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Liquid−Liquid Equilibria for the System 1-Methyl Propyl Ethanoate (1) + Acetic Acid (2) + Water (3) at (283.15 and 323.15) K

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Liquid−liquid equilibrium (LLE) data for the system 1-methyl propyl ethanoate + acetic acid + water were measured at temperatures of (283.15 and 323.15) K. The temperature influence on the LLE data is very small in the temperature range studied. The NRTL and UNIQUAC models were used to correlate the data for both ternary systems. The interaction parameters obtained from both models successfully correlated the equilibrium compositions.

Introduction

Liquid−liquid equilibrium (LLE) data are of interest in extraction operations and recovery of valuable products. Nowadays, liquid−liquid extraction has become one of the main separation technologies for separation of complex liquid mixtures. Owing to that, there has been a significant growth in the number of publications devoted to the study on LLE of ternary and quaternary mixtures, including experimental data and correlation parameters. In this way, phase equilibria studies supply essential information to select adequate solvents and the design of extractors. Although simulation programs provide a variety of possibilities for process synthesis, design, and optimization, the quality of the results depends on the quality of the models used.[1] In some cases, the results obtained predicting with group contribution methods might be sufficient, and in other cases exact experimental data and a good description of them with the thermodynamic models are necessary.[1] Hence, the experimental data and a modeling study of the system are required.

In this sense, although LLE for the acetic acid + water + acetate systems have been investigated[2−8] extensively because of their wide application in industrial processes, such as the synthesis of acetic esters, to the authors' knowledge, the experimental data for LLE in the mixture 1-methyl propyl ethanoate + acetic acid + water are not available in the literature. So, in this work, LLE of the 1-methyl propyl ethanoate + acetic acid + water have been measured at (283.15 and 323.15) K. The influence of temperature on the system has been studied. Finally, the NRTL[9] and UNIQUAC[10] models were used to correlate the experimental data for the ternary system discussed here. The models and parameters provide a basis for simulation and design of the commercial acetic acid LLE extraction.

Experimental Section

Materials. Ethanol ($w > 99.5$ %, analytical grade) was purchased from Panreac; 1-methyl propyl ethanoate ($w \geq 99$ % (GC)) was purchased from Sigma-Aldrich; and acetic acid ($w = 99.8$ % for analysis ACS) was supplied by Acros organics. Water from Merck (for chromatography, $w > 99.99$ %) was used. The reagents were used without further purification since impurities are smaller than the detection limit of the analytical method used. The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ± 0.01 K with a thermostatted bath. The uncertainty in refractive index and density measurements is ± 0.0002 and ± 0.01 $\text{kg}\cdot\text{m}^{-3}$, respectively.

The experimental values of these properties are given in Table 1 together with those given in the literature.[11,12] Appropriate precautions, such as adding zeolite pellets on the bottles, were taken when handling the reagents to avoid hydration.

Apparatus and Procedure. The equipment and liquid−liquid equilibrium measuring procedures were previously reported.[8]

The composition of the sampled liquid phases was determined using an HP 6890 Series chromatograph equipped with a thermal conductivity detector (TCD), an HP3395 integrator, and a 2 m × 1/8 in. column packed with Porapack Q-S 80/100. The detector temperature was 523 K, whereas the injector and column temperatures were 483 K. Very good peak separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. To obtain homogeneous mixtures of the standard, 1 mL of ethanol has been added to the calibration vials. The uncertainty in the mole fraction was usually less than 0.002 and ± 0.1 K in the temperature measurements.

Moreover, an experimental point near the plait point for the ternary system 1-methyl propyl ethanoate + acetic acid + water at (283.15 and 323.15) K was determined by the cloud point method. Experiments were conducted in sealed, heated vials with a total liquid volume of approximately 4 mL. Water was progressively added to a 1-methyl propyl ethanoate + acetic acid mixture of known composition until the mixture became cloudy.

