Liquid−Liquid Equilibria for Binary System of Ethanol + Hexadecane at Elevated Temperature and the Ternary Systems of Ethanol + Heterocyclic Nitrogen Compounds + Hexadecane at 298.15 K

In-Chan Hwang,[†] Kyung-Lok Kim,[†] So-Jin Park,*,[†] and Kyu-Jin Han[‡]

Department of Chemical Engineering, College of Engineering, Chungnam National University, Daejeon 305-764, Korea, and Department of Ammunition, Daeduk College, Daejeon 305-715, Korea

Liquid−liquid equilibrium data from 294.40 K to 323.15 K are reported for the binary system of ethanol (1) + hexadecane (2). Ternary systems at 298.15 K with six heterocyclic nitrogen-containing compounds were experimentally determined by using tie-line measuring method. The experimental data were correlated by the non random two liquid and universal quasi-chemical equations, and the correlated values were compared with the measured values. Additionally, the extracting capabilities of ethanol for heterocyclic nitrogen-containing compounds were investigated with respect to distribution coefficient and selectivity.

Introduction

Air pollution by nitrogen compounds (NOx) and particulate matter (PM) of diesel exhaust is now a serious common problem in the whole world. In the very early 2000s, most governmental regulatory limits for highway vehicle diesel was within the mass fraction range of (300 to 500)·10^{-6} by weight of total sulfur. However, recently the U.S. Environmental Protection Agency passed rules requiring the use of ultralow sulfur diesel (ULSD) for diesel vehicles, which allows a mass fraction of only 15·10^{-6} of sulfur. This ULSD oil will be expected to reduce dramatically NOx and PM; however, many gasoline producers are faced with technical and economic challenges to meet these new specifications.

The hydrodesulfurization (HDS) process so far is most commonly used in the oil industry to reduce sulfur content in diesel fuel by converting sulfur compounds into hydrogen sulfide.[1−4] The refinery HDS feedstocks (naphtha, kerosene, diesel oil, and heavier oils) contain a wide range of organic sulfur compounds, including thiols, thiophenes, organic sulfides, and disulfides, etc. These organic sulfur compounds are products of the degradation of sulfur-containing biological components, present during the natural formation of the fossil fuel, petroleum crude oil. Recently, there are some reports that conventional HDS process will be successfully applied for producing ultralow sulfur diesel if heterocyclic nitrogen-containing compounds are removed effectively from the middle distillate feedstock. Heterocyclic nitrogen-containing compounds, which act as an inhibitor for the desulfurization process, in the middle distillates are classified as basic and nonbasic compounds. Basic compounds include six-membered heterocyclics such as quinoline, pyridine, acridine, and aniline. Nonbasic compounds include five-membered heterocyclics such as pyrrole and indole. Adsorption and solvent extraction could be an effective process to remove these nitrogen-containing compounds from the middle distillates. However, solvent extraction may have some advantages in the

* Corresponding author. E-mail address: sjpark@cnu.ac.kr. Tel.: +82-42-821-5684. Fax: +82-42-823-6414.
[†] Chungnam National University.
[‡] Daeduk College.

Table 1. The Purity of Chemicals Used in These Experiments

chemicals	ρ/g·cm^3 at 298.15 K		GC analysis	UNIQUAC	
	this work	reference^a		r-value^a	q-value^a
ethanol	0.78532	0.78500	> 99.9	2.1055	1.9720
hexadecane	0.77014	0.77330	> 99.8	11.2438	9.2560
quinoline	1.08930	1.09290^b	> 99.5	4.7923	3.1530
pyridine	0.97813	0.97820	> 99.5	2.9993	2.1130
acridine	1.07352	1.10040^b	> 97.0		
indole	1.21665	1.21950^b	> 99.0	4.2820	2.6920
pyrrole	0.96595	0.96980^b	> 97.0	2.5734	1.8240
aniline	1.01738	1.01750	> 99.6	3.7165	2.8160

^{a} Ref 10. ^{b} At 293.15 K.

Table 2. Experimental Data for the Binary System of Ethanol (1) + Hexadecane (2)

	x_1	
T/K	ethanol-rich phase	hexadecane-rich phase
294.40	0.9621	0.2551
298.15	0.9597	0.2918
308.15	0.9510	0.3836
318.15	0.9359	0.4907
323.15	0.9054	0.5544

Table 3. The G^E Model Parameters and Mean Deviation between the Calculated and Experimental for the Binary System

	NRTL		UNIQUAC	
	$ij = 12$	$ij = 21$	$ij = 12$	$ij = 21$
	ethanol (1) + hexadecane (2)			
A_{ij}/K	−696.338	2574.058	−90.228	1139.604
B_{ij}/K	5.795	−8.603	0.156	−2.344
α	0.2000			
Δx_1	0.0032		0.0045	

adsorption of removing nitrogen compounds, because it would be operated at atmospheric pressure and a moderate temperature. Besides, it does not need additional catalyst.

