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Measurement and Correlation of Liquid−Liquid Equilibria of Methylcyclohexane + Toluene + *N*-Formylmorpholine at (293, 303, 313, and 323) K

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Liquid−liquid equilibrium (LLE) data for ternary systems methylcyclohexane (1) + toluene (2) + *N*-formylmorpholine (NFM) (3) were determined under atmospheric pressure and at temperatures of (293.15, 303.15, 313.15, and 323.15) K. Complete phase diagrams were obtained by determining solubility and tie-line data. Tie-line compositions were correlated by the Othmer−Tobias and Bachman methods. The universal quasichemical activity coefficient (UNIQUAC) and the nonrandom two-liquid (NRTL) equation were used to correlate the phase equilibrium in the system using the interaction parameters determined from experimental data. Distribution coefficients, separation factors, and selectivity were evaluated for the immiscibility regions.

Introduction

Liquid−liquid equilibrium (LLE) data of the different mixtures in a given process are required for the design of liquid extraction processes. To understand and provide further information about the phase behavior of solvents + aromatics + alkanes, a large amount of investigations have been carried out in the recent years on LLE measurements of such systems.[1−12]

High-purity aromatic compounds are used for chemical synthesis with ever-increasing demands. These compounds can be obtained by extractive distillation. Many solvents such as sulfolane,[1−5] *N*-methylpyrrolidone,[6] glycol,[7,8] and *N*-formylmorpholine are used in this process. *N*-Formylmorpholine has been found to be an excellent solvent for industrial extraction of aromatics from feed stocks, such as hydrogenated pyrolysis gasoline and hydrorefined coke oven oil.[9−12]

LLE data of methylcyclohexane + toluene + NFM are scarce in the literature,[10−12] which are not available for multicomponent system. The objective of this work is to determine LLE data of methylcyclohexane + toluene + NFM at several temperatures and to test the capability of the various equilibrium models to correlate these data. The compositions were measured at (293.15, 303.15, 313.15, and 323.15) K and regressed by the UNIQUAC[13] and NRTL[14] models.

Experimental

Chemicals. The purities and refractive indices of all chemicals used in this study are presented in Table 1. The refractive indice was measureed by a refractometer (WAY-S). The purity of the chemicals was determined by gas chromatography (Agilent GC6890), and the results confirmed the mass fraction purity was higher than 99.5 %. All chemicals were used without further purification.

Apparatus and Procedure. The experimental apparatus used in the previous study was modified and used in this study.[5] The apparatus consists of a glass cell with a water jacket to maintain a constant temperature. The temperature was controlled with an electronic device (DF-101B, made in China) within ± 0.5 K inside the cell. The cell was connected to a water bath, which was controlled within ± 0.1 K. The condenser ensures complete condensation of evaporated compounds. A mixture of known composition and mass was placed in the extraction vessel and vigorously stirred for 1 h, and the mixture was then left to settle for 3 h. Samples were taken by a syringe from the upper and lower phases. A series of LLE measurements were made by changing either the temperature or the composition of the mixture.

Table 1. Details of the Chemicals: Purities, UNIQUAC Structural Parameters, and Refractive Indices

			UNIQUAC structural parameter		n_D^{20}	
compound	supplier	purity (%)	*r*	*q*	exptl	lit.[a]
NFM	Sigma	99.5325	4.2248	3.440	1.4840	1.4848
methylcyclohexane	Sigma	99.7370	5.1742	4.396	1.4230	1.4221
toluene	Sigma	99.8457	3.9228	2.968	1.4873	1.4960

[a] Lange's Handbook of chemistry, 15th ed. (1999).

The composition of the mixture was determined by gas chromatography. The temperatures of the injector and the detector were maintained at 520 K. The column temperature was controlled by programming the temperature, and after 1 min of holding at 340 K, the column temperature was raised to the final temperature of 430 K at the rate of 15 $K \cdot min^{-1}$. Nitrogen was used as the carrier gas at the rate of 40 $cm^3 \cdot min^{-1}$. Single-phase samples of known composition were used to calibrate the gas chromatograph in the composition range of interest. The analysis for the calibration indicated that a precision of $\pm 3 \cdot 10^{-4}$ area ratio was obtained for each composition. The samples of each phase at the same temperature were analyzed three times at least, and the average values were used. The average deviation of the area ratio is $\pm 3 \cdot 10^{-4}$.

