J. Chem. Eng. Data **2008,** *53,* 89–93

Liquid–Liquid Equilibria of Mixtures Containing Methyl Acetate + Methanol + Hexane or Heptane

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This paper reports the results of a new experimental study of liquid–liquid equilibria for the mixtures methyl acetate + methanol + hexane or heptane at atmospheric pressure and at (268.15, 278.15, 288.15, and 298.15) K. The equilibrium compositions were measured by gas chromatography from samples split isothermally into a glass-stirred device, and phase diagrams are reported at each temperature. The experimentally determined liquid−liquid equilibria were satisfactorily correlated by the NRTL and UNIQUAC equations. A comparative analysis was performed by application of UNIFAC group contribution method and its modifications to predict experimental liquid–liquid equilibria (LLE) behavior of these ternary mixtures. A poor prediction was observed from these contribution methods.

Introduction

Nowadays, liquid–liquid extraction has become one of the main separation technologies for separation of complex liquid mixtures. Hence, there has been a significant growth in the number of publications devoted to the study on liquid–liquid equilibria (LLE) of ternary and quaternary mixtures, including experimental data and correlation parameters. Phase equilibria studies supply essential information to select appropriate solvents and to design 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 data and models used. In some cases, the results obtained predicted with group contribution methods might be sufficient; in other cases, experimental data and a good description of them with the thermodynamic models is necessary. Hence, experimental data and a study to determine the predictive capability of group contribution methods are required.

In this work, we extend our measurements of experimental liquid–liquid data[1,2] to the mixtures methyl acetate + methanol + *n*-alkanes (C_6 to C_7) at atmospheric pressure and (268.15, 278.15, 288.15, and 298.15) K. Experimental data for these mixtures are not available in the open literature.

A study of the predictive capability of the UNIFAC group contribution method[3] and its modifications is presented for these ternary mixtures. Group contribution methods are extensively used in the chemical industry, especially during the development of chemical processes,[4] and UNIFAC stand out because it is highly used, due to its wide application range, and its parameter matrix is the most comprehensive. VLE parameters obtained from extensive series of revisions and extensions of the parameter matrix can be used.[5–11] Or, special LLE data-fitted parameters can be used as those proposed by Magnussen et al.,[12] originating the UNIFAC-LLE model. Owing to some inherent limitations of the UNIFAC model,[13] several modifications to this model have been proposed. Some of these modifications are the UNIFAC−Dortmund,[14–17] the UNIFAC−Lyngby,[18] and, more recently, the A-UNIFAC.[19–21]

Experimental Section

Materials. The chemicals used, of chromatographic quality, were supplied by Sigma. The mass fraction purities were better than 99.6 % for methyl acetate, 99.8 % for methanol, 99.1 % for hexane, and 99.7 % for heptane. The maximum water mass fraction (determined with a Coulometric Moisture Model CA-06) were $6.8 \cdot 10^{-3}$, $1.5 \cdot 10^{-2}$, $7.8 \cdot 10^{-4}$, and $8.1 \cdot 10^{-4}$, for methyl acetate, methanol, hexane, and heptane, respectively. Prior to use, the liquids were degassed in an ultrasonic bath for 4 h, stored into inert argon (N55, volume fraction of water less than $3 \cdot 10^{-6}$), and dried over molecular sieves type 3Å for methanol and 4Å for methyl acetate and *n*-alkanes, 1/16 in. (Aldrich cat. no. 20,860-4 or 20,858-2, respectively). The chemicals were checked using gas chromatography, and the purities were better than those from vendor specifications. These purities were checked periodically during manipulation.

Apparatus and Procedure. The device for liquid–liquid equilibria determination consists of 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 given uncertainty of $\pm 5 \cdot 10^{-2}$ K 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 $\pm 4 \cdot 10^{-4}$ mol 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 of approximately 2 mL were taken from the upper and lower phase with a syringe.

