Liquid−Liquid Equilibria of Ternary and Six-Component Systems Including Cyclohexane, Benzene, Toluene, Ethylbenzene, Cumene, and Sulfolane at 303.15 K

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Liquid−liquid equilibrium (LLE) data for four ternary systems comprising cyclohexane + (benzene, toluene, ethylbenzene, or cumene) + sulfolane have been measured at 303.15 K and at atmospheric pressure. The LLE data for a six-component system including (cyclohexane + benzene + toluene + ethylbenzene + cumene + sulfolane) has also been measured at the above conditions. The reliability of the experimental data was tested using the Othmer−Tobias correlation. The LLE data were then analyzed using a UNIFAC model with group-interaction parameters extracted from the UNIFAC-LLE data bank and a NRTL version with temperature-dependent binary parameters determined from the experimental LLE data (NRTL/2), both as programmed by the Aspen Plus simulator. Based on the analysis of these data, both models represented the experimental data with sufficient accuracy as revealed from the very small values of the root mean square error and the average absolute deviation in composition.

Introduction

Extraction is the most widely used process for the separation of aromatics from different paraffins. Solvents used for the extraction should have high selectivity for aromatics, high capacity, high density, low viscosity, and partial miscibility with the hydrocarbon mixtures at reasonably low temperatures.[1] They also must have good thermal stability, low reactivity, and minimum corrosion characteristics in addition to being environmentally friendly. Sulfolane (tetraethylene sulfone), among the organic solvents, has been widely used as a solvent in the recovery of high-purity aromatics such as benzene, toluene, ethylbenzene, isopropyl benzene (cumene), and xylenes from refinery process streams and products.

Accurate phase equilibrium data are important parameters for the design and evaluation of industrial unit operations for the extraction processes. Although the technical literature is very rich on the subject of solvent extraction of some aromatics such as benzene, toluene, and xylene ternary systems, liquid−liquid equilibrium data for cyclohexane + (benzene, toluene, ethylbenzene, or cumene) + sulfolane systems are very limited in the literature.[3,4,6,18] Table 1 lists the available literature (including this work) on LLE data of benzene, toluene, ethylbenzene, and cumene with sulfolane. Ternary phase equilibrium data are essential for the proper understanding of the solvent extraction processes, selection of solvents, and design of extractors. Few examples on quaternary systems containing nonaromatics + benzene + toluene + sulfolane are also available[7,9] and are listed in Table 1.

The objective of the present work is to measure the LLE data for the ternary systems cyclohexane + (benzene, toluene,

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ethylbenzene, or cumene) + sulfolane at 303.15 K at atmospheric pressure. The liquid−liquid equilibrium data for the six-component system (cyclohexane + benzene + toluene + ethylbenzene + cumene + sulfolane) were also measured at the above conditions. Additionally, a predictive activity coefficient model (UNIF-LL, as it is called in the Aspen Plus) will be used to demonstrate its predictive capacity for the resulting data. This UNIF-LL model uses group-interaction parameters extracted from the UNIFAC-LLE data bank.[16] Also, a Non-Random Two Liquid model (called NRTL/2) will be used to correlate the experimental LLE data. The NRTL/2 model is usually suitable for highly nonideal systems and has temperature-dependent binary parameters determined from the user measured LLE data.[16] The UNIF-LL model gave accurate predictions in comparison with other models used in previous studies.[14,17] The NRTL/2 model correlated very accurately the LLE data of various ternary systems including sulfolane.[6,9,18] In addition, Chen et al.[9] used only the NRTL ternary system parameters to predict the LLE of three quaternary and two quinary systems. The predicted LLE data were found to compare well with the experimental LLE data with an average RMSD of 0.0059 and 0.0092, respectively.[9]

Experimental Section

The chemicals used in this work were supplied as follows: sulfolane by Merck with a stated mass fraction of 0.99 (<0.002 H_2O); benzene, toluene, ethylbenzene, and cumene by BDH with stated mass fractions of >0.99 (<0.001 H_2O), >0.995 (<0.0003 H_2O), >0.99, and >0.981 (no H_2O), respectively; and cyclohexane by Riedel-DeHaen with a stated mass fraction of >0.995 (<0.0001 H_2O). All materials were used as received without any further purification.

