

# Liquid–Liquid Equilibria for the Ternary System Water + Decane + Diethylene Glycol Monobutyl Ether at 20 °C, 30 °C, and 40 °C

Yi-Lu Liu, Bo-Jiun Lin, and Li-Jen Chen\*

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106, Republic of China

Liquid–liquid equilibria measurements of the ternary system water + decane + diethylene glycol monobutyl ether at 20.0, 30.0, and 40.0 °C were made at atmospheric pressure. The experimental data were correlated well with the UNIQUAC model.

## Introduction

Several industrial applications, for example, herbicides, tertiary oil recovery, and the production of drugs,<sup>1,2</sup> need precise liquid–liquid equilibrium data of mixtures of the type water + oil + surfactant. Nonionic surfactants of the homologous series of polyoxyethylene alcohols  $\text{CH}_3(\text{CH}_2)_{i-1}(\text{OCH}_2\text{CH}_2)_j\text{OH}$ , abbreviated by  $\text{C}_i\text{E}_j$ , are widely used as emulsifying agents and detergents. In addition, the phase behavior of mixtures of the type water + oil +  $\text{C}_i\text{E}_j$  also plays an important role in the fundamental research of critical phenomena, phase conductivity, and wetting transitions.<sup>3–7</sup> In our laboratory, we have performed liquid–liquid equilibrium measurements on water +  $\text{C}_i\text{E}_j$  binary systems<sup>8</sup> and four ternary systems: water + dodecane +  $\text{C}_4\text{E}_1$ ,<sup>9</sup> water + octane +  $\text{C}_4\text{E}_2$ ,<sup>10</sup> water + dodecane +  $\text{C}_6\text{E}_2$ ,<sup>11</sup> and water + tetradecane +  $\text{C}_6\text{E}_2$ .<sup>12</sup>

In this study, liquid–liquid equilibrium measurements of the ternary system water + decane + diethylene glycol monobutyl ether ( $\text{C}_4\text{E}_2$ ) were preformed at 20.0 °C, 30.0 °C, and 40.0 °C at atmospheric pressure. The experimental data were further correlated with the universal quasi-chemical (UNIQUAC) model<sup>13</sup> to estimate six effective binary interaction parameters at different temperatures.

## Experimental Section

Decane was obtained from Merck with a purity of 99%. The nonionic surfactant diethylene glycol monobutyl ether was an Aldrich Chemical product with a purity of 99%. These two chemicals were used as received without further purification. Water was purified with a Millipore Milli-RO PLUS 10 and Milli-Q system to a resistivity > 18.2 M $\Omega$ -cm.

All samples were prepared with known compositions and sealed in test tubes with septa. These samples were placed in a homemade, computer controlled thermostat,<sup>9</sup> whose temperature was controlled within  $\pm 0.005$  °C, and left for at least 24 h for equilibration. After equilibrium was reached, each phase was withdrawn with a Hamilton syringe and was analyzed with a gas chromatograph (China Chromatography 9800, Taiwan) equipped with a thermal conductivity detector and connected to an integrator (C-R6A, Chromatopac, Shimadzu Co., Japan). The temperatures of the injector port and the thermal conductivity detector were held at 270 °C and 300 °C, respectively. The flow rate of the carrier gas, helium, was maintained

**Table 1. Average Deviations of Calibration Curves of the Gas Chromatograph**

binary system	conc <sup>a</sup> range of $\text{C}_4\text{E}_2$	avg error <sup>b</sup>
water + $\text{C}_4\text{E}_2$	0.6940–1	0.0003
	0–0.7951	0.0006
decane + $\text{C}_4\text{E}_2$	0.8501–1	0.0002
	0–0.9096	0.0008

<sup>a</sup> Mass fraction. <sup>b</sup> Average error =  $(1/N)\sum_{i=1}^N |w_i^{\text{cal}} - w_i^{\text{act}}|$ , where  $N$  is the number of calibration points and  $w$  is the mass fraction of  $\text{C}_4\text{E}_2$ . The superscript cal stands for the calculated value from the calibration curve, and the superscript act refers to the actual value.

at 60 mL·min<sup>-1</sup>. The oven temperature was initially held at 195 °C and then raised to a final temperature of 240 °C at a speed of 10 °C·min<sup>-1</sup> after 2 min. The sample was separated in a 2 m long  $\times$  3.175 mm diameter stainless steel column packed with Poropak P 80/100 mesh. Each analysis took about 10 min. Single-phase binary mixtures, water +  $\text{C}_4\text{E}_2$  and decane +  $\text{C}_4\text{E}_2$ , with known compositions were used to calibrate the instrument in the composition range of interest. The calibration results were further fitted to a polynomial equation. The deviations of the calibration curves from the actual values are tabulated in Table 1.