Sample Analysis. The compositions were determined by gas chromatography using a Hewlett-Packard HP-6890 Series GC

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10.1021/je700397g CCC: $40.75

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) + hexane (3)							
T = 268.15 K							
0.000	0.104	0.000	0.909	0.057	0.164	0.074	0.792
0.005	0.110	0.007	0.904	0.068	0.183	0.088	0.763
0.015	0.113	0.021	0.889	0.089	0.221	0.112	0.701
0.023	0.124	0.032	0.867	0.104	0.250	0.127	0.659
0.041	0.147	0.058	0.823	0.125	0.308	0.148	0.552
T = 278.15 K							
0.000	0.137	0.000	0.873	0.042	0.187	0.053	0.775
0.008	0.139	0.009	0.861	0.052	0.216	0.065	0.748
0.016	0.147	0.020	0.844	0.060	0.237	0.074	0.725
0.026	0.170	0.031	0.829	0.071	0.275	0.085	0.691
0.034	0.180	0.042	0.802				
T = 288.15 K							
0.000	0.186	0.000	0.835	0.033	0.267	0.040	0.738
0.008	0.200	0.010	0.812	0.041	0.301	0.048	0.704
0.016	0.216	0.020	0.796	0.055	0.387	0.060	0.627
0.025	0.239	0.030	0.769				
T = 298.15 K							
0.000	0.267	0.000	0.801	0.020	0.319	0.024	0.724
0.017	0.301	0.019	0.747	0.027	0.374	0.029	0.686
methyl acetate (1) + methanol (2) + heptane (3)							
T = 268.15 K							
0.000	0.076	0.000	0.953	0.080	0.137	0.101	0.810
0.012	0.087	0.014	0.935	0.101	0.152	0.131	0.770
0.028	0.097	0.033	0.910	0.121	0.162	0.159	0.726
0.045	0.110	0.055	0.878	0.136	0.190	0.176	0.691
0.060	0.119	0.077	0.845	0.177	0.247	0.223	0.604
0.065	0.122	0.082	0.836				
T = 278.15 K							
0.000	0.095	0.000	0.936	0.081	0.190	0.105	0.772
0.022	0.117	0.028	0.894	0.102	0.217	0.131	0.729
0.041	0.131	0.053	0.859	0.132	0.275	0.159	0.664
0.060	0.153	0.078	0.821				
T = 288.15 K							
0.000	0.127	0.000	0.915	0.061	0.212	0.074	0.790
0.024	0.161	0.028	0.875	0.084	0.266	0.101	0.729
0.043	0.183	0.051	0.834	0.084	0.270	0.101	0.730
0.052	0.195	0.063	0.813	0.118	0.392	0.128	0.628
T = 298.15 K							
0.000	0.153	0.000	0.904	0.038	0.246	0.046	0.806
0.008	0.166	0.009	0.879	0.044	0.267	0.052	0.790
0.011	0.176	0.014	0.867	0.067	0.350	0.073	0.728
0.021	0.205	0.025	0.845	0.075	0.389	0.082	0.693
0.026	0.217	0.030	0.836	0.082	0.429	0.089	0.661

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) + Hexane (3)						
NRTL						
	12	21	13	31	23	32
a	−5560.492	2526.703	−1593.132	1844.571	2341.315	1987.802
b	24.215	−11.267	6.691	−4.994	−5.268	−3.481
	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$		
T = 268.15 K	0.002	0.021	0.002	0.015		
T = 278.15 K	0.001	0.013	0.001	0.006		
T = 288.15 K	0.001	0.031	0.001	0.013		
T = 298.15 K	0.000	0.014	0.000	0.021		
UNIQUAC						
	12	21	13	31	23	32
a	−1084.297	2714.862	1333.594	−99.137	1648.191	477.276
b	4.942	−9.659	−2.634	−0.316	−1.744	−1.580
	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$		
T = 268.15 K	0.007	0.036	0.004	0.012		
T = 278.15 K	0.001	0.014	0.001	0.007		
T = 288.15 K	0.001	0.029	0.001	0.016		
T = 298.15 K	0.000	0.013	0.000	0.017		
Methyl Acetate (1) + Methanol (2) + Heptane (3)						
NRTL						
	12	21	13	31	23	32
a	−6861.834	2852.944	−461.823	−4785.382	2382.586	2115.020
b	29.190	−12.379	1.885	21.129	−5.096	−3.169
	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$		
T = 268.15 K	0.001	0.004	0.001	0.004		
T = 278.15 K	0.003	0.015	0.001	0.004		
T = 288.15 K	0.006	0.041	0.003	0.009		
T = 298.15 K	0.005	0.058	0.002	0.012		
UNIQUAC						
	12	21	13	31	23	32
a	−3152.262	1926.945	−2382.830	938.680	1440.329	477.570
b	12.324	−6.917	10.018	−3.576	−0.606	−1.546
	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$		
T = 268.15 K	0.001	0.009	0.001	0.005		
T = 278.15 K	0.004	0.019	0.002	0.009		
T = 288.15 K	0.007	0.045	0.003	0.011		
T = 298.15 K	0.006	0.060	0.002	0.009		

