JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Liquid−Liquid Equilibria Measurement of Systems Involving Alkanes (Heptane and Dodecane), Aromatics (Benzene or Toluene), and Furfural

U. K. Arun Kumar and Ratan Mohan*

Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi 110016, India

ABSTRACT: Liquid−liquid equilibria (LLE) of alkane + aromatic + solvent systems is of interest in connection with the extraction of aromatics from petroleum fractions, for example, naphtha, distillates, lube oil, and so forth. Though the actual industrial systems contain a large number of compounds, LLE studies on a smaller number of representative compounds are also important in the development of theoretical/semiempirical LLE models for use in the design of extraction processes. In the present work LLE data has been experimentally obtained for the ternary systems heptane + benzene + furan-2-carbaldehyde (furfural) and heptane + methylbenzene (toluene) + furfural at two temperatures (298.15 and 303.15) K, and for the quaternary systems heptane + dodecane + benzene or toluene + furfural at 298.15 K. The data are seen to be correlated excellently by the nonrandom two-liquid model. The model parameters were determined by data regression using the Nelder−Mead optimization technique. The model also enabled tie line calculations between the last experimental tie line and the plait point, thereby giving the shape of the full two-phase region.

INTRODUCTION

Liquid extraction is a widely used process for separation of aromatics from petroleum fractions such as naphtha, lube oil, and so forth, as distillation is not viable because of the presence of several close boiling components. Accordingly, measurement of liquid−liquid equilibrium (LLE) data and development of theoretical models for alkanes + aromatics + solvent systems is an important goal toward extraction process design needs. Various organic solvents have been studied and used in extraction industry for this separation, for example, sulfolane, *N*-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), ethylene glycols, and propylene carbonate. Ashour and Abu-Eishah[1] and Banerjee et al.[2] give an extensive list of LLE studies of mixtures involving above solvents (particularly sulfolane) and alkane and aromatic compounds.

In recent years, interest in the search for more environmentally friendly, biodegradable solvents has also been observed. Solvents like ionic liquids have shown promising selectivity results but have not seen much commercial use due to engineering problems. Other solvents in this category are furfural and related compounds like furfuryl alcohol and tetrahydrofurfuryl alcohol (THFA), obtained as byproducts of the sugar industry. LLE studies for dearomatization using these as solvents have also been made in the past. In an early study dating back to the fifties, Kenny[3] reported experimental LLE data and predictions for furfural + iso-octane + benzene system. In recent works, Morawski et al.[4] studied LLE of furfuryl alcohol with aromatics benzene, toluene, and xylenes and alkanes hexane, dodecane, and hexadecane. Letcher et al.[5] studied the LLE of furfural + aromatics (benzene, toluene, xylenes) + alkanes (hexane, dodecane, hexadecane). Skrollahzadeh et al.[6] investigated the removal of benzene and toluene from AW-406 (a petroleum solvent, mainly hexane and cyclohexane with some benzene and toluene) using THFA and water as solvent. The partition coefficient of benzene in THFA + water was found to be comparable to that in furfuryl alcohol and to that in sulfolane. Coto et al.[7] and Espada et al.[8] studied the LLE of furfural and lube oil cuts (light, medium, and heavy neutral distillates) for the removal of aromatics from lube oils.

In the present work LLE measurements have been made for the ternary systems heptane + benzene + furan-2-carbaldehyde (furfural) and heptane + methylbenzene (toluene) + furfural at two temperatures, (298.15 and 303.15) K. Measurements for the quaternary systems heptane + dodecane + benzene (or toluene) + furfural at 298.15 K have also been made. Nonrandom two-liquid (NRTL) activity coefficient model has been used to correlate the experimental data, after obtaining the model parameters by data regression using the Nelder−Mead[9] optimization technique.

EXPERIMENTAL SECTION

Materials. Benzene was supplied by Ranbaxy Fine Chemicals, India, and heptane and toluene were supplied by Qualigens, India. All three were HPLC grade materials. Furfural was supplied by CDH Laboratories, India. The purities of all these chemicals were rated to be > 99 % by the manufacturers. It was reconfirmed by gas chromatography, and the mass fractions were found to be 0.994 for heptane, 0.996 for dodecane, 0.999 for benzene, 0.999 for toluene, and 0.995 for furfural. The materials were used as supplied by the manufacturers, without any further purification.