Results and Discussion

The solubility data for the binary system of methylcyclohexane (1) + *N*-formylmorpholine (2) at four temperatures are given

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Table 2. Experimental and Calculated Liquid−Liquid Equilibrium Mole Fractions for the Binary System Methylcyclohexane (1) + *N*-Formylmorpholine (3)

	methylcyclohexane-rich phase, x_{11}			*N*-formylmorpholine-rich phase, x_{12}		
T/K	exptl	NRTL	UNIQUAC	exptl	NRTL	UNIQUAC
293	0.9797	0.9703	0.9623	0.0231	0.0175	0.0371
303	0.9705	0.9617	0.9447	0.0276	0.0248	0.0439
313	0.9613	0.9549	0.9357	0.0311	0.029	0.0487
323	0.9531	0.9482	0.9267	0.0497	0.0429	0.0657

Table 3. Experimental Data for the Ternary System Methylcyclohexane (1) + Toluene (2) + NFM (3) at Different Temperatures

	methylcyclohexane-rich phase		NFM-rich phase				
T/K	x_1	x_2	x_1	x_2	*K*	β	*S*
293.15	0.8991	0.0773	0.0222	0.0106	0.1371	5.5537	4.0821
	0.8288	0.1399	0.0227	0.0278	0.1987	7.2552	3.8118
	0.7652	0.1945	0.0244	0.0514	0.2643	8.2876	3.3459
	0.6974	0.2499	0.0278	0.0857	0.3429	8.6030	2.8622
	0.5981	0.3242	0.0371	0.1511	0.4661	7.5137	2.2840
	0.5368	0.3650	0.0462	0.1983	0.5433	6.3125	2.0038
	0.4505	0.4135	0.0653	0.2694	0.6515	4.4947	1.6818
303.15	0.8964	0.0766	0.0249	0.0116	0.1514	5.4517	4.0369
	0.8261	0.1386	0.0256	0.0297	0.2143	6.9149	3.7382
	0.7623	0.1928	0.0275	0.0541	0.2806	7.7783	3.2843
	0.6939	0.2479	0.0314	0.0889	0.3586	7.9249	2.8075
	0.6246	0.2999	0.0377	0.1328	0.4428	7.3364	2.4011
	0.5307	0.3623	0.0517	0.2025	0.5589	5.7374	1.9635
	0.4467	0.4079	0.0715	0.2705	0.6632	4.1431	1.6571
313.15	0.8935	0.0758	0.0278	0.0126	0.1662	5.3426	3.9882
	0.8231	0.1373	0.0287	0.0316	0.2302	6.6007	3.6657
	0.7590	0.1911	0.0310	0.0566	0.2962	7.2516	3.2123
	0.6901	0.2458	0.0353	0.0920	0.3743	7.3172	2.7517
	0.6198	0.2976	0.0423	0.1364	0.4583	6.7157	2.3530
	0.5241	0.3595	0.0577	0.2064	0.5741	5.2149	1.9209
	0.4399	0.4033	0.0790	0.2734	0.6779	3.7748	1.6221
323.15	0.8903	0.0750	0.0309	0.0136	0.1813	5.2246	3.9335
	0.8198	0.1360	0.0321	0.0335	0.2463	6.2908	3.5890
	0.7554	0.1893	0.0347	0.0591	0.3122	6.7965	3.1443
	0.6552	0.2664	0.0424	0.1135	0.4261	6.5837	2.5186
	0.5819	0.3171	0.0520	0.1626	0.5128	5.7381	2.1481
	0.5168	0.3567	0.0642	0.2110	0.5915	4.7618	1.8776
	0.4405	0.3951	0.0846	0.2700	0.6834	3.5582	1.6103

in Table 2, and the measured equilibrium mole fractions for methylcyclohexane (1) + toluene (2) + *N*-formylmorpholine (3) are shown in Table 3. The experimental and the predicted tie-lines for the system at (293.15, 303.15, 313.15, and 323.15) K are shown in Figures 1 to 4. The reliability of experimentally measured tie-line data can be ascertained by the Othmer−Tobias correlation (eq 1) and the Bachman correlation (eq 2) at tie-line data,[5] where x_{11} is the mole fraction of methylcyclohexane in the methylcyclohexane-rich phase and x_{32} is the mole fraction of NFM in the NFM-rich phase. The parameters of the Othmer−Tobias correlation were given in Table 4. The Bachman correlation is an empirical equation describing the distribution of components in the three-component two-phase liquid system, and the parameters of the Bachman correlation were given in Table 4. The approximation of the correlation factor (r^2) to 1 indicates the degree of consistency of the related data. Othmer−Tobias and Bachman plots at different temperatures were made in Figures 5 and 6, respectively.