Table 1. Liquid−Liquid Equilibrium Studies of Systems Containing Sulfolane (3) and Benzene, Toluene, Ethylbenzene, and/or Cumene

nonaromatics	aromatics	T/K	ref
pentane	benzene	290.15, 298.15, 323.15	2
hexane	benzene	282.15, 323.15, 348.15, 373.15	6, 7, 8
cyclohexane	benzene	298.15, 303.15	6, this work
heptane	benzene	298.15, 303.15	5, 16
octane	benzene	298.15, 308.15, 313.15, 318.15, 323.15, 343.15, 348.15, 372.15, 373.15, 402.15	6, 7, 11−13
decane	benzene	303.15	5
dodecane	benzene	303.15	5
hexane, octane	benzene	298.15	7
pentane	toluene	290.15, 298.15, 323.15	2
hexane	toluene	290.15, 298.15, 308.15, 313.15, 323.15	3, 4, 7, 10
cyclohexane	toluene	290.15, 298.15, 303.15, 323.15	3, 4, 6, this work
2-methylpentane	toluene	298.15	4
1-hexene	toluene	298.15	4
heptane	toluene	298.15	6, 15
octane	toluene	298.15, 308.15, 313.15, 318.15, 323.15, 343.15, 348.15, 372.15, 373.15, 402.15	7, 11−13
hexane, heptane	toluene	298.15	9
cyclohexane	ethylbenzene	303.15, 313.15, 323.15	18
cyclohexane	cumene	303.15	this work
heptane	benzene, toluene	298.15	9
hexane, octane	benzene, toluene	298.15	7
cyclohexane	benzene, toluene, ethylbenzene, cumene	303.15	this work

The equilibrium experimental data were determined using a tightly closed, jacketed equilibrium cell with 100 mL volume. The temperature was measured with a mercury-in-glass thermometer with uncertainty of ± 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) 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 sulfolane, aromatic(s), and cyclohexane were introduced into the cell, stirred for 2 h, and then left for 8 h to equilibrate and settle down into a lower layer (sulfolane-rich phase) and an upper layer (cyclohexane-rich phase) under 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 long × 0.32 mm i.d. WCOT (wall-coated-open-tube) fused silica capillary column coated with a 1.2 μm stationary film (CP-Sil 5CB). The inlet pressure of the carrier nitrogen gas was set to 30 kPa, and the temperatures of the detector and the injector were set to 573.15 K and 548.15 K, respectively. The oven temperature was programmed as follows: the initial temperature was set to 373.15 K for 2 min followed by a constant heating rate of 20 K·min^{-1} until a final temperature of 523.15 K was attained. The final temperature was kept for 8 min, and then the cycle was repeated. Mixtures of known compositions of reagents were used to calibrate the gas chromatograph. Mass fraction measurements were reproducible to within ± 0.1 %. The greatest error in the material balance in these experiments was found to be less than 1 %.

Results and Discussion

A summary of citations of LLE studies of ternary systems involving the aromatics under study, namely, benzene, toluene, ethylbenzene, and cumene (including this work), are given in Table 1. The cited literature data spans a temperature range of (290.15 to 402.15) K in a 57 isothermal data sets with about 400 experimental data points.

The experimental liquid−liquid equilibrium data for the ternary systems cyclohexane + (benzene, toluene, ethylbenzene,

Table 2. Experimental LLE Data for the Four Ternary Systems in This Work at 303.15 K

| mole fractions in upper layer (cyclohexane-rich phase)			mole fractions in lower layer (sulfolane-rich phase)		
X_1	X_2	X_3	X_1	X_2	X_3
Cyclohexane (1) + Benzene (2) + Sulfolane (3) System					
0.9969	0.0000	0.0031	0.0313	0.0000	0.9687
0.9312	0.0639	0.0049	0.0315	0.0407	0.9246
0.8701	0.1227	0.0072	0.0397	0.0773	0.8770
0.7553	0.2295	0.0152	0.0490	0.1456	0.7941
0.7215	0.2627	0.0159	0.0539	0.1809	0.7512
0.6747	0.3042	0.0211	0.0556	0.2009	0.7279
0.5911	0.3754	0.0335	0.0618	0.2501	0.6687
Cyclohexane (1) + Toluene (2) + Sulfolane (3) System					
0.9961	0.0000	0.0039	0.0436	0.0000	0.9564
0.9295	0.0652	0.0053	0.0429	0.0254	0.9317
0.8657	0.1264	0.0079	0.0493	0.0524	0.8983
0.7636	0.2214	0.0150	0.0535	0.0948	0.8518
0.7121	0.2715	0.0165	0.0537	0.1198	0.8265
0.6698	0.3073	0.0229	0.0586	0.1382	0.8032
0.5995	0.3663	0.0343	0.0632	0.1724	0.7644
Cyclohexane (1) + Ethylbenzene (2) + Sulfolane (3) System					
0.9984	0.0000	0.0016	0.0410	0.0000	0.9590
0.9349	0.0610	0.0041	0.0411	0.0189	0.9400
0.8717	0.1221	0.0062	0.0443	0.0372	0.9185
0.7732	0.2165	0.0104	0.0426	0.0673	0.8901
0.6782	0.3044	0.0174	0.0462	0.0960	0.8578
0.6082	0.3655	0.0263	0.0454	0.1151	0.8395
0.5385	0.4290	0.0325	0.0318	0.1012	0.8670
Cyclohexane (1) + Cumene (2) + Sulfolane (3) System					
0.9971	0.0000	0.0029	0.0397	0.0000	0.9603
0.9328	0.0630	0.0042	0.0366	0.0144	0.9490
0.8645	0.1275	0.0080	0.0390	0.0281	0.9329
0.7650	0.2231	0.0119	0.0408	0.0495	0.9097
0.7184	0.2699	0.0117	0.0392	0.0594	0.9013
0.6739	0.3099	0.0162	0.0408	0.0701	0.8891

