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Phase Equilibria for Liquid Mixtures of (an Alkane + Toluene + Dimethyl Phthalate)

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This study aims to investigate the efficiency of dimethyl phthalate (DMP), having low water solubility, low density, and a high boiling point compared to alkanes, as a solvent to extract toluene from its multicomponent hydrocarbon mixtures. Liquid–liquid equilibrium (LLE) data of the solubility (binodal) curves and tie-line end compositions were examined for mixtures of {heptane or hexane or cyclohexane (1) + toluene (2) + DMP (3)} at $T = 298.15$ K and 101.3 kPa. The reliability of the experimental tie-line data was verified by using the Othmer–Tobias correlation. Distribution coefficients and separation factors were evaluated for the immiscibility region. The experimental tie-line data were correlated by the universal quasichemical activity coefficient (UNIQUAC) equation and also predicted with the universal functional group activity coefficient (UNIFAC) model. The experimental data were compared with the calculated results.

Introduction

Oil refineries manufacture a variety of useful products. The refining of petroleum products via chemical separation methods by adding a compound does cause a chemical change in the material. Thus, some of the components are lost, and generally, byproducts are formed. In addition, the chemicals required are expensive. Mechanical separation methods are better applied in the petroleum industry. Extraction processes are suitable to separate an aliphatic–aromatic mixture existing in a homogeneous form by means of introducing the second phase into the system in the form of a solvent that selectively dissolves the component required in the feed mixture.^{1,2}

The choice of solvent used in extraction is extremely important for the success of separation. Therefore, some factors like polarity, boiling point, reactivity, viscosity, stability, safety in use, cost, existence in substantial quantities, and suitability for reuse should be taking into consideration. Considerable laboratory effort is required just to find a solvent which is consistent with the considerations above. Liquid–liquid equilibrium (LLE) data related to selected solvent must be acquainted previously. Phase equilibrium data with respect to that system is definitely necessary for the design of separation equipment; since they know the principles of separation operations, chemical engineers can successfully develop, design, and operate industrial processes. Varied solvents have been tested to discover the best separation for the aliphatic–aromatic mixtures of this kind so far.^{3–10} There have not been any articles in the literature related to LLE consisting of aliphatic–aromatic mixtures and dimethyl phthalate (DMP). That is why it is worth investigating the phase equilibria for liquid mixtures of {an alkane + toluene + DMP}.

Experimental Section

Materials. Heptane, hexane, cyclohexane, toluene, and DMP were supplied by Merck and were of > 0.99, 0.99, 0.98, > 0.99, and > 0.99 mass fraction purity, respectively.

Procedure. The solubility curves were determined by the cloud-point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions.^{11–16} The temperature in the cell was kept constant by circulating water from a water bath (NUVE, BS 302 model), which was equipped with a temperature controller capable of maintaining the temperature within ± 0.1 K. The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of (alkane + solvent) with toluene until the turbidity had disappeared. For the alkane-side and solvent-side, binary mixtures of either (alkane + toluene) or (solvent + toluene) were titrated against the third component until the transition from homogeneity to heterogeneity was observed. All initial mixtures were prepared in 10 mL volume by mass using with a Mettler scale accurate to within $\pm 10^{-7}$ kg.

Mutual solubility values of the binary mixture (alkane + solvent) were measured using the method based on the detection of the cloud point. The transition point between the homogeneous and the heterogeneous zones was determined visually. The reliability of the method depends on the precision of the Metrohm microburet with an accuracy of $\pm 3 \cdot 10^{-9}$ m³ and is limited by the visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved by waiting for about 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least twice to acquire high accuracy.

End-point determinations of the tie-lines were carried out by the independent analysis of the conjugate phases that were regarded as being in equilibrium. Approximately, 10 cm³ of mixture in known masses of alkane, toluene, and solvent lying within the heterogeneous gap were introduced into the extraction cell and stirred for 4 h and then left for 6 h (the time necessary to attain equilibrium was established in preliminary experiments) to settle down into the two layers. DMP did not create any problems related to phase separation like forming foam or emulsions.