To develop the extraction process of nitrogen compounds from the middle distillate, we report the liquid−liquid equilibrium (LLE) data at (294.40, 298.15, 308.15, 318.15, 323.15) K for the binary system of ethanol (1) + hexadecane (2). Hexadecane (cetane) was taken as the model compound for diesel fuel. Quinoline, pyridine, acridine, indole, pyrrole, and

Table 4. Experimental LLE Data of the System Ethanol (1) + Nitrogen-Containing Compounds (2) + Hexadecane (3) at 298.15K

nitrogen-containing compounds	ethanol-rich phase		hexadecane-rich phase		nitrogen-containing compounds	ethanol-rich phase		hexadecane-rich phase	
	x_{11}	x_{21}	x_{13}	x_{23}		x_{11}	x_{21}	x_{13}	x_{23}
quinoline	0.9112	0.0244	0.3658	0.0194	pyrrole (continued)	0.6404	0.3212	0.1939	0.1112
	0.8788	0.0455	0.4416	0.0398		0.6044	0.3608	0.1760	0.1202
	0.7840	0.0783	0.5687	0.0663		0.5681	0.3956	0.1677	0.1289
	0.6742	0.0924	0.6700	0.0910		0.5409	0.4241	0.1566	0.1379
	0.7801	0.0793	0.5739	0.0707		0.5100	0.4600	0.1408	0.1370
	0.7540	0.0853	0.6016	0.0763		0.4356	0.5399	0.1188	0.1532
pyridine	0.8850	0.0729	0.3109	0.0494		0.3511	0.6279	0.0833	0.1529
	0.8026	0.1406	0.3451	0.0967		0.3009	0.6822	0.0723	0.1631
	0.7262	0.1915	0.3843	0.1381		0.2648	0.7181	0.0608	0.1627
	0.6656	0.2359	0.4020	0.1825		0.1916	0.7954	0.0436	0.1666
	0.5716	0.2841	0.4493	0.2517		0.1909	0.7932	0.0412	0.1585
acridine	0.8630	0.0161	0.2895	0.0118		0.1501	0.8335	0.0319	0.1575
	0.7899	0.0293	0.3402	0.0230		0.1163	0.8717	0.0243	0.1646
	0.7429	0.0390	0.3697	0.0260		0.0786	0.9091	0.0180	0.1641
	0.6653	0.0450	0.4397	0.0314		0.0382	0.9535	0.0164	0.1683
indole	0.9024	0.0409	0.3373	0.0188		0.0061	0.9843	0.0156	0.1630
	0.8521	0.0817	0.3426	0.0395	aniline	0.9339	0.0356	0.2734	0.0165
	0.8143	0.1172	0.3543	0.0610		0.8941	0.0753	0.2564	0.0313
	0.7194	0.2198	0.3272	0.0919		0.8573	0.1130	0.2419	0.0430
	0.7160	0.2245	0.3033	0.0947		0.8161	0.1552	0.2165	0.0529
	0.6902	0.2511	0.2742	0.1014		0.7894	0.1873	0.2007	0.0632
	0.6369	0.3138	0.2305	0.1093		0.7502	0.2279	0.1847	0.0701
	0.5976	0.3620	0.2074	0.1125		0.7167	0.2633	0.1650	0.0751
	0.5345	0.4213	0.1787	0.1183		0.6833	0.2956	0.1537	0.0823
	0.4598	0.4912	0.1528	0.1228		0.6455	0.3351	0.1376	0.0840
	0.3778	0.5688	0.1373	0.1258		0.6099	0.3726	0.1236	0.0854
	0.3097	0.6332	0.1079	0.1305		0.5795	0.4046	0.1103	0.0878
	0.2485	0.7083	0.0899	0.1357		0.5210	0.4715	0.1002	0.0957
	0.1849	0.7732	0.0685	0.1375		0.4909	0.5023	0.0836	0.0931
	0.1363	0.8367	0.0393	0.1431		0.4566	0.5360	0.0778	0.0967
	0.0779	0.8878	0.0181	0.1491		0.4132	0.5796	0.0682	0.0989
	0.0351	0.9344	0.0156	0.1532		0.2636	0.7295	0.0320	0.1005
pyrrole	0.9029	0.0459	0.2841	0.0177		0.1537	0.8410	0.0186	0.1038
	0.8281	0.1247	0.2610	0.0455		0.1160	0.8786	0.0172	0.1053
	0.7486	0.2065	0.2355	0.0768		0.0648	0.9308	0.0074	0.1074
	0.6802	0.2805	0.2090	0.1023		0.0000	0.9949	0.0000	0.1118