Received: September 4, 2010
Accepted: January 18, 2011
Published: February 10, 2011

Table 1. Experimental LLE Data for the Ternary System Heptane (1) + Benzene (2) + Furfural (3) at T = 298.15 K and T = 303.15 K

	mole fraction					
T/K	x_1	x_2	x_3	x_1	x_2	x_3
	Alkane-Rich Layer			Furfural-Rich Layer		
298.15	0.907	0.029	0.064	0.054	0.024	0.921
	0.851	0.076	0.073	0.064	0.063	0.873
	0.798	0.120	0.082	0.072	0.103	0.825
	0.750	0.162	0.088	0.075	0.138	0.786
	0.708	0.196	0.096	0.094	0.187	0.719
	0.603	0.263	0.134	0.131	0.244	0.625
303.15	0.842	0.038	0.120	0.057	0.025	0.918
	0.790	0.085	0.125	0.062	0.063	0.875
	0.744	0.122	0.134	0.072	0.103	0.825
	0.699	0.163	0.138	0.080	0.138	0.782
	0.631	0.213	0.156	0.090	0.189	0.721
	0.531	0.273	0.196	0.123	0.254	0.623

Table 2. Experimental LLE Data for the Ternary System Heptane (1) + Toluene (2) + Furfural (3) at T = 298.15 K and T = 303.15 K

	mole fraction					
T/K	x_1	x_2	x_3	x_1	x_2	x_3
	Alkane-Rich Layer			Furfural-Rich Layer		
298.15	0.847	0.043	0.110	0.054	0.019	0.927
	0.779	0.112	0.109	0.061	0.052	0.887
	0.724	0.167	0.109	0.065	0.077	0.858
	0.652	0.225	0.123	0.082	0.133	0.785
	0.587	0.271	0.142	0.099	0.189	0.712
	0.536	0.294	0.170	0.106	0.224	0.670
303.15	0.794	0.060	0.146	0.054	0.018	0.928
	0.723	0.136	0.141	0.060	0.045	0.895
	0.652	0.196	0.152	0.066	0.075	0.859
	0.572	0.276	0.152	0.093	0.147	0.760
	0.485	0.325	0.190	0.123	0.217	0.660

Procedure. A 100 mL glass cell with a magnetic stirrer was used as the equilibrium cell for the experiments. The temperature of the cell was controlled and maintained by a constant temperature water bath. The cell had two sampling ports and a small hole with needle to maintain pressure atmospheric. The liquid temperature was measured by a thermocouple inside. Temperatures were observed to be within ± 0.1 °C of the set temperature and were taken to be uniform for the cell liquids, as the total volume inside was not more than about (60 to 70) mL and the liquid was well-stirred. Feed mixture compositions were taken such that the mixture would form two phases. Essentially equal volumes of furfural and heptane (~ 20 mL each) were taken, and the amount of benzene or toluene added was varied, thus yielding different tie lines. The feed mixture was first stirred by the magnetic stirrer for about an hour to form an emulsion and was then allowed to settle for (3 to 5) h, until it formed two clear phases. Samples from each phase were withdrawn using syringes.

Table 3. Experimental LLE Data for the Quaternary System Heptane (1) + Dodecane (2) + Benzene (3) + Furfural (4) at T = 298.15 K

	mole fraction							
T/K	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
	Alkane-Rich Layer				Furfural-Rich Layer			
298.15	0.748	0.165	0.033	0.054	0.038	0.007	0.021	0.934
	0.681	0.177	0.071	0.071	0.044	0.004	0.048	0.904
	0.637	0.136	0.142	0.085	0.047	0.005	0.104	0.844
	0.567	0.150	0.193	0.090	0.053	0.006	0.147	0.794
	0.525	0.113	0.259	0.103	0.063	0.008	0.189	0.740
	0.463	0.110	0.303	0.123	0.076	0.009	0.237	0.678
	0.424	0.111	0.335	0.130	0.084	0.009	0.284	0.622