For each tie line, three samples were prepared at the same mass fraction. After equilibration, at least three gas chromatograph measurements were performed for each phase in every sample. The reported value was an average over three samples. The experimental uncertainty among three samples was within  $\pm 0.0008$  mass fraction.

When the water content in the oil-rich phase was very low, a Karl Fischer moisture titrator (MKC-210, Kyoto Electronics Co., Japan) was used to determine the water content in these phases. The experimental uncertainty of the Karl Fischer moisture measurements was within  $\pm 0.00002$  mass fraction for the water content.

## Results and Discussion

For the ternary system water + decane +  $\text{C}_4\text{E}_2$ , there is only one two-liquid-phase-coexisting region in the triangle phase diagram of the system at 20 °C, 30 °C, and 40 °C, as shown in Figures 1–3. Tables 2–4 give all the experimental data of the tie lines. In Figures 1–3, the symbol filled triangle stands for the prescribed total composition of each tie line. The fitting coefficient of a linear expression to each tie line and its corresponding total composition data point is always better than 0.999, indicating the consistency of our experimental data.

\* Corresponding author. E-mail: ljchen@ccms.ntu.edu.tw.

**Table 2. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Decane (2) + C<sub>4</sub>E<sub>2</sub> (3) at 20.0 °C**

experimental data				calculated results			
oil-rich phase		water-rich phase		oil-rich phase		water-rich phase	
W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>
0.000 18	0.0129	0.8317	0.1683	0.000 17	0.0130	0.8270	0.1725
0.000 22	0.0134	0.7539	0.2461	0.000 22	0.0161	0.7477	0.2514
0.000 26	0.0165	0.6724	0.3252	0.000 26	0.0179	0.6748	0.3237
0.000 31	0.0183	0.5733	0.4211	0.000 29	0.0197	0.5767	0.4199
0.000 31	0.0198	0.4972	0.4932	0.000 32	0.0208	0.5017	0.4920
0.000 32	0.0221	0.3941	0.5882	0.000 37	0.0231	0.3980	0.5876
0.000 35	0.0236	0.3301	0.6444	0.000 42	0.0254	0.3315	0.6439
0.000 44	0.0270	0.2773	0.6874	0.000 46	0.0280	0.2795	0.6833
0.000 48	0.0330	0.2068	0.7346	0.000 60	0.0345	0.2035	0.7287
0.000 80	0.0458	0.1380	0.7621	0.000 83	0.0461	0.1353	0.7487
0.001 29	0.0600	0.1033	0.7538	0.001 00	0.0562	0.1003	0.7446
0.008 4	0.2000	0.0413	0.5958	0.001 39	0.0878	0.0490	0.7053
				0.000 64	0.0107	0.0038	0.0131

avg error:  $\sum_{i=1}^N |W_i^{\text{exp}} - W_i^{\text{calc}}|/N$ .  
The symbol  $N$  is the number of tie lines.

**Table 3. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Decane (2) + C<sub>4</sub>E<sub>2</sub> (3) at 30.0 °C**

experimental data				calculated results			
oil-rich phase		water-rich phase		oil-rich phase		water-rich phase	
W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>
0.000 23	0.0195	0.8333	0.1667	0.000 12	0.0101	0.8250	0.1747
0.000 27	0.0212	0.7530	0.2470	0.000 18	0.0133	0.7455	0.2538
0.000 32	0.0228	0.6507	0.3454	0.000 24	0.0166	0.6443	0.3540
0.000 33	0.0241	0.5672	0.4257	0.000 29	0.0191	0.5656	0.4312
0.000 35	0.0263	0.4820	0.5055	0.000 36	0.0221	0.4835	0.5100
0.000 37	0.0278	0.4151	0.5659	0.000 42	0.0252	0.4183	0.5703
0.000 43	0.0315	0.3321	0.6384	0.000 55	0.0308	0.3328	0.6436
0.000 44	0.0333	0.2865	0.6740	0.000 62	0.0346	0.2883	0.6772
0.000 60	0.0382	0.2405	0.7059	0.000 79	0.0410	0.2382	0.7091
0.000 76	0.0471	0.1747	0.7422	0.001 09	0.0535	0.1723	0.7352
0.001 62	0.0679	0.1191	0.7457	0.001 54	0.0729	0.1160	0.7325
0.004 0	0.1199	0.0752	0.6976	0.003 0	0.1141	0.0756	0.7010
				0.000 19	0.0048	0.0033	0.0061