aniline were taken as the basic or nonbasic heterocylic nitrogen-containing compounds in the middle distillate feedstock. The tie-line end compositions for these six different heterocyclic compounds containing the systems ethanol (1) + nitrogen-containing compounds (2) + hexadecane (3) were experimentally determined at 298.15 K. Additionally, the extraction selectivity of ethanol as a solvent was analyzed with respect to distribution and selectivity curves.
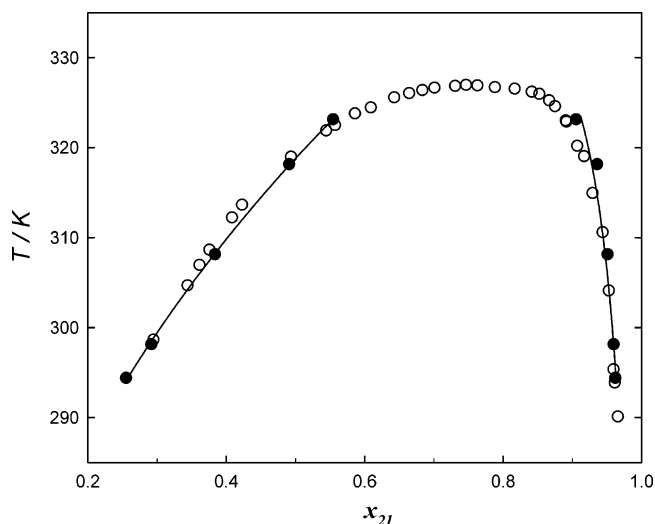
Experimental Section

Materials. The chemicals used in this investigation were analytical commercial grade purity. Ethanol was provided by J.T Baker Chemical Co., and hexadecane, pyrrole, and acridine were obtained from Aldrich. Quinoline was from Junsei (Japan),
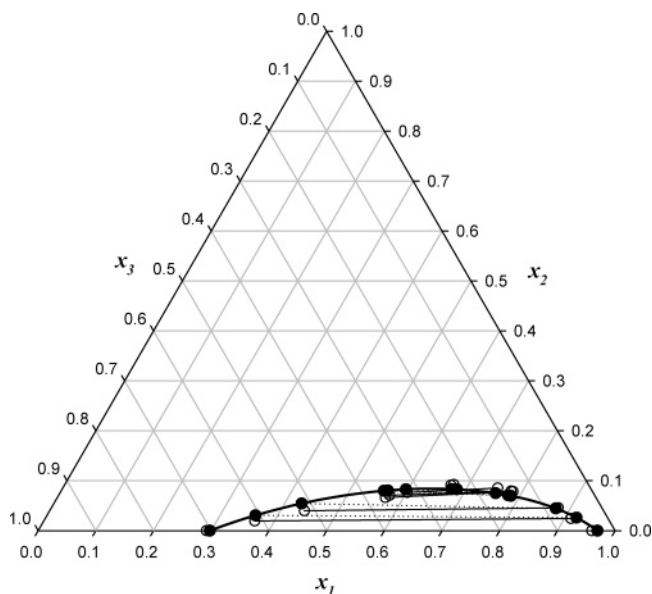

Figure 1. LLE for the binary system; ●, ethanol (1) + hexadecane (2); ○, ethanol (1) + hexadecane (2) by Matsuda et al.[6] Solid curves were calculated from NRTL equation.

