Liquid−Liquid Equilibrium for the System Heptane + *o*-Xylene + Diethylene Glycol over the Temperature Range of 288.15 K to 318.15 K

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Liquid−liquid equilibrium data for the system heptane + *o*-xylene + diethylene glycol have been experimentally measured over the temperature range of 288.15 to 318.15 K. The equilibrium data of this study are analyzed using the UNIQUAC, NRTL, UNIFAC, UNIFAC-LL, and UNIFAC-DMD models as programmed by the Aspen Plus simulator. On the basis of the analyses of the experimental data of this work, UNIFAC-LL showed the best predictive performance for the mole fraction of the target species (*o*-xylene) in both upper (heptane-rich) and lower (DEG-rich) phases, whereas UNIFAC-DMD showed poor predictive performance in comparison with the other models.

Introduction

The extraction of aromatics from catalytic reformates pyrolysis naphtha, kerosene, and superior kerosene has potential commercial importance in the oil refining industry. There are many processes used to separate aromatics, for instance, processes utilizing transition metals.[1] The most widely used process for separating aromatics from different paraffins is liquid extraction. In 1976, Rawat et al.[2] studied 19 organosulfur solvents as potential solvents for the extraction of aromatics using gas chromatography. Solvents for extraction should have high selectivity for aromatics, high capacity, high density, low viscosity, and partial miscibility with the hydrocarbon mixtures at reasonably low temperature.[3] They also must have good thermal stability, low reactivity, and minimum corrosion characteristics, in addition to being environmentally friendly. Many organic solvents have been investigated for extracting aromatics. They include sulfolane,[4−7] triethylene glycol,[8,9] tetraethylene glycol,[10,11] propylene carbonate,[12] dimethyl sulfoxide,[13] *n*-methyl pyrrolidone,[14] ethylene carbonate,[15] and *γ*-butrolactone.[16] Combinations of solvents to balance selectivity and solvency have also been investigated.[17−19]

Accurate phase equilibrium data are important parameters for the design and evaluation of industrial unit operations for extraction processes. Liquid−liquid equilibrium data for diethylene glycol (DEG) + aromatic + hydrocarbons systems are scarce in the literature. Although the technical literature is very rich on the subject of solvent extraction of some aromatics such as benzene and toluene, ternary system studies involving xylenes in general and *o*-xylenes in particular are relatively scarce. Moreover, ternary phase equilibrium data are essential for a proper understanding of solvent extraction processes, selection of solvents, and design of extractors.

The objective of the present study is the measurement of LLE data for the ternary system heptane + *o*-xylene + diethylene glycol over the temperature range of 288.15 K to 318.15 K under atmospheric pressure conditions. Additionally, five activity coefficient models, which are predictive in nature, are used to demonstrate their predictive capacities for the resulting data behavior. These models are UNIQUAC, NTRL, and three versions of UNIFAC, which differ only in the database used for the group interaction parameters. UNIFAC has group interaction parameters extracted from the vapor−liquid equilibrium (VLE) data bank, UNIFAC-LL has group interaction parameters extracted from the LLE data bank, and UNIFAC-DMD has group interaction parameters extracted from the Dortmund Data Bank.[20]

Experimental Section

The diethylene glycol used in this work was supplied by Riedel-de Haen with a stated purity of 98%. Heptane and *o*-xylene were supplied by Fluka with a purity of 99%. All materials were used as received without further purification.

The equilibrium experimental data were determined using a tightly closed, jacketed equilibrium cell with 100-cm^3 volume. The temperature was measured with a mercury-in-glass thermometer with a precision of better than 0.1 K. The temperature in the jacket of the cell was kept constant by circulating water from a water bath (Julabo Labortechnik GMBH-Germany), which was equipped with a temperature controller (Julabo PC) capable of maintaining the temperature at a fixed value within ±0.1 K. Mixtures of known masses of diethylene glycol, *o*-xylene, and heptane were introduced into the cell and stirred for 2 h and then left for 8 h to equilibrate and settle down into a raffinate (aqueous-phase) layer and an extract (organic-phase) layer at the same temperature.