Table 4. Experimental LLE Data for the Quaternary System Heptane (1) + Dodecane (2) + Toluene (3) + Furfural (4) at T = 298.15 K

	mole fraction							
T/K	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
	Alkane-Rich Layer				Furfural-Rich Layer			
298.15	0.682	0.184	0.063	0.071	0.034	0.004	0.037	0.924
	0.627	0.168	0.123	0.082	0.041	0.004	0.075	0.880
	0.570	0.156	0.177	0.096	0.049	0.006	0.113	0.832
	0.529	0.137	0.226	0.108	0.053	0.007	0.147	0.793
	0.482	0.130	0.263	0.125	0.062	0.008	0.180	0.750
	0.434	0.118	0.303	0.145	0.069	0.010	0.212	0.709

Phase compositions were measured using gas chromatography, employing the internal standard method of analysis. The gas chromatograph (GC) used in this study was ULTIMA 2100 by NETEL, India. It was equipped with a flame ionization (FID) detector and 10 % OV-17 Chrom WHP (2 m × 1/8″) column. The injector and detector temperatures both were maintained at 548.15 K. The column temperature was programmed for an initial temperature of 348.15 K maintained for 1 min and a final temperature of 498.15 K. Heating was done at the rate of 18 $\text{K}\cdot\text{min}^{-1}$. The flow rate of nitrogen carrier gas was kept at 20 $\text{mL}\cdot\text{min}^{-1}$. In the internal standard method, GC calibration plots were obtained by employing six to seven sample mixtures of known compositions as the standard references. Each sample was prepared by adding known masses of the components, and octane or ethanol was used as the internal standard. A Denver Instruments analytical balance with an accuracy of ± 0.0001 g was used for weighing. After obtaining the calibration plots, other known mixtures (different from those used for calibration) were analyzed and their mass compositions determined. The differences in the mass values were found to be in the range (0.001 to 0.005) g. From this the accuracy in mole fractions was estimated to be ± 0.005. Each tie line experiment was done twice, and in both cases three samples from each phase were taken and analyzed; that is, the final reported value of each composition is the average of six measurements.

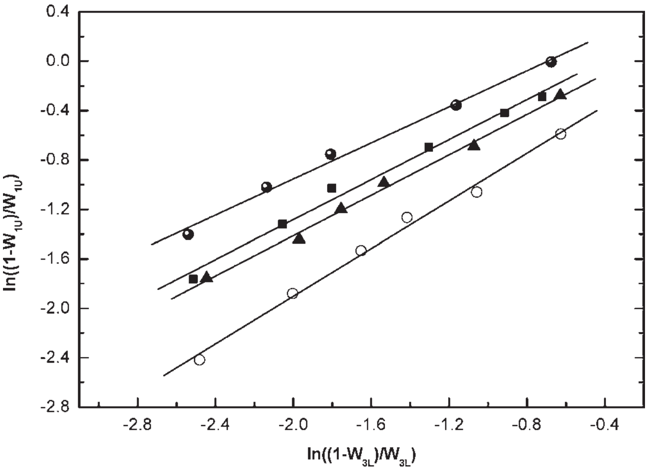

Figure 1. Othmer−Tobias plots for heptane + benzene + furfural system at ○, 298.15 K; ▲, 303.15 K and heptane + toluene + furfural system at ■, 298.15 K; ●, 303.15 K. W_{1U}, mass fraction of heptane in upper layer, $W_{3\ L}$, mass fraction of furfural in the lower layer.

