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Liquid−Liquid Equilibria of Acetone + Methanol + *n*-Alkane (C_6−C_8) at Different Temperatures

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Liquid−liquid equilibria have been measured for the systems acetone + methanol + *n*-alkane (C_6−C_8) at 278.15, 288.15, and 298.15 K. Phase compositions were measured by gas chromatography from samples splitted isothermally in a glass stirred device. The tie line data were correlated with the UNIQUAC model and the corresponding fitting parameters being gathered. The UNIFAC group contribution method and its modifications were applied to test their capability to predict liquid−liquid equilibrium, only poor accuracy being obtained for these ternary systems.

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1. Introduction

Liquid−liquid extraction and modified rectification are usual operations in the solvent separation processes where the miscibility of chemicals develops a key role for the design and development of such unit operations. Despite time-consuming theoretical research and experimental work to obtain accurate data, the most widespread predictive methods, such as group contribution models, are of scarce utility to compute liquid equilibrium. In accordance with these reasons, the experimental data related to phase equilibrium are of present interest for practical and theoretical application.

Continuing our research for thermodynamic characterization of mixtures (Iglesias et al., 1998, 1999a−c), we present the dependence of the liquid−liquid equilibria on temperature for the ternary systems acetone + methanol + (hexane, heptane, or octane), focusing on analyzing short linear hydrocarbons as alternative solvents for heterogeneous extractive distillation. The liquid−liquid equilibria data for the binary systems methanol + *n*-alkane have been previously published (Orge et al., 1997). The measured experimental data were correlated by means of the UNIQUAC equation (Abrams and Prausnitz, 1975), the corresponding fitting parameters being gathered. UNIFAC group contribution method (Fredenslund et al., 1975; Magnussen et al., 1981) and its modifications (Gmehling and Weidlich, 1986; Larsen et al., 1987) were applied to test their prediction capability, with only a qualitative description being obtained.

2. Experimental Section

The chemicals used were supplied by Merck and were of chromatographic quality. The purities are >99.8 mass % for acetone and methanol and >99.0 mass % for *n*-alkanes. The liquids were degassed in an ultrasonic bath for 4 h, stored in inert argon (<3 ppmv in water), and dried over molecular sieves type 3 Å for acetone and methanol and 4 Å for *n*-alkanes, 1/16 in. (Aldrich cat. no. 20,860-4 or 20,858-2, respectively). The chemicals were checked using gas chromatography, better purities being obtained than those from vendor specifications. The densities and refractive indexes of pure substances were measured and compared (Table 1) with other recent literature values at 298.15 K and atmospheric pressure. The densities of the pure substances were measured with an Anton Paar DSA-48 densimeter and a sound analyzer, with a precision of ±0.000 05 $g \cdot cm^{-3}$, and the refractive indexes, with an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of ±0.000 01; finally, the accuracy of the data was found to be ±0.0001 $g \cdot cm^{-3}$ and ±0.000 04 for the densities and the refractive indexes, respectively. The experimental procedure of density and refractive index measurement in our laboratory was explained previously (Iglesias et al., 1998). The liquid−liquid equilibria of the systems acetone + methanol + (hexane, heptane, or octane) at 278.15, 288.15, and 298.15 K and atmospheric pressure were measured experimentally by means of a 5.0×10^{-5} m^3 jacketed glass cell with a magnetic stirrer and a controlled-temperature bath, PolyScience model 9510, whose temperature stability was $\pm 10^{-2}$ K. The temperature in the cell 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 range of the work. The sample was stirred for 30 min and then left to settle for at least 5 h. After equilibrium was attained, the phases were allowed to separate and small samples of approximately 2 mL were taken from each phase with a syringe. The compositions were determined by gas chromatography, with an internal standard calibration method.