System chromatograph equipped with a flame ionization detector and a HP-1 19091Z-215 (methyl siloxane, 50 m × 3.2 × 10^{-4} m × 1.05 × 10^{-6} m film thickness) capillary column. The carrier gas used was helium, and the flow rate was 0.8 mL·min^{-1}. 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. An internal standard calibration method was used. The reference samples were analyzed using the same chromatographic conditions as the equilibrium samples.

Results and Discussion

Experimental Results. The experimental tie-line data of the mixtures methyl acetate + methanol + *n*-alkanes (C_6 to C_7) at (268.15, 278.15, 288.15, and 298.15) K and atmospheric pressure are reported in Table 1. The estimated uncertainty in mole fraction for these 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 liquid–liquid equilibria data for the binary systems methanol + *n*-alkanes have been previously published.[22]

As expected, the size of the two-phase region decreases with increase in temperature. On the other hand, it can be observed that the immiscibility region also decreases with decrease in the alkane chain length.

LLE Correlation. The UNIQUAC[23] and NRTL[24] equations were applied to correlate the experimental data, using these temperature dependence parameters, respectively:

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

$$\tau_{ij} = (a_{ij} + b_{ij}T)/RT \tag{2}$$

where a_{ij} (cal·mol^{-1}) and b_{ij} (cal·K^{-1}·mol^{-1}) are temperature independent parameters.

These fitting parameters (a_{ij} and b_{ij}) and the root-mean-square deviations are given in Table 2. The nonrandom parameter (α)

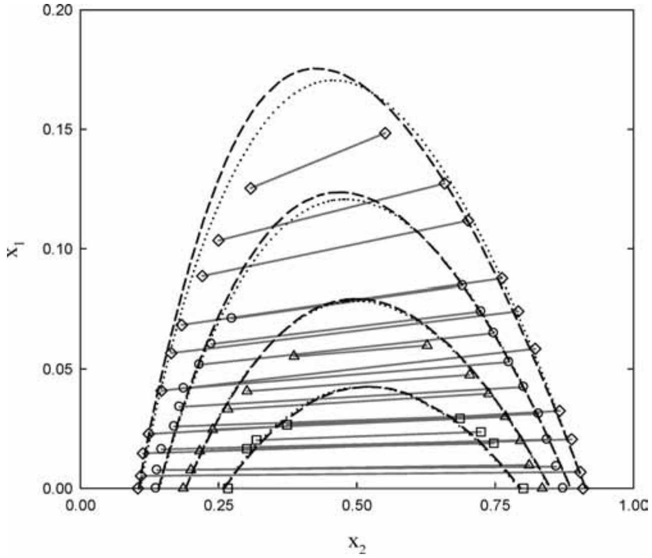

Figure 1. Experimental tie-lines and binodal curves for methyl acetate (1) + methanol (2) + hexane (3) correlated by the NRTL and UNIQUAC equations. Experimental tie-lines at ◇, 268.15 K; ○, 278.15 K; Δ, 288.15 K; and □, 298.15 K; •••, NRTL equation; and - - -, UNIQUAC equation.

