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Liquid−Liquid Equilibria for Binary Systems Containing *N*-Formylmorpholine

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Liquid−liquid equlilibrium (LLE) data were measured for four binary systems containing *N*-formylmorpholine and alkanes (i.e. pentane, hexane, heptane, and octane) over the temperature range 298 K to 413 K using circulation type equipment with an equilibrium view cell. The compositions of both light and heavy phases were analyzed by on-line gas chromatography. The mutual solubility increased as the temperature increased for all these systems. The binary liquid−liquid equilibrium data were correlated with the NRTL and UNIQUAC equations using temperature-dependent parameters. Both models correlate the experimental data well. The solubility in *N*-formylmorpholine increased in the following order at the same temperature: pentane, hexane, heptane, and octane.

Introduction

There have been ever-increasing demands for high-purity aromatic compounds as a feedstock for chemical synthesis. Many solvents such as sulfolane,[1−5] *N*-methylpyrrolidone,[6] glycol,[7,8] and *N*-formylmorpholine[9−11] are used to extract aromatics such as benzene, toluene, and xylene from hydrocarbon mixtures.

The *N*-formylmorpholine extractive distillation process separates aromatics from the reformates. It minimizes aromatic content in gasoline and refines the extracted aromatics, which are used as raw materials for petrochemical processes. This process can recover most of the benzene. The solvent-to-feed ratio by mass of this process is around 3.5. The operating cost and the initial equipment cost for the overall plant can be reduced by optimization. Commercial process simulators such as PROΠ(SimSci), HYSYS (Hyprotech), and ASPEN-PLUS (Aspentech)[12] have been used to determine the optimum solvent rate. However, liquid−liquid equilibrium (LLE) data are not available for these mixtures.

In this work, a newly designed circulating apparatus equipped with a equilibrium view cell and connected directly to a gas chromatograph has been constructed to obtain the equilibrium T, x, x data for the *N*-formylmorpholine (NFM) and *n*-alkane (pentane, hexane, heptane, and octane) systems in the operating temperature range of the NFM extractive distillation process. LLE data for the four binary systems were measured in the temperature range from 298 K to 413 K, and these data were compared with the existing data at different temperatures (293 K to 333 K).[10,11] Experimental data were correlated with the NRTL[13] and UNIQUAC[14] models with the function of temperature-dependent parameters.

Table 1. Suppliers and Purities of the Used Chemicals

chemical	supplier	spec %[a]	purity[b]/%
NFM	ACROS	99+	99.99+
NFM	Samsung Chemical Co., Ltd.	98+	99.14+
pentane	Kanto Chemical Co., Ltd.	99+	99.99+
hexane	Junsei Chemical Co., Ltd.	99.5	99.99+
heptane	Aldrich	99+	99.93+
octane	ACROS	99+	99.94+

[a] The purity reported by the supplier. [b] The purity determined as an area ratio by gas chromatography with a thermal conductivity detector.

Experimental Section

Chemicals. The suppliers and purities of the chemicals are listed in Table 1 together with the purities determined using a HP 5890 gas chromatograph with a thermal conductivity detector. The *N*-formylmorpholine supplied by Samsung Chemical Co., Ltd., was used after distillation and filtration treatment through the 0.45 μm membrane. The rest of the chemicals were used without purification.

Experimental Apparatus. The sampling parts of the recirculation type apparatus used in the previous studies were modified and used in this study.[4,5] A schematic diagram of the apparatus is shown in Figure 1. The system consists of eight major parts: an equilibrium cell, a magnetic pump for circulation, one vapor and two liquid sampling valves, a constant temperature air bath, a magnetic stirrer, a charge−discharge device, temperature and pressure measurement devices, and an analysis system. The volume of the equilibrium cell was 240 cm^3. The cell was made of stainless steel (SUS. 316) and placed inside the air bath, controlled by a PID temperature controller to the desired temperature within ±0.1 K (maximum temperature 573.2 K). The cell and the quartz window were sealed with PTFE (Teflon) gaskets. The mixing was promoted by the magnetic stirrer and magnetic recirculation pumps. The sampling system consists of a sample valve, a sample loop, and a pneumatic actuator. The sample injection valve was a two-position rotary

