1266 *J. Chem. Eng. Data* **2010,** *55,* 1266–1270

(Liquid + Liquid) Equilibrium for (*N*,*N*-Dimethylformamide (DMF) + Hexadecane) at Temperatures between (293.15 and 313.15) K and Ternary Mixtures of (DMF + Hexadecane) with Either Quinoline, or Pyridine, or Pyrrole, or Aniline, or Indole at $T = 298.15$ K

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(Liquid + liquid) equilibrium for (*N*,*N*-dimethylformamide (DMF) + *n*-hexadecane) at temperatures from (293.15 to 313.15) K and for ternary mixtures of (DMF + hexadecane) with either quinoline, or pyridine, or pyrrole, or aniline, or indole at $T = 298.15$ K were determined at atmospheric pressure with stirred and thermoregulated cells. The NRTL and UNIQUAC models were used to correlate the experimental data. In addition, the extraction capability of DMF for heterocyclic nitrogen compounds was investigated with respect to distribution and selectivity.

Introduction

Air pollution by nitrogen compounds (NO*x*) and particulate matter (PM) of diesel exhaust is now a serious problem in the whole world. In the very early 2000s, most governmental regulatory limits for total sulfur for highway vehicle diesel were within the mass fraction range of $(300 \text{ to } 500) \cdot 10^{-6}$. However, the US Environmental Protection Agency (EPA) recently passed rules requiring use of ultralow sulfur diesel (ULSD) for diesel vehicles, which allows a mass fraction $15 \cdot 10^{-6}$ for sulfur. This ULSD will be expected to reduce dramatically NO*x* and PM. However, many gasoline producers are faced with technical and economic challenges to meet these new specifications.

The hydrodesulfurization (HDS) process is so far the most commonly used process in the oil industry to reduce the sulfur content in diesel fuel by converting sulfur compounds into hydrogen sulfide.[1,2] There are some reports that the conventional HDS process can be applied successfully for producing ultralow sulfur diesel, if heterocyclic nitrogen-containing compounds are removed effectively from the middle distillate feedstock. This means that heterocyclic nitrogen-containing compounds act as inhibitors for the desulfurization process in the middle distillates. These nitrogen-containing compounds are classified as basic and nonbasic compounds. Basic compounds include six-membered heterocyclics such as quinoline, pyridine, and aniline. Nonbasic compounds include five-membered heterocyclics such as pyrrole and indole. Solvent extraction could be an effective process to remove these nitrogen-containing compounds from the middle distillates.

To develop the extraction process of nitrogen compounds from the middle distillate, we reported some (liquid + liquid) equilibrium (LLE) data and excess properties.[3,4] As a continuation of our systematic study on the phase equilibrium data, this paper reports the binary liquid−liquid equilibrium (LLE) data for (*N*,*N*-dimethylformamide (DMF) + hexadecane) at temperatures from (293.15 to 313.15) K and ternary LLE data for (DMF + hexadecane) with quinoline, or pyridine, or pyrrole, or aniline, or indole at $T = 298.15$ K and at atmospheric pressure. The experimental LLE data for the binary and ternary systems are correlated using two activity coefficients: NRTL[5] and UNIQUAC.[6] In addition, the extraction capabilities of DMF for heterocyclic nitrogen compounds were investigated with respect to distribution and selectivity.

Table 1. Density ρ at $T = 298.15$ K and Mass Fraction Purity w Determined by gc of the Pure Components along with UNIQUAC Parameters

	$\rho/\text{g}\cdot\text{cm}^{-3}$			UNIQUAC	
chemicals	this work	ref[a]	100 w	r value[a]	q value[a]
DMF	0.94421	0.94440	> 99.7	2.4317	2.1920
hexadecane	0.77319	0.77330	> 99.8	11.2438	9.2560
quinoline	1.08945	1.09290[b]	> 99.6	4.7923	3.1530
pyridine	0.97825	0.97820	> 99.5	2.9993	2.1130
indole	1.21668	1.21950[b]	> 99.0	4.2820	2.6920
pyrrole	0.96590	0.96980[b]	> 97.0	2.5734	1.8240
aniline	1.01742	1.01750	> 99.6	3.7165	2.8160

[a] Ref 12. [b] At 293.15 K.