Results and Discussion

The determination of composition of the equilibrium liquid phases for the system of 1-methyl propyl ethanoate + acetic acid + water was carried out at (283.15 and 323.15) K at

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Table 1. Densities ρ, Refractive Indexes n_D, and UNIQUAC Structural Parameters of the Used Pure Components

	ρ (T = 298.15 K)/(kg·m^{-3})		n_D (T = 298.15 K)		UNIQUAC parameters	
compound	exptl	lit.[a]	exptl	lit.[a]	r_i[b]	q_i[b]
1-methyl propyl ethanoate	865.22	866.00	1.3870	1.3875	4.8266	4.1920
water	997.06	997.05	1.3325	1.3325	0.9200	1.3997
acetic acid	1043.90	1043.90	1.3696	1.3698	2.2023	2.0720

[a] Taken from TRC tables.[11] [b] DECHEMA.[12]

Table 2. LLE Data for the 1-Methyl Propyl Ethanoate (1) + Acetic Acid (2) + Water (3) System

	1-methyl propyl ethanoate rich phase		water rich phase	
T/K	x_1	x_2	x_1	x_2
283.15	0.944	0.000	0.001	0.000
	0.884	0.027	0.002	0.009
	0.824	0.057	0.002	0.018
	0.786	0.087	0.002	0.027
	0.728	0.125	0.003	0.041
	0.677	0.157	0.003	0.053
	0.627	0.183	0.004	0.063
	0.576	0.212	0.004	0.081
	0.533	0.233	0.004	0.092
	0.485	0.252	0.006	0.108
	0.428	0.274	0.007	0.128
	0.406	0.281	0.009	0.138
	0.366	0.292	0.011	0.156
	0.328	0.297	0.013	0.171
	0.238	0.292	0.021	0.193
	0.198	0.288	0.031	0.212
	0.189	0.283	0.029	0.201
	0.134	0.268	0.051	0.224
323.15	0.906	0.000	0.001	0.000
	0.856	0.031	0.001	0.010
	0.801	0.055	0.002	0.017
	0.758	0.093	0.002	0.029
	0.696	0.128	0.002	0.042
	0.666	0.143	0.002	0.052
	0.510	0.225	0.004	0.086
	0.481	0.248	0.006	0.113
	0.416	0.257	0.007	0.133
	0.389	0.270	0.009	0.144
	0.338	0.285	0.012	0.164
	0.292	0.277	0.018	0.177
	0.249	0.281	0.023	0.197
	0.201	0.273	0.037	0.213
	0.580	0.181	0.003	0.068
	0.520	0.224	0.004	0.084

atmospheric pressure and is presented in Table 2. All concentrations are expressed in mole fractions. The NRTL[9] and UNIQUAC[10] models were used to correlate the experimental data for the ternary systems discussed. To fit the UNIQUAC interaction parameters, the structural parameters (r_i and q_i) recommended by DECHEMA[12] were used for the pure components and are listed in Table 1. The nonrandomness parameter (α_{ij}) of the NRTL equation was fixed at 0.2 or 0.3. The binary interaction parameters were obtained using the CHEMCAD 6.0 Chemstations Inc. software, and the values which give the best results are given in Table 3.

There are two effective binary interaction parameters for a binary subsystem. Therefore, six effective binary interaction parameters are required for a ternary system. The corresponding sets of binary interaction parameters were determined by minimizing the differences between the experimental and calculated equilibrium mole fractions for each of the components for all the experimental tie lines. The objective function (OF) used is

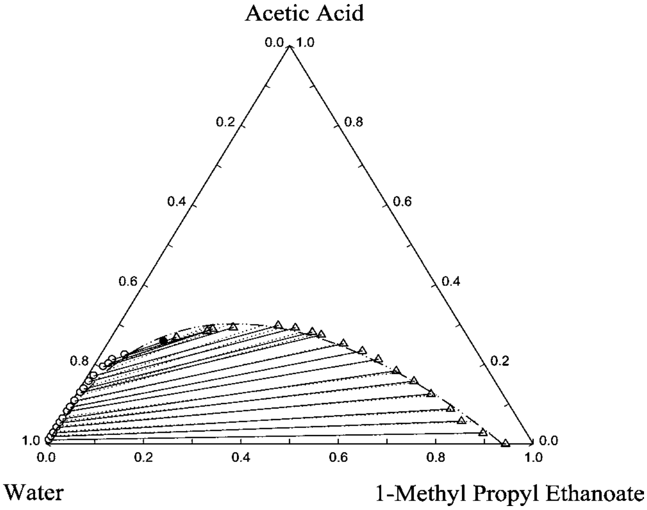

Figure 1. Liquid−liquid equilibria of the 1-methyl propyl ethanoate (1) + acetic acid (2) + water (3) system at T = 283.15 K. Experimental data: Δ, the 1-methyl propyl ethanoate rich phase; ○, the aqueous phase; —, experimental lines. Calculated using the UNIQUAC model: ••—••—••, binodal curve; •••••, tie lines; ●, experimental cloud point.

$$\mathrm{OF} = \sum_{k=1}^{M} \sum_{j=1}^{2} \sum_{i=1}^{3} (x_{ijk} - \hat{x}_{ijk})^2 \tag{1}$$

where M is the number of tie lines; x indicates the experimental mole fraction; $\hat{x}$ is the calculated mole fraction; and subscripts i, j, and k denote, respectively, component, phase, and tie line.