Table 3. Root-Mean-Square Deviations, σ (I, Alkane-Rich Phase; II, Methanol-Rich Phase) Obtained from Prediction with UNIFAC, UNIFAC-LLE, UNIFAC−Dortmund, and UNIFAC−Lyngby Models

	UNIFAC				UNIFAC-LLE			
T/K	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$
methyl acetate (1) + methanol (2) + hexane (3)								
268.15	0.006	0.121	0.004	0.073	0.007	0.507	0.007	0.495
278.15	0.003	0.119	0.002	0.070	0.005	0.087	0.005	0.085
288.15	0.003	0.181	0.002	0.121	0.006	0.029	0.005	0.017
298.15	0.002	0.220	0.004	0.137	0.005	0.042	0.005	0.041
methyl acetate (1) + methanol (2) + heptane (3)								
268.15	0.005	0.074	0.002	0.032	0.015	0.697	0.013	0.648
278.15	0.004	0.098	0.001	0.047	0.007	0.151	0.007	0.090
288.15	0.005	0.147	0.002	0.076	0.006	0.157	0.007	0.109
298.15	0.003	0.175	0.001	0.089	0.005	0.064	0.005	0.039

	UNIFAC−Dortmund				UNIFAC−Lyngby			
T/K	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$
methyl acetate (1) + methanol (2) + hexane (3)								
268.15	0.007	0.102	0.002	0.035	0.016	0.124	0.011	0.061
278.15	0.003	0.103	0.001	0.012	0.008	0.125	0.006	0.065
288.15	0.003	0.154	0.001	0.039	0.006	0.188	0.004	0.117
298.15	0.001	0.179	0.000	0.040	0.003	0.229	0.002	0.135
methyl acetate (1) + methanol (2) + heptane (3)								
268.15	0.008	0.066	0.002	0.021	0.023	0.090	0.014	0.026
278.15	0.005	0.084	0.001	0.013	0.015	0.115	0.009	0.047
288.15	0.005	0.123	0.001	0.026	0.013	0.165	0.008	0.080
298.15	0.003	0.146	0.001	0.033	0.008	0.196	0.005	0.098

in the NRTL equation has been fixed to 0.3 for all cases. A good accuracy has been achieved for all studied mixtures. For instance, Figure 1 shows the correlation using both UNIQUAC and NRTL equations of methyl acetate + methanol + hexane at all temperatures studied.

LLE Prediction. Prediction of LLE for the ternary systems studied has been carried out by the UNIFAC group contribution method[3] with parameters obtained from vapor–liquid[11] or liquid–liquid[12] (UNIFAC-LLE) equilibrium data and its modifications, UNIFAC−Dortmund,[14–17] UNIFAC−Lyngby,[8] and A-UNIFAC,[19–21] which takes into account association effects. This model adds a group contribution association term to the residual and combinatorial contributions to the activity coefficients.

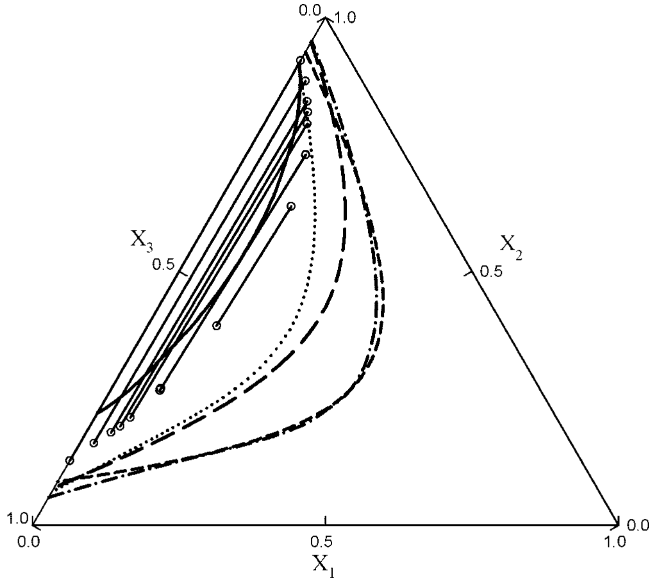

Figure 2. ○, Experimental tie-lines; and prediction by - - -, UNIFAC; –, UNIFAC-LLE; •••, UNIFAC−Dortmund; - • -, UNIFAC−Lyngby; and - - -, A-UNIFAC for methyl acetate (1) + methanol (2) + heptane (3) at 288.15 K.