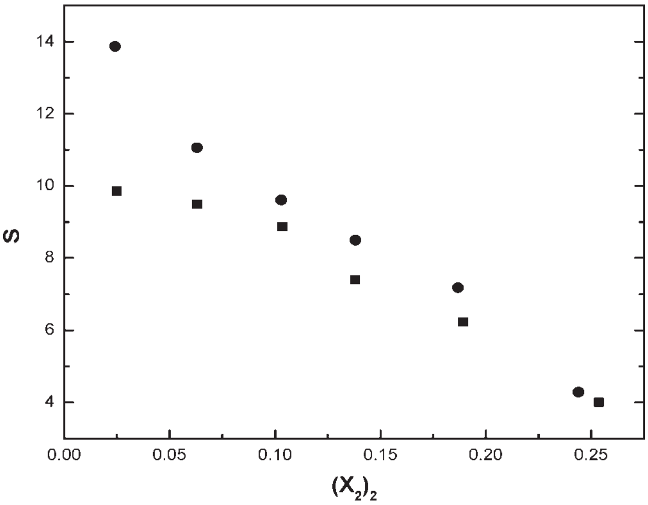

Figure 2. Selectivity (S) plots for the heptane (1) + benzene (2) + furfural (3) system at ●, 298.15 K; ■, 303.15 K; $(x_2)_2$, benzene mole fraction in the furfural-rich layer.

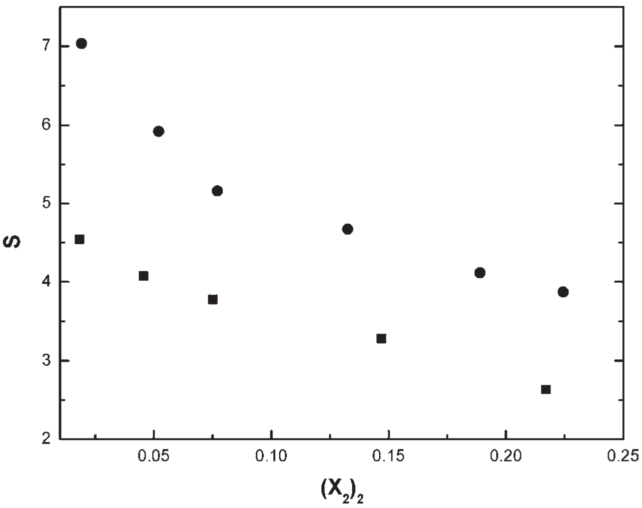

Figure 3. Selectivity (S) plots for heptane (1) + toluene (2) + furfural (3) system at ●, 298.15 K; ■, 303.15 K; $(x_2)_2$, toluene mole fraction in the furfural-rich layer.

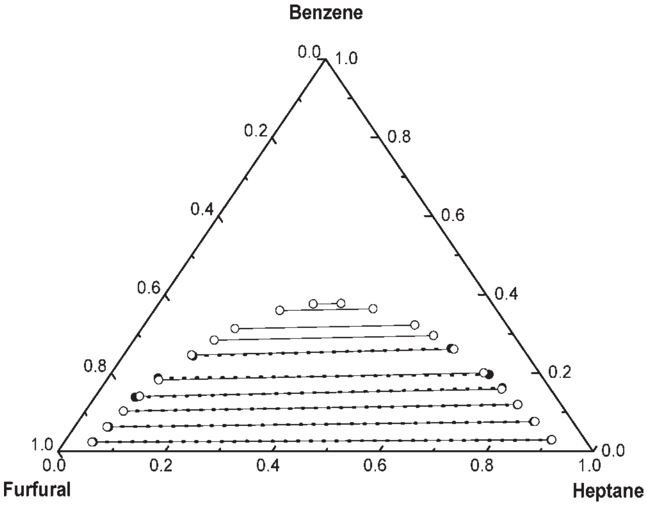

Figure 4. Ternary LLE of the heptane (1) + benzene (2) + furfural (3) system at 298.15 K; · · • · ·, experimental, —○—, NRTL.

RESULTS AND DISCUSSION

Experimental Data. The experimental LLE data for heptane + benzene + furfural systems at (298.15 and 303.15) K are reported in Table 1 and that for heptane + toluene + furfural systems at the same two temperatures in Table 2. The composition entries (x_1, x_2, x_3) in these tables, as well as in other tables, are mole fractions. Likewise data for heptane + benzene (or toluene) + furfural systems at 298.15 K are given in Tables 3 and 4. The ternary phase diagrams with tie lines are shown later in Figures 4 to 9, where comparisons with NRTL model results are also made.