or cumene) + sulfolane measured at 303.15 K and at atmospheric pressure are shown in Table 2 and displayed on the triangular diagrams shown in Figures 1 to 4 for benzene, toluene, ethylbenzene, and cumene, respectively. It is clear from the data shown in Figures 1 to 4 that the aromatics under study have a much higher affinity toward cyclohexane in the upper layer than sulfolane in the lower layer, while the lower layer is almost free of cyclohexane. The experimental LLE data for the six-component system cyclohexane + benzene + toluene + ethylbenzene + cumene + sulfolane at 303.15 K and at atmospheric pressure are displayed in Table 3.
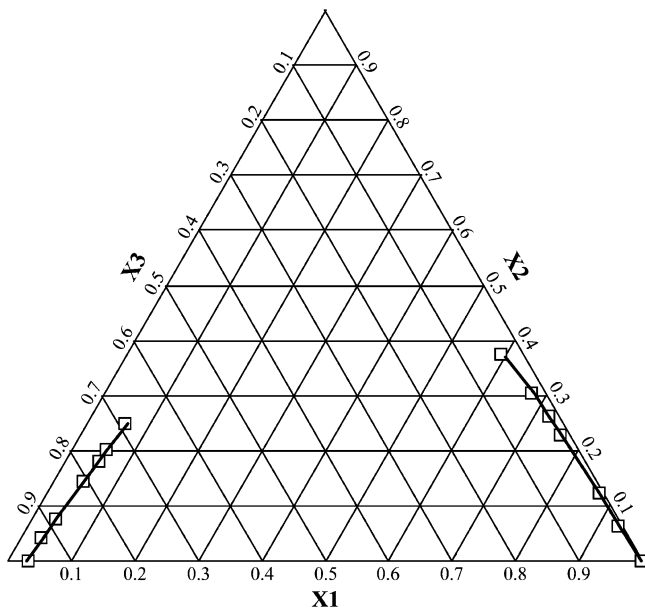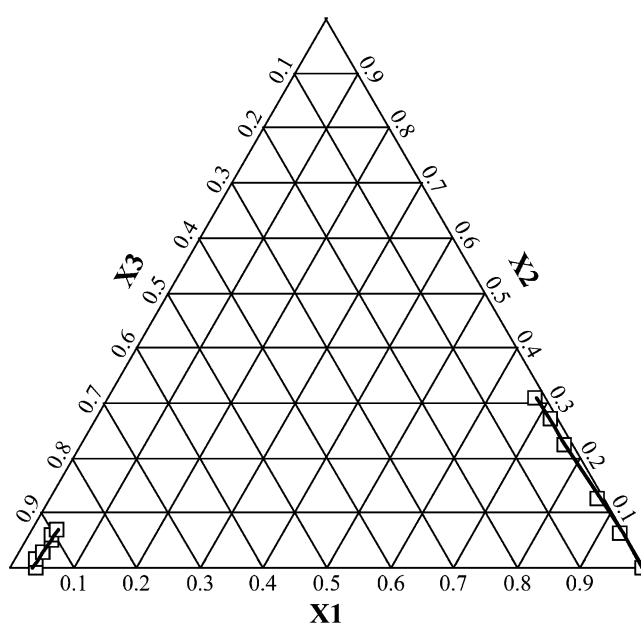
Figure 1. Experimental LLE data equilibrium molar compositions of the ternary system cyclohexane (1) + benzene (2) + sulfolane (3) at 303.15 K: □, experimental; —, UNIF-LL prediction.
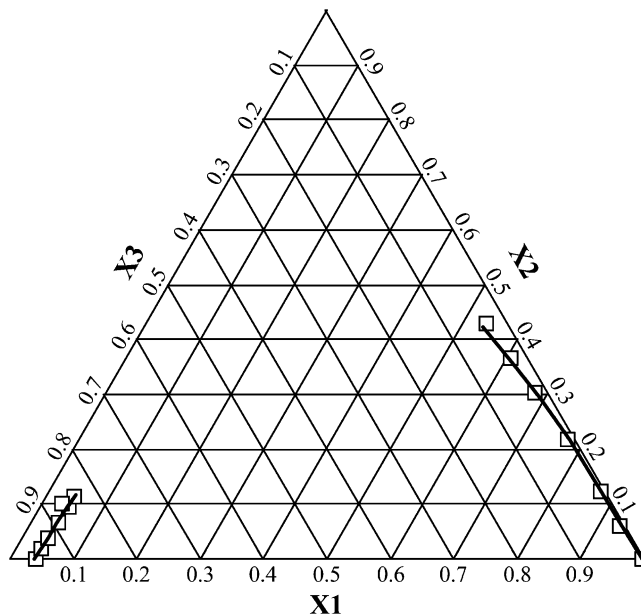
Figure 3. Experimental LLE data equilibrium molar compositions of the ternary system cyclohexane (1) + ethylbenzene (2) + sulfolane (3) at 303.15 K: □, experimental; —, UNIF-LL prediction.
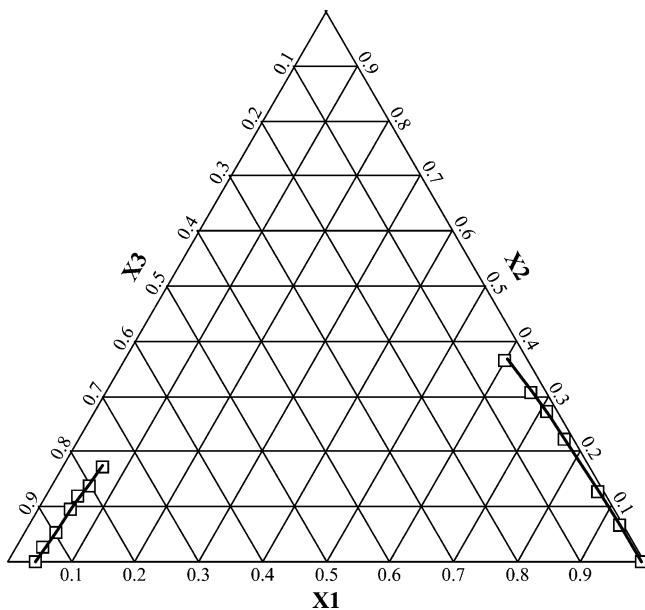
Figure 2. Experimental LLE data equilibrium molar compositions of the ternary system cyclohexane (1) + toluene (2) + sulfolane (3) at 303.15 K: □, experimental; —, UNIF-LL prediction.