Figure 2. LLE for the ternary system of ethanol (1) + quinoline (2) + hexadecane (3) at 298.15 K; ○, experimental value; ●, calculated value. Dashed lines were calculated from UNIQUAC equation.
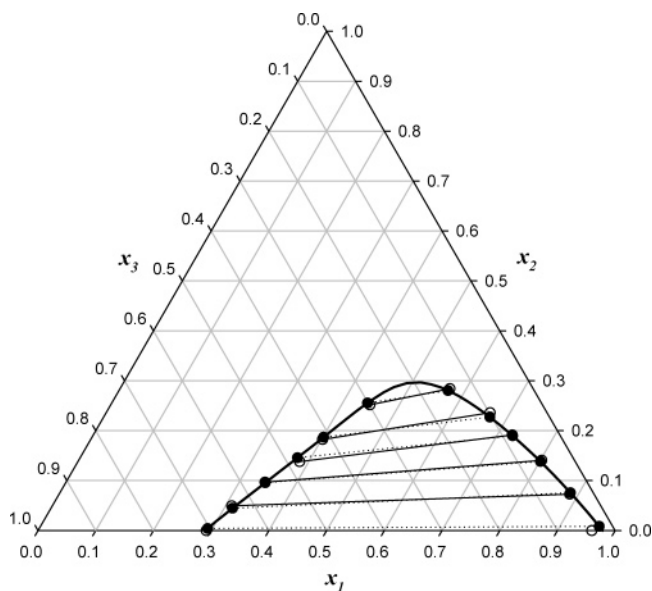
Figure 3. LLE for the ternary system of ethanol (1) + pyridine (2) + hexadecane (3) at 298.15 K; ○, experimental value; ●, calculated value. Dashed lines were calculated from NRTL equation.
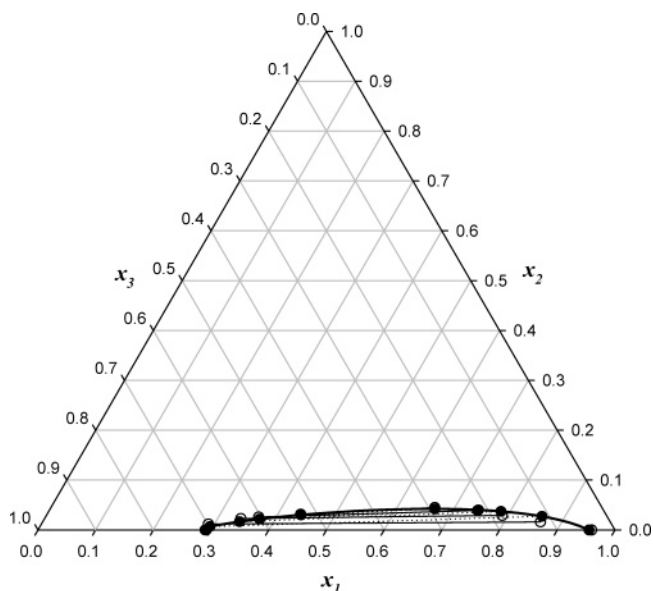

Figure 4. LLE for the ternary system of ethanol (1) + acridine (2) + hexadecane (3) at 298.15 K; ○, experimental value; ●, calculated value. Dashed lines were calculated from NRTL equation.

Table 5. The NRTL Model Parameters for the Ternary Systems of Ethanol (1) + Nitrogen-Containing Compounds (2) + Hexadecane (3) at 298.15 K

nitrogen-containing compounds	NRTL parameters (K)				
	i-j	$(g_{ij} - g_{ii})/R$	$(g_{ji} - g_{jj})/R$	α_{ij}	RMSD
quinoline	1-2	−252.95	−246.98	0.20	0.0083
	2-3	−494.33	243.54	0.20	
	1-3	1031.20	−5.35	0.20	
pyridine	1-2	932.16	−826.92	0.20	0.0050
	2-3	1641.80	−526.12	0.20	
	1-3	1222.90	−44.72	0.20	
acridine	1-2	−144.57	−1736.20	0.20	0.0042
	2-3	−1391.30	105.66	0.20	
	1-3	998.80	19.02	0.20	
indole	1-2	1471.60	−652.85	0.20	0.0131
	2-3	995.73	148.71	0.20	
	1-3	1089.60	−26.13	0.20	
pyrrole	1-2	834.80	−484.14	0.20	0.0103
	2-3	1514.90	47.97	0.20	
	1-3	932.73	50.03	0.20	
aniline	1-2	−894.66	1484.60	0.20	0.0124
	2-3	2390.30	260.31	0.20	
	1-3	1007.70	18.37	0.20	

