.832
319.73	6.478	338.76	15.515
323.07	7.615	340.86	17.015
327.64	9.470	344.09	19.462
330.00	10.560	346.28	21.263

Apparatus and Procedure

A Stage-Muller double recirculation still was used to measure the pure component vapor pressures and the $P-T-x-y$ data. The dynamic still and its method of operation have been described previously (Shealy and Sandler, 1985). This equipment is useful for obtaining data below and near atmospheric pressure, and at temperatures above 288 K. The pressure was measured using a Wallace-Tiernan precision mercury manometer with an accuracy of 0.02 kPa. The temperature was measured using a Rosemount high-precision platinum resistance thermometer and a Fluke multimeter with 0.01 K accuracy. Considering the fluctuations in bath temperature during the measurements, the overall uncertainty in the reported pressure is estimated to be ±0.05 kPa. Similarly, the overall uncertainty in the reported temperature is estimated to be ±0.02 K.

A Hewlett-Packard 5890 Series II gas chromatograph equipped with an FID detector and a capillary column (HP5 cross-linked 5% phenyl methyl silicone, 50 m × 32 mm ×

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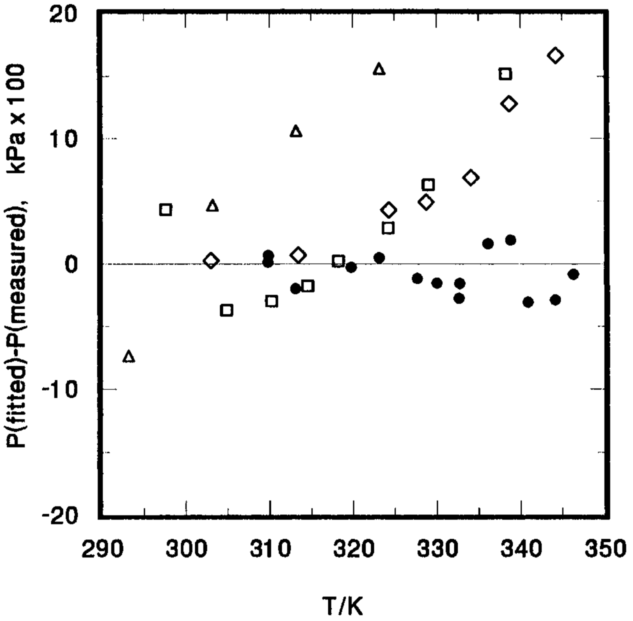

Figure 1. Comparison of acetic acid pure component saturation pressure from various sources: (●) measured in this work; (◇) Boublik et al. (1973); (△) Vargaftik (1975) (□) TRC Thermodynamic Tables (1990). See text for details.

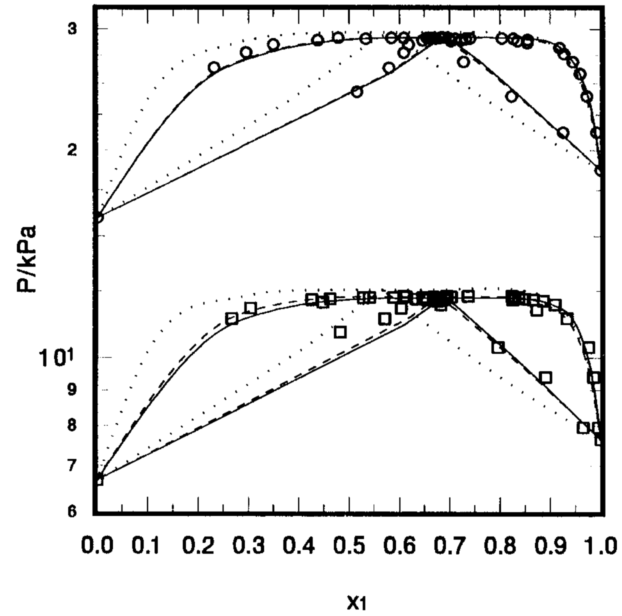

Figure 2. Vapor−liquid equilibrium of acetic acid (1) + octane (2) at 323.15 K and 343.15 K. Points are data measured in this work. Dotted lines are predictions by the original UNIFAC activity coefficient model, solid lines are correlations using the modified UNIQUAC model of Fu et al. (1995), and the dashed lines are predictions using the modified UNIFAC model of Fu et al. (1996).

