Liquid−Liquid Equilibria of Methyl Acetate + Methanol + Octane or Nonane

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Liquid−liquid equilibria for the ternary systems methyl acetate + methanol + octane and methyl acetate + methanol + nonane were studied at (278.15, 288.15, and 298.15) K and at atmospheric pressure. Composition analysis of each phase was carried out by gas chromatography. The nonrandom two-liquid and universal quasichemical models were used to correlate the experimental results. A good fit has been obtained as a function of temperature for all cases studied. The UNIFAC group contribution method and its modifications have been applied to test their prediction capability. A poor prediction was observed from the contribution methods.

Introduction

Ternary-phase equilibrium data are essential for the proper understanding of solvent extraction processes, selection of solvents, and design of extractors. It is necessary to know, using experimental data or theory and semiempirical predictive methods, the compositions of the two phases in equilibrium. In this way, the phase equilibrium study supplies essential information for the separation processes design and optimization. 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. In some cases, the results based on calculations using group contribution methods might be sufficient; in other cases, experimental data and a good description of them with the used thermodynamic models is required. Hence, experimental data and knowledge of the predictive capability of group contribution methods are required. In this work liquid−liquid equilibria (LLE) of the methyl acetate + methanol + octane and methyl acetate + methanol + nonane mixtures have been measured. Experimental data for these mixtures are not available in open literature.

Experimental Section

Materials. The chemicals were supplied by Sigma. Further purification was achieved by ultrasonic degassing and molecular sieves drying (type 3Å for methanol and 4Å for methyl acetate and *n*-alkanes, $^{1}/_{16}$ in.). The chemicals were stored in inert argon (N55, less than 3 ppm by volume in water). The purity of materials was checked by gas chromatography and found to be better than 99.6 mass % for methyl acetate, 99.8 mass % for methanol, 99.7 mass % for octane, and 99.2 mass % for nonane and the maximum water contents of the pure liquids (Coulometric Moisture Model CA-06) were (6.8×10^{-3}, 1.5×10^{-2}, 8.0×10^{-4}, and 2.6×10^{-3}) mass % for methyl acetate, methanol, octane, and nonane, respectively.

Apparatus and Procedure. LLE measurements were carried out in a jacketed glass cell with a magnetic stirrer. The cell was connected to a PolyScience bath model 9510, whose temperature stability was $\pm 10^{-2}$ K. The cell temperature was measured with a Yokogawa 7563 digital thermometer with a precision of $\pm 10^{-2}$ K, calibrated with an Anton Paar MKT-100 digital thermometer (precision $\pm 10^{-3}$ K, temperature scale ITS-90) over the entire temperature range. The samples were prepared by mass using a Mettler AX 205 DeltaRange balance with a precision of ±0.00008 g, which gives an uncertainty of $\pm 4 \times 10^{-4}$ mole fraction. Each mixture was stirred for 60 min and then left to settle for at least 12 h. After equilibrium was attained, the phases were allowed to separate and small samples were taken from the upper and lower phase with a syringe. The compositions were determined by gas chromatography using a Hewlett-Packard HP-6890 Series GC System chromatograph equipped with a flame ionization detector and a HP-1 19091Z-215 (methyl siloxane, 50 m $\times$ 3.2×10^{-4} m $\times$ 1.05×10^{-6} m film thickness) capillary column. The carrier gas used was helium and the flow rate was 0.8 mL/min. Both injector and detector temperatures were maintained at 503.15 K. The initial column temperature was 363.15 K, and the final temperature was 523.15 K. The peak areas were converted to the mole fractions using weight factors determined by the gas chromatographic analysis of mixtures of known composition. Estimated uncertainties for mole fractions were determined as $\pm 3 \times 10^{-3}$ in the *n*-alkane-rich region (phase I) and $\pm 2 \times 10^{-3}$ in the methanol-rich region (phase II).

Results and Discussion

The tie-line compositions of the mixtures methyl acetate + methanol + octane or nonane at (278.15, 288.15, and 298.15) K are given in Table 1.

The LLE data for the binary systems methanol + *n*-alkane have been previously published.[1,2] As expected, the size of the two-phase region decreases with an increase in temperature. On the other hand, it can be observed that the immiscibility region also decreases with the alkane chain decreasing.