$$\ln\left(\frac{1-x_{32}}{x_{32}}\right) = a + b\ln\left(\frac{1-x_{11}}{x_{11}}\right) \tag{1}$$

$$x_{32} = a + b(x_{32}/x_{11}) \tag{2}$$

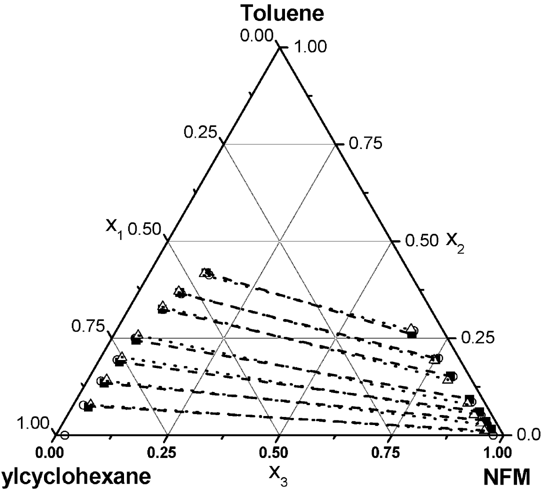

Figure 1. Experimental and predicted LLE data for methylcyclohexane (1) + toluene (2) + NFM (3) at 293 K: ○, experimental; ■, NRTL; △, UNIQUAC.

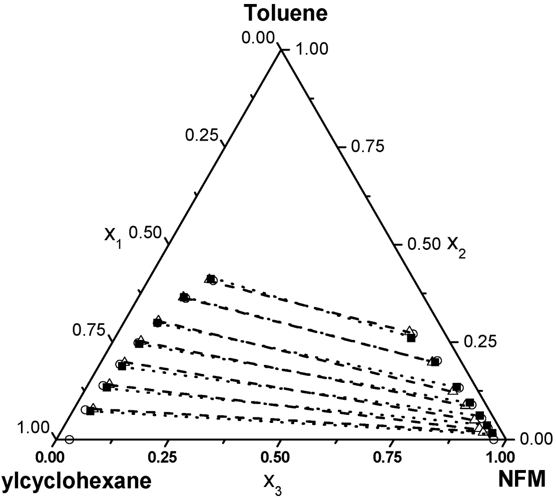

Figure 2. Experimental and predicted LLE data for methylcyclohexane (1) + toluene (2) + NFM (3) at 303 K: ○, experimental; ■, NRTL; △, UNIQUAC.

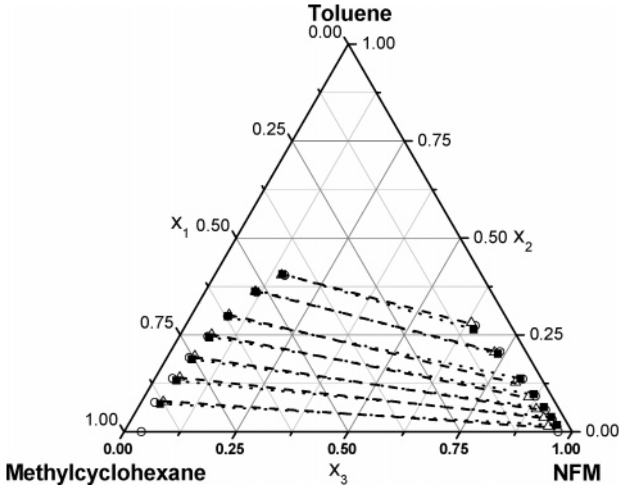

Figure 3. Experimental and predicted LLE data for methylcyclohexane (1) + toluene (2) + NFM (3) at 313 K: ○, experimental; ■, NRTL; △, UNIQUAC.