Figure 4. Experimental LLE data equilibrium molar compositions of the ternary system cyclohexane (1) + cumene (2) + sulfolane (3) at 303.15 K: □, experimental; —, UNIF-LL prediction.

The reliability of the experimental data can be ascertained by applying the Othmer–Tobias correlation,[19] depicted in eq 1, for each of the above mixtures at the test temperature:

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

or

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

where w_{3L} = mass fraction of sulfolane (3) in the lower layer (sulfolane-rich phase), w_{1U} = mass fraction of cyclohexane (1) in the upper layer (cyclohexane-rich phase), and a and b are the fitting parameters of Othmer–Tobias correlation. The first

data point, where no aromatic exists in the mixture (i.e., $w_2 = 0$) is usually not included in this correlation.[18] The values of a, b, and correlation factor R^2 are given in Table 4 at 303.15 K for the systems under study. The linearity of the Othmer–Tobias plot and the value of the R^2 (close to 1.0) reveal the degree of the consistency of the experimental data of this work. The measured LLE data of this work are in excellent agreement with the available LLE data[3,4,6] for benzene and toluene (see Table 1). The standard deviations (σ) of the studied systems are listed in Table 4 for reference. The σ values range from 0.034 to 0.050 for the four ternary systems and reach 0.135 for the six-component system. The relatively high σ for the six-component system could be attributed to the deficiency of the Othmer–Tobias model in describing LLE systems with more than four species.[20]

Table 3. Experimental LLE Data of Cyclohexane (1) + Benzene (2) + Toluene (3) + Ethylbenzene (4) + Cumene (5) + Sulfolane (6) System at 303.15 K