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Table 1. Experimental LLE Data of the Studied Ternary Mixtures (I, Alkane-Rich Phase; II, Methanol-Rich Phase)

x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}
Methyl Acetate (1) + Methanol (2) + Octane (3)							
278.15 K							
0.000	0.088	0.000	0.957	0.151	0.191	0.187	0.713
0.019	0.091	0.024	0.929	0.163	0.206	0.201	0.692
0.039	0.104	0.052	0.895	0.181	0.233	0.217	0.660
0.059	0.119	0.079	0.862	0.201	0.260	0.240	0.614
0.079	0.134	0.105	0.825	0.206	0.267	0.243	0.604
0.109	0.155	0.137	0.785	0.222	0.296	0.254	0.567
0.124	0.161	0.157	0.754	0.235	0.327	0.262	0.529
0.142	0.184	0.177	0.724				
288.15 K							
0.000	0.095	0.000	0.952	0.106	0.206	0.124	0.778
0.015	0.110	0.018	0.928	0.124	0.233	0.145	0.741
0.032	0.130	0.039	0.898	0.149	0.279	0.172	0.688
0.051	0.147	0.061	0.871	0.159	0.300	0.185	0.658
0.065	0.161	0.078	0.846	0.172	0.333	0.194	0.626
0.086	0.186	0.102	0.811	0.181	0.364	0.201	0.599
298.15 K							
0.000	0.115	0.000	0.940	0.090	0.238	0.101	0.786
0.023	0.147	0.024	0.908	0.104	0.267	0.114	0.760
0.043	0.173	0.050	0.866	0.125	0.326	0.136	0.698
0.066	0.207	0.076	0.825	0.138	0.363	0.149	0.658
Methyl Acetate (1) + Methanol (2) + Nonane (3)							
x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}
278.15 K							
0.000	0.063	0.000	0.974	0.178	0.165	0.234	0.690
0.020	0.074	0.026	0.944	0.214	0.194	0.268	0.639
0.037	0.084	0.050	0.918	0.243	0.218	0.300	0.589
0.063	0.094	0.085	0.877	0.263	0.240	0.318	0.552
0.091	0.107	0.123	0.832	0.263	0.239	0.319	0.552
0.112	0.119	0.154	0.794	0.272	0.251	0.324	0.539
0.132	0.137	0.173	0.771	0.282	0.265	0.329	0.517
0.148	0.147	0.197	0.744				
288.15 K							
0.000	0.082	0.000	0.968	0.140	0.191	0.166	0.760
0.023	0.095	0.027	0.935	0.157	0.205	0.188	0.731
0.039	0.104	0.047	0.913	0.184	0.236	0.214	0.689
0.065	0.122	0.079	0.873	0.198	0.255	0.228	0.657
0.085	0.137	0.101	0.847	0.219	0.290	0.248	0.621
0.103	0.158	0.121	0.821	0.248	0.330	0.271	0.539
0.125	0.178	0.147	0.787				
298.15 K							
0.000	0.098	0.000	0.963	0.139	0.253	0.159	0.747
0.022	0.114	0.027	0.933	0.158	0.280	0.175	0.714
0.041	0.138	0.047	0.904	0.164	0.292	0.182	0.707
0.068	0.165	0.076	0.862	0.165	0.295	0.183	0.702
0.087	0.184	0.098	0.835	0.177	0.315	0.195	0.674
0.103	0.203	0.122	0.803	0.193	0.362	0.209	0.641
0.124	0.230	0.144	0.771	0.206	0.407	0.218	0.596

Correlation of Tie Lines. The universal quasichemical (UNIQUAC)[3] and nonrandom two-liquid (NRTL)[4] equations were applied to correlate the experimental data, using these temperature-dependence parameters,[5] respectively

$$\tau_{ij} = \exp\left(-\frac{a_{ij} + b_{ij}T}{RT}\right) \tag{1}$$

$$\tau_{ij} = \frac{a_{ij} + b_{ij}T}{RT} \tag{2}$$

where a_{ij} is a temperature-independent parameter (J·mol^{-1}) and b_{ij} is a dependent parameter (J·mol^{-1}·K^{-1}).

Table 2. Parameters of NRTL and UNIQUAC Equations and Root-Mean-Square Deviations σ (I, Alkane-Rich Phase; II, Methanol-Rich Phase)