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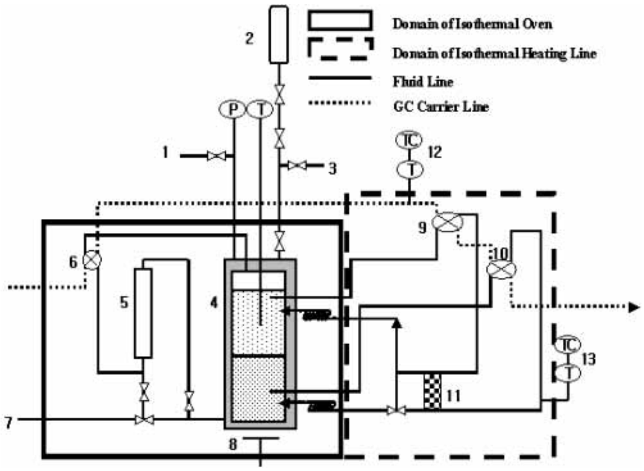

Figure 1. Flow diagram of the apparatus: 1, vacuum line for the removal of air with a vacuum pump; 2, bottle for charging a reagent; 3, air line (8 kg_f/cm^2) for the leak test; 4, equilibrium cell with the view window (quartz); 5, magnetic pump (chromium plating); 6, six-way valve for vapor; 7, discharge line with vacuum; 8, magnetic stirrer; 9, sampling loop for the light phase; 10, sampling loop for the heavy phase; 11, circulating minipump; 12, temperature controller (domain of preheating carrier line); 13, temperature controller (domain of circulating fluid line).

Table 2. Experimental and Calculated LLE Data for the Pentane (1) + *N*-Formylmorpholine (2) System

	top phase, x_{11}			bottom phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
304.49	0.9944	0.9925	0.9934	0.0397	0.0376	0.0380
308.16	0.9907	0.9917	0.9924	0.0415	0.0399	0.0400
313.07	0.9905	0.9904	0.9908	0.0432	0.0432	0.0430
317.88	0.9901	0.9890	0.9891	0.0455	0.0467	0.0463
322.86	0.9895	0.9874	0.9871	0.0497	0.0506	0.0501
327.57	0.9856	0.9857	0.9850	0.0555	0.0545	0.0539
333.28	0.9813	0.9833	0.9822	0.0573	0.0596	0.0592
338.01	0.9771	0.9810	0.9796	0.0606	0.0643	0.0639
342.83	0.9748	0.9785	0.9767	0.0650	0.0693	0.0692
348.02	0.9711	0.9754	0.9734	0.0717	0.0752	0.0753
352.23	0.9680	0.9726	0.9705	0.0827	0.0803	0.0807
357.79	0.9654	0.9684	0.9665	0.0899	0.0877	0.0883
363.45	0.9643	0.9635	0.9621	0.0952	0.0958	0.0967
368.48	0.9591	0.9586	0.9579	0.1022	0.1038	0.1048
373.60	0.9516	0.9529	0.9535	0.1128	0.1126	0.1136
378.41	0.9496	0.9469	0.9492	0.1262	0.1217	0.1224
383.17	0.9468	0.9401	0.9448	0.1376	0.1315	0.1317
388.10	0.9455	0.9323	0.9401	0.1494	0.1426	0.1419

Table 3. Experimental and Calculated LLE Data for the Hexane (1) + *N*-Formylmorpholine (2) System

	top phase, x_{11}			bottom phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
299.46	0.9865	0.9853	0.9850	0.0311	0.0319	0.0330
306.31	0.9826	0.9833	0.9832	0.0346	0.0337	0.0340
314.24	0.9797	0.9808	0.9809	0.0365	0.0360	0.0355
324.31	0.9756	0.9770	0.9774	0.0408	0.0395	0.0384
333.24	0.9737	0.9733	0.9737	0.0428	0.0430	0.0417
344.01	0.9689	0.9680	0.9684	0.0452	0.0481	0.0469
353.74	0.9641	0.9623	0.9626	0.0523	0.0536	0.0529
363.47	0.9536	0.9557	0.9557	0.0589	0.0603	0.0606
374.03	0.9488	0.9470	0.9464	0.0730	0.0694	0.0711
383.69	0.9363	0.9372	0.9360	0.0848	0.0801	0.0835
394.37	0.9252	0.9232	0.9215	0.0947	0.0963	0.1010
402.95	0.9060	0.9079	0.9067	0.1135	0.1154	0.1192
413.33	0.8785	0.8792	0.8835	0.1597	0.1600	0.1479