X_1	X_2	X_3	X_4	X_5	X_6
		Mole Fractions in Upper Layer (Cyclohexane-Rich Phase)			
0.9967	0.0000	0.0000	0.0000	0.0000	0.0033
0.9320	0.0147	0.0051	0.0157	0.0165	0.0050
0.8693	0.0295	0.0102	0.0310	0.0316	0.0066
0.7626	0.0563	0.0199	0.0554	0.0541	0.0133
0.7161	0.0669	0.0241	0.0675	0.0656	0.0145
0.6781	0.0780	0.0290	0.0742	0.0715	0.0199
0.5046	0.1151	0.0484	0.1122	0.1072	0.0435
		Mole Fractions in Lower Layer (Sulfolane-Rich Phase)			
0.0340	0.0000	0.0000	0.0000	0.0000	0.9660
0.0184	0.0104	0.0071	0.0046	0.0023	0.9571
0.0091	0.0194	0.0140	0.0095	0.0051	0.9429
0.0391	0.0388	0.0263	0.0177	0.0140	0.8642
0.0418	0.0462	0.0314	0.0217	0.0166	0.8423
0.0398	0.0540	0.0374	0.0256	0.0194	0.8238
0.0496	0.0814	0.0590	0.0438	0.0328	0.7333

Table 4. Constants of the Othmer−Tobias Correlation and the Correlation Factor, R^2, for the Systems Studied in This Work at 303.15 K (Based on Mass Fractions)

system	N	a	b	R^2	σ
cyclohexane + benzene + sulfolane	6	2.6031	1.2337	0.9971	0.044
cyclohexane + toluene + sulfolane	6	6.9957	1.4928	0.9983	0.034
cyclohexane + ethylbenzene + sulfolane	6	20.0348	1.7791	0.9956	0.050
cyclohexane + cumene + sulfolane	5	54.0058	1.9699	0.9967	0.045
cyclohexane + benzene + toluene + ethylbenzene + cumene + sulfolane	6	4.4163	1.1126	0.9780	0.135

Table 5. UNIFAC LLE Group-Interaction Parameters, a_{ij}, in Kelvin

$i−j$	CH_3	CH_2	ACH	ACCH	$ACCH_2$	$ACCH_3$	sulfolane
CH_3	0.0	0.0	−114.80	−115.70	−115.70	−115.70	561.40
CH_2	0.0	0.0	−114.80	−115.70	−115.70	−115.70	561.40
ACH	156.50	156.50	0.0	167.00	167.00	167.00	21.97
ACCH	104.30	104.30	−146.80	0.0	0.0	0.0	238.00
$ACCH_2$	104.30	104.30	−146.80	0.0	0.0	0.0	238.00
$ACCH_3$	104.30	104.30	−146.80	0.0	0.0	0.0	238.00
sulfolane	67.84	67.84	59.16	26.59	26.59	26.59	0.0

Table 6. UNIFAC Group Volume, R_k, and Surface-Area, Q_k, Parameters

group	R_k	Q_k	group	R_k	Q_k
CH_3	0.9011	0.848	$ACCH_2$	1.0396	0.660
CH_2	0.6744	0.540	$ACCH_3$	1.2663	0.968
ACH	0.5313	0.400	sulfolane	4.0358	3.200
ACCH	0.8121	0.348			

The experimental data of this work were also used to examine the LLE predictive capability of the UNIF-LL model (with group-interaction parameters extracted from the LLE data bank stored in the Aspen Plus simulator). These parameters are listed in Tables 5 and 6 for reference. In addition, the NRTL/2 model (with binary parameters, A_{ij}, determined from the fitting of the current measured LLE data) was used to correlate these data. Both models were used as programmed in the Aspen Plus simulator.[16] The regression method used in Aspen Plus simulator is the generalized least-squares method based on the maximum likelihood principles. The Britt−Luecke algorithm[21] is used in the Aspen Plus to obtain the NRTL/2 model parameters.[16] Table 7 shows the NRTL/2 binary parameters, $A_{ij} = \{(g_{ij} - g_{jj})/R$ for each pair of components in each ternary mixture with $A_{ii} = A_{jj} = 0$ and $A_{ij} \neq A_{ji}$. R is the universal gas constant, and g_{ij} is the energy parameter in the NRTL equation (in K). The Aspen Plus simulator default values of the non-randomness factor, α_{ij}, were used for all four ternary systems studied in this work; $\alpha_{12} = \alpha_{23} = 0.3$, $\alpha_{13} = 0.2$, with $\alpha_{ij} = \alpha_{ji}$.