Methyl Acetate (1) + Methanol (2) + Octane (3)						
NRTL						
	12	21	13	31	23	32
a	−30586.3	11299.0	−16693.7	25963.4	9121.21	5929.78
b	122.607	−47.420	59.331	−78.200	−17.591	−0.262
	$\sigma(x_1^{I})$	$\sigma(x_2^{I})$	$\sigma(x_1^{II})$	$\sigma(x_2^{II})$		
278.15 K	0.004	0.019	0.002	0.008		
288.15 K	0.004	0.029	0.004	0.014		
298.15 K	0.004	0.027	0.004	0.018		
UNIQUAC						
	12	21	13	31	23	32
a	−13017.9	7800.81	−13909.5	10978.1	6406.48	994.311
b	48.501	−27.468	52.205	−37.733	−2.672	−2.864
	$\sigma(x_1^{I})$	$\sigma(x_2^{I})$	$\sigma(x_1^{II})$	$\sigma(x_2^{II})$		
278.15 K	0.004	0.019	0.002	0.009		
288.15 K	0.005	0.030	0.004	0.014		
298.15 K	0.004	0.023	0.003	0.019		
Methyl Acetate (1) + Methanol (2) + Nonane (3)						
NRTL						
	12	21	13	31	23	32
a	−23662.6	14543.6	2003.01	1169.05	11863.9	5926.63
b	96.006	−58.555	−8.817	12.104	−26.033	2.639
	$\sigma(x_1^{I})$	$\sigma(x_2^{I})$	$\sigma(x_1^{II})$	$\sigma(x_2^{II})$		
278.15 K	0.002	0.007	0.001	0.004		
288.15 K	0.003	0.010	0.001	0.007		
298.15 K	0.003	0.018	0.001	0.011		
UNIQUAC						
	12	21	13	31	23	32
a	−8501.86	7522.47	−867.247	624.933	8350.77	849.312
b	31.696	−26.229	5.423	−0.789	−8.241	−2.259
	$\sigma(x_1^{I})$	$\sigma(x_2^{I})$	$\sigma(x_1^{II})$	$\sigma(x_2^{II})$		
278.15 K	0.002	0.009	0.001	0.004		
288.15 K	0.003	0.015	0.003	0.010		
298.15 K	0.004	0.028	0.003	0.015		

For the NRTL model, the third randomness parameter (α_{ij}) was set at a value of 0.3. The parameters calculated in this way (a_{ij} and b_{ij}), and the root-mean-square deviations for the NRTL and UNIQUAC equations, are shown in Table 2. As it can be observed from Table 2, the correlations obtained with both models are similar, presenting a good accuracy. For instance, Figure 1 shows the correlation results using the NRTL equation.

Prediction Models. Prediction of LLE for the ternary systems studied has been carried out by the UNIFAC group contribution method[6] with parameters obtained from vapor−liquid[7] or LLE[8] data and its modifications: UNIFAC Dortmund[9−11] and UNIFAC-Lyngby.[12] As shown in Figure 2, all of them overestimate the split region at each temperature with the exception of UNIFAC with parameters obtained from LLE data (UNIFAC-LLE), which underestimates this region. Perhaps it is due to insufficient ester group information in the contribution method database. This fact could be clearly observed by the predicted immiscibility by the nonsymmetric tendency toward methyl acetate + nonane linear mixture, which estimate an LLE for these binary mixture at 278.15