Table 4. Experimental and Calculated LLE Data for the Heptane (1) + *N*-Formylmorpholine (2) System

	top phase, x_{11}			bottom phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
301.12	0.9889	0.9903	0.9902	0.0244	0.0249	0.0251
311.31	0.9871	0.9864	0.9864	0.0256	0.0263	0.0262
319.37	0.9847	0.9826	0.9826	0.0288	0.0278	0.0276
329.08	0.9801	0.9769	0.9770	0.0310	0.0301	0.0299
339.00	0.9658	0.9696	0.9698	0.0339	0.0331	0.0330
343.75	0.9637	0.9656	0.9657	0.0350	0.0348	0.0347
358.43	0.9463	0.9504	0.9506	0.0380	0.0412	0.0413
368.50	0.9347	0.9373	0.9374	0.0481	0.0469	0.0472
373.48	0.9320	0.9299	0.9300	0.0512	0.0502	0.0505
378.02	0.9213	0.9226	0.9226	0.0545	0.0535	0.0539
387.64	0.9121	0.9051	0.9050	0.0605	0.0617	0.0620
398.85	0.8774	0.8809	0.8806	0.0701	0.0736	0.0736
403.46	0.8753	0.8696	0.8691	0.0786	0.0795	0.0792
412.16	0.8422	0.8456	0.8451	0.0969	0.0924	0.0913

Table 5. Experimental and Calculated LLE Data for the Octane (1) + *N*-Formylmorpholine (2) System

	top phase, x_{11}			bottom phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
297.00		0.9850	0.9842	0.0120	0.0143	0.0148
305.67		0.9811	0.9808	0.0171	0.0165	0.0166
308.20	0.9730	0.9798	0.9797	0.0214	0.0172	0.0172
313.10	0.9729	0.9772	0.9775	0.0197	0.0187	0.0184
322.80	0.9712	0.9716	0.9724	0.0205	0.0218	0.0213
332.68	0.9634	0.9651	0.9664	0.0233	0.0255	0.0248
342.48	0.9615	0.9580	0.9595	0.0326	0.0297	0.0290
353.22	0.9530	0.9492	0.9505	0.0342	0.0351	0.0348
362.83	0.9463	0.9406	0.9411	0.0403	0.0408	0.0411
372.50	0.9351	0.9309	0.9301	0.0457	0.0477	0.0487
384.17	0.9161	0.9175	0.9143	0.0573	0.0579	0.0603
392.83	0.8990	0.9058	0.9003	0.0683	0.0678	0.0710
402.27	0.8806	0.8893	0.8824	0.0800	0.0820	0.0852
413.66	0.8523	0.8553	0.8560	0.1127	0.1102	0.1072
416.18	0.8452	0.8389	0.8493	0.1211	0.1203	0.1129

switching valve with an internal sample loop of 0.5 μL. This was connected with the pneumatic actuator that actuates positions. The actuator was operated with a solenoid valve. The vacuum pump was used for discharge of the mixture. The temperature was measured using a sheath type 100 Ω-platinum resistance thermometer. Its uncertainty was estimated to be within 0.05 K. The sampling system was connected to a gas chromatograph (Hewlett-Packard 5890 Series Π) which had a thermal conductivity detector (TCD) and a 1.828 8 m × 0.003 175 m column packed with Chromosorb WHP 100/120 coated with OV-101. The liquid-phase compositions were determined with a maximum relative error of 0.1%.