avg error:  $\sum_{i=1}^N |W_i^{\text{exp}} - W_i^{\text{calc}}|/N$ .  
The symbol  $N$  is the number of tie lines.

**Table 4. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Decane (2) + C<sub>4</sub>E<sub>2</sub> (3) at 40.0 °C**

experimental data				calculated results			
oil-rich phase		water-rich phase		oil-rich phase		water-rich phase	
W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>	W <sub>1</sub>	W <sub>3</sub>
0.000 38	0.0276	0.8425	0.1575	0.000 13	0.0123	0.8261	0.1729
0.000 41	0.0303	0.7624	0.2376	0.000 19	0.0159	0.7476	0.2507
0.000 41	0.0311	0.6853	0.3109	0.000 23	0.0187	0.6743	0.3229
0.000 42	0.0321	0.6227	0.3704	0.000 27	0.0210	0.6110	0.3847
0.000 45	0.0334	0.5391	0.4492	0.000 33	0.0239	0.5332	0.4593
0.000 46	0.0351	0.4595	0.5228	0.000 40	0.0273	0.4585	0.5288
0.000 48	0.0375	0.4096	0.5668	0.000 45	0.0304	0.4047	0.5766
0.000 53	0.0401	0.3367	0.6300	0.000 57	0.0362	0.3339	0.6349
0.000 70	0.0440	0.2728	0.6780	0.000 74	0.0442	0.2692	0.6809
0.000 81	0.0478	0.2379	0.7010	0.000 86	0.0503	0.2333	0.7018
0.000 85	0.0551	0.1979	0.7229	0.001 08	0.0597	0.1942	0.7188
0.001 41	0.0659	0.1539	0.7362	0.001 42	0.0748	0.1504	0.7274
0.002 8	0.0999	0.1006	0.7189	0.002 1	0.1033	0.1021	0.7150
				0.000 16	0.0078	0.0066	0.0082

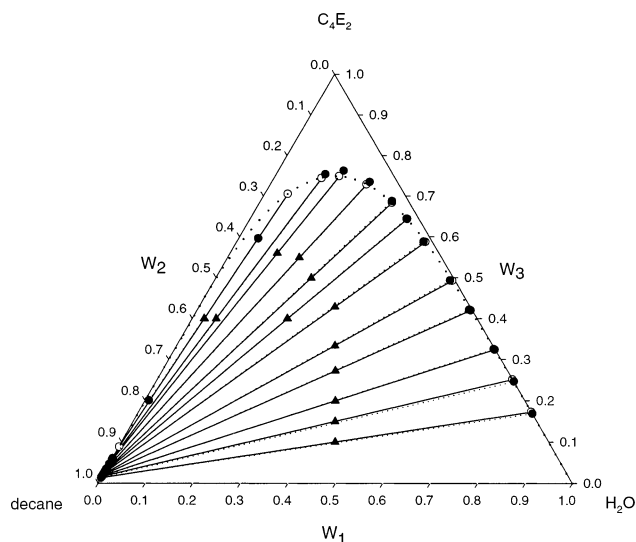
avg error:  $\sum_{i=1}^N |W_i^{\text{exp}} - W_i^{\text{calc}}|/N$ .  
The symbol  $N$  is the number of tie lines.