The correlation of experimental data was carried out separately at each temperature. The binary interaction parameters calculated in this way are given in Table 3. Also, the root-mean-square deviation (rmsd) of the phase compositions is included in this table

$$\mathrm{rmsd} = 100 \cdot \left(\sum_{k=1}^{M} \sum_{j=1}^{2} \sum_{i=1}^{3} \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M} \right)^{1/2} \tag{2}$$

The rmsd is a measure of the agreement between the experimental and calculated data. In Table 3, it can be observed

Table 3. UNIQUAC and NRTL Binary Interaction Parameters for the System 1-Methyl Propyl Ethanoate (1) + Acetic Acid (2) + Water (3)

	UNIQUAC parameters				NRTL parameters			
T/K	$i-j$	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}	100 rmsd	α	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}	100 rmsd
283.15	1−2	−1542.21	1278.82	1.02	0.2	−3261.24	609.45	1.19
	1−3	4126.01	1048.92		0.2	2845.60	11973.57	
	2−3	−1676.73	1375.24		0.3	−3432.02	5116.52	
323.15	1−2	−2008.41	478.26	0.999	0.2	−4112.55	2175.38	1.11
	1−3	4480.21	639.87		0.2	2162.66	12465.36	
	2−3	−1271.74	−400.63		0.3	−3246.69	5528.24	

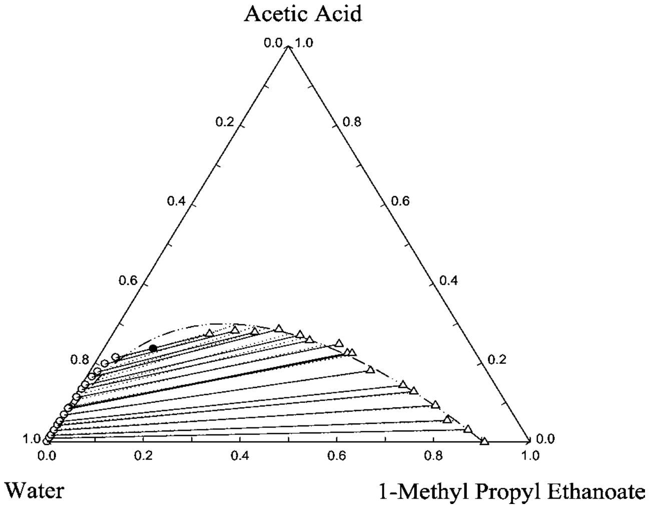

Figure 2. Liquid−liquid equilibria of the 1-methyl propyl ethanoate (1) + acetic acid (2) + water (3) system at $T = 323.15$ K. Experimental data: Δ, 1-methyl propyl ethanoate rich phase; ○, aqueous phase; —, experimental lines. Calculated using the UNIQUAC model: ••—••—••, binodal curve; •••••, tie lines; ●, experimental cloud point.

that both models were found to properly correlate the data for the 1-methyl propyl ethanoate + acetic acid + water system, but the UNIQUAC model gives the best results. In Figures 1 and 2, the experimental data at (283.15 and 323.15) K have been plotted for 1-methyl propyl ethanoate + acetic acid + water together with binodal curves calculated using the UNIQUAC model and some experimental and calculated tie lines. As was shown in Figures 1 and 2, the temperature influence on the LLE data is very small in the temperature range studied. On the other hand, to check the shape of the binodal curve near to the plait-point, the cloud method was used to obtain one point for each temperature. This point was shown in Figures 1 and 2.

Conclusions

Liquid−liquid equilibrium data of 1-methyl propyl ethanoate + acetic acid + water have been measured at (283.15 and 323.15) K. The temperature has practically no effect on the size of the immiscibility region in the investigated temperature range. The LLE data were correlated using the NRTL and UNIQUAC activity coefficient models. The correlation with the UNIQUAC equation gives better results for the system 1-methyl propyl ethanoate + acetic acid + water. The models and parameters provide a basis for simulation and design of the commercial acetic acid LLE extraction.

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