Table 2. Experimental LLE Mole Fraction x as a Function of Temperature T Data for DMF (1) + Hexadecane (2)

	DMF phase	hexadecane phase
T/K	x_1	x_1
293.15	0.9971	0.0812
298.15	0.9960	0.0858
303.15	0.9957	0.0861
308.15	0.9935	0.0863
313.15	0.9929	0.0873

Experimental Section

Materials. Commercial grade DMF (C_3H_7NO, $M = 73.10$ $\text{g}\cdot\text{mol}^{-1}$, CAS-RN 68-12-2), hexadecane ($C_{16}H_{34}O$, $M = 226.45$ $\text{g}\cdot\text{mol}^{-1}$, CAS-RN 544-76-3), pyridine (C_5H_5N, $M =$

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10.1021/je9006234

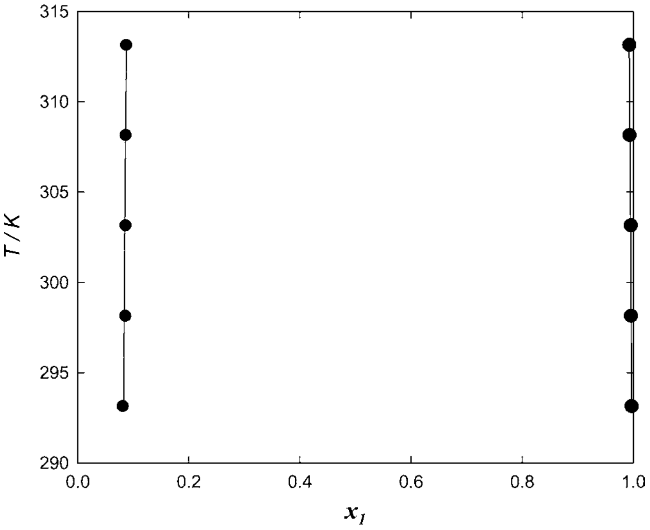

Figure 1. LLE for the binary system DMF (1) + hexadecane (2): ●, experimental value. Solid lines were calculated from the UNIQUAC model.

Table 3. G^E Model Parameters and rmsd between the Calculated and Experimental Values for DMF (1) + Hexadecane (2)

DMF (1) + hexadecane (2)	NRTL $ij = 12$	NRTL $ij = 21$	UNIQUAC $ij = 12$	UNIQUAC $ij = 21$
A_{ij} (K)[a]	3949.9109	5.6501	602.6904	−563.9268
B_{ij}	−8.3909	0.9149	−1.9597	3.0220
α	0.20		−	
rmsd	0.0013		0.0012	

[a] Parameters (K): $a_{ij} = A_{ij} + B_{ij}T$.