On the other hand, the experimental LLE data for systems containing species of very limited solubility, like the systems studied in this work, represent a tough test for the predictive

Table 7. NRTL/2 Binary Parameter, $\{(g_{ij} - g_{jj})/R$, in Kelvin$\}$ for the Four Ternary Systems Studied in This Work at 303.15 K and at Atmospheric Pressure

component	$j = 1$	$j = 2$	$j = 3$
	Cyclohexane (1) + Benzene (2) + Sulfolane (3)		
$i = 1$	0	195.4139	1925.9201
$i = 2$	−97.0454	0	414.5144
$i = 3$	1154.5952	−15.3628	0
	Cyclohexane (1) + Toluene (2) + Sulfolane (3)		
$i = 1$	0	373.3710	1919.3685
$i = 2$	−143.2766	0	1.316259
$i = 3$	1061.5719	−0.52951	0
	Cyclohexane (1) + Ethylbenzene (2) + Sulfolane (3)		
$i = 1$	0	−75.1534	2126.4566
$i = 2$	174.3284	0	259.0932
$i = 3$	1067.5610	318.0283	0
	Cyclohexane (1) + Cumene (2) + Sulfolane (3)		
$i = 1$	0	2175.0695	1974.8179
$i = 2$	−761.3521	0	609.4586
$i = 3$	1101.7958	175.7614	0

Table 8. RMSE and AAD in Liquid Mole Fractions as Obtained from UNIF-LL and NRTL/2 Models for the Four Ternary Systems Cyclohexane (1) + Aromatic (2) + Sulfolane (3) at 303.15 K

	cyclohexane		benzene		sulfolane	
model	RMSE	AAD	RMSE	AAD	RMSE	AAD
	Upper Layer (Cyclohexane-Rich Phase)					
UNIF-LL	0.017	0.011	0.019	0.015	0.008	0.005
NRTL/2	0.004	0.003	0.004	0.003	0.001	0.001
	Lower Layer (Sulfolane-Rich Phase)					
UNIF-LL	0.015	0.011	0.055	0.036	0.066	0.042
NRTL/2	0.002	0.001	0.005	0.003	0.006	0.004

	cyclohexane		toluene		sulfolane	
model	RMSE	AAD	RMSE	AAD	RMSE	AAD
	Upper Layer (Cyclohexane-Rich Phase)					
UNIF-LL	0.015	0.013	0.018	0.016	0.002	0.002
NRTL/2	0.004	0.003	0.005	0.004	0.002	0.001
	Lower Layer (Sulfolane-Rich Phase)					
UNIF-LL	0.008	0.008	0.008	0.007	0.003	0.003
NRTL/2	0.001	0.001	0.003	0.002	0.002	0.002

	cyclohexane		ethylbenzene		sulfolane	
model	RMSE	AAD	RMSE	AAD	RMSE	AAD
	Upper Layer (Cyclohexane-Rich Phase)					
UNIF-LL	0.043	0.035	0.040	0.038	0.006	0.004
NRTL/2	0.007	0.006	0.009	0.008	0.004	0.002
	Lower Layer (Sulfolane-Rich Phase)					
UNIF-LL	0.008	0.007	0.015	0.013	0.021	0.019
NRTL/2	0.002	0.002	0.002	0.002	0.002	0.002

	cyclohexane		cumene		sulfolane	
model	RMSE	AAD	RMSE	AAD	RMSE	AAD
	Upper Layer (Cyclohexane-Rich Phase)					
UNIF-LL	0.073	0.066	0.074	0.071	0.005	0.004
NRTL/2	0.006	0.004	0.008	0.006	0.001	0.001
	Lower Layer (Sulfolane-Rich Phase)					
UNIF-LL	0.010	0.008	0.024	0.019	0.025	0.020
NRTL/2	0.002	0.001	0.001	0.001	0.002	0.001

models. Table 8 shows the root mean square error (RMSE) and the average absolute deviation (AAD) in mole fraction obtained using UNIF-LL (predictive) model and NRTL/2 (correlative) model at 303.15 K. The RMSE and AAD are defined as follows:

$$\text{RMSE} = \sqrt{\frac{1}{N}\sum_i (X_i^{\text{exp}} - X_i^{\text{pred}})^2} \qquad (3)$$

$$\text{AAD} = \frac{1}{N}\sum_i |X_i^{\text{exp}} - X_i^{\text{pred}}| \qquad (4)$$

Table 9. RMSE and AAD in Liquid Mole Fractions as Obtained from UNIF-LL Model for the Six-Component System Cyclohexane (1) + Benzene (2) + Toluene (3) + Ethylbenzene (4) + Cumene (5) + Sulfolane (6) at 303.15 K[a]

	cyclohexane		benzene		toluene		ethylbenzene		cumene		sulfolane	
phase	RMSE	AAD	RMSE	AAD	RMSE	AAD	RMSE	AAD	RMSE	AAD	RMSE	AAD
ULL	0.258	0.210	0.085	0.072	0.021	0.019	0.076	0.065	0.069	0.059	0.079	0.049
LLL	0.019	0.016	0.075	0.057	0.012	0.010	0.029	0.022	0.015	0.011	0.117	0.085

[a] ULL, upper liquid layer; LLL, lower liquid layer.