Table 6. The UNIQUAC Model Parameters for the Ternary Systems of Ethanol (1) + Nitrogen-Containing Compounds (2) + Hexadecane (3) at 298.15 K

nitrogen-containing compounds	UNIQUAC parameters (K)			
	i-j	$(u_{ij} - u_{ii})/R$	$(u_{ji} - u_{jj})/R$	RMSD
quinoline	1-2	147.12	−270.93	0.0075
	2-3	−241.34	207.73	
	1-3	−31.50	417.08	
pyridine	1-2	189.02	−207.22	0.0085
	2-3	29.19	117.92	
	1-3	−17.91	396.02	
indole	1-2	−314.44	516.82	0.0161
	2-3	−91.12	340.72	
	1-3	−29.40	392.57	
pyrrole	1-2	−373.40	993.99	0.0088
	2-3	0.73	455.12	
	1-3	−48.06	444.62	
aniline	1-2	201.42	−235.33	0.0117
	2-3	−38.25	427.80	
	1-3	371.65	65.88	

and the others were from Kanto (Japan). The mass fraction purity of the chemicals was checked by gas chromatographic analysis. Their impurities were less than 0.5 % except acridine (< 3.0 %), pyrrole (< 3.0 %) and indole (< 1.0 %). All chemicals were used without further purification and were stored in a desiccator with a drying agent before their use. The density and purity of the substances are listed in Table 1.

Apparatus and Procedure. LLE measurement has been carried out by measuring the end point of tie-lines for all the binary and ternary systems. The self-designed LLE measuring system was used and consists of three parts: equilibrium glass cell, thermostat (Lauda MD 20 with DLK15 cooler) with precision temperature-measuring system, and Corning PC-320 magnetic stirrer. The sample was prepared by adding the nitrogen compound to the mother solution of hexadecane and ethanol with a mass ratio of 50:50. When the system temperature was reached, the sample mixture was stirred rigorously in an equilibrium cell for about 12 h and then settled down for about 24 h at constant system temperature, brought the mixture into equilibrium. Temperature fluctuation was less than ± 0.02 K. After equilibriate, the sample mixture from each liquid phase was taken and analyzed using gas chromatography (HP 6890N) with HP-5 (5 % diphenyl:95 % dimethylsiloxane, 30 m × 0.32 mm × 0.25 μm) capillary column and a thermal conductivity detector. The liquid mole fraction was decided with the GC analysis. The uncertainty of the calculated mole fraction is ± 1·10[−4]. The procedure is described in detail elsewhere.[5]

Results and Discussion

Tie Lines and Data Correlation Using Non Random Two Liquid (NRTL) and Universal Quasi-Chemical (UNIQUAC) Equation. Liquid−liquid equilibria for the binary system of ethanol (1) + hexadecane (2) at (294.40, 298.15, 308.15, 318.15, 323.15) K are listed in Table 2. These data were plotted and compared with the reference data[6] as shown in Figure 1. The binary LLE data were correlated also with NRTL and UNIQUAC equation. The adjustable binary parameters of each equation are furnished in Table 3 along with the mean deviations between experimental and calculated values. The NRTL model gave a slightly better correlation result with 0.32 % mean deviation of ethanol mole fraction. The dashed lines in Figure 1 represent the calculated values by NRTL equation. The
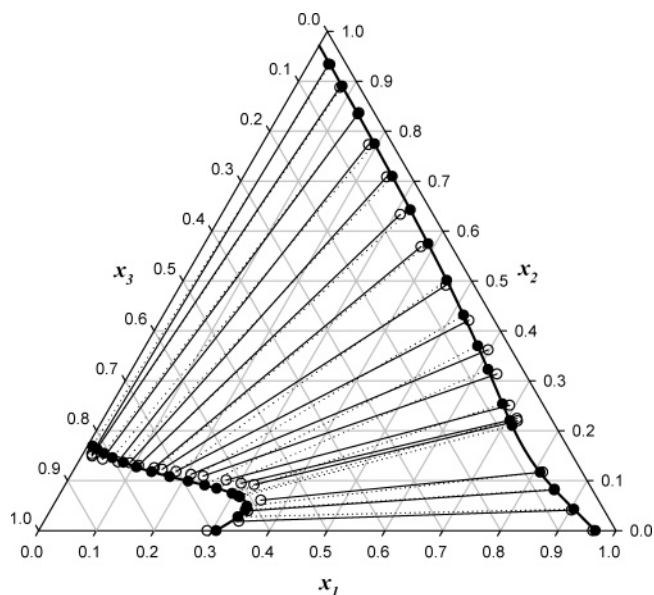
Figure 5. LLE for the ternary system of ethanol (1) + indole (2) + hexadecane (3) at 298.15 K; ○, experimental value; ●, calculated value. Dashed lines were calculated from NRTL equation.
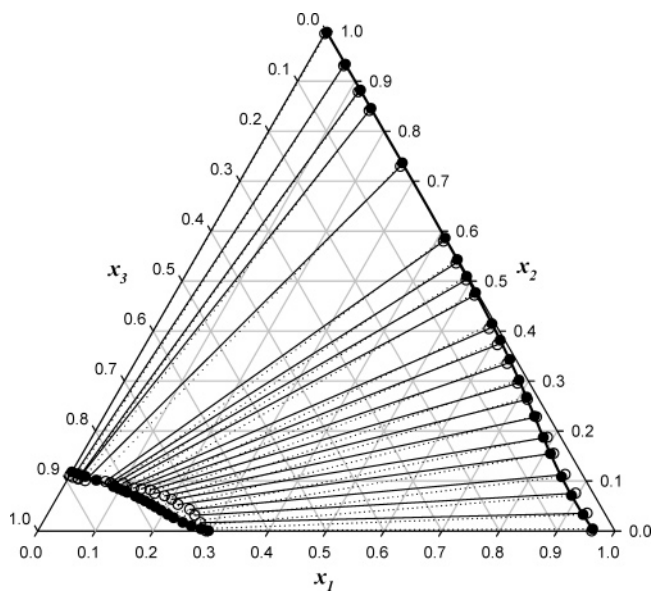