Note that the surfactant C<sub>4</sub>E<sub>2</sub> mainly partitions into the lower aqueous phase and the composition of C<sub>4</sub>E<sub>2</sub> is relatively small in the upper oil-rich phase. The body of the two-liquid-phase-coexisting region slightly shrinks along with an increase in temperature, as shown in Figure 4, consistent with previous work for the system water + C<sub>4</sub>E<sub>2</sub> + octane.<sup>10</sup> Kilpatrick et al.<sup>14</sup> pointed out that the partitioning of C<sub>4</sub>E<sub>2</sub> between aqueous and oil-rich phases is fairly insensitive to alkane chain length. To be more precise, the two-phase region of the mixture water + C<sub>4</sub>E<sub>2</sub> + alkane slightly enlarges along with an increase of oil chain length, as demonstrated in Figure 4.<sup>14</sup>

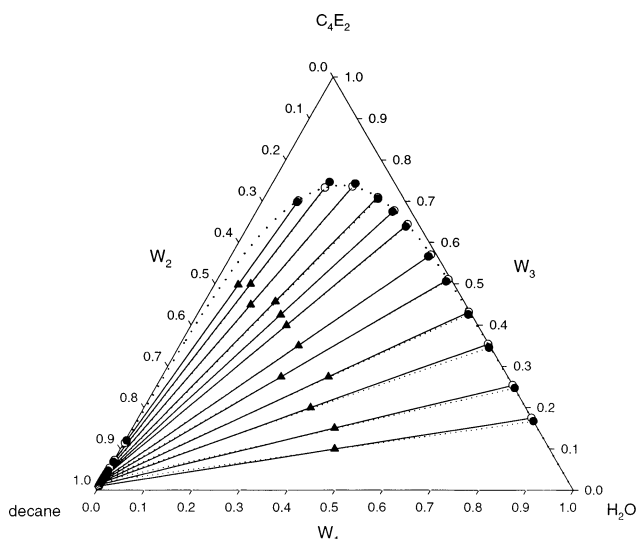
The UNIQUAC model of Abrams and Prausnitz<sup>14</sup> was used to correlate the experimental data. In this study, the relative van der Waals volume  $r_i$  and van der Waals surface area  $q_i$  were adopted from the UNIFAC group contribution of Hansen *et al.*,<sup>15</sup> listed in Table 5. The effective binary interaction parameter,  $a_{ij}$ , is defined by

$$a_{ij} = \frac{u_{ij} - u_{jj}}{R} \quad (1)$$

where  $R$  is the gas constant and  $u_{ij}$  is the UNIQUAC interaction parameter between molecules  $i$  and  $j$ .



**Figure 1.** Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + decane (2) +  $C_4E_2$  (3) at 20.0 °C: experimental tie lines (●, solid line); calculated binodal curve (dotted curve) and tie lines (○, dotted line); total compositions (▲).

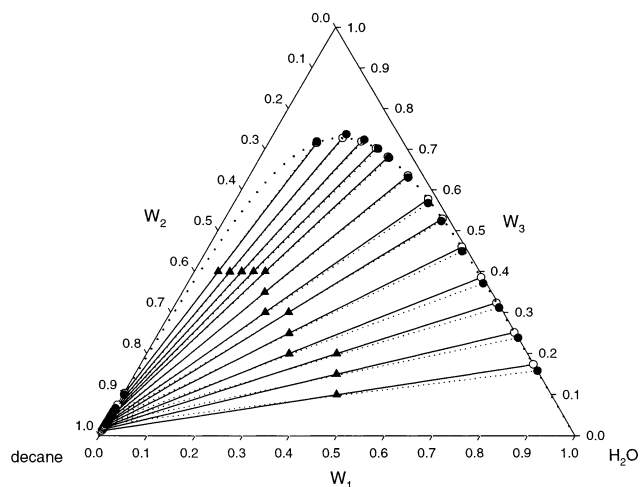


**Figure 2.** Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + decane (2) +  $C_4E_2$  (3) at 30.0 °C: experimental tie lines (●, solid line); calculated binodal curve (dotted curve) and tie lines (○, dotted line); total compositions (▲).