Table 10. RMSE and AAD in Temperature as Obtained from UNIF-LL and NRTL/2 Models for the Four Ternary Systems Cyclohexane (1) + Aromatic (2) + Sulfolane (3) at 303.15 K

	benzene (2)		toluene (2)		ethylbenzene (2)		cumene (2)		six-component mixture	
model	RMSE	AAD	RMSE	AAD	RMSE	AAD	RMSE	AAD	RMSE	AAD
UNIF-LL	0.73	0.48	1.02	0.65	0.32	0.29	0.80	0.63	4.72	4.02
NRTL/2	0.07	0.05	0.11	0.09	0.25	0.19	0.15	0.13		

where N is the number of data points and x_i is the mole fraction of component i. For the four ternary LLE systems studied in this work, both UNIF-LL and NRTL/2 models represent the experimental data quite well, and the predictions are accurate enough as demonstrated by the very small values of the RMSE and the AAD in mole fractions presented in Table 8. Table 9 shows the values of the RMSE and the AAD in mole fractions in each phase of the six-component system as obtained by the UNIF-LL model; these values are generally higher than their counterpart is in the ternary systems. It is clear from Tables 8 and 9 that the NRTL/2 correlative model as compared to the predictive UNIF-LL model better represents the experimental LLE data of the studied four ternary systems. Table 10 shows the values of the RMSE and the AAD in temperature using the UNIF-LL and NRTL/2 models for these ternary systems. It should be mentioned that the NRTL/2 correlative model was applied in this work to the six-component system; this is a tedious problem that requires up to 30-nonzero parameters (out of 36) to fit such a system. In addition, although the RMSE and AAD in mole fraction for the six-component system (using UNIF-LL, Table 10) seem acceptable, the corresponding RMSE and AAD in temperature are relatively high. This might be attributed to the limited capability of the UNIFAC binary parameters in predicting the temperature for a six-component system, especially if we recall that the UNIFAC model treats the whole sulfolane compound as one group represented by a single set of parameters.

It is obviously impossible to measure all possible equilibrium compositions because there are infinitely many of them. Therefore, only a finite set of these compositions can be measured, and thermodynamic models are used to provide estimates for intermediate compositions. Among the thermodynamic models most commonly used for this kind of work are the UNIFAC and the NRTL models. In the presence of these models parameters, as it is the case of this work, one can calculate a continuous set of equilibrium compositions, which form a continuous curve; the *bimodal curve*. This curve only *looks* like a single continuous curve, but it consists of two branches, each of which represents a phase and they meet in what is called the *plait point*. The plait point represents a condition where the three-component mixture separates into two phases that have identical compositions. Usually, this point is located near the top of the two-phase envelope, at the inflection point. For those interested, the UNIFAC and NRTL parameters listed in Tables 5, 6, and 7 can be used to predict the LLE at high aromatics' concentrations and, eventually, the plait point.

Conclusions

The LLE data for the four ternary systems comprising cyclohexane + (benzene, toluene, ethylbenzene, or cumene) + sulfolane were measured at 303.15 K and at atmospheric pressure. The LLE data for the six-component system (cyclohexane + benzene + toluene + ethylbenzene + cumene + sulfolane) were also measured at the above conditions. The linearity of the Othmer−Tobias plots and the values of the correlation factor (R^2 very close to 1.0) as well as the low standard deviations (σ less than 0.05) proved the consistency of the experimental measurements for the four ternary systems studied. The standard deviations for the six-component system is relatively high ($\sigma = 0.135$). The LLE data of this work were then analyzed using the UNIFAC-LLE (or UNIF-LL) predictive model and the NRTL/2 correlative model as programmed by the Aspen Plus simulator. Based on the analysis of these data, both models represented the experimental data with sufficient accuracy as revealed from the very small RMSE and AAD values in mole fractions for both the four ternary systems and the six-component system studied in this work.

Literature Cited

(1) Rawat, B. S.; Naithani, J. Basic consideration in the selection of solvents for aromatic extraction. *Hydrocarbon Technol.* **1993**, 51−60.