Figure 7. LLE for the ternary system of ethanol (1) + aniline (2) + hexadecane (3) at 298.15 K; ○, experimental value; ●, calculated value. Dashed lines were calculated from UNIQUAC equation.
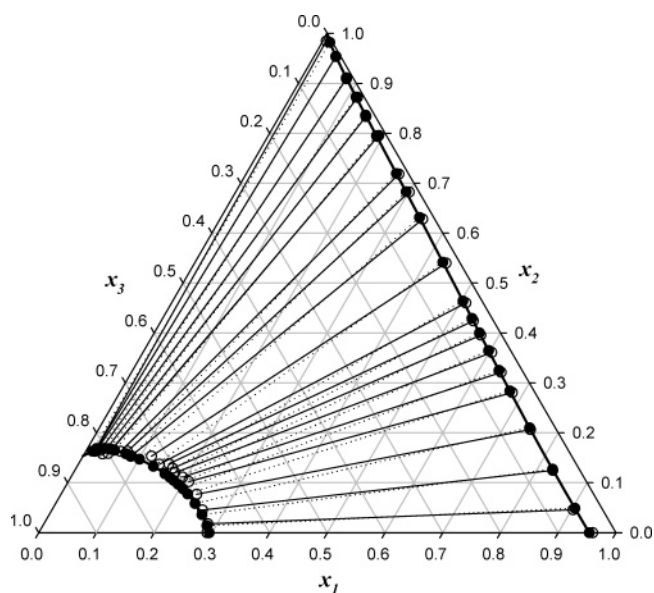

Figure 6. LLE for the ternary system of ethanol (1) + pyrrole (2) + hexadecane (3) at 298.15 K; ○, experimental value; ●, calculated value. Dashed lines were calculated from UNIQUAC equation.

Figure 8. Distribution coefficient (*D*) against x_{21} for the ternary systems of ethanol (1) + nitrogen-containing compounds (2) + hexadecane (3) at 298.15 K.; ○, quinoline; □, pyridine; ▲, acridine; ◇, pyrrole; ■, aniline; ▽, indole.

experimental tie-line data for the ternary systems, ethanol (1) + nitrogen-containing compounds (2) + hexadecane (3) at 298.15 K, are given in Table 4. Ternary tie-line data were also correlated using NRTL[7] and UNIQUAC[8] models except for acridine-contained systems, because there are no UNIQUAC parameters for acridine.

The binary parameters were determined by minimizing the differences between the experimental and calculated mole fractions for each of the components over all the measured tie-lines of ternary systems. The simplex function in DDBSP software package was applied for the minimization procedure. The used object function (OF) was