Analysis. Samples from both layers were carefully taken and analyzed by a gas chromatograph, Clarius 500 model. A flame ionization detector (FID) was used with a Valco-Bond capillary

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Table 1. Experimental Solubility Curve Data for Alkane (1) + Toluene (2) + DMP (3) Ternary Systems at 298.15 K and 101.3 kPa

w_1	w_2	w_3
Heptane (1) + Toluene (2) + DMP (3)		
0.9458	0	0.0542
0.8401	0.0901	0.0698
0.6955	0.1753	0.1292
0.5919	0.2263	0.1818
0.4972	0.2521	0.2507
0.3728	0.2578	0.3694
0.2332	0.2295	0.5373
0.1482	0.1695	0.6823
0.1025	0.0899	0.8076
0.0764	0	0.9236
Hexane (1) + Toluene (2) + DMP (3)		
0.9198	0	0.0802
0.8259	0.0813	0.0928
0.7053	0.1752	0.1195
0.6009	0.2186	0.1805
0.4653	0.2299	0.3048
0.3375	0.2158	0.4467
0.2044	0.1881	0.6075
0.1441	0.1654	0.6905
0.0846	0.0949	0.8205
0.0705	0	0.9295
Cyclohexane (1) + Toluene (2) + DMP (3)		
0.9221	0	0.0779
0.7620	0.0886	0.1494
0.6802	0.1144	0.2054
0.5268	0.1350	0.3382
0.3533	0.1288	0.5179
0.2981	0.1119	0.5900
0.2171	0.0820	0.7009
0.1569	0	0.8431

column of 30 m × 320 μm × 1 μm. Injections were performed on the split 150/1 mode. Helium was used as a carrier gas, the flow rate of which is 1 mL·min⁻¹. The injection volume of the samples was 1 μL. The internal standard used was isopropanol. The detector temperature were kept at 543 K. The oven temperature program was as follows: The initial temperature was set to 373 K. It is followed by a heating rate of 10 K·min⁻¹ until the final temperature of 473 K was acquired. The samples of each phase were analyzed twice, and the average values were used.

Models and Predictions

The experimental data were correlated by the universal quasichemical activity coefficient (UNIQUAC) and universal

functional group activity coefficient (UNIFAC) models. The UNIQUAC interaction parameters were estimated using the numerical technique, Newton–Raphson for simultaneous non-linear equations. The objective function (OF) given below¹⁷ is employed for the evaluation of the best estimates of these interaction parameters from LLE data, because of the property weighing small and large activities equally; that is, it operates on the ratio of rather than the difference between activities.

$$OF = \sum_k \sum_i [\ln(x'_{ik} \gamma'_{ik}) - \ln(x''_{ik} \gamma''_{ik})]^2 \quad (1)$$

x'_{ik} and x''_{ik} refer to the mole fraction of component i in phase I and II, respectively, at tie-line k .

The experimental tie-line data were correlated using these estimated UNIQUAC parameters, and the optimization results were judged by calculating the corresponding root-mean-square deviation (rmsd) values using the following equation;

$$\text{rmsd} = \left[\frac{\sum_k \sum_j \sum_i (x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2}{6n} \right]^{0.5} \quad (2)$$

where n is the number of tie-lines. The indices i , j , and k refer to component, phase, and tie-line, respectively.

The experimental tie-line data were also predicted using UNIFAC model using eq 2.

Results and Discussion

Experimental Data. The compositions of mixture on the binodal curve, as well as the mutual binary solubility of alkane and solvent at $T = 298.15$ K are given in Table 1, in which w_i denotes the mass fraction of component i . The measured equilibrium tie-line data are given in Table 2. The experimental solubility curve and tie-line data are plotted in Figures 1, 2, and 3.

The reliability of the experimental tie-line data is verified by using the Othmer–Tobias correlation.¹⁸ This correlation is stated by the equation below;

$$\ln\left(\frac{1 - w_{33}}{w_{33}}\right) = a + b \ln\left(\frac{1 - w_{11}}{w_{11}}\right) \quad (3)$$

w_{33} refers to the mass fraction of DMP in the solvent-rich phase and w_{11} refers to mass fraction of the alkane in the alkane-rich phase; a and b are the constants of this equation. Othmer–Tobias plots constructed of the $\ln((1 - w_{11})/(w_{11}))$ versus $\ln((1 - w_{33})/$