The experimental tie-line data were used to determine the optimum UNIQUAC and NRTL interaction parameters between methylcyclohexane, toluene, and NFM. The values of these

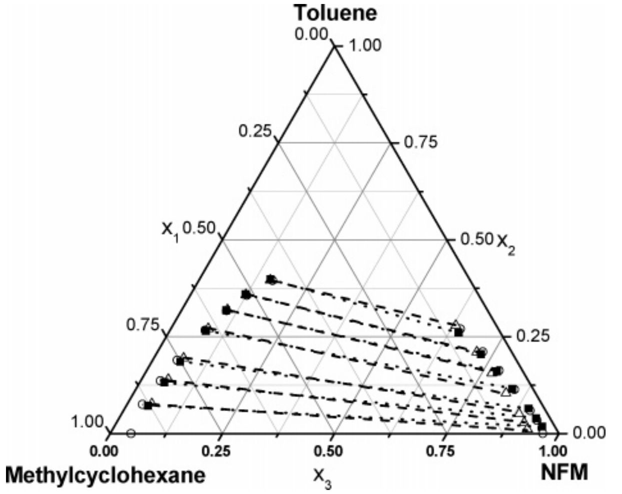

Figure 4. Experimental and predicted LLE data for methylcyclohexane (1) + toluene (2) + NFM (3) at 323 K: ○, experimental; ■, NRTL; △, UNIQUAC.

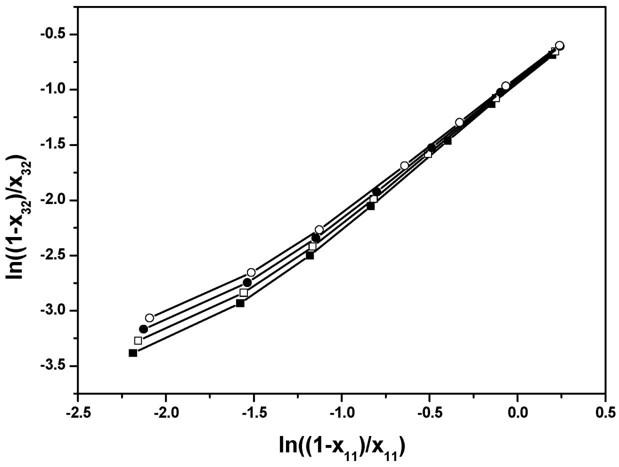

Figure 5. Othmer−Tobias correlation for the methylcyclohexane (1) + toluene (2) + NFM (3) system at different temperatures: ■, 293 K; □, 303 K; ●, 313 K; ○, 323 K.

Table 4. Constants of Othmer−Tobias and Bachman Equations for the Methylcyclohexane + Toluene + NFM System

	Othmer−Tobias			Bachman		
T/K	*a*	*b*	r^2	*a*	*b*	r^2
293.15	−1.0004	1.1667	0.9884	0.3904	0.6757	0.9597
303.15	−0.9834	1.1361	0.9884	0.3813	0.6842	0.9597
313.15	−0.9609	1.1106	0.9888	0.3713	0.6927	0.9624
323.15	−0.9324	1.0869	0.9902	0.3687	0.6899	0.9682

parameters for the two equations are shown in Table 5. The UNIQUAC and NRTL equations were fitted to experimental data using an iterative compound computer program with the objective function developed by Sørensen.[15] The objective function in this case was determined by minimizing the square of the difference between the mole fractions predicted by the respective method and those experimentally measured over all the tie-lines in the ternary system. The objective function, OF, used is

$$\mathrm{OF} = \min \sum_i \sum_j \sum_k (x_{ijk}^{\mathrm{exptl}} - x_{ijk}^{\mathrm{calcd}})^2 \qquad (3)$$

where x_{ijk}^{exptl} and x_{ijk}^{calcd} are the experimental and calculated mole fractions, respectively. The subscripts *i*, *j*, and *k* denote component, phase, and tie-line, respectively.

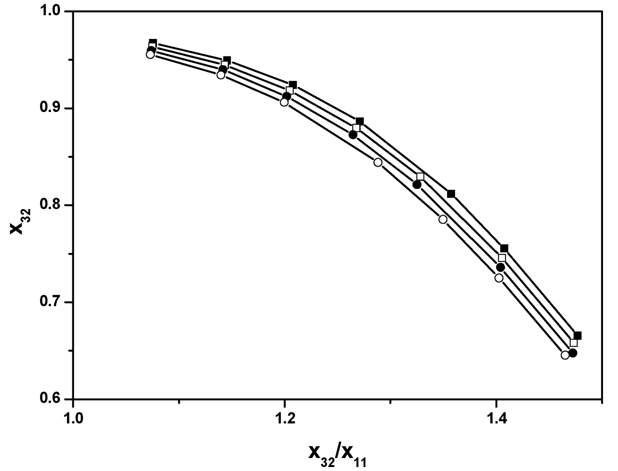

Figure 6. Bachman correlation for the methylcyclohexane (1) + toluene (2) + NFM (3) system at different temperatures: ■, 293 K; □, 303 K; ●, 313 K; ○, 323 K.