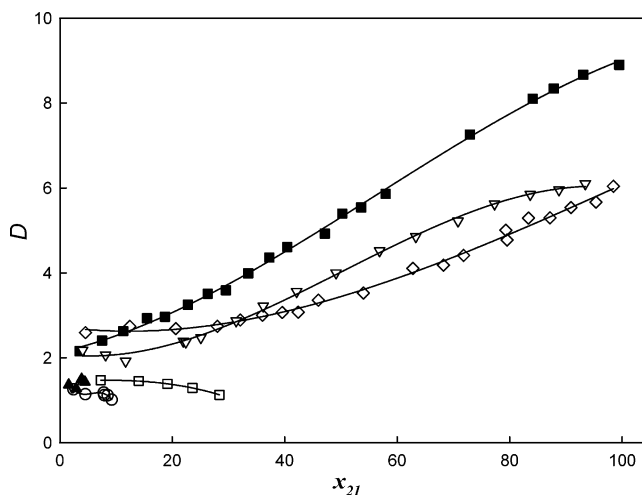$$OF = \min \sum_i \sum_j \sum_k (x_{ij_k} - x_{ij_k}^C)^2 \qquad (1)$$

where *x* and x^c are the experimental and calculated mole fractions, respectively. The subscripts *i*, *j*, and *k* denote component, phase, and tie-line, respectively. The parameters calculated are listed in Table 5 and 6, together with the root-mean-square deviation (RMSD) values between experimental and calculated data, defined as

$$RMSD = \left[\frac{\sum_i \sum_j \sum_k (x_{ijk} - x_{ij_k}^C)^2}{6N} \right]^{1/2} \qquad (2)$$

where *N* is the number of tie-lines.

The ternary LLE of each system at 298.15 K are plotted in Figures 2 to 7. The dashed lines are calculated tie-lines. The experimental and calculated LLE data agreed relatively well as shown in the Figures 2 to 7. The slopes of the tie-lines presented in Figures 2 to 7 show that pyridine, indole, pyrrole, and aniline are more soluble in ethanol than in hexadecane, while quinoline and acridine show almost the same solubility in ethanol or

Table 7. Experimental Distribution Values *D* and Selectivity Values *S* for Each Tie-Line

nitrogen-containing compounds	x_{21}	D	S	nitrogen-containing compounds	x_{21}	D	S
quinoline	0.0244	1.2577	8.9826	pyrrole (continued)	0.3212	2.8885	6.4750
	0.0455	1.1432	5.2671		0.3608	3.0017	6.2522
	0.0783	1.1810	2.3582		0.3956	3.0690	5.9143
	0.0924	1.0154	1.0285		0.4241	3.0754	5.6498
	0.0793	1.1216	2.1734		0.5399	3.3577	5.8876
	0.0853	1.1180	1.8105		0.5399	3.5242	5.5023
pyridine	0.0729	1.4757	8.8427		0.6279	4.1066	5.8014
	0.1406	1.4540	4.8238		0.6822	4.1827	5.5504
	0.1915	1.3867	3.1182		0.7181	4.4136	5.6383
	0.2359	1.2926	2.3115		0.7954	4.7743	5.6484
	0.2841	1.1287	1.4510		0.7932	5.0044	5.9303
acridine	0.0161	1.3644	7.0760		0.8335	5.2921	6.0281
	0.0293	1.2739	4.0006		0.8717	5.295	5.8472
	0.0390	1.5000	3.6774		0.9091	5.5399	5.9043
	0.0450	1.4331	2.3991		0.9535	5.6655	5.7939
indole	0.0409	2.1813	14.8172		0.9843	6.0387	5.9809
	0.0817	2.0681	9.1908	aniline	0.0356	2.1576	23.7170
	0.1172	1.9207	6.6769		0.0753	2.4058	16.8925
	0.2198	2.3918	5.7343		0.1130	2.6279	13.9609
	0.2245	2.3707	5.8163		0.1552	2.9338	12.4995
	0.2511	2.4768	5.8030		0.1873	2.9636	11.2479
	0.3138	2.8705	6.0830		0.2279	3.2511	10.6109
	0.3620	3.2183	6.3394		0.2633	3.5060	10.3336
	0.4213	3.5609	6.2832		0.2956	3.5917	9.5980
	0.4912	4.0000	6.2732		0.3351	3.9893	9.7048
	0.5688	4.5215	6.2692		0.3726	4.3630	9.8019
	0.6332	4.8521	6.2706		0.4046	4.6082	9.7501
	0.7083	5.2196	6.3212		0.4715	4.9269	9.2551
	0.7732	5.6233	6.4263		0.5023	5.3953	9.7117
	0.8367	5.8470	6.5036		0.5360	5.5429	9.4068
	0.8878	5.9544	6.3404		0.5796	5.8605	9.3060
	0.9344	6.0992	6.2225		0.7295	7.2587	9.5416
pyrrole	0.0459	2.5932	19.1193		0.8410	8.1021	9.3955
	0.1247	2.7407	11.7821		0.8786	8.3438	9.2763
	0.2065	2.6888	8.1766		0.9308	8.6667	9.1986
	0.2805	2.7419	6.7820		0.9949	8.8989	8.8989

hexadecane and their immiscible regions are very small. Among measured systems, quinoline-, pyridine-, and acridine-contained systems show only one binary immiscibility; on the other hand, the other systems have more than two immiscible systems. The correlated parameters of NRTL and UNIQUAC models for ternary systems and mean deviations of comparison results are given in the Tables 5 and 6. The experimental ternary LLE data are correlated well with both NRTL and UNIQUAC equations. Their RMSDs between calculated and measured mole fraction are less than 1 % for almost all the systems.