Table 2. Experimental Tie-Line Data of Alkane (1) + Toluene (2) + DMP (3) Ternary Systems at 298.15 K and 101.3 kPa

alkane-rich (1) phase			solvent-rich (3) phase			d_2	S
w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}		
Heptane (1) + Toluene (2) + DMP (3)							
0.9080	0.0375	0.0545	0.0895	0.0353	0.8752	0.9413	9.5501
0.8621	0.0727	0.0652	0.0822	0.0634	0.8544	0.8721	9.1462
0.7761	0.1331	0.0908	0.0987	0.1124	0.7889	0.8445	6.6403
0.6775	0.1901	0.1324	0.1380	0.1536	0.7084	0.8080	3.9668
0.5800	0.2220	0.1780	0.1837	0.2004	0.6159	0.9027	2.9484
Hexane (1) + Toluene (2) + DMP (3)							
0.8856	0.0348	0.0796	0.0732	0.0264	0.9004	0.7586	9.1781
0.8297	0.086	0.0843	0.0819	0.0781	0.84	0.9081	9.2000
0.7531	0.1468	0.1001	0.1033	0.1338	0.7629	0.9114	6.6448
0.6696	0.1973	0.1331	0.1633	0.174	0.6627	0.8819	3.6162
Cyclohexane (1) + Toluene (2) + DMP (3)							
0.8784	0.0258	0.0958	0.1621	0.0158	0.8221	0.6124	3.3185
0.8128	0.0629	0.1243	0.1868	0.0512	0.762	0.8140	3.5418
0.7391	0.1008	0.1601	0.2115	0.0879	0.7006	0.8720	3.0473
0.6591	0.12	0.2201	0.2715	0.1079	0.6206	0.8992	2.1828

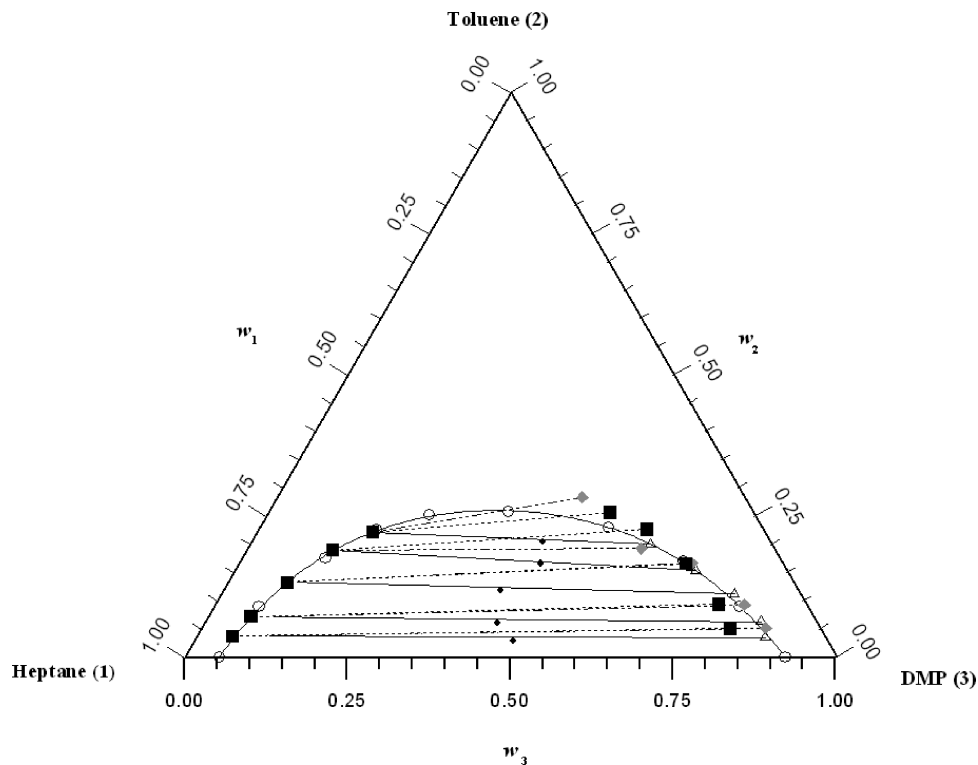


Figure 1. Ternary diagram of {heptane (1) + toluene (2) + DMP (3)} at 298.15 K; \circ , experimental solubility curve; Δ , experimental tie-lines; \blacklozenge , calculated UNIQUAC tie-lines; \blacksquare , calculated UNIFAC tie-lines.