Table 1. Comparison of Measured Pure Component Property Data with Literature Values at 298.15 K

	$\rho/(g \cdot cm^{-3})$		n_D	
component	exptl	lit.	exptl	lit.
acetone	0.7844	0.78429[a] 0.78547[b]	1.35580	1.35596[b]
methanol	0.7866	0.78664[b]	1.32645	1.32652[b]
hexane	0.6551	0.65484[b] 0.6549[c]	1.37234	1.37226[b]
heptane	0.6794	0.6794[b]	1.38512	1.3850[d]
octane	0.6985	0.69862[b]	1.39514	1.39505[b]

[a] Hnedkovsky and Cibulka (1993). [b] *TRC Thermodynamic Tables* (1994). [c] Aminabhavi et al. (1996). [d] Sastry and Valand (1996).

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Table 2. Experimental Data of the Liquid−Liquid Equilibrium of the Systems Acetone (1) + Methanol (2) + (Hexane or Heptane or Octane) (3) and Root Mean Square Deviations σ

278.15 K				288.15 K				298.15 K			
x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}
Acetone + Methanol + Hexane											
0.000	0.137	0.000	0.873	0.000	0.186	0.000	0.835	0.000	0.267	0.000	0.801
0.005	0.142	0.013	0.847	0.006	0.201	0.016	0.820	0.005	0.288	0.010	0.761
0.013	0.146	0.033	0.821	0.010	0.206	0.025	0.803	0.008	0.308	0.015	0.744
0.022	0.157	0.055	0.798	0.022	0.236	0.051	0.746	0.016	0.322	0.024	0.717
0.038	0.176	0.081	0.746	0.061	0.342	0.077	0.637	0.022	0.339	0.030	0.687
0.070	0.227	0.116	0.663	0.066	0.389	0.079	0.605				
0.126	0.319	0.166	0.537								
	$\sigma(x_1^{\mathrm{I}})$			$\sigma(x_2^{\mathrm{I}})$			$\sigma(x_1^{\mathrm{II}})$			$\sigma(x_2^{\mathrm{II}})$	
	0.001			0.004			0.001			0.005	
Acetone + Methanol + Heptane											
0.000	0.095	0.000	0.936	0.000	0.127	0.000	0.915	0.000	0.153	0.000	0.904
0.004	0.098	0.020	0.901	0.005	0.129	0.015	0.893	0.005	0.184	0.014	0.880
0.013	0.100	0.041	0.873	0.011	0.129	0.031	0.860	0.009	0.191	0.028	0.854
0.018	0.106	0.066	0.843	0.020	0.132	0.055	0.822	0.027	0.207	0.048	0.827
0.030	0.110	0.096	0.805	0.041	0.144	0.099	0.773	0.064	0.264	0.107	0.710
0.045	0.122	0.173	0.702	0.057	0.158	0.126	0.729	0.102	0.391	0.124	0.603
0.078	0.134	0.212	0.646	0.087	0.201	0.165	0.647				
0.121	0.154	0.252	0.574	0.155	0.355	0.195	0.541				
0.166	0.177	0.279	0.481								
	$\sigma(x_1^{\mathrm{I}})$			$\sigma(x_2^{\mathrm{I}})$			$\sigma(x_1^{\mathrm{II}})$			$\sigma(x_2^{\mathrm{II}})$	
	0.002			0.006			0.005			0.009	
Acetone + Methanol + Octane											
0.000	0.088	0.000	0.957	0.000	0.095	0.000	0.952	0.000	0.105	0.000	0.939
0.091	0.125	0.156	0.777	0.022	0.125	0.053	0.888	0.014	0.120	0.029	0.899
0.128	0.142	0.222	0.695	0.041	0.148	0.084	0.851	0.024	0.132	0.050	0.874
0.163	0.154	0.294	0.599	0.073	0.174	0.123	0.810	0.040	0.157	0.084	0.835
0.220	0.175	0.369	0.502	0.091	0.193	0.177	0.719	0.062	0.192	0.114	0.796
0.289	0.206	0.415	0.450	0.117	0.207	0.225	0.662	0.085	0.215	0.146	0.745
				0.154	0.230	0.267	0.614	0.106	0.232	0.171	0.709
				0.237	0.285	0.316	0.524	0.129	0.256	0.208	0.661
	$\sigma(x_1^{\mathrm{I}})$			$\sigma(x_2^{\mathrm{I}})$			$\sigma(x_1^{\mathrm{II}})$			$\sigma(x_2^{\mathrm{II}})$	
	0.003			0.007			0.006			0.008	