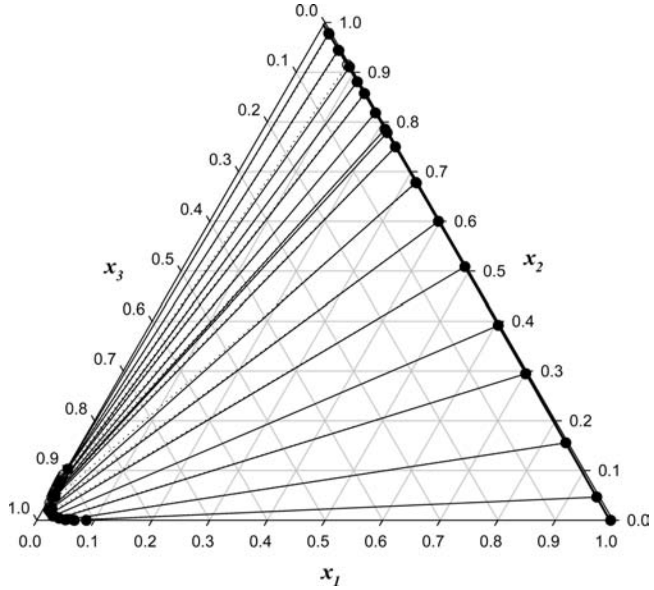

Figure 2. LLE for the ternary system DMF (1) + aniline (2) + hexadecane (3) at $T = 298.15$ K: ●, experimental value; ○, calculation value. Dashed lines were calculated from the UNIQUAC model.

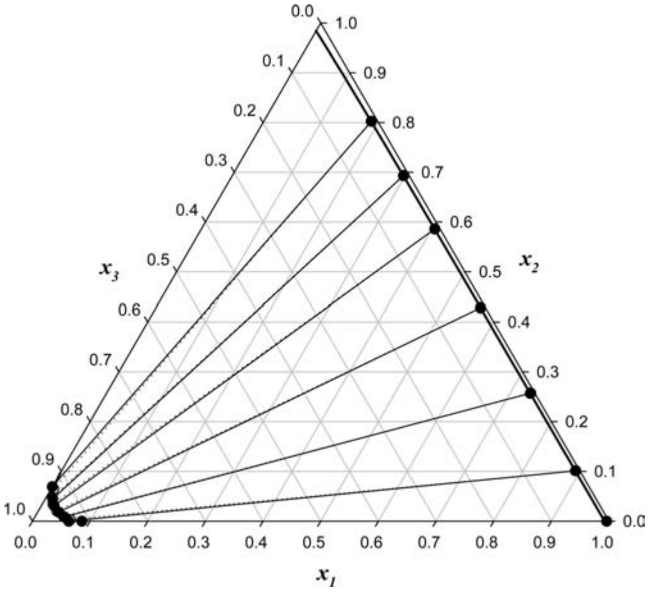

Figure 3. LLE for the ternary system DMF (1) + indole (2) + hexadecane (3) at $T = 298.15$ K: ●, experimental value; ○, calculation value. Dashed lines were calculated from the NRTL model.

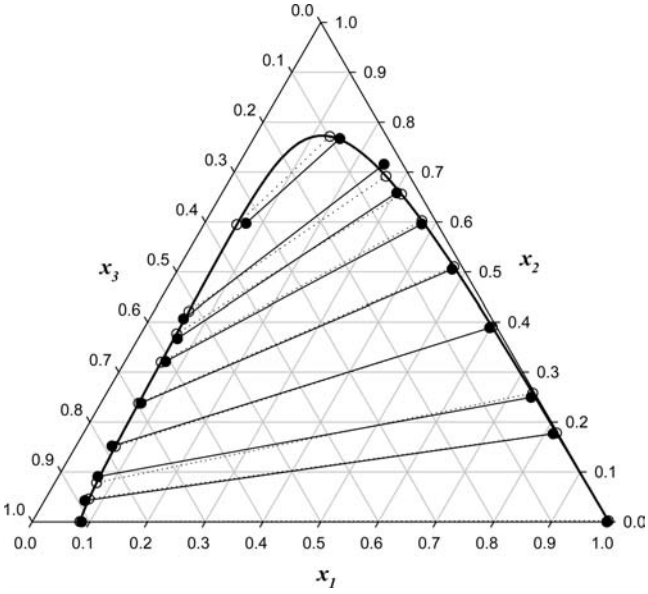

Figure 4. LLE for the ternary system DMF (1) + pyridine (2) + hexadecane (3) at $T = 298.15$ K: ●, experimental value; ○, calculation value. Dashed lines were calculated from the UNIQUAC model.