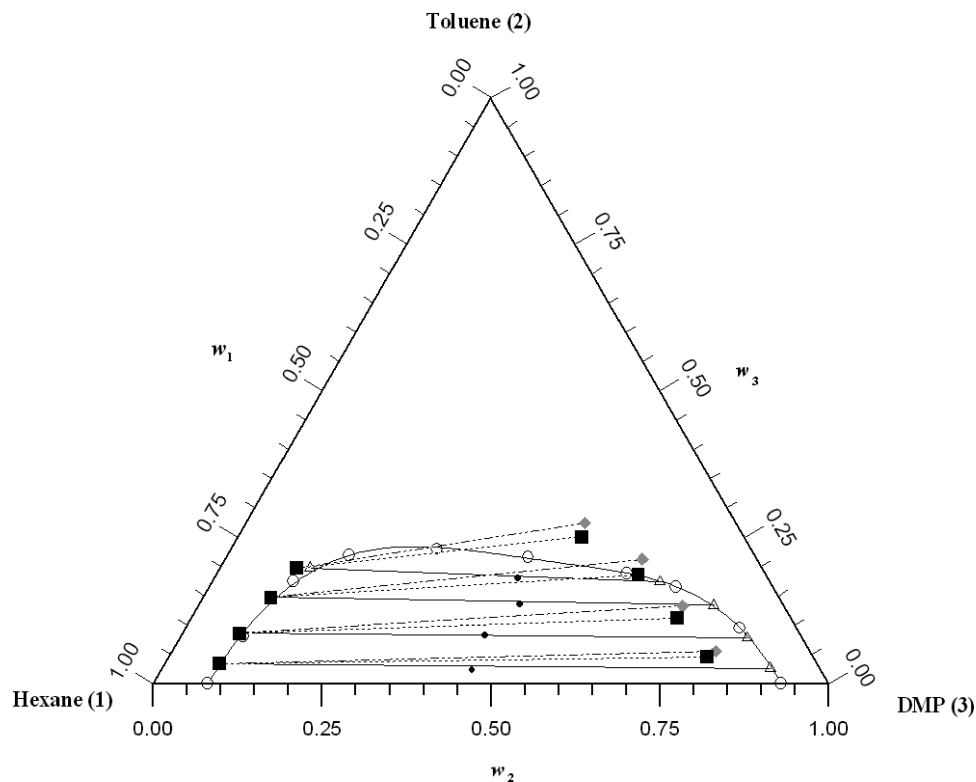


Figure 2. Ternary diagram of {hexane (1) + toluene (2) + DMP (3)} at 298.15 K; \circ , experimental solubility curve; Δ , experimental tie-lines; \blacklozenge , calculated UNIQUAC tie-lines; \blacksquare , calculated UNIFAC tie-lines.

(w_{33})) are shown in Figure 4 at $T = 298.15$ K. The correlation being linear indicates the degree of consistency of the related data.

The distribution coefficient, d_i , and separation factor, S , are evaluated for the immiscibility region and also given in Table 2. These parameters represent extraction performance of the so-

lvent. Distribution coefficient, the capacity of solvent for the extracted component, is calculated as follows:

$$d_i = w_{i3}/w_{i1} \quad (4)$$

w_{i1} and w_{i3} are the mass fraction of component i in alkane-rich phase and in solvent-rich phase, respectively. Higher distribution