To examine the quality of the experimental tie line data, the Othmer−Tobias[10] test was made for each ternary system. The Othmer−Tobias correlation

$$\left(\frac{1-w_{3L}}{w_{3L}}\right) = a\left(\frac{1-w_{1U}}{w_{1U}}\right)^{b} \qquad (1)$$

in the logarithm form is

$$\ln\left(\frac{1-w_{3L}}{w_{3L}}\right) = a + b\ln\left(\frac{1-w_{1U}}{w_{1U}}\right) \qquad (2)$$

where w_{3L} = mass fraction of furfural (3) in the furfural-rich layer (lower layer), w_{1U} = mass fraction of heptane (1) in the heptane-rich layer (upper layer), and a and b are the parameters of Othmer−Tobias correlation. The linearity of the plot indicates the consistency of the data. Figure 1 shows the Othmer−Tobias plots for the four ternary systems. In all four plots the experimental data points are seen to be very close to the straight lines, thus confirming that the data is consistent over the experimental range.

The experimental selectivity data for heptane + benzene + furfural systems are shown in Figure 2, and those for heptane + toluene + furfural systems are shown in Figure 3. Selectivity S, the measure of the solvent ability to extract aromatics from

Table 5. NRTL Binary Interaction Parameters for the System Heptane (1) + Benzene (2) + Furfural (3)

T/K	i	j	τ_{ij}	τ_{ji}	100·rmsd
298.15	1	2	−1545.6	148.5	0.4032
	1	3	641.91	699.83	
	2	3	369.94	−1583.9	
303.15	1	2	−1148.01	260.536	0.3503
	1	3	486.78	748.572	
	2	3	428.263	−1138.67	

Table 6. NRTL Binary Interaction Parameters for the System Heptane (1) + Toluene (2) + Furfural (3)

T/K	i	j	τ_{ij}	τ_{ji}	100·rmsd
298.15	1	2	−1537.2	18.11	0.5111
	1	3	510.44	733.58	
	2	3	682.72	−1509.1	
303.15	1	2	−810.25	−75.25	0.5037
	1	3	443.24	768.01	
	2	3	3882.2	−409.38	

Table 7. NRTL Binary Interaction Parameters for the System Heptane (1) + Dodecane (2) + Benzene (3) + Furfural (4)

T/K	i	j	τ_{ij}	τ_{ji}	100·rmsd
298.15	1	2	−2797.4	−325.79	0.2690
	1	3	−78.215	83.206	
	1	4	802.03	649.85	
	2	3	1088.1	−640.67	
	2	4	215.64	−1875	
	3	4	318.31	86.363	

alkanes, is defined as

$$S = \frac{(x_2/x_1)^{\mathrm{S}}}{(x_2/x_1)^{\mathrm{A}}} \tag{3}$$

$(x_2/x_1)^{\mathrm{S}}$ is the ratio of aromatic concentration (mole fraction) x_2 to alkane concentration x_1 in the solvent-rich phase, and $(x_2/x_1)^{\mathrm{A}}$ is the ratio of aromatic concentration to alkane concentration in the raffinate (alkane-rich) phase. From the figures it is seen that selectivity decreases with increasing aromatic concentration x_2 in the solvent (furfural) rich phase, that is, when the feed has more aromatics. Also the selectivity decreases with increasing temperature. In all cases, however, the value of selectivity is seen to be greater than about 3, implying that extraction of aromatics by furfural can be done.

Modeling and Data Correlation. The NRTL activity coefficient model[11] is a frequently used model to represent experimental LLE data. In this study too it has been employed to see how well it correlates experimental data. The main equations of the NRTL model are the excess Gibbs free energy equation

$$\frac{g^{\mathrm{E}}}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{n} G_{li} x_i} \tag{4}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad \text{where } \tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \text{ and } \alpha_{ij} = \alpha_{ji} \tag{5}$$

Table 8. NRTL Binary Interaction Parameters for the System Heptane (1) + Dodecane (2) + Toluene (3) + Furfural (4)

T/K	i	j	τ_{ij}	τ_{ji}	100·rmsd
298.15	1	2	−1011.3	9.2392	0.0785
	1	3	67.16	−0.68763	
	1	4	1239.7	722.37	
	2	3	0.84511	52.029	
	2	4	29.645	636.48	
	3	4	441.1	25.247	