Table 3. Parameters of the UNIQUAC Equation

i	j	a_{ij}	a_{ji}	b_{ij}/K	b_{ji}/K
Acetone + Methanol + Hexane					
acetone	methanol	2.512 823	69.660 05	−632.9674	−19456.52
acetone	*n*-hexane	37.744 49	60.157 63	−11292.41	−16676.06
methanol	*n*-hexane	0.368 464	2.447 340	−112.7674	−1278.591
Acetone + Methanol + Heptane					
acetone	methanol	−1.139 710	19.572 23	461.4783	−5598.379
acetone	*n*-heptane	−0.614 722 4	18.553 80	137.6429	−5373.369
methanol	*n*-heptane	0.343 202 2	2.588 562	−112.0708	−1388.782
Acetone + Methanol + Octane					
acetone	methanol	0.703 563 2	9.157 445	−163.9125	−2673.614
acetone	*n*-octane	−6.925 900	7.764 735	1843.627	−2284.951
methanol	*n*-octane	1.574 742	3.004 333	−470.6289	−1536.035

To this aim, we have prepared mixtures near the immiscibility region by mass using a Mettler AE-240 balance with a precision of $\pm 10^{-4}$ g, which led to an accuracy of $\pm 5 \times 10^{-5}$ molar fraction in the standards used in the calibration. The reference samples were analyzed using the same chromatographic conditions as those for the equilibrium samples. The accuracy estimated in mole fraction for the equilibrium data was 3×10^{-3} in the *n*-alkane-rich region (phase I) and 2×10^{-3} in the methanol-rich region (phase II). The chromatograph device was a Hewlett Packard 6890 Series GC System equipped with a flame ionization detector and a HP-INNOWax 19091N-133 of cross-linked poly(ethylene glycol) [30 m × $(2.5 \times 10^{-4}$ m) × $(2.5 \times 10^{-7}$ m) film thickness]. The injector and detector temperatures were maintained at 448.15 K and 473.15 K, respectively. The column temperature was maintained at 313.15 K, and the flow rate of the nitrogen carrier gas was 6×10^{-7} mL/min.

3. Results and Discussion

The equilibrium compositions are gathered in Table 2. The UNIQUAC equation was applied to correlate the experimental data, and good accuracy has been achieved for all cases with temperature dependence parameters:

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

The fitting parameters (a_{ij} and b_{ij}) are enclosed in Table 3, and the root-mean-square deviations are gathered in Table 2. Parts a, b, and c of Figure 1 show the experimental and correlated tie lines of the ternary systems with the UNIQUAC model. The effect of temperature on the equilibrium for all the ternary systems is shown in Figure 2. As expected, the size of the two-phase region decreases with an increase in temperature. Nagata (1994) published liquid−liquid equilibrium data for the ternary system