These UNIFAC modifications have been also applied to predict the studied mixtures and compared with the values obtained for the liquid–liquid equilibria of mixtures methyl acetate + methanol + *n*-alkanes (C_8 to C_{12}). The experimental values of these mixtures have been previously published.[1,2]

Table 3 reports the root-mean-square deviations obtained in the prediction of the ternary mixtures studied in the present work with the UNIFAC model and its modifications, UNIFAC-LLE, UNIFAC−Dortmund, and UNIFAC−Lyngby.

On the other hand, in order to predict the liquid–liquid equilibria using the A-UNIFAC model, it has been necessary to estimate previously the methanol (CH3OH) and acetate (CCOO) group interaction parameters. The addition of an association term to the UNIFAC model makes it necessary not only to estimate the association parameter but also to reparameterize the residual term, since the earlier group interaction parameters incorporated the association effects, which are treated explicitly. The self- and cross-association parameters have been given by Ferreira et al.[21] The residual group interaction parameters were estimated in this work using experimental VLE data of 14 binary mixtures with 200 points.[25] Their values are 200.2 and 18.49 K for CH3OH−CCOO and CCOO−CH3OH interactions, respectively. Table 4 reports the root-mean-square deviations obtained in the prediction of not only the ternary mixtures studied in this work but also the mixtures methyl acetate + methanol + *n*-alkanes (C_8 to C_{12}) with the A-UNIFAC model. These mixtures have been included to study the effect of the alkane chain length in the prediction with this group contribution method.

For instance, Figure 2 shows the predicted results for methanol + methyl acetate + heptane at 288.15 K. An unsatisfactory description was obtained by means of these group contribution methods. All methods except UNIFAC-LLE overestimate the split region at each temperature and the UNIFAC−Lyngby method provided the worst prediction. This fact could be more clearly observed by the predicted immiscibility by the nonsymmetric tendency toward the methyl acetate + *n*-alkane linear mixture, which estimates the liquid–liquid equilibria for these binary mixtures at low temperatures from *n*-nonane to *n*-dodecane. On the contrary, these binary mixtures show a

Table 4. Root-Mean-Square Deviations, σ (I, Alkane-Rich Phase; II, Methanol-Rich Phase) Obtained from Prediction with the A-UNIFAC Model for the Methyl Acetate (1) + Methanol (2) + *n*-Alkane (3) Mixtures

T/K	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$	$\sigma(x_1^{\mathrm{I}})$	$\sigma(x_2^{\mathrm{I}})$	$\sigma(x_1^{\mathrm{II}})$	$\sigma(x_2^{\mathrm{II}})$
	methyl acetate + methanol + hexane				methyl acetate + methanol + heptane			
268.15	0.006	0.109	0.008	0.084	0.011	0.060	0.012	0.044
278.15	0.007	0.105	0.007	0.091	0.024	0.082	0.040	0.082
288.15	0.006	0.157	0.006	0.141	0.009	0.113	0.009	0.092
298.15	0.001	0.192	0.001	0.151	0.010	0.126	0.009	0.109
	methyl acetate + methanol + octane				methyl acetate + methanol + nonane			
278.15	0.032	0.077	0.037	0.088	0.022	0.030	0.025	0.058
288.15	0.015	0.091	0.011	0.071	0.017	0.052	0.013	0.055
298.15	0.009	0.080	0.009	0.076	0.013	0.080	0.013	0.068
	methyl acetate + methanol + decane				methyl acetate + methanol + undecane			
278.15	0.031	0.015	0.031	0.043	0.025	0.003	0.114	0.143
288.15	0.021	0.010	0.021	0.040	0.023	0.031	0.081	0.115
298.15	0.019	0.033	0.015	0.045	0.030	0.095	0.021	0.099
308.15	0.010	0.050	0.011	0.043	0.008	0.036	0.021	0.073
	methyl acetate + methanol + dodecane							
278.15	0.014	0.030	0.096	0.105				
288.15	0.018	0.010	0.077	0.092				
298.15	0.019	0.025	0.020	0.041				
308.15	0.012	0.036	0.014	0.025				

homogeneous experimental trend over the whole range of temperatures.[1,2] Figure 3 is an example of this behavior.