Table 2. Vapor−Liquid Equilibria for Acetic Acid (1) + Octane (2)

1	y_1	P/kPa	x_1	y_1	P/kPa
		T = 343.15 K			
0.0000	0.0000	15.942	0.7409	0.6733	29.090
	0.5169	24.299	0.8039	0.6992	29.080
0.2313	0.5794	26.348	0.8268	0.7324	29.032
0.2946	0.6088	27.693	0.8556	0.7243	28.922
0.3492	0.6184	28.450	0.8351	0.7035	28.793
0.4372	0.6463	28.890	0.8543		28.598
0.4781	0.6599	29.105	0.9181		28.165
0.5330	0.6644	29.050	0.9272		27.600
0.5844	0.6679	29.100	0.9448	0.7284	26.847
0.6093	0.6820	29.115	0.9591		25.797
0.6554	0.6812	29.123	0.9731	0.8232	23.930
0.6864	0.6864	29.150	0.9921	0.9254	21.220
0.7119		29.050	1.0000	1.0000	18.722
		T = 323.15 K			
0.0000	0.0000	6.667	0.8303	0.7035	12.250
	0.4818	10.902	0.8372	0.6554	12.232
0.2660	0.5709	11.390	0.8475	0.6733	12.170
0.3038	0.6038	11.797	0.8254		12.125
0.4477		12.030	0.8661	0.6899	12.132
0.4619	0.6332	12.160	0.8855	0.6759	12.080
0.4252	0.6554	12.138	0.9085	0.6823	11.943
0.5277	0.6777	12.215	0.8727		11.730
0.5404	0.6509	12.232	0.9330		11.400
0.5893	0.6463	12.228	0.9758	0.7965	10.360
0.6136	0.6688	12.250	0.9860	0.8902	9.388
0.7365	0.6088	12.278	0.9952	0.9647	7.950
0.8232	0.6950	12.270	1.0000	1.0000	7.637

0.52 mm film thickness) was used for analyzing samples. The temperature of the injection port, detector, and oven were 120, 200, and 90 °C, respectively, during the analysis of the samples. A splitter was used on the helium carrier gas line to reduce the sample size fed to the detector. The total carrier gas flow rate was about 260 mL/min, with a septum purge rate of 2 mL/min, and the carrier gas flow through the column was 2.47 mL/min, all measured at the room temperature.

Gravimetrically prepared samples of 0.3 μL were analyzed over the entire concentration range to calibrate the gas chromatograph. The uncertainty in the mole fractions is estimated to be about ±0.005, except for mixtures containing less than about 20 mol % acid, where uncertainty increased sharply due to the low response of the FID detector to acetic acid. Consequently, we do not report experimental data in that region. Samples of the equilibrium phases were taken approximately 30 min after a composition change when conditions in the still had stabilized, and at least three analyses were made on each sample with intermittent checking of the calibration with gravimetrically prepared samples.

Results and Discussion

The vapor−liquid equilibrium data obtained for the two isotherms are presented in Table 2. The compositions of the liquid phase (x_1) and of the vapor phase (y_1) are given in mole fraction of acetic acid. From the data it is evident that this mixture is highly nonideal. Preliminary trials with several equation of state models and with the original UNIFAC activity coefficient model that do not take association into account did not give very successful results for the VLE correlation and prediction of this system, especially for the vapor phase. The predictions from the original UNIFAC activity coefficient model are shown as dotted lines in Figure 2.