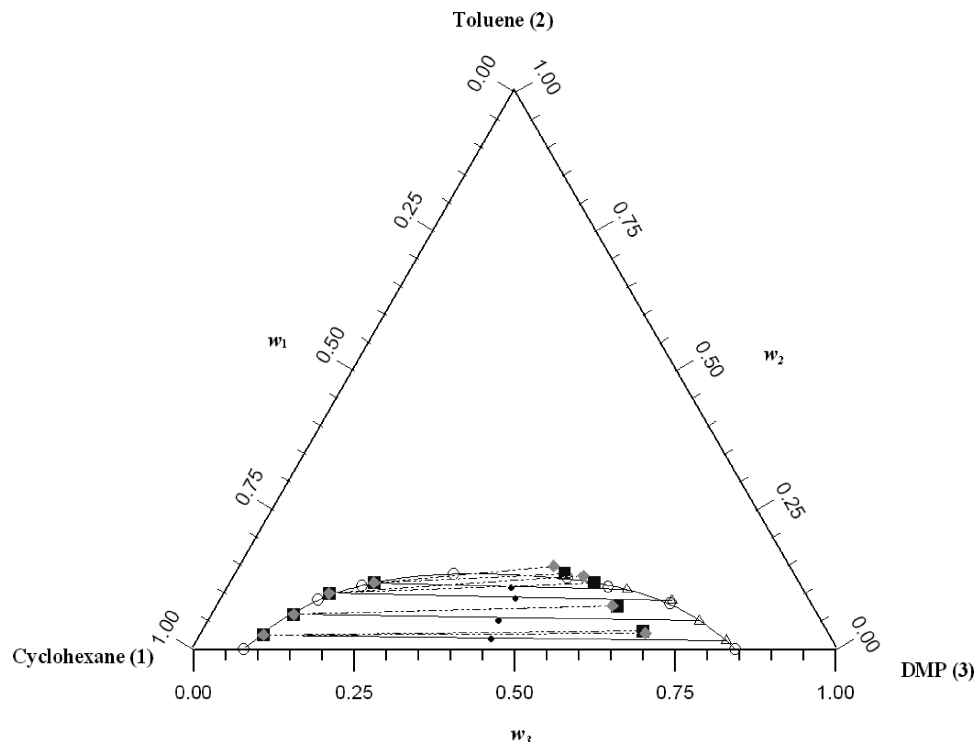


Figure 3. Ternary diagram of {cyclohexane (1) + toluene (2) + DMP (3)} at 298.15 K; ○, experimental solubility curve; △, experimental tie-lines; ◇, calculated UNIQUAC tie-lines; ■, calculated UNIFAC tie-lines.

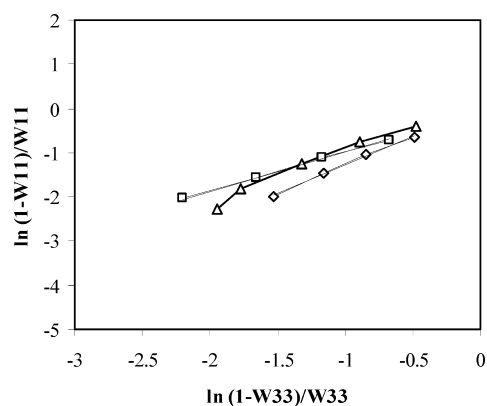


Figure 4. Othmer–Tobias plots of the {alkane (1) + toluene (2) + DMP (3)} ternary systems at $T = 298.15$ K; ◇, cyclohexane; □, hexane; △, heptane.

coefficients allow use of lower solvent-to-alkane flow ratios.

The effectiveness of a solvent can be expressed by the separation factor of the solvent. The separation factor of DMP, a measure of the ability of DMP to separate toluene from alkane, is given by

$$S = d_2/d_1 \quad (5)$$

The extracting power of the solvents is given in Figures 5 and 6 by means of the distribution coefficient (d_2) of toluene between alkane and solvent phases and separation factors (S), respectively. The distribution coefficient increased in Figure 5 and the separation factor in Figure 6, respectively, as the concentration of toluene increased. Since the separation factor in all cases is greater than 1, the extraction is possible.

Correlation and Prediction. The values of UNIQUAC interaction parameters with OF values calculated from eq 1 and the correlation results of the experimental tie-line data by means of rmsd values are given in Table 3. Table 4 includes rmsd values of the UNIFAC model. The rmsd values of the following

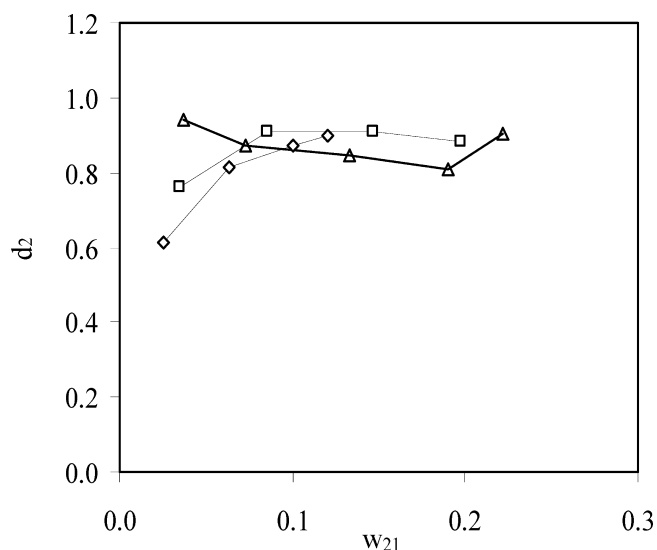


Figure 5. Distribution coefficient of toluene, d_2 , plotted against the mass fraction of toluene in alkane phase, w_{21} ; ◇, cyclohexane; □, hexane; △, heptane.

ternary systems for the UNIQUAC and UNIFAC models, respectively, were calculated as follows: 0.0805 as compared to 0.0799 for {heptane + toluene + DMP}; 0.1166 as compared to 0.1153 for {hexane + toluene + DMP}; and finally 0.1323 as compared to 0.1323 for {cyclohexane + toluene + DMP}, which are in poor agreement. Comparisons of tie-line experimental data with calculated UNIQUAC and UNIFAC values are plotted in Figures 1 to 3, respectively.