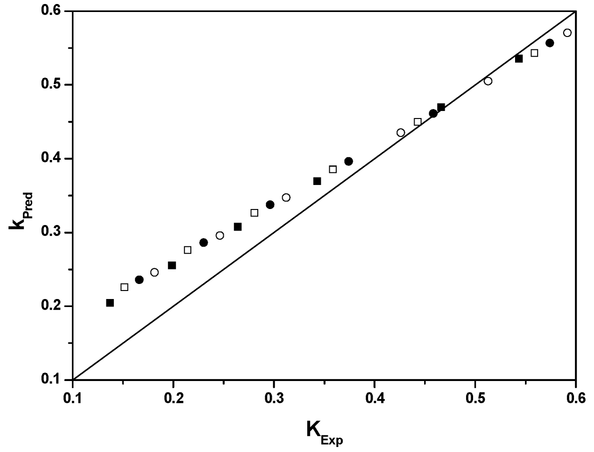

Figure 7. Measured and predicted distribution coefficient by NRTL for the methylcyclohexane (1) + toluene (2) + NFM (3) system at different temperatures: ■, 293 K; □, 303 K; ●, 313 K; ○, 323 K.

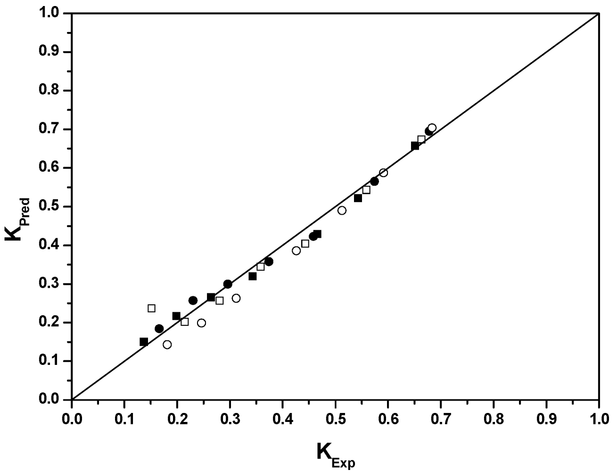

Figure 8. Measured and predicted distribution coefficient by UNIQUAC for the methylcyclohexane (1) + toluene (2) + NFM (3) system at different temperatures: ■, 293 K; □, 303 K; ●, 313 K; ○, 323 K.

For the NRTL, we have set α_{ij} and α_{ji} as temperature independent with fixed values of α for each pair of compounds. A fixed value of $\alpha = 0.3$ between each pair of compounds was found to be satisfactory. A fixed value of the nonrandomness parameter, $a = 0.3$, between each pair of components was found to be satisfactory.

Table 5. UNIQUAC and NRTL Interaction Parameters for the Ternary Systems

		UNIQUAC		NRTL	
i	j	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	$(g_{ji} - g_{ii})/R$	$(g_{ij} - g_{jj})/R$
NFM	methylcyclohexane	74.2209	303.8576	802.4546	739.4515
NFM	toluene	−106.3842	−53.2705	573.0537	266.3876
methylcyclohexane	toluene	−260.0480	−46.7526	−20.3385	937.6354

Table 6. Root-Mean-Square Deviation (rmsd) Values for Ternary Mixtures

T/K	UNIQUAC	NRTL
293.15	0.0047	0.0027
303.15	0.0060	0.0027
313.15	0.0059	0.0028
323.15	0.0084	0.0028

The UNIQUAC structural parameters r and q listed in Table 1 were calculated from the group contribution data. The corresponding values for reformate were calculated from the equivalent sum of the component constituting the reformate and their respective compositions.

The goodness of fit for UNIQUAC and NRTL equations was measured by the root-mean-square deviation (rmsd) values. The rmsd values are calculated from the difference between the experimental data and the predictions of each method at a given temperature according to following formula

$$\text{rmsd} = \left\{\frac{\sum_k \sum_j \sum_i (x_{ijk}^{\text{exptl}} - x_{ijk}^{\text{calcd}})}{6n}\right\}^{1/2} \tag{4}$$

where n is the number of tie-lines; x^{calcd} is the calculated mole fraction; and x^{exptl} is the experimental mole fraction. The results of rmsd values are reported in Table 6. These data may be compared with the results of Sørensen et al.[15] for many data sets of different systems, which gave rmsd values ranging from 0.18 to 1.37. These results show that UNIQUAC and NRTL equations fit our experimental data satisfactorily.