Experimental Procedure. The mixture was fed into the equilibrium cell that was initially evacuated. The mixture was stirred for at least 1 h with the magnetic stirrer and then left to settle for at least 2 h. The samples were analyzed by gas chromatography. The temperatures of the injector and the detector were maintained at 523.15 K. After 1 min of holding at 353.15 K, the column temperature was raised to the final temperature of 423.15 K at the rate of 25 $K\cdot min^{-1}$. Helium was used as the carrier gas at the rate of 23 $cm^3\cdot min^{-1}$. Single-phase samples of known composition were used to calibrate the gas chromatograph in the composition range of interest. The analysis for the calibration indicated that a precision of $\pm 3 \times 10^{-5}$ area ratio was obtained for each composition. The samples of each phase at the same temperature were analyzed three times at least, and the average values were used. The average deviation of the area ratio is $\pm 3 \times 10^{-5}$.

Results and Discussion

The experimental liquid−liquid equilibrium data for the systems pentane (1) + *N*-formylmorpholine (2), hexane (1) + *N*-formylmorpholine (2), heptane (1) + *N*-formylmorpholine (2), and octane (1) + *N*-formylmorpholine (2) are given in Tables 2−5 and Figures 2−5. Concentrations of compo-

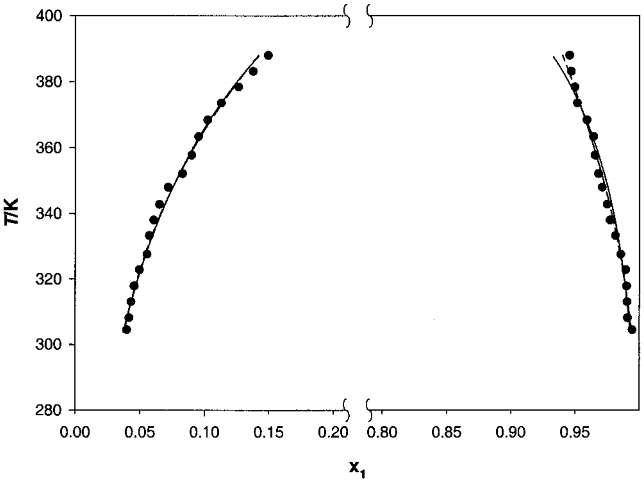

Figure 2. Experimental and calculated liquid–liquid equilibrium data for the pentane (1) + *N*-formylmorpholine (2) mixture: points, experimental results; solid line, NRTL with α = 0.3; dashed line, UNIQUAC.

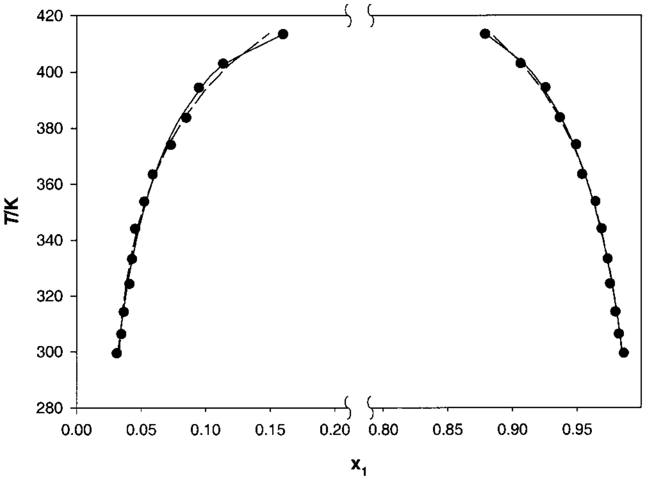

Figure 3. Experimental and calculated liquid–liquid equilibrium data for the hexane (1) + *N*-formylmorpholine (2) mixture: points, experimental results; solid line, NRTL with α = 0.3; dashed line, UNIQUAC.