Samples from both layers were carefully taken and analyzed using a gas chromatograph (Chrompack CP 9001) with a flame ionization detector (FID). Chromatographic separation of the mixture constituents was achieved using a 50 m × 0.32 mm i.d. WCOT (wall-coated open-tube) capillary column of fused silica coated with a 1.2-μm stationary film (CP-Sil 5 CB). The inlet pressure of the carrier nitrogen gas was set to 40 kPa, and the tempera-

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Table 1. Experimental LLE Data of the DEG (1) + *o*-Xylene (2) + Heptane (3) System over the Temperature Range of 288.15 K to 318.15 K

upper (heptane-rich) phase			lower (DEG-rich) phase		
x_1	x_2	x_3	x_1	x_2	x_3
288.15 K					
0.0004	0	0.9996	0.9950	0	0.0049
0.0012	0.1066	0.8922	0.9850	0.0100	0.0049
0.0010	0.1867	0.8122	0.9776	0.0175	0.0048
0.0015	0.3344	0.6641	0.9665	0.0290	0.0044
0.0020	0.4266	0.5713	0.9581	0.0373	0.0046
0.0023	0.4980	0.4997	0.9527	0.0431	0.0041
0.0028	0.5641	0.4331	0.9471	0.0490	0.0038
298.15 K					
0.0024	0.000	0.9976	0.9946	0	0.0054
0.0030	0.1018	0.8951	0.9852	0.0097	0.0051
0.0038	0.1953	0.8008	0.9777	0.0174	0.0048
0.0044	0.3529	0.6427	0.9658	0.0297	0.0044
0.0049	0.4048	0.5902	0.9566	0.0385	0.0048
0.0052	0.5380	0.4567	0.9474	0.0479	0.0047
0.0054	0.5282	0.4664	0.9472	0.0475	0.0053
0.0053	0.5747	0.4201	0.9441	0.0515	0.0043
308.15 K					
0.0048	0.0000	0.9952	0.9928	0.0000	0.0072
0.0053	0.0992	0.8955	0.9834	0.0098	0.0068
0.0058	0.1787	0.8155	0.9742	0.0183	0.0075
0.0061	0.3112	0.6827	0.9629	0.0302	0.0069
0.0081	0.3997	0.5922	0.9504	0.0422	0.0074
0.0088	0.4750	0.5162	0.9418	0.0509	0.0073
318.15 K					
0.0051	0.0000	0.9949	0.9926	0.0000	0.0074
0.0065	0.1024	0.8911	0.9827	0.0097	0.0076
0.0053	0.1827	0.8121	0.9752	0.0175	0.0073
0.0055	0.3162	0.6783	0.9637	0.0293	0.0071
0.0060	0.4083	0.5858	0.9530	0.0400	0.0070
0.0060	0.4606	0.5333	0.9451	0.0480	0.0070

tures of both the detector and injector were set to 250 °C. The oven temperature was programmed as follows: the initial temperature was set to 75 °C for 5 min followed by a constant heating rate of 15 °C/min until a final temperature of 240 °C was attained. The final temperature was kept for 9 min, and then the cycle was repeated. Mixtures of known compositions of the reagents were used to calibrate the gas chromatograph. The reproducibility of the composition measurements was found to be better than 0.1%.

Results and Discussion

The experimental liquid−liquid equilibrium data for the heptane + *o*-xylene + DEG system are shown in Table 1. It is clear that the extracting solvent (DEG) has high solubility in the lower phase (raffinate), called the DEG-rich phase, and the solubility of heptane is very low in the DEG-rich phase. The solubility of DEG in the upper phase (heptane-rich phase) is quite low. *o*-Xylene, however, is distributed between the two phases. Figure 1 demonstrates the experimental data of the first two isotherms in a typical ternary (triangular) diagram.

The experimental data of this work have been used to test the LLE predictive capability of some liquid-phase models. The models used in this study were UNIQUAC, NRTL, and three versions of UNIFAC (i.e., UNIFAC, with group interaction parameters extracted from the VLE data bank, UNIFAC-LL, with group interaction parameters extracted from the LLE data bank, and UNIFAC-DMD, with group interaction parameters extracted from the Dortmund Data Bank).[20] All models were used as programmed in the Aspen Plus simulator.[20] The availability of a rich data bank of the required interaction parameters for these models as employed by many simulators such as the Aspen Plus provides, on one hand, a good means of testing the cross consistency of the emerging experimental LLE data[21] (i.e., agreement between different data sets when treated by the same model that uses the same interaction parameters for the different data sets). On the other hand, experimental LLE data for systems containing species of very limited solubility, such as the systems under experimental investigation in this study, represent a tough test for predictive models. Tables 2 and 3 reveal the average absolute relative deviations (AARD) of the compositions (mole fractions) obtained from the UNIQUAC, NRTL, UNIFAC, UNIFAC-LL, and UNIFAC-DMD models (in the predictive mode). The AARD is