Next we used a correlative and a predictive activity coefficient model recently proposed by Fu et al. (1995, 1996), both of which account for the association in both phases. One of these models (Fu et al., 1995) is a modification of the UNIQUAC model, based on the association theory of Wertheim (1984), in which the hydrogen bond is treated as a strong physical interaction rather than a chemical reaction. This model considers the association term as an additional contribution to the activity coefficient term of the UNIQUAC model:

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} + \ln \gamma_i^{\text{assoc}} \tag{2}$$

The first two terms are the combinatorial and residual contributions, respectively, to the activity coefficient of species i as given by the original UNIQUAC model. The last term represents the association contribution. If none

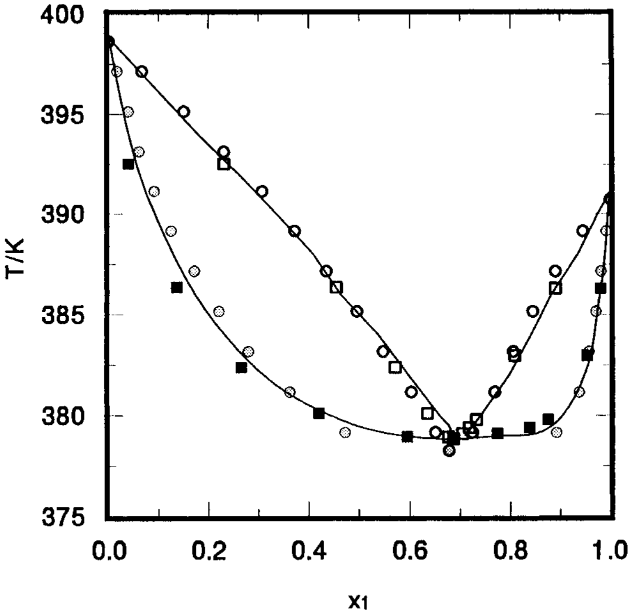

Figure 3. Vapor−liquid equilibrium of acetic acid (1) + octane (2) at 101.33 kPa. Points are data as compiled in the TRC Data Base (1996) from two different sources. Solid lines are predictions using the modified UNIQUAC model of Fu et al. (1995), with parameters linearly extrapolated with respect to temperature using parameter values obtained at 323.15 K and 343.15 K.

of the components in a mixture hydrogen bonds, then the association term vanishes and the original UNIQUAC model is recovered. The activity coefficient contribution due to association is obtained from a residual Helmholtz energy term derived by Chapman et al. (1990) from Wertheim's association theory. This activity coefficient model contains two parameters for each pair of compounds in the mixture. The model also accounts for the vapor phase association by including a monomer−dimer reaction model of hydrogen bonding in the vapor. The details of the model are given by Fu et al. (1995). The results obtained with this model by fitting the two model parameters to the total pressure versus liquid composition data are shown as dashed lines in Figure 2. This model predicts a reasonably accurate azeotropic point and gives a good correlation of the vapor phase composition at both temperatures.

Next we extrapolated the model parameters obtained at 323.15 K and 343.15 K linearly with absolute temperature in order to predict the higher temperature isobaric phase behavior reported earlier (TRC Data Base, 1996). The results are shown in Figure 3. The agreement between the model predictions and the experimental data is very good. This indicates the compatibility between the isothermal data measured in this work and the isobaric data measured earlier at atmospheric pressure (between 380 K and 398 K), and also the extrapolation capability of the modified UNIQUAC model of Fu et al. (1995).

Finally, we tested a modification of the UNIFAC group contribution model by Fu et al. (1996). This model also makes use of eq 2; however, in this case, the first two terms are obtained from the original UNIFAC model. The last term is obtained from a functional group based association model, again developed from Wertheim's model. For the vapor phase the same monomer−dimer association model used in the modified UNIQUAC model described above was also used. With the binary group interaction parameters obtained earlier by Fu et al. for this model, the model could be used in a completely predictive manner. The results obtained are shown as solid lines in Figure 2. The results are very similar to those obtained using the modified UNIQUAC correlative model considered earlier.

Conclusion

Vapor−liquid equilibrium data for the acetic acid + octane binary system were obtained at 323.15 K and 343.15 K. This system was found to be highly nonideal with azeotropes at both temperatures. As a result of the self-association of acetic acid, only the models that account for association can represent the VLE behavior of this system accurately. We found that the recent models proposed by Fu et al. (1995, 1996) are adequate for this purpose.

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