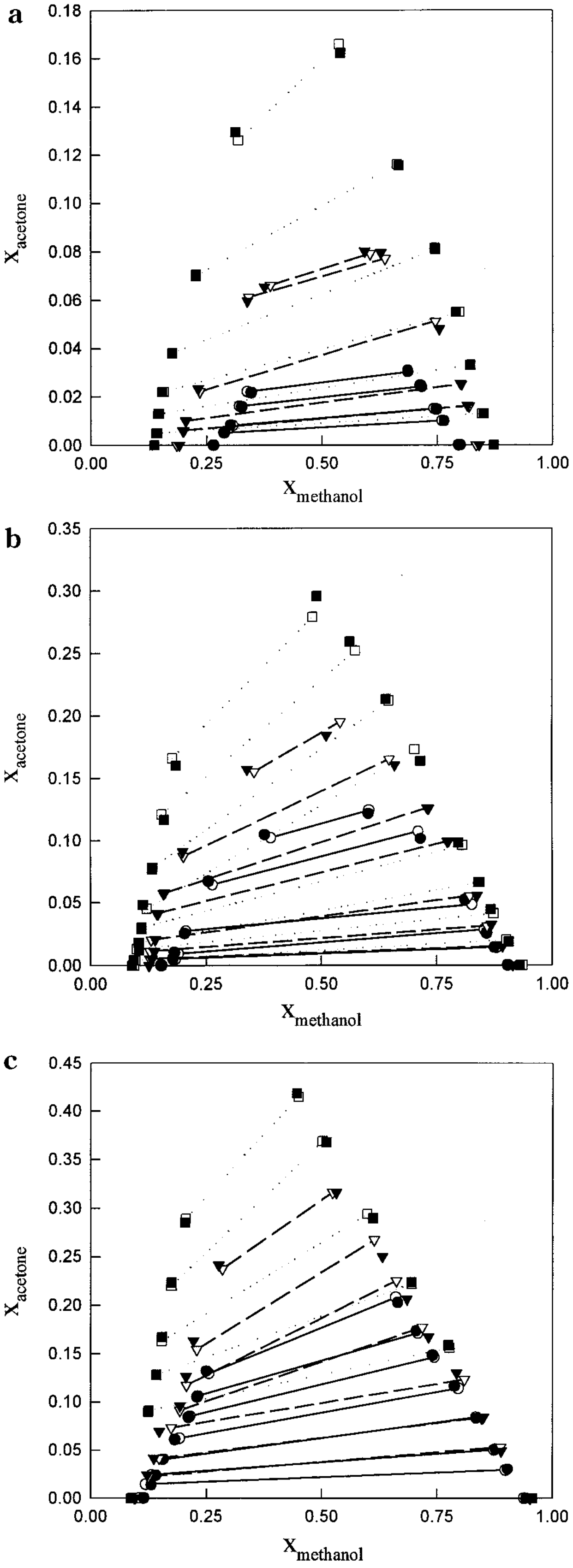

Figure 1. Experimental tie lines and estimated data from the UNIQUAC model at the temperatures 278.15 K (■, exp; □, corr), 288.15 K (▼, exp; ▽, corr), and 298.15 K (●, exp; ○, corr) for (a) (—) acetone (1) + methanol (2) + hexane (3), (b) (– – –) (1) acetone + methanol (2) + heptane (3), and (c) (· · ·) acetone (1) + methanol (2) + octane (3).

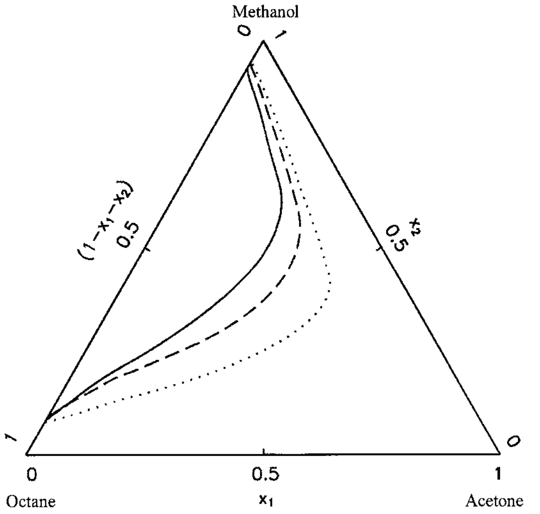

Figure 2. Effect of temperature on the liquid–liquid equilibrium for the ternary system acetone (1) + methanol (2) + octane (3) (curves computed by the UNIQUAC equation): (· · ·) 278.15 K; (– – –) 288.15 K; (—) 298.15 K.