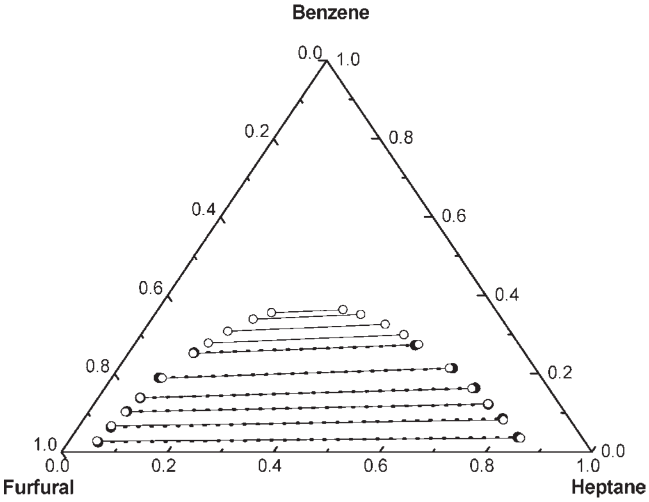

Figure 5. Ternary LLE of the heptane (1) + benzene (2) + furfural (3) system at 303.15 K; ··•··, experimental, —○—, NRTL.

and the activity coefficient given as

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{n} G_{li} x_l} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{l=1}^{n} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{k=1}^{n} \tau_{kj} G_{kj} x_k}{\sum_{l=1}^{n} G_{lj} x_l} \right) \tag{6}$$

In the above equations, τ_{ij} and $\propto_{ij}$ are the interaction parameters of the NRTL model, x_i are the mole fractions, and T is the temperature in Kelvin. The parameters $\propto_{ij}$ and τ_{ij} are determined by data regression. However the nonrandomness parameter $\propto_{ij}$ is often not varied; here too it was fixed at a value of 0.3. τ_{ij} were obtained by minimizing the objective function F defined below.

$$F = \min \sum_{i} \sum_{j} \sum_{k} (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2 \tag{7}$$

where $x_{ijk}{}^{\mathrm{exp}}$ and $x_{ijk}{}^{\mathrm{cal}}$ are the experimental and calculated mole fractions, respectively, i is the number of components, j is the number of phases, and k is the number of tie lines. The parameters τ_{ij} are 6 in number for the ternary systems and 12 for the quaternary systems. The minimization of the objective function was carried out by Nelder—Mead optimization technique, by means of a computer program written in MATLAB for the purpose.

Root mean square deviation (rmsd), the measure of agreement between the experimental and calculated data, is defined as

$$\mathrm{rmsd} = \left[\sum_{i} \sum_{j} \sum_{k} \frac{(x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2}{6M} \right]^{1/2} \tag{8}$$

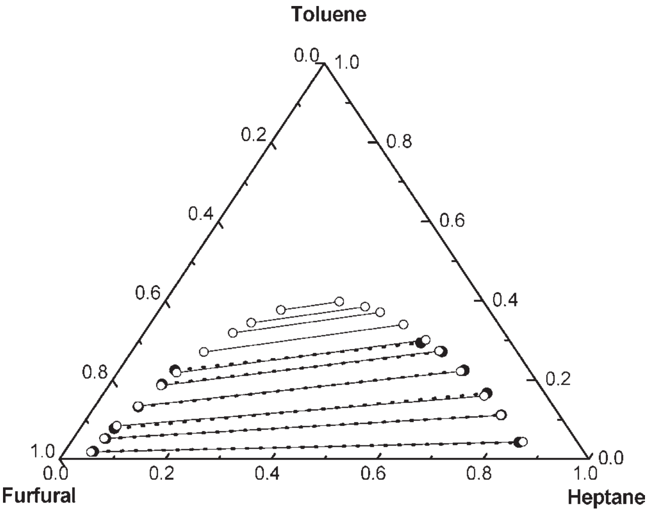

Figure 6. Ternary LLE of the heptane (1) + toluene (2) + furfural (3) system at 298.15 K; ··•··, experimental, —○—, NRTL.