79.10 g·mol^{-1}, CAS-RN 110-86-1), and aniline (C_6H_7N, $M = 93.13$ g·mol^{-1}, CAS-RN 62-53-3) were obtained from Aldrich. Pyrrole (C_4H_5N, $M = 67.09$ g·mol^{-1}, CAS-RN 109-97-7) was obtained from Fluka, and quinoline (C_9H_7N, $M = 129.16$ g·mol^{-1}, CAS-RN 91-22-5) was obtained from Junsei Chemical Co. All the chemicals were dried using molecular sieves with a pore diameter of 0.4 nm. The purity of the chemicals was examined by gas chromatography and by comparing the densities with values reported in the literature. According to the gas chromatographic analysis, their impurities were less than 0.5 wt %, except for pyrrole (< 3.0 wt %) and indole (< 1.0 wt %). The measured densities and purities of the samples are summarized in Table 1 with UNIQUAC parameters of relative surface and volume fractions.

Apparatus and Procedure. The equilibrium vessel was housed in a thermostat (Lauda MD 20 with DLK 15 cooler) and the temperature determined with an AΣA F250 to be constant within ± 0.02 K. The samples in the equilibrium vessel were stirred vigorously for a time of about 8 h with a magnetic stirrer (Corning PC-320) and allowed to settle for a time of more than 16 h at constant temperature. After both liquid phases settled, sampling was carried out from the upper phase and the bottom phase without contamination of both phases. The chemical analysis of each sample was done using a gas

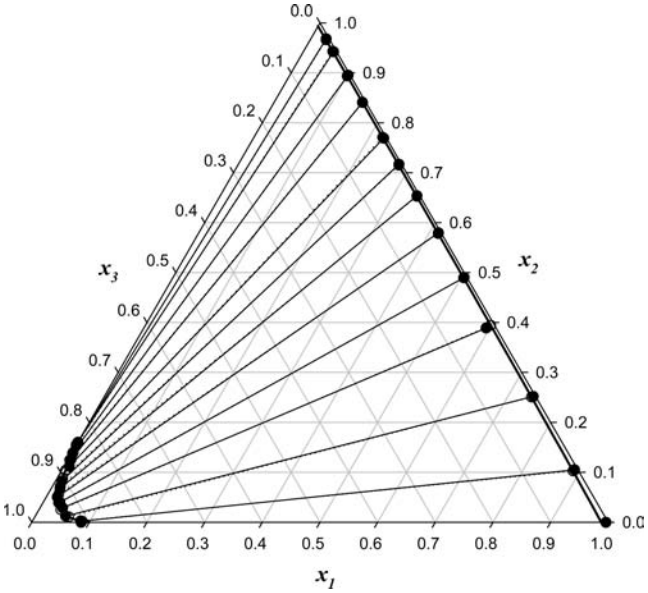

Figure 5. LLE for the ternary system DMF (1) + pyrrole (2) + hexadecane (3) at T = 298.15 K: ●, experimental value; ○, calculation value. Dashed lines were calculated from the NRTL model.