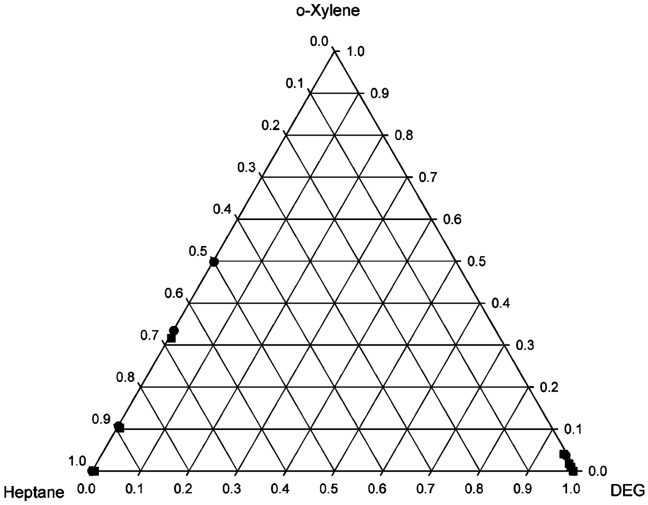

Figure 1. Experimental LLE data equilibrium compositions of the ternary system DEG + *o*-xylene + heptane at ●, 288.15 K and ■, 318.15 K.

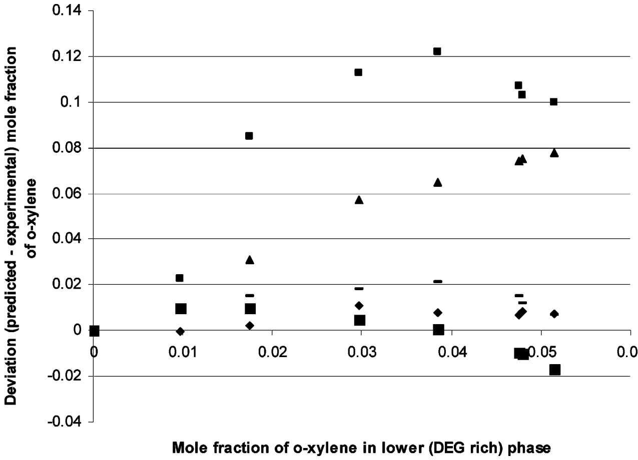

Figure 2. Comparison between deviations in mole fractions of *o*-xylene in the lower (DEG-rich) phase as predicted by different models for the system DEG (1) + *o*-xylene (2) + heptane (3) at 298.15 K: ▲, UNIFAC; ◆, UNIFAC-LL; ■, UNIFAC-DMD; black rectangle, NRTL; −, UNIQUAC.

$$\mathrm{AARD} = \frac{1}{N}\sum \left| \frac{x_i^{\mathrm{exptl}} - x_i^{\mathrm{pred}}}{x_i^{\mathrm{exptl}}} \right|$$

The general observations for the five models on the predictive accuracy for the very limited solubility components in both phases, namely, heptane in the DEG-rich phase and DEG in the heptane-rich phase, are very poor. This may be attributed to errors in activity coefficients, and

Table 2. Average Absolute Relative Deviation (AARD) in Mole Fraction as Obtained from UNIQUAC and NRTL Predictive Models for the System Heptane (1) + *o*-Xylene (2) + DEG (3)

	UNIQUAC						NRTL					
	heptane-rich phase			DEG-rich phase			heptane-rich phase			DEG-rich phase		
T/K	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$
288.15	0.50	0.86	2.31	1.62	0.45	0.04	0.50	0.84	2.33	2.88	0.38	0.01
298.15	0.54	0.79	1.49	5.68	0.52	0.04	0.55	0.76	1.42	2.63	0.41	0.01
308.15	0.28	0.67	0.52	2.67	0.92	0.04	0.28	0.59	0.44	1.13	0.70	0.02
318.18	0.29	0.68	0.48	2.69	0.93	0.04	0.28	0.60	0.41	1.13	0.67	0.02

Table 3. Average Absolute Relative Deviation (AARD) in Mole Fraction as Obtained from UNIFAC Predictive Models for the System Heptane (1) + *o*-Xylene (2) + DEG (3)

	UNIFAC						UNIFAC-LL						UNIFAC-DMD					
	heptane-rich phase			DEG-rich phase			heptane-rich phase			DEG-rich phase			heptane-rich phase			DEG-rich phase		
T/K	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$	AARD$_1$	AARD$_2$	AARD$_3$
288.15	0.20	0.29	0.30	4.69	1.04	0.05	0.31	0.59	7.80	1.84	0.35	0.02	0.47	0.94	0.74	0.84	1.75	0.05
298.15	0.35	0.54	0.54	3.91	1.58	0.07	0.26	0.42	1.69	1.96	0.17	0.02	0.63	1.26	0.74	0.87	2.94	0.09
308.15	0.29	0.71	0.74	3.17	1.72	0.07	0.16	0.40	1.37	1.73	0.06	0.01	0.55	1.75	0.82	0.91	3.75	0.10
318.15	0.21	0.51	0.67	3.45	1.46	0.06	0.19	0.45	1.64	1.90	0.16	0.02	0.41	1.25	0.80	1.00	2.38	0.06

these small errors lead to large errors in LLE data predictions.[22]