Distribution and Selectivity. The distribution coefficient (*D*) of the solute (nitrogen-containing compounds) over the two liquid phases in the equilibrium is defined as

$$D = \frac{x_{21}}{x_{23}} \qquad (3)$$

where x_{21} is the mole fraction of solute in ethanol-rich phase and x_{23} is the mole fraction of solute in hexadecane-rich phase. Calculated *D* values of each solute are presented in Table 7 and plotted in Figure 8. As shown in Figure 8, the *D* values of indole, pyrrole, and aniline are greater than that of quinoline, pyridine, and acridine in the measured systems. The effectiveness of extraction of nitrogen-containing compounds by ethanol could be given by its selectivity (*S*), which is a measure of the ability of ethanol as a separating agent of nitrogen-containing compounds from the hexadecane, that is, middle distillates.

$$S = \frac{x_{21}(x_{21} + x_{31})}{x_{23}(x_{23} + x_{33})} \qquad (4)$$

The experimental values of *S* are listed also in Table 7. As shown in Figure 9, selectivity decreases when going through the tie-line end compositions from low concentration to high concentration of nitrogen-containing compounds. It means the higher the concentration of nitrogen-containing compounds in the feed, the lower the selectivity of ethanol to nitrogen-containing compounds. The selectivity of ethanol follows in the order of aniline > pyrrole > indole > pyridine > quinoline > acridine, because the distribution coefficients in all the ternaries are slightly greater than unity, and selectivities are not sufficiently
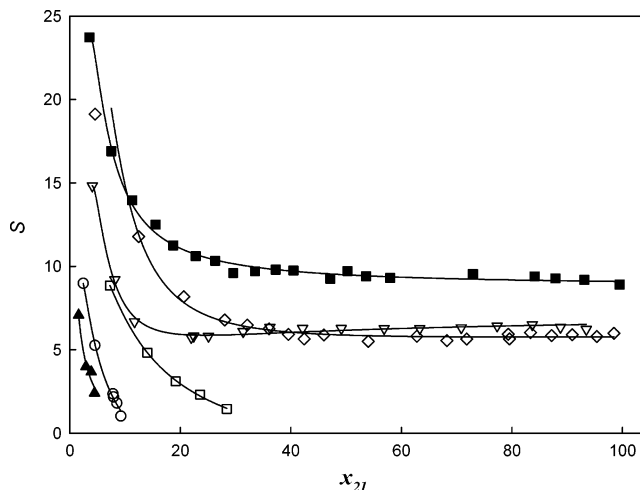

Figure 9. Selectivity(*S*) against x_{21} for the ternary systems of ethanol (1) + nitrogen-containing compounds (2) + hexadecane (3) at 298.15 K.; ○, quinoline; □, pyridine; ▲, acridine; ◇, pyrrole; ■, aniline; ▽, indole.

high compared to the result of methanol.[5] Ethanol is therefore not better than methanol as an effective extracting solvent of nitrogen-containing compounds from the middle distillates.

Conclusion

Binary LLE for the ethanol + 00hexadecane was measured at the temperature ranges from 294.40 K to 323.15 K and ternary tie-line data for six different ethanol (1) + nitrogen-containing compounds (2) + hexadecane (3) systems were also measured at 298.15 K. The binary LLE curve has upper critical solution temperature and correlated well with NRTL equation. Among the ternary systems, quinoline-, pyridine-, and acridine-contained systems show only one binary immiscibility, while the others have more than two immiscible systems. They also correlated well with NRTL and UNIQUAC equations, and their RMSDs between calculated and measured values are mostly less than 1 mol %. The extracting capabilities of ethanol to heterocyclic nitrogen-contained compounds revealed that their κ values and selectivity were not sufficiently high enough, and the κ values of indole, pyrrole, and aniline systems are greater than that of quinoline, pyridine, and acridine systems. The selectivity of ethanol follows in the order of aniline > pyrrole > indole > pyridine > quinoline > acridine.

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