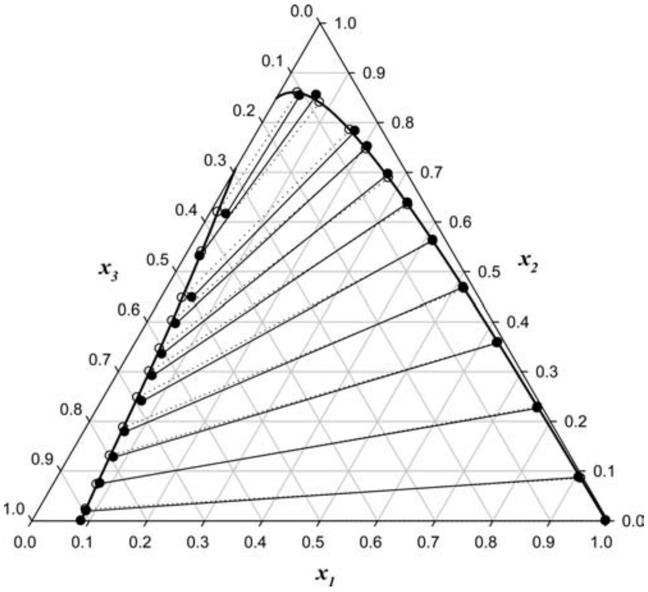

Figure 6. LLE for the ternary system DMF (1) + quinoline (2) + hexadecane (3) at T = 298.15 K: ●, experimental value; ○, calculation value. Dashed lines were calculated from the UNIQUAC model.

chromatograph (HP 6890N) with an HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column and a thermal conductivity detector. The uncertainty of the calculated mole fraction was estimated less than ca. $\pm 1 \cdot 10^{-3}$. The analytical procedure is described in detail elsewhere.[7]

Densities were measured by a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Graz, Austria). The uncertainty of the density meter is stated by manufacturer as $5 \cdot 10^{-6}$ g·cm^{-3} in the range of (0 to 3) g·cm^{-3}. Temperature is controlled within ± 0.01 K in the range from (273.15 to 363.15) K. The details of operating procedures have been described elsewhere.[8,9]

Results and Discussion

The LLE data for the binary system (DMF + hexadecane) at temperatures of (293.15, 298.15, 303.15, 308.15, and 313.15) K under atmospheric pressure are listed in Table 2 and plotted in Figure 1. The solubility of DMF in hexadecane increased slightly ($x_{\mathrm{DMF}} < 0.09$) with temperature in the temperature range investigated, while that of hexadecane in DMF was negligible ($x_{\mathrm{C16}} < 0.008$). The binary LLE data were correlated with the NRTL and the UNIQUAC model. The adjustable binary parameters of the NRTL and the UNIQUAC models are listed in Table 3, along with the root-mean-square-deviations (rmsd) between experimental and recalculated values. The UNIQUAC model gave slightly better correlation with a mean deviation of DMF mole fraction of 0.12 %. The solid lines in Figure 1 represent the values calculated using the UNIQUAC model.

The measured ternary LLE data for (DMF (1) + (either quinoline, or pyridine, or pyrrole, or aniline, or indole) (2) + hexadecane (3)) at T = 298.15 K are given in Table 4. The ternary LLE data for each system are shown in Figures 2 to 6.

Experimental LLE data were correlated using NRTL and UNIQUAC models. Minimizing the differences between the experimental and calculated mole fractions for each component determined the constituent binary parameters of both models over all the measured LLE data of the ternary systems. The objective function (OF) used was

$$\mathrm{OF} = \min \sum_i \sum_j \sum_k (x_{ijk} - x_{ijk}^{c})^2 \qquad (1)$$

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 quality of the parameters can be evaluated according to the mean deviation in the compositions of coexisting phases.[10] The binary parameters optimized of NRTL and UNIQUAC models for the ternary systems are listed in Table 5, with the rmsd values between experimental and calculated data, defined as

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

where N is the number of tie lines. The digit number 6 means the three components in two phases. The experimental ternary LLE data are correlated well with both the NRTL and the UNIQUAC equations. Their rmsd between measured and calculated mole fractions is less than 0.9 % for almost all the systems. In the figures, the dashed lines are calculated tie lines. The slopes of the tie lines presented in the figures show that quinoline, pyridine, pyrrole, aniline, and indole are more soluble in solvent (DMF) than in hexadecane when enough solvent is added. Only the ternary system DMF + pyridine + hexadecane is a Treybal's type I[11] system, which shows partial miscibility of the solvent and the diluent hexadecane, while DMF + pyrrole or aniline or indole or quinoline + hexadecane are ternary systems of a Treybal's type II, where two immiscible binaries exist.