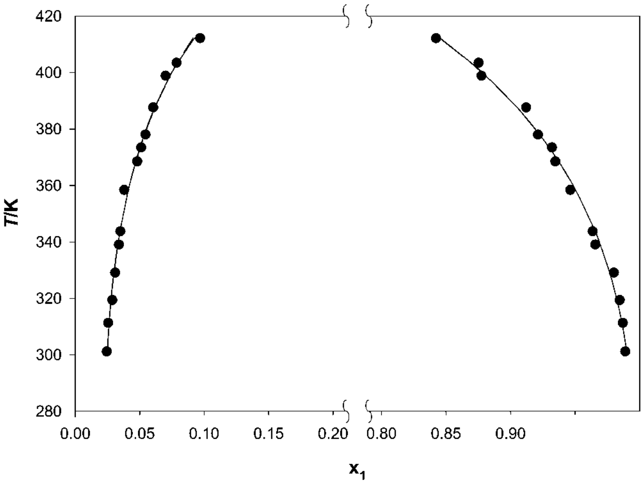

Figure 4. Experimental and calculated liquid–liquid equilibrium data for the heptane (1) + *N*-formylmorpholine (2) mixture: points, experimental results; solid line, NRTL with α = 0.3; dashed line, UNIQUAC.

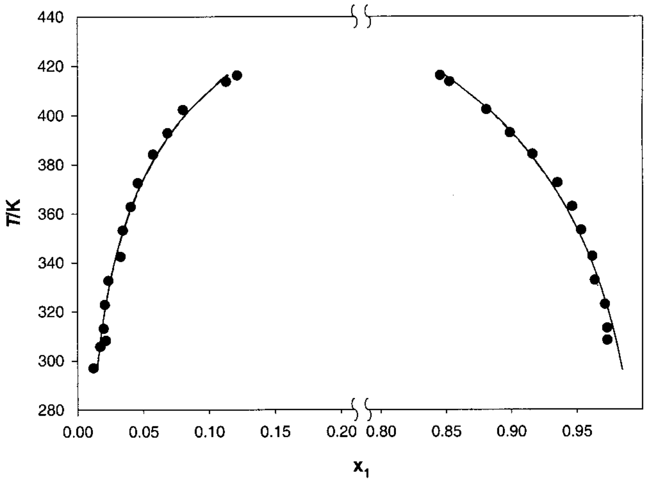

Figure 5. Experimental and calculated liquid–liquid equilibrium data for the octane (1) + *N*-formylmorpholine (2) mixture: points, experimental results; solid line, NRTL with α = 0.3; dashed line, UNIQUAC.

Table 6. Temperature Dependence of the Parameters of the NRTL Equation for the *n*-Alkane (1) + *N*-Formylmorpholine (2) Binary Systems[a]

parameter	pentane	hexane	heptane	octane
a_{12}	−3.462 66	−10.695 26	−62.593 35	−27.818 91
a_{21}	−1.561 02	37.690 74	71.964 65	40.841 01
b_{12}/K	2240.924 69	1555.790 02	5137.815 99	3089.473 48
b_{21}/K	1244.168 79	−1440.303 61	−2902.831 30	−719.764 15
d_{21}/K^{-1}	0.000 34	0.000 89	0.000 50	−0.000 42
$e_{12}/(\ln \mathrm{K})^{-1}$	0.002 79	1.553 54	8.621 37	3.607 94
$e_{21}/(\ln \mathrm{K})^{-1}$	−0.000 55	−5.292 13	−10.415 88	−6.189 97

[a] $c_{12} = c_{21} = 0.3$; $d_{12}/\mathrm{K}^{-1} = 0$.

nents *i* in phase *j* (*j* = 1, top phase; *j* = 2, bottom phase) are given in the mole fraction x_{ij}. The binary liquid–liquid equilibrium data were correlated with the NRTL and UNIQUAC equations.

The binary parameters have the temperature dependence function

for the NRTL model:

$$\tau_{ij} = a_{ij} + b_{ij}/T + e_{ij} \ln T \qquad (1)$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15\ \mathrm{K}) \qquad (2)$$

where τ_{ij} is dimensionless and *T* is in kelvin.

for the UNIQUAC model:

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T + c_{ij} \ln T) \qquad (3)$$

The binary parameters for the models were evaluated by a nonlinear regression method based on the maximum-likelihood principle. The objective function was minimized during optimization of the parameters in each of the equations:

$$\mathrm{OF} = \sum_{k=1}^{N} \left\{ \left(\frac{T_k^{\mathrm{cal}} - T_k^{\mathrm{exp}}}{\sigma_{T_k}} \right)^2 + \sum_{i=1}^{2} \sum_{j=1}^{2} \left(\frac{x_{ij}^{\mathrm{cal}} - x_{ij}^{\mathrm{exp}}}{\sigma_{x_{ijk}}} \right)^2 \right\} \qquad (4)$$

where *N* is the number of experimental data points in each group *k*.