The distribution coefficient of toluene K, which is the measure of the solvent power or capacity of NFM, is given by

$$K = \frac{x_{23}}{x_{21}} \tag{5}$$

where x_{23} and x_{21} are, respectively, the mole fractions of toluene (2) in the NFM-rich phase and the methylcyclohexane-rich phase. The distribution coefficients of toluene are displayed in Table 3, which represent the relationship of the toluene concentration in the methylcyclohexane-rich phase, with the measured distribution coefficients K for the three ternary systems methylcyclohexane (1) + toluene (2) + NFM (3) at temperatures of (293 to 323) K. The distribution coefficient values increased as the temperature and/or x_{21} increased.

The distribution coefficient was predicted by the NRTL and UNIQUAC models using the interaction parameters generated in Table 5. Figures 7 and 8 show a good agreement between the experimental and predicted (rmsd for NRTL is 0.0399 and for UNIQUAC is 0.0297) distribution coefficients for the three ternary systems, respectively. The deviation of the distribution coefficients for the NRTL model is larger than that for the UNIQUAC model because the NRTL model only gave slightly more positive deviations to the concentration of toluene in the NFM-rich phase at a low concentration range of toluene and the UNIQUAC model gave the same negative deviation to the concentrations of toluene in two phases. The results predicted by the UNIQUAC model seemed good. In fact, the NRTL fit better than the UNIQUAC, as can be seen from Figures 1 to 4.

The effectiveness of extraction can be expressed by the separation factor, β, of NFM. The separation factor of NFM, which is an indication of the ability of NFM to separate toluene from methylcyclohexane, is given by

$$\beta = \frac{(x_{23}/x_{13})}{(x_{21}/x_{11})} \tag{6}$$

Here x_{23} and x_{13} are, respectively, the mole fractions of toluene and methylcyclohexane in the NFM-rich phase, and x_{21} and x_{11} are, respectively, the mole fractions of toluene and methylcyclohexane in the methylcyclohexane-rich phase. The experimental values of β are listed in Table 3. As can be seen from the results in this table, the separation factor values are not constant over the whole two-phase region. For the three ternary systems methylcyclohexane (1) + toluene (2) + NFM (3) at temperatures of (293 to 323) K, the higher the temperature, the lower the separation factor. The separation factor changed as the concentration of toluene varied, which means that optimal concentrations of toluene in the feed exist to get a good separation capacity of NFM. Because the separation factors in all cases are greater than 1, the extraction is possible.

The effectiveness of extraction of toluene by NFM can be given by its selectivity (S), which is also a measure of the ability of NFM to separate toluene from methylcyclohexane. Selectivity on a solvent-free basis is given by

$$S = \frac{x_{23}/(x_{23} + x_{13})}{x_{21}/(x_{21} + x_{11})} \tag{7}$$

where x_{23} and x_{13} are, respectively, the mole fractions of methylcyclohexane (1) and toluene (2) in the NFM-rich phase and x_{21} and x_{11} are, respectively, the mole fractions of methylcyclohexane (1) and toluene (2) in the methylcyclohexane-rich phase. The experimental values of S are listed in Table 3. This may contribute to the determination of the degree of suitability of solvent for extraction of toluene. As shown in Table 3, selectivity in all cases is greater than 1, and selectivity decreases when going through the tie-line end compositions from low concentration to high concentration of toluene. It means the higher the concentration of toluene compounds in the feeds, the lower the selectivity of NFM to toluene.

Conclusions

An experimental investigation of equilibrium behavior of liquid−liquid and methylcyclohexane + toluene + NFM ternary systems was carried out at temperatures of (293 to 323) K and at atmospheric pressure. It can be seen from Figures 1 to 4 that as the temperature increases the solubility of NFM in the methylcyclohexane-rich phase increases, but it has little effect on the solubility of methylcyclohexane in the NFM-rich phase. Increasing the temperature and the concentration of toluene increases the mutual NFM + methylcyclohexane solubility. Both the NRTL and UNIQUAC equations satisfactorily correlate the LLE experimental data. The calculations based on both UNIQUAC and NRTL equations give a good representation of the tie-line data for the system studied. However, according to the rmsd, the values based on the NRTL model are found to be better than those based on the UNIQUAC model. The reliability of experimentally measured tie-line data can be correlated by the Othmer−Tobias and Bachman equations, by correlation factors (r^2) approximate to 1. Because the separation factor and selectivity in all cases are greater than 1, NFM can be used to extract toluene from methylcyclohexane mixtures.

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