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

$$\beta = \frac{x_2^{\mathrm{I}}}{x_2^{\mathrm{II}}} \qquad (3)$$

where x_2^{I} is the mole fraction of solute in the DMF-rich phase and x_2^{II} is the mole fraction of solute in the hexadecane-rich phase. Calculated β values of each solute are presented in Table 4 and plotted in Figure 7. As shown in Figure 7, the β values for indole, pyrrole, and aniline are greater than that of quinoline

Table 4. Experimental LLE Mole Fractions *x* for DMF (1) + Either Pyrrole or Aniline or Indole or Quinoline (2) + Hexadecane (3) at *T* = 298.15 K, with Solute Distribution Ratio *β* and Selectivity *S* Values

	DMF-rich phase		hexadecane-rich phase			
system	x_1^{I}	x_2^{II}	x_1^{II}	x_2^{II}	β	S
DMF (1) + aniline (2) + hexadecane (3)	0.9960	0.0000	0.0858	0.0000	–	–
	0.9485	0.0466	0.0652	0.0000	–	–
	0.8403	0.1556	0.0491	0.0007	222.29	12.99
	0.7011	0.2945	0.0366	0.0038	77.50	4.05
	0.4887	0.5086	0.0184	0.0139	36.59	1.38
	0.3969	0.6000	0.0142	0.0245	24.49	0.88
	0.6051	0.3918	0.0239	0.0083	47.20	1.86
	0.3188	0.6782	0.0099	0.0209	32.45	1.01
	0.2477	0.7496	0.0079	0.0478	15.68	0.50
	0.2116	0.7853	0.0058	0.0496	15.83	0.43
	0.2189	0.7783	0.0056	0.0477	16.32	0.42
	0.1784	0.8183	0.0049	0.0535	15.30	0.42
	0.1407	0.8568	0.0039	0.0695	12.33	0.34
	0.1155	0.8807	0.0034	0.0680	12.95	0.38
	0.0875	0.9105	0.0023	0.1028	8.86	0.23
	0.0509	0.9446	0.0007	0.0759	12.45	0.17
	0.0176	0.9781	0.0005	0.0803	12.18	0.35
DMF (1) + indole (2) + hexadecane (3)	0.9960	0.0000	0.0858	0.0000	–	–
	0.8917	0.1014	0.0630	0.0000	30.28	2.11
	0.7355	0.2574	0.0512	0.0085	23.54	1.52
	0.5631	0.4285	0.0363	0.0182	18.79	1.03
	0.4050	0.5861	0.0222	0.0312	15.52	0.67
	0.2974	0.6939	0.0129	0.0447	11.58	–
	0.1870	0.8022	0.0000	0.0693	–	–
DMF (1) + pyridine (2) + hexadecane (3)	0.9960	0.0000	0.0858	0.0000	–	–
	0.8146	0.1765	0.0702	0.0424	4.16	0.36
	0.7400	0.2495	0.0686	0.0907	2.75	0.26
	0.5985	0.3890	0.0624	0.1516	2.57	0.27
	0.4751	0.5051	0.0696	0.2381	2.12	0.31
	0.3773	0.5958	0.0708	0.3213	1.85	0.35
	0.3028	0.6581	0.0681	0.3672	1.79	0.40
	0.2522	0.7154	0.0590	0.4067	1.76	0.41
	0.1925	0.7655	0.0535	0.4635	1.65	0.46
DMF (1) + pyrrole (2) + hexadecane (3)	0.9960	0.0000	0.0858	0.0000	–	–
	0.8890	0.1051	0.0859	0.0023	45.70	4.42
	0.7441	0.2518	0.0528	0.0123	20.47	1.45
	0.5938	0.3889	0.0394	0.0288	13.50	0.90
	0.5051	0.4901	0.0292	0.0399	12.28	0.71
	0.4157	0.5796	0.0193	0.0505	11.48	0.53
	0.3414	0.6537	0.0155	0.0677	9.66	0.44
	0.2787	0.7168	0.0112	0.0830	8.64	0.35
	0.2262	0.7689	0.0095	0.1120	6.87	0.29
	0.1536	0.8406	0.0056	0.1259	6.68	0.24
	0.1011	0.8953	0.0022	0.1382	6.48	0.14
	0.0526	0.9421	0.0000	0.1595	5.91	–
	0.0269	0.9680	0.0000	0.1549	6.25	–
DMF (1) + quinoline (2) + hexadecane (3)	0.9960	0.0000	0.0858	0.0000	–	–
	0.9058	0.0874	0.0851	0.0196	4.46	0.32
	0.7641	0.2266	0.0812	0.0752	3.01	0.32
	0.6289	0.3577	0.0784	0.1279	2.80	0.35
	0.5146	0.4689	0.0725	0.1789	2.62	0.37
	0.4146	0.5633	0.0711	0.2405	2.34	0.40
	0.3335	0.6383	0.0636	0.2914	2.19	0.42
	0.2707	0.6959	0.0585	0.3351	2.08	0.45
	0.2069	0.7516	0.0520	0.3962	1.90	0.48
	0.1702	0.7825	0.0543	0.4481	1.75	0.56
	0.0667	0.8551	0.0264	0.5312	1.61	0.64
	0.0384	0.8539	0.0296	0.6157	1.39	1.07