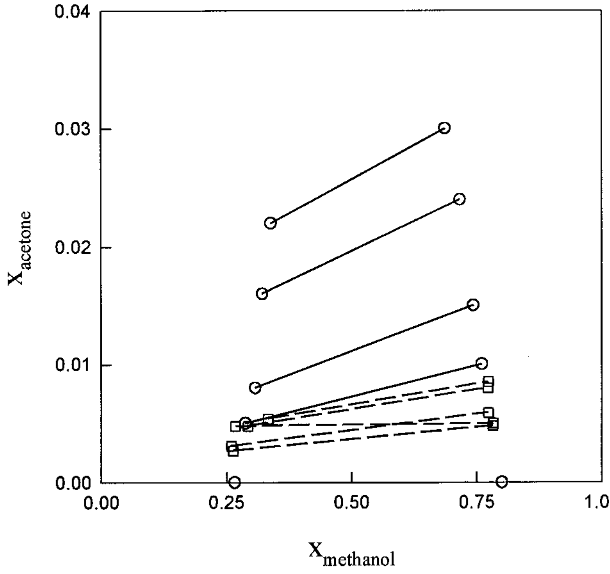

Figure 3. Comparison of gathered experimental data (—) with those reported by Nagata (1994) (– – –) for acetone (1) + methanol (2) + hexane (3) at 298.15 K.

acetone + methanol + hexane at 298.15; those data have been compared with the data from this study in Figure 3. No bibliographic data were found from the open literature of the acetone + methanol + heptane or octane ternary systems at the used conditions. The UNIFAC group contribution method and its modifications, UNIFAC-Lyngby and UNIFAC-Dortmund, were applied to predict the inmiscibility region. A poor description was obtained by means of this group contribution method: only the model of UNIFAC with specific parameters for liquid–liquid equilibria shows a qualitative accuracy; UNIFAC-Lyngby shows the worst results. All of these models overestimate the splitted region at each temperature, perhaps due to insufficient ketone molecular group information in the contribution method database. This fact could be clearly observed by the predicted inmiscibility for the mixture acetone + octane at low temperatures (Figure 4b) when such a mixture shows a homogeneous experimental trend in the whole range of temperatures (Orge et al., 1997). Such an effect reveals the importance of a wider disposal of thermodynamic liquid split data for an adequate description of multicomponent heterogeneous systems by means of contribution methods.

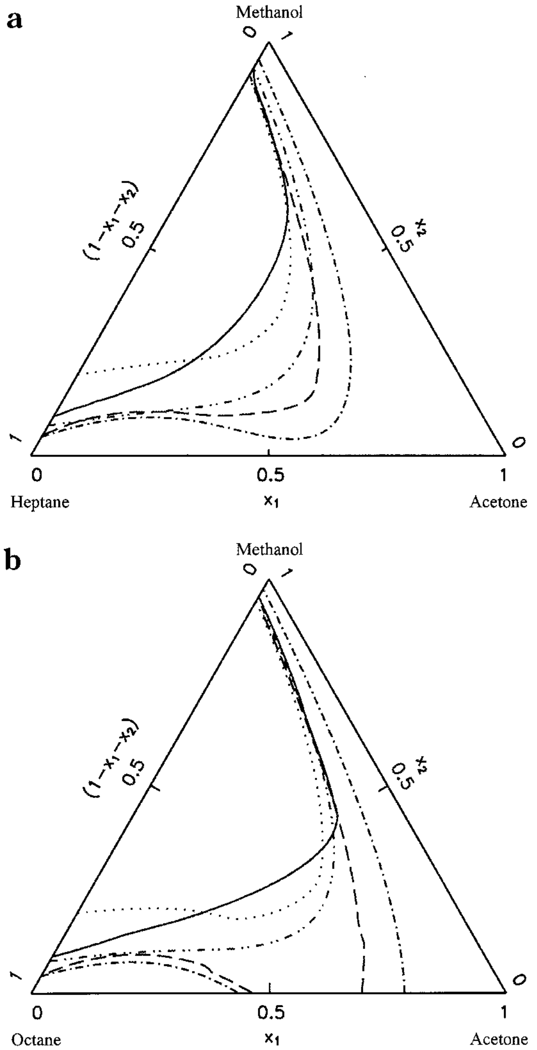

Figure 4. Immiscibility region [(—) experimental; (− · · −) UNIFAC; (· · ·) UNIFAC-LLE; (− − −) UNIFAC-Dortmund; (− · −) UNIFAC-Lyngby] at the temperature 278.15 K for (a) acetone (1) + methanol (2) + heptane (3) and (b) acetone (1) + methanol (2) + octane (3).

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