The four resulting NRTL and UNIQUAC parameters optimized for the liquid–liquid equilibrium data are listed in Tables 6 and 7. The absolute average deviations of the NRTL and UNIQUAC equations are listed in Table 8. The NRTL model showed slightly smaller deviations in the

Table 7. Temperature Dependence of the Parameters of the UNIQUAC Equation for the *n*-Alkane (1) + *N*-Formylmorpholine (2) Binary Systems

parameter	pentane	hexane	heptane	octane
a_{12}	59.653 86	8.355 16	23.909 00	14.715 76
a_{21}	−33.994 93	−34.691 92	−18.803 55	−20.092 80
b_{12}/K	−3501.076 52	−768.568 26	−1910.536 76	−1084.385 20
b_{21}/K	1549.879 87	1657.696 94	1105.737 43	885.630 03
$c_{12}/(\ln K)^{-1}$	−8.577 48	−1.142 97	−3.240 34	−2.077 96
$c_{21}/(\ln K)^{-1}$	4.974 10	5.039 81	2.603 71	2.944 10

Table 8. Absolute Average Deviations (AAD%)[a] of the NRTL and UNIQUAC Equations for the *n*-Alkane (1) + *N*-Formylmorpholine (2) Binary Systems

	x_{11}		x_{12}	
system	NRTL	UNIQUAC	NRTL	UNIQUAC
pentane + NFM	0.30	0.19	3.19	3.06
hexane + NFM	0.14	0.17	2.72	3.85
heptane + NFM	0.33	0.33	2.90	3.08
octane + NFM	0.47	0.36	5.78	7.36

[a] AAD% = $(1/N)\sum_{i=1}^{N} |(x_{1,\mathrm{cal}} - x_{1,\mathrm{exp}})/x_{1,\mathrm{exp}}| \times 100$.

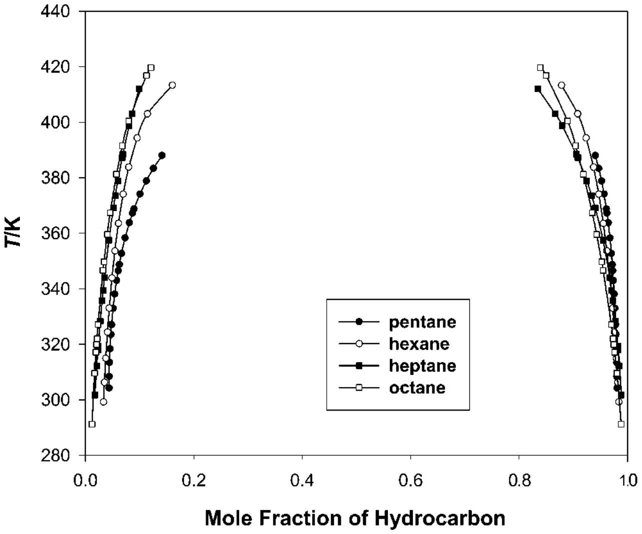

Figure 6. Mutual solubility for the *N*-formylmorpholine and nonaromatic mixtures.

bottom phase. However, in the top phase, the UNIQUAC model has smaller deviations. The mutual solubility increased as the temperature increased in all these systems. The solubility of *n*-paraffin in *N*-formylmorpholine, that is, the bottom phase, increased in the following order at the same temperature: pentane, hexane, heptane, and octane. The results are displayed in Figure 6.

Conclusions

In this work, we have determined the interaction parameters of the NRTL and UNIQUAC equations for the *N*-formylmorpholine + *n*-alkane systems (i.e. pentane, hexane, heptane, and octane) from experimental binary liquid−liquid equilibrium data at 331.15 K up to 413.15 K. The temperature dependency of the parameters of NRTL and UNIQUAC models can be expressed by eqs 1 and 3, respectively. Thus, a quantitative description of liquid−liquid equilibria of industrial interest containing *N*-formylmorpholine and *n*-alkanes is available to accurately simulate and optimize the extractive distillation units where these systems are involved.

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