and pyridine in the systems measured. The effectiveness of extraction of nitrogen-containing compounds by DMF could be given by its selectivity (S), which is a measure of the ability of DMF as a separating agent of nitrogen-containing compounds from the hexadecane, i.e., middle distillates.

$$S = \frac{x_2^{\mathrm{I}} x_1^{\mathrm{II}}}{x_2^{\mathrm{II}} x_1^{\mathrm{I}}} \tag{4}$$

x_2^{I} is the mole fraction of solute in the DMF-rich phase; x_2^{II} is the mole fraction of solute in the hexadecane-rich phase; x_1^{II} is the mole fraction of DMF in the hexadecane-rich phase; and x_1^{I} is the mole fraction of DMF in the DMF-rich phase.

The experimental values of S are listed also in Table 4. As shown in Figure 8, selectivity decreases when going through the tie-line end compositions from low concentration to high concentration of the nitrogen-containing compounds.

In addition, the calculated selectivity was compared with methanol,[7] ethanol,[3] and *N*-methylformamide[4] (NMF), which can be used as separating agents of heterocyclic nitrogen compounds from the hexadecane. As a result, the selectivity follows in the order of methanol > DMF > NMF > ethanol.

Table 5. NRTL and UNIQUAC Model Parameters for the Ternary Systems DMF (1) + Either Pyrrole or Aniline or Indole or Quinoline (2) + Hexadecane (3) at T = 298.15 K

	NRTL parameters/K				
system	$i - j$	$(g_{ij} - g_{ii})/R$	$(g_{ji} - g_{jj})/R$	α_{ij}	rmsd
DMF (1) + aniline (2) + hexadecane (3)	1 − 2	−670.71	−168.92	0.20	0.0049
	2 − 3	1379.80	253.50		
	1 − 3	1238.70	348.90		
DMF (1) + Indole (2) + hexadecane (3)	1 − 2	−585.08	191.04	0.20	0.0021
	2 − 3	1043.30	287.98		
	1 − 3	1217.00	331.16		
DMF (1) + pyridine (2) + hexadecane (3)	1 − 2	−11.76	−350.25	0.20	0.0091
	2 − 3	985.02	−301.64		
	1 − 3	1740.60	272.19		
DMF (1) + pyrrole (2) + hexadecane (3)	1 − 2	−328.09	1133.5	0.20	0.0034
	2 − 3	1420.50	87.46		
	1 − 3	1133.50	261.29		
DMF (1) + quinoline (2) + hexadecane (3)	1 − 2	186.00	−380.11	0.20	0.0078
	2 − 3	1056.80	−224.89		
	1 − 3	1568.30	269.27		