(2) Cassell, G. W.; Dural, N.; Hines, A. L. Liquid−liquid equilibrium of sulfolane−benzene−pentane and sulfolane−toluene−pentane. *Ind. Eng. Chem. Res.* **1989**, *28*, 1369−1374.

(3) Cassell, G. W.; Hassan, M. M.; Hines, A. L. Phase equilibria of the cyclohexane−toluene−sulfolane and hexane−toluene−sulfolane ternary systems. *Chem. Eng. Commun.* **1989**, *85*, 233−243.

(4) Modragon-Garduno, M.; Romero-Martinez, A.; Trejo, A. Liquid−liquid equilibria systems. I. C₆-isomers + sulfolane + toluene at 298.15 K. *Fluid Phase Equilib.* **1991**, *64*, 291−303.

(5) Letcher, T. M.; Redhi, G. G.; Radloff, S. E.; Liquid−liquid equilibria of the ternary mixtures with sulfolane at 303.15 K. *J. Chem. Eng. Data* **1996**, *41*, 634−638.

(6) Chen, J.; Li, Z.; Duan, L. Liquid−liquid equilibria of the ternary and quaternary systems including cyclohexane, 1-heptene, benzene, toluene, and sulfolane at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 689−692.

(7) Chen, J.; Duan, L.-P.; Mi, J.-G.; Fei, W.-Y.; Li, Z.-C. Liquid−liquid equilibria of multicomponent systems including *n*-hexane, *n*-octane, benzene, toluene, xylene and sulfolane at 298.15 K and atmospheric pressure. *Fluid Phase Equilib.* **2000**, *173*, 109−119.

(8) De Fre, R. M.; Verhoeye, L. A. Phase equilibria in systems composed of an aliphatic and an aromatic hydrocarbon and sulpholane. *J. Appl. Chem. Biotechnol.* **1976**, *26*, 469−487.

(9) Chen, J.; Mi, J.; Fei, W.; Li, Z. Liquid−liquid equilibria of quaternary and quinary systems including sulfolane at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 169−171.

(10) Rappel, R.; de Gois, L. M. N.; Mattedi, S. Liquid−liquid equilibria data for systems containing aromatic + non-aromatic + sulfolane at 308.15 and 323.15 K. *Fluid Phase Equilib.* **2002**, *202*, 263−276.

(11) Lee, S.; Kim, H. Liquid−liquid equilibria for the ternary systems sulfolane + octane + benzene, sulfolane + octane + toluene, and sulfolane + octane + *p*-xylene. *J. Chem Eng. Data* **1995**, *40*, 499−503.

(12) Lee, S.; Kim, H. Liquid−liquid equilibria for the ternary systems sulfolane + octane + benzene, sulfolane + octane + toluene, and sulfolane + octane + *p*-xylene at elevated temperature. *J. Chem Eng. Data* **1998**, *43*, 358−361.

(13) Lin, W.-C.; Kao, N.-H. Liquid−liquid equilibria of octane + (benzene or toluene, or *m*-xylene) + sulfolane at 323.15, 348.15, and 373.15 K. *J. Chem. Eng. Data* **2002**, *47*, 1007−1011.

(14) Ashour, I.; Abdulkarim, M. M. Liquid−liquid equilibrium for the system heptane + *o*-xylene + diethylene glycol over the temperature range of 288.15 K to 318.15 K. *J. Chem. Eng. Data* **2005**, *50*, 924−927.

(15) Rawat, B. S.; Gulati, I. B.; Mallik, K. L. Study of some sulphur-group solvents for aromatics extraction by gas chromatography. *J. Appl. Chem. Biotechnol.* **1976**, *26*, 247−252.

(16) *ASPEN-PLUS Sequential Process Simulator*, Release 12.1; Aspen Technology Inc.: Cambridge, MA, 2003.

(17) Ashour, I. Liquid−liquid equilibrium of MTBE + ethanol + water and MTBE + 1-hexanol + water over the temperature range of 288.15 K to 318.15 K. *J. Chem. Eng. Data* **2005**, *50*, 113−118.

(18) 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.

(19) Othmer, D. F.; Tobias, P. E. Liquid−liquid extraction data of toluene and acetaldehyde systems. *Ind. Eng. Chem.* **1942**, *21*, 690−697.

(20) Darwish, N. A.; Abdelkarim, M. M.; Hilal, N.; Ashour, I. Analysis and evaluation of the liquid−liquid equilibrium data of the extraction of aromatics from hydrocarbons by tetraethylene glycol. *J. Chem. Eng. Data* **2003**, *48*, 1614−1619.

(21) Britt, H. I.; Luecke, R. H. The estimation of parameters in nonlinear implicit models. *Techometrics* **1973**, *15*, 223−228.