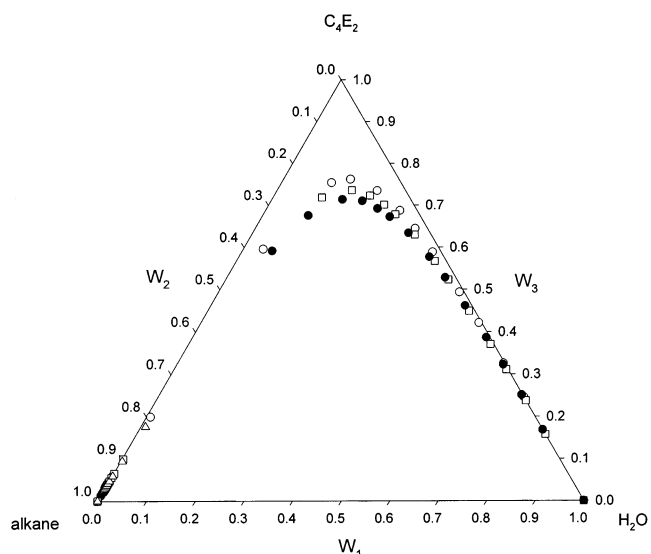
There are two effective binary interaction parameters for each pair of substances. Therefore, six effective binary interaction parameters are required for a ternary system. The six effective binary interaction parameters of the ternary system water + decane +  $C_4E_2$  were determined by numerically minimizing the following objective function.<sup>16</sup>

$$F_x = \sum_{k=1}^2 \sum_{j=1}^3 \sum_{i=1}^3 \left( \frac{X_{ijk}^{\text{exp}} - X_{ijk}^{\text{calc}}}{X_{ijk}^{\text{exp}}} \right)^2 \quad (2)$$

where  $X_{ijk}^{\text{exp}}$  and  $X_{ijk}^{\text{calc}}$  are the experimental and calculated, respectively, mole fractions of component  $i$  in phase  $j$  along a tie line  $k$ . The liquid–liquid equilibrium flash calculation<sup>17</sup> was applied to evaluate the compositions of both liquid phases along each tie line by using the experimental total compositions as input data. As one can see in Figures 1–3, the predicted binodal curve was in very good agreement with the experimental results, except for the very first



**Figure 3.** Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + decane (2) +  $C_4E_2$  (3) at 40.0 °C: experimental tie lines (●, solid line); calculated binodal curve (dotted curve) and tie lines (○, dotted line); total compositions (▲).



**Figure 4.** Experimental binodal curves for the system water (1) + decane (2) +  $C_4E_2$  (3) at 20.0 °C (○) and 40.0 °C (□) and for the system water (1) + octane (2) +  $C_4E_2$  (3) at 20.0 °C (■).

**Table 5.** Relative van der Waals Volume  $r$  and van der Waals Surface Area  $q$ <sup>15</sup>

compound	$r$	$q$
water	0.9200	1.4000
decane	7.1974	6.0160
$C_4E_2$	6.1695	5.0760

**Table 6.** Effective UNIQUAC Interaction Parameters for the System Water (1) + Decane (2) +  $C_4E_2$  (3)

$t$ /°C	$a_{12}$	$a_{21}$	$a_{13}$	$a_{31}$	$a_{23}$	$a_{32}$
20.0	155.4	2451	44.12	-39.12	255.2	-94.81
30.0	177.8	2464	25.19	-58.68	251.2	-104.6
40.0	117.6	2432	-78.17	35.54	236.8	-105.2

tie line next to the  $C_4E_2$ /decane side in Figure 1. It is believed that this tie line is very close to the plait point of the system. It is well understood that the UNIQUAC model is based on mean field theory, which is unable to precisely describe any phase behavior near a critical point, such as a plait point. As consequence, the UNIQUAC model describes this tie line relatively poorly. One may also see the calculated result listed in the bottom line of Table 2.

The subroutine DUMPOL of the IMSL library<sup>18</sup> was used to minimize the objective function  $F_v$ , eq 2. The regression results of the UNIQUAC effective binary interaction parameters are shown in Table 6. The calculated results for each tie line are given in Tables 2–4 to make a comparison with experimental data. As one can see in Figures 1–3, the phase behavior of the system water + decane +  $C_4E_2$  is successfully described by the UNIQUAC model.