Conclusions

Binary LLE data for (DMF + hexadecane) were measured at temperatures ranging from (293.15 to 313.15) K, and ternary tie-line data for five different (DMF + hexadecane) with either quinoline, or pyridine, or pyrrole, or aniline, or indole were measured at a temperature of 298.15 K. The UNIQUAC model gave a slightly better correlation result than the NRTL model with 0.12 % mean deviation of DMF mole fraction for the binary system. The ternary system (DMF + pyridine + hexadecane) is a Treybal's type I having a plait point, while (DMF + hexadecane) with either pyrrole or aniline or indole or quinoline are ternary mixtures of type II, having two partially miscible binaries. The measured systems were also correlated well with the NRTL and UNIQUAC equations, and the root-mean-square-deviations between calculated and measured values are mostly less than a mole fraction of 0.009. The β values of indole, pyrrole, and aniline are greater than that of quinoline and pyridine in the measured systems. Selectivity decreases when going through the tie-line end compositions from low concentration to high concentration of nitrogen-containing compounds.

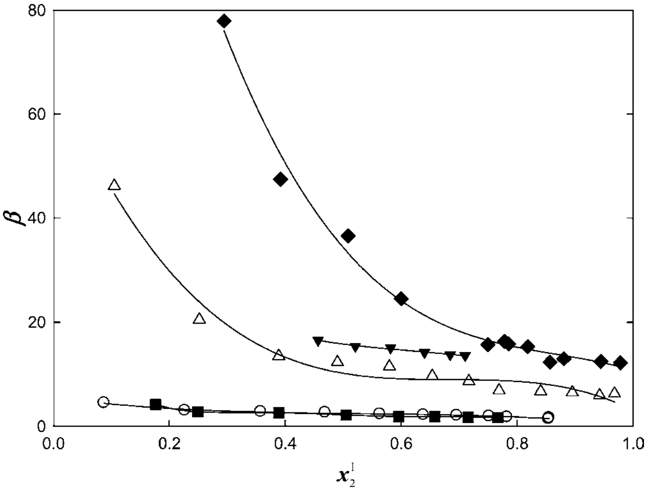

Figure 7. Solute distribution ratio (β) against x_2^{I} for the ternary systems DMF (1) + nitrogen-containing compounds (2) + hexadecane (3) at T = 298.15 K: ○, quinoline; ■, pyridine; △, pyrrole; ◆, aniline; ▼, indole.

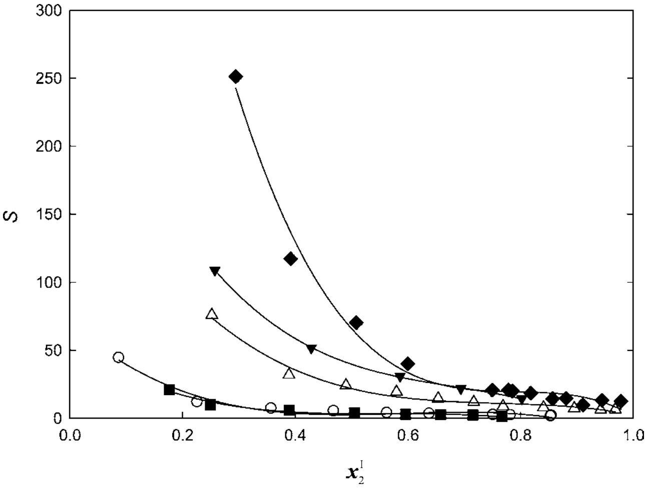

Figure 8. Selectivity (S) against x_2^{I} for the ternary systems DMF (1) + nitrogen-containing compounds (2) + hexadecane (3) at T = 298.15 K: ○, quinoline; ■, pyridine; △, pyrrole; ◆, aniline; ▼, indole.

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Received for review July 21, 2009. Accepted September 8, 2009.

JE9006234