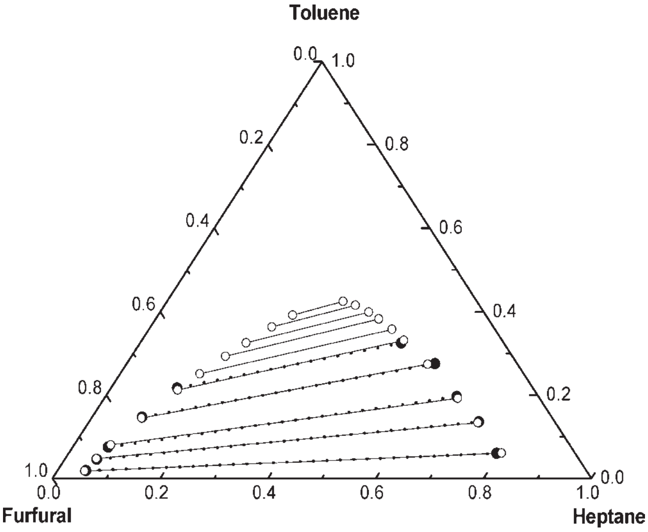

Figure 7. Ternary LLE of the heptane (1) + toluene (2) + furfural (3) system at 303.15 K; ··•··, experimental, —○—, NRTL.

where M is the number of tie lines measured and 6 is the number of compositions measured per tie line for ternary systems. For quaternary systems this number is 8. The rmsd values for all four ternary systems are presented in Tables 5 and 6 along with the NRTL parameters. For the quaternary systems Tables 7 and 8 show the rmsd values. The low values show that the experimental and calculated data are in very good agreement with each other. The comparison of the experimental and calculated tie lines on the phase diagram is shown in Figures 4 to 9. Except for one or two tie lines in Figures 6 and 7, all of the tie lines in these figures show excellent correlation by the NRTL model. The figures also show the calculated tie lines in the region above the uppermost experimental tie line, up to very near the plait point. The shape of the two-phase dome can thus be seen clearly.

■ CONCLUSIONS

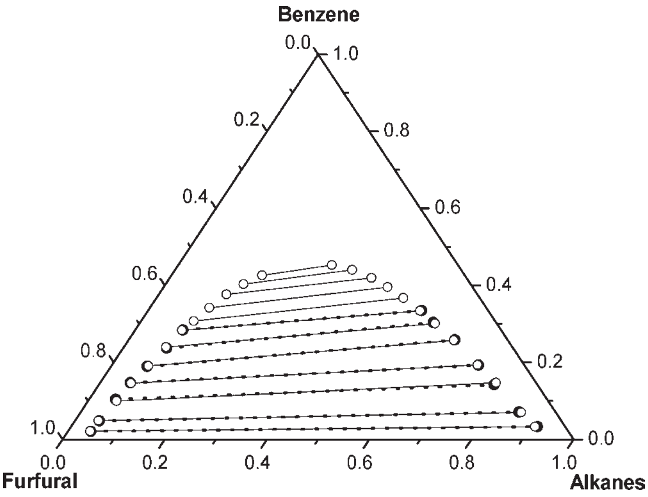

Figure 8. Quaternary LLE of the alkanes (heptane (1) + dodecane (2)) + benzene (3) + furfural (4) system at 298.15 K; ··•··, experimental, —○—, NRTL.