For the four LLE data sets of the system under study in Table 1, UNIFAC-LL outperforms the other four models as shown in Tables 2 and 3. As shown in Figure 2, the worst prediction is made by the UNIFAC-DMD model. These results could be attributed to the fact that the interaction parameters used by UNIFAC-LL are all extracted from LLE data, which makes their predictive capability far better than that of UNIQUAC, NRTL, and UNIFAC, whose parameters are mainly derived by regressing VLE data rather than LLE data. However, this interpretation is not valid in the case of UNIFAC-DMD, and a general trend cannot be seen based on the accuracy of the predictions of only one constituent. Overall, however, UNIFAC-LL is once again the preeminent model among the models used. It is not to be concluded, however, that UNIFAC-LL always exceeds the other models in its LLE predictive capacity. For example, it shows the poorest performance when the ternary LLE data[23] are analyzed using these different models.[24] It is therefore a questionable approach to base judgments solely on such models. There is never a better alternative to a careful, cautious, and considerate experimental approach. Generally, the errors are high because the prediction accuracy of the data is very sensitive to small errors in activity coefficients.[22] Deviations in the mole fraction of *o*-xylene in the DEG-rich phase obtained from the five models examined in this study at 298.15 K are shown in Figure 2. It is clearly shown that UNIFAC-LL surpasses the other models and this model predicts negative and positive deviations similar to those predicted by the NRTL model, but the deviations for the later mentioned model are large in comparison with UNIFAC-LL. In contrast to UNIFAC-LL and NRTL, which predict positive and negative deviations, UNIQUAC, UNIFAC, and UNIFAC-DMD predict only positive deviations. However, UNIFAC-DMD shows the worst deviation. Figure 3 displays the deviations in the mole fraction of *o*-xylene, as given by UNIFAC-LL, in the DEG-rich phase for four isotherms. It is shown clearly for isotherm 308.15 K that the deviations are lying within ±0.005, followed by isotherm 298.15 K in which the deviations have positive and negative values. On the contrary, for isotherms 288.15 and 318.15 K, all deviations are positive and large, especially above a 0.03 mole fraction of *o*-xylene. The performance of these models is dependent on the databases on which each model is based. UNIFAC-LL is expected to yield the best performance when it is used to predict LLE data, upon which this model is based.

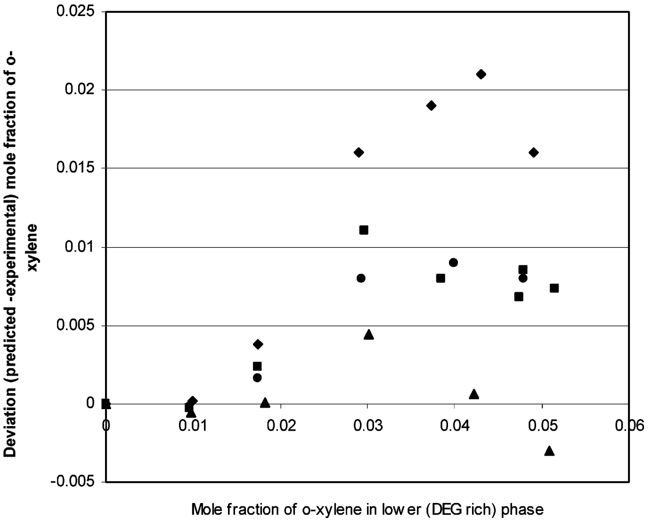

Figure 3. Comparison between deviations in mole fractions of *o*-xylene in the lower (DEG rich) phase as predicted by UNIFAC-LL for the system DEG(1) + *o*-xylene (2) + heptane (3): ◆, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

Conclusions

Liquid−liquid equilibrium data for the DEG + *o*-xylene + heptane system were produced in the temperature range of 288.15 K to 318.15 K. The equilibrium data of this work were analyzed using five models in the predictive mode as programmed by the Aspen Plus simulator. The models used in this work were UNIQUAC, NRTL, UNIFAC, UNIFAC-LL, and UNIFAC-DMD. UNIFAC-LL showed the best predictive performance and surpassed the other models, and UNIFAC-DMD had poor prediction accuracy for the target species *o*-xylene.

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