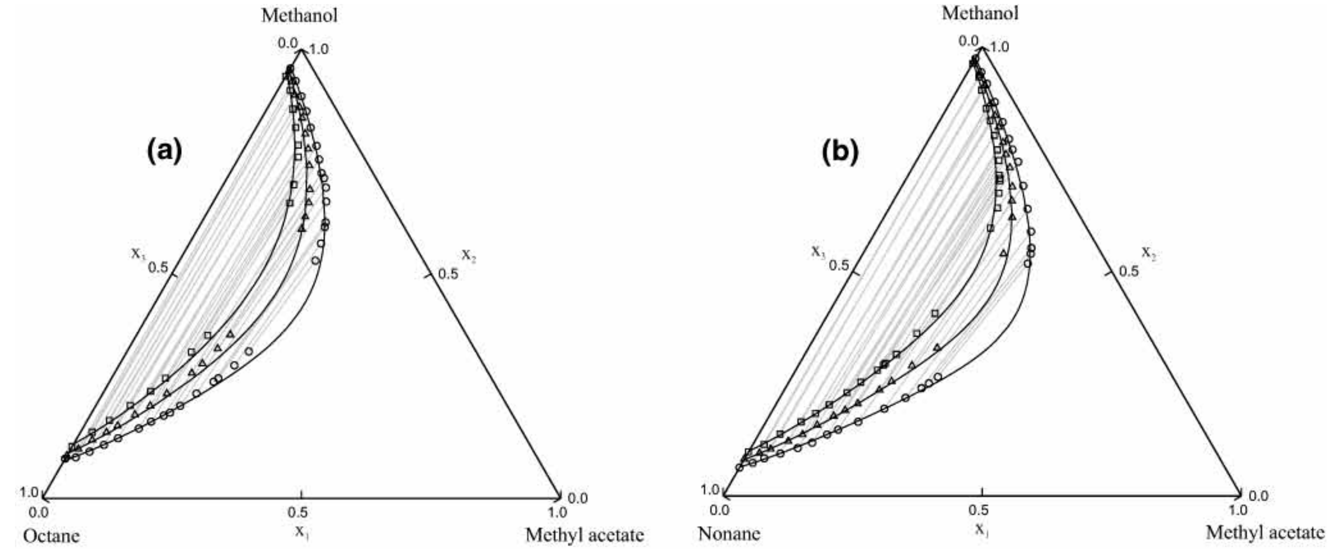

Figure 1. Experimental tie lines and binodal curves correlation by NRTL equation for (a) methyl acetate (1) + methanol (2) + octane (3) and (b) methyl acetate (1) + methanol (2) + nonane (3). Experimental tie lines: (○), 278.15 K; (△), 288.15 K; (□), 298.15 K; (solid line) NRTL equation.

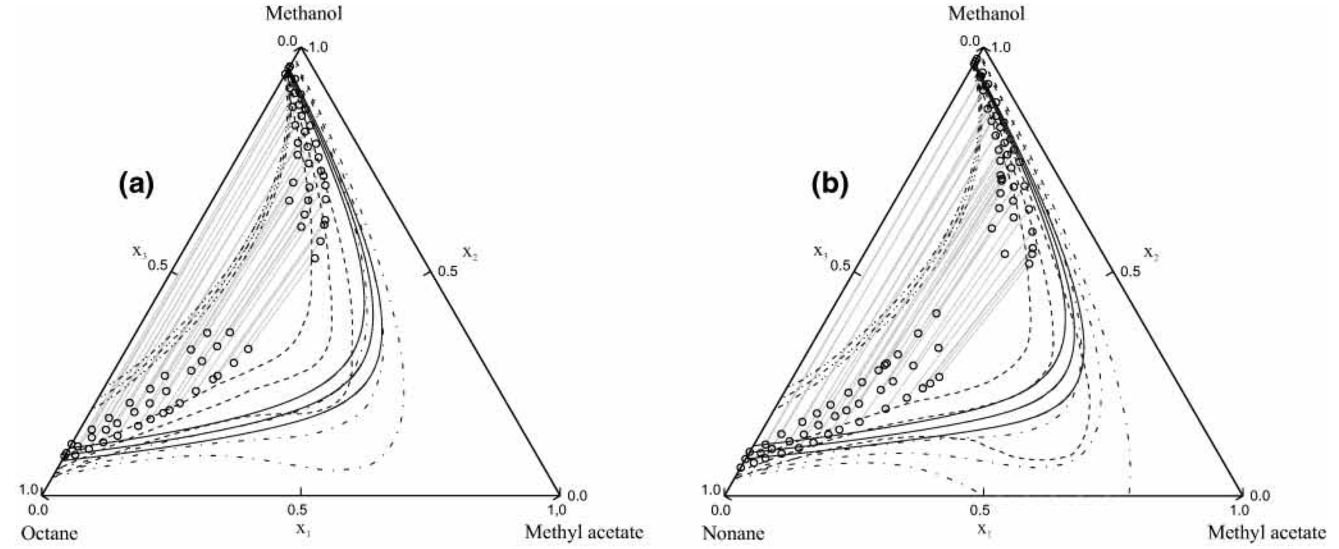

Figure 2. Experimental tie lines (○) and prediction by UNIFAC-Original (solid line), UNIFAC-LLE (dot-dot-dashed line), UNIFAC-Dortmund (dashed line), UNIFAC-Lyngby (dot-dashed line) for (a) methyl acetate (1) + methanol (2)+ octane (3) and (b) methyl acetate (1) + methanol (2) + nonane (3) at 278.15 K, 288.15 K, and 298.15 K.

K. On the contrary, this binary mixture shows a homogeneous experimental trend in the whole range of temperatures[2].

Conclusions

The LLE experimental data for the systems methyl acetate + methanol + octane or nonane were determined at (278.15, 288.15, and 298.15) K and at atmospheric pressure. These data have been satisfactorily correlated as a function of temperature by both UNIQUAC and NRTL equations.

UNIFAC group contribution method and its modifications have been applied to predict these mixtures. No method has been able to predict adequately the split region of these mixtures. Such effect reveals the importance of a wider disposal of thermodynamic liquid split data for an adequate description of multicomponent heterogeneous mixtures in order to design separation units.

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