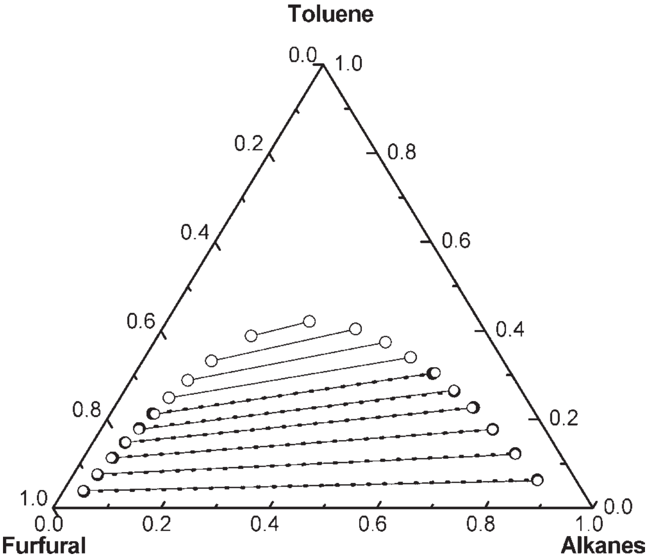

Figure 9. Quaternary LLE of alkanes (heptane (1) + dodecane (2)) + toluene (3) + furfural (4) system at 298.15 K; ··•··, experimental, —○—, NRTL.

Liquid−liquid equilibrium data for the ternary systems heptane + benzene + furfural and heptane + toluene + furfural at (298.15 and 303.15) K were experimentally measured. LLE data for the quaternary systems heptane + dodecane + benzene (or toluene) + furfural at 298.15 K were also measured. The Othmer−Tobias test confirmed the consistency of the experimental data. High selectivity values were observed, from about 3 to 14. Selectivities are higher at the lower temperature 298.15 K than at 303.15 K.

For the theoretical description, the NRTL model was found to give a very good representation of the tie lines, giving very low rmsd values. The binary interaction parameters of the NRTL model needed for these calculations were determined by regression using the measured LLE data. Tie line calculations from the model for the upper two-phase region showed this extrapolated part to be a smooth extension of the lower, experimentally determined region.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +91-11-26591033. Fax: +91-11-26581120. E-mail: ratan@chemical.iitd.ac.in.

REFERENCES

(1) Ashour, I.; Abu-Eishah, S. I. Liquid-Liquid Equilibria for Cyclohexane + Ethylbenzene + Sulfolane at (303.15, 313.15 and 323.15) K. *J. Chem. Eng. Data* **2006**, *51*, 859–863.

(2) Banerjee, T.; Sahoo, R. K.; Rath, S. S.; Kumar, R.; Khanna, A. Multicomponent Liquid-Liquid Equilibria for Aromatic Extraction Systems Using COSMO-RS. *Ind. Eng. Chem. Res.* **2007**, *46*, 1292–1304.

(3) Kenny, J. W. Prediction of ternary liquid liquid equilibrium from binary data (for the system furfural-iso-octane-benzene. *Chem. Eng. Sci.* **1957**, *6*, 116–122.

(4) Morawski, P.; Letcher, T. M.; Naicker, P. K. Liquid-Liquid Equilibria for Mixtures of (Furfuryl Alcohol + an Aromatic Hydrocarbon + an Alkane) at T = 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 1453–1456.

(5) Letcher, T. M.; Zondi, S.; Naicker, P. K. Liquid-Liquid Equilibria for Mixtures of (Furfural + an Aromatic Hydrocarbon + an Alkane) at T = 298.15 K. *J. Chem. Eng. Data* **2003**, *48*, 23–28.

(6) Skrollahzadeh, S.; Sadeghi Fateh, D.; Shokouhi, H.; Shahvelayati, A.; Golmohammad, F. Liquid Extraction of Aromatic Hydrocarbons by Tetrahydrofurfuryl Alcohol, An Environmentally Friendly Solvent. *J. Appl. Sci.* **2008**, *8*, 1320–1324.

(7) Coto, B.; van Grieken, R.; Pena, J. L.; Espada, J. J. A generalized model to predict the liquid-liquid equilibrium in the systems furfural + lubricating oils. *Chem. Eng. Sci.* **2006**, *61*, 8028–8039.

(8) Espada, J. J.; Coto, B.; Pena, J. L. Liquid-liquid equilibrium in the systems furfural + light lubricating oils using UNIFAC. *Fluid Phase Equilib.* **2007**, *259*, 201–209.

(9) Nelder, J. A.; Mead, R. A simplex method for minimization. *J. Comput.* **1965**, *7*, 308–313.

(10) Othmer, D. F.; Tobias, P. E. Tie Line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–696.

(11) Renon, H.; Prausnitz, J. M. Local compositions in the thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.