### Literature Cited

- (1) Fleming, P. D., III; Vinatieri, J. E. The Role of Critical Phenomena in Oil Recovery Systems Employing Surfactants. *J. Colloid Interface Sci.* **1981**, *81*, 319–331.
- (2) Gullickson, N. D.; Scamehorn, J. F.; Harwell, J. H. In *Surfactant-Based Separation Processes*; Scamehorn, J. F., Harwell, J. F., Eds.; Surfactant Science Series vol. 33; Marcel Dekker: New York, 1989; Chapter 6.
- (3) Kunieda, H.; Friberg, S. E. Critical Phenomena in a Surfactant/Water/Oil System. Basic Study on the Correlation between Solubilization, Microemulsion, and Ultralow Interfacial Tensions. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1010–1014.
- (4) Yeh, M.-C.; Chen, L.-J. Wetting Transitions at the Air–Liquid Interface of Water + Tetradecane +  $C_6E_2$  Mixtures. *J. Chem. Phys.* **2001**, *115*, 8575–8582.
- (5) Chen, L.-J.; Yan, W.-J.; Hsu, M.-C.; Tyan, D.-L. Wetting Transitions at Liquid–Liquid Interfaces in Three-Component Water + Oil + Nonionic Surfactant Systems. *J. Phys. Chem.* **1994**, *98* (8), 1910–1917.
- (6) Chen, L.-J.; Lin, S.-Y.; Xyu, J.-W. Wetting/Nonwetting Behaviors in a Ternary Amphiphilic System. *J. Chem. Phys.* **1996**, *104*, 225–232.
- (7) Kahlweit, M.; Busse, G.; Winkler, J. Electric Conductivity in Microemulsions. *J. Chem. Phys.* **1993**, *99*, 5605–5614.
- (8) Lai, H.-H.; Chen, L.-J. Liquid–Liquid Equilibrium Phase Diagram and Density of Three Water + Nonionic Surfactant  $C_jE_j$  Binary Systems. *J. Chem. Eng. Data* **1999**, *44*, 251–253.
- (9) Lin, B.-J.; Chen, L.-J. Liquid–Liquid Equilibrium for the Ternary System Water + Docecane + Diethylene Glycol Monobutyl Ether. *J. Chem. Eng. Data* **2002**, *47*, 992–996.
- (10) Liu, Y.-L.; Chiou, D.-R.; Chen, L.-J. Liquid–Liquid Equilibrium for the Ternary System Water + Octane + Diethylene Glycol Monobutyl Ether. *J. Chem. Eng. Data* **2002**, *47*, 310–312.
- (11) Hu, H.; Chiu, C.-D.; Chen, L.-J. Liquid–Liquid Equilibria for the Ternary System Water + *n*-Dodecane + 2-(2-*n*-Hexyloxyethoxy)-ethanol. *Fluid Phase Equilib.* **1999**, *164*, 187–194.
- (12) Hu, H.; Chen, L.-J. Liquid–Liquid Equilibria for the Ternary System Water + *n*-Tetradecane + 2-(2-*n*-Hexyloxyethoxy) ethanol at 293.15 K and 303.15 K. *J. Chem. Eng. Data* **2000**, *45*, 304–307.
- (13) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116–128.
- (14) Kilpatrick, P. K.; Gorman, C. A.; Davis, H. T.; Scriven, L. E.; Miller, W. G. Patterns of Phase Behavior in Ternary Ethoxylated Alcohol-*n*-Alkane-Water Mixtures. *J. Phys. Chem.* **1986**, *90*, 5292–5299.
- (15) Hansen, H. K.; Coto, B.; Kuhlmann, B. UNIFAC with Lineary Temperature-Dependent Group-Interaction Parameters, IVC-SEP, Phase Equilibria and Separation Processes, SEP 9212, May, 1992, Danmarks Techniske Universitet, Danmark.
- (16) García-Sánchez, F.; Schwartzentruber, J.; Ammar, M. N.; Renon, H. Modeling of Multiphase Liquid Equilibria for Multicomponent Mixtures. *Fluid Phase Equilib.* **1996**, *121*, 207–225.
- (17) Ammar, M. N.; Renon, H. The Isothermal Flash Problem: New Methods for Phase Split Calculations. *AIChE J.* **1987**, *33*, 926–939.
- (18) *IMSL Math/Library FORTRAN Subroutines for Mathematical Applications*; IMSL, Inc.: Houston, TX, 1991; Chapter 8.

Received for review July 9, 2002. Accepted December 8, 2002. This work was supported by the Chinese Petroleum Company and the National Science Council of Taiwan, Republic of China.

JE0255776