Conclusion

LLE data for three ternary systems comprising of {heptane or hexane or cyclohexane + toluene + DMP} were measured at $T = 298.15$ K and 101.3 kPa. The reliability of the

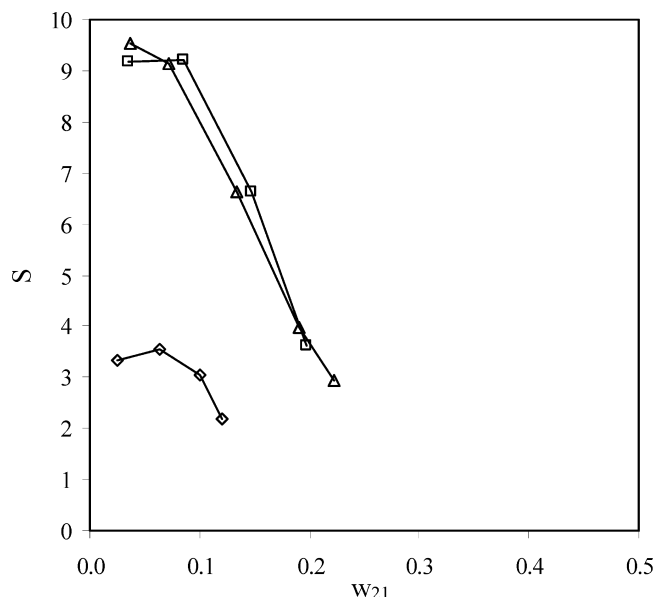


Figure 6. Separation factor, S , plotted against the mass fraction of toluene in the alkane phase, w_{21} ; ◇, cyclohexane; □, hexane; △, heptane.

Table 3. UNIQUAC Interaction Parameters, OF, and rmsd Values for Ternary Systems

i	j	τ_{ij}	τ_{ji}	OF	rmsd
Heptane (1) + Toluene (2) + DMP (3)					
1	2	2.0844	4.0100	0.8865	0.0805
1	3	1.8180	1.1201		
2	3	4.2070	2.7002		
Hexane (1) + Toluene (2) + DMP (3)					
1	2	1.2207	1.3456	0.0248	0.1166
1	3	1.2110	1.5062		
2	3	0.9090	1.7165		
Cyclohexane (1) + Toluene (2) + DMP (3)					
1	2	6.8579	2.0830	0.0081	0.1323
1	3	1.1249	1.5884		
2	3	2.3770	5.5891		

Table 4. rmsd Values of UNIFAC Model for Ternary Systems

system	rmsd
heptane + toluene + DMP	0.0799
hexane + toluene + DMP	0.1153
cyclohexane + toluene + DMP	0.1323

experimentally measured tie-line data of each ternary system was correlated by the Othmer–Tobias correlation. Othmer–Tobias correlation coefficients being linear (for heptane: 0.9752; hexane: 0.9993; cyclohexane: 0.9961) indicates the reliability of the experiments. The parameters of UNIQUAC model were calculated for {heptane or hexane or cyclohexane + toluene + DMP} with OF's given in Table 3 as 0.8865, 0.0248, and 0.0081, respectively. These OF's show that the calculated UNIQUAC parameters can be satisfactorily used to correlate the experimental tie-line data, except for the {heptane + toluene + DMP} ternary system, having relatively less satisfactory results than the other ternary systems. Both the UNIQUAC and the UNIFAC models calculate the tie-line data in a poor agreement with the experimental data, which can be seen from Figures 1 to 3 and rmsd values of Tables 3 and 4. The inconsistency became more revealed, especially on the solvent hand of the ternary systems. Separation factors, which are indications of the ability of DMP to separate toluene from

heptane, hexane, or cyclohexane, were found varying between 2.1828 and 9.5501. This result means that extraction of toluene from the systems reported here by DMP is possible, since the separation factors are bigger than 1. Because of the fact that the heterogeneous gaps, the regions under the each solubility curve, are almost the same in Figures 1 and 2, DMP has nearly equal extraction ability for these two ternary systems. According to Figures 2 and 6, toluene can be extracted from cyclohexane the least easily. This may be because of the cyclic structure of cyclohexane, showing more reactivity than n-alkanes, which contributes difficulties for the separation from toluene.

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