On the other hand, the UNIFAC, UNIFAC-LLE, and A-UNIFAC models predict a similar split region, without appreciable changes, in the studied temperature range for each mixture. Owing to that, good predicted results in some mixtures at certain temperatures are achieved. This is true of the case of A-UNIFAC in Figure 3.

Conclusion

The LLE of the mixtures methyl acetate + methanol + *n*-alkane (C_6 to C_7) were determined in the temperature range (268.15 to 298.15) K and at atmospheric pressure. Both the UNIQUAC and NRTL equations were able to describe the behavior of these mixtures, showing low deviation values from the experimental data.

The UNIFAC method and its modifications UNIFAC-LLE, Unifac−Dortmund, UNIFAC−Lyngby, and A-UNIFAC were applied to predict the LLE of the studied systems. The results were compared with the predictions of the methyl acetate + methanol + *n*-alkane (C_8 to C_{12}) mixtures. These methods have been shown to be incapable of adequately predicting the split region of the mixtures studied, above all, at low temperatures. Not even the UNIFAC-LLE method, which uses specific parameters from the liquid−liquid equilibria data, or A-UNIFAC, that takes into account the association effects, were good enough. Such results reveal the importance of obtaining a wider range of the liquid–liquid equilibria data for an adequate description of heterogeneous multicomponent systems by means of the group contribution methods.

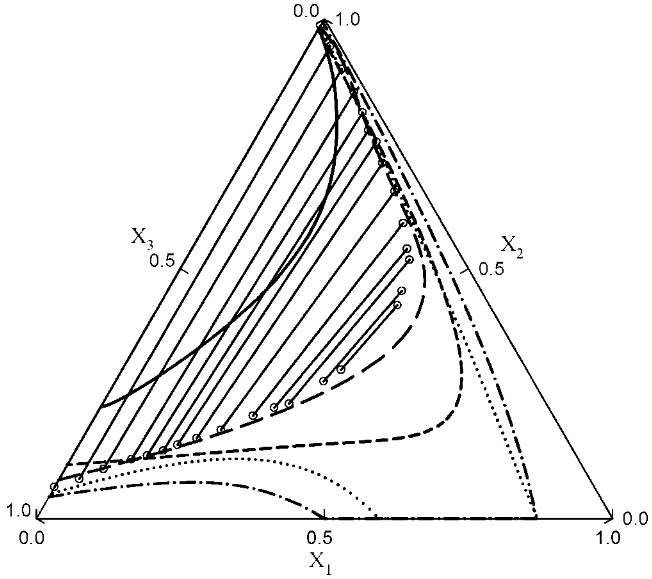

Figure 3. ○, Experimental tie-lines; and prediction by - - -, UNIFAC; –, UNIFAC-LLE; •••, UNIFAC−Dortmund; - • -, UNIFAC−Lyngby; and - - -, A-UNIFAC for methyl acetate (1) + methanol (2) + *n*-undecane (3) at 288.15 K.

These methods, which are extensively used in the prediction of physical properties and vapor–liquid equilibria, are inefficient in the prediction of liquid–liquid equilibria, and they should not be used in the design of operation units. The use of the results obtained from chemical process simulators would produce an ineffective design. This is due to several limitations such as the scarcity of experimental heterogeneous mixture data with different functional groups at wide operational conditions, inadequate thermodynamic consistency tests for experimental equilibrium data quality control, etc. Solutions to these problems are the following: first, the modification of the present models or the proposal of new ones; second, the careful use of the existing equilibria data in the literature. Since a test for thermodynamic consistency is nonexistent, it is difficult to know if the data are “good” (in the literature, it is possible to find data for the same system at a determined pressure and temperature, which differ by more than 100 % in the composition value; see refs 26 and 27). Finally, the use of an extensive range of temperatures and pressures, as well as different sized molecules, is also important in estimating group interaction parameters.

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Received for review July 12, 2007. Revised October 19, 2007. Accepted November 13, 2007. L. M. C. expresses thanks for the financial support from the programa FPU of Ministerio de Educación y Ciencia, Spain.

JE700397G