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Liquid−Liquid Equilibria for the Binary Systems of *N*-Formylmorpholine with Branched Cycloalkanes

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Liquid−liquid equilibrium (LLE) data were measured for three binary systems containing *N*-formylmorpholine and branched cycloalkanes (methylcyclopentane, methylcyclohexane, and ethylcyclohexane) over the temperature range around 300 K to close to the upper critical solution temperature (UCST) using circulation type equipment with an equilibrium view cell. The compositions of both branched cycloalkane rich and *N*-formylmorpholine rich phases were analyzed by on-line gas chromatography. The binary liquid−liquid equilibrium data were correlated with the NRTL and UNIQUAC equations using temperature-dependent parameters. Although clear deviation was observed in the vicinity of the UCST, the NRTL and UNIQUAC equations fitted the experimental data well. The solubility of cycloalkane in the *N*-formylmorpholine increases in the following order at the same temperature: methylcyclopentane, methylcyclohexane, and ethylcyclohexane.

Introduction

Many pairs of liquids of industrial importance have limited mutual solubilities. Liquid−liquid equilibrium (LLE) data are essential when considering separation processes. Recently, there have been ever-increasing demands for high-purity aromatic compounds as a feedstock for chemical synthesis. The aromatics are obtained by separating out the reformates, which are the products of catalytic reforming of naphtha. Extractive distillation and extraction processes are used to separate aromatics from hydrocarbon mixtures, especially to recover aromatics from reformates. Also, many solvents such as sulfolane,[1−5] *N*-methylpyrrolidone,[6] glycol,[7,8] and *N*-formylmorpholine[9−11] are used in these processes. The extractive distillation process using *N*-formylmorpholine as a solvent is suitable for aromatics separation from reformates.[12] This process minimizes aromatic content in gasoline and refines the extracted aromatics, which are used as raw materials for petrochemical processes.

These days, commercial simulators are used for optimization of chemical processes. The optimum variable in the extractive distillation unit is a solvent-to-feed ratio. The operating cost and the initial equipment cost for the overall plant can be reduced by optimizing the solvent-to-feed ratio. Binary LLE data containing *N*-formylmorpholine for wide temperature ranges have become necessary because of the extractive distillation process to separate aromatics from hydrocarbon mixtures.[13] However, LLE data for these mixtures are not available in the literature and the databank of simulators.

The liquid−liquid equilibria for the *N*-formylmorpholine and branched cycloalkane (methylcyclopentane, methylcyclohexane, and ethylcyclohexane) binary systems were measured in the temperature range from about 300 K to the vicinity of the upper critical solution temperature (UCST). Experimental data were correlated with the nonrandom two-liquid (NRTL)[14] and universal quasi-chemical (UNIQUAC)[15] models with the temperature-dependent parameters.

Table 1. Suppliers and Purity of the Used Chemicals

chemical	supplier	spec %[a]	purity %[b]
N-formylmorpholine	ACROS	>99.00	>99.99
methylcyclopentne	ACROS	>95.00	>99.15
methylcyclohexane	Junsei Chemical Co., Inc.	>99.00	>99.89
ethylcyclohexane	ACROS	>99.00	>99.94

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

Experimental Section

Chemicals. The chemicals were purchased and further purified with molecular sieves 13X. The suppliers and specification of the chemicals are listed in Table 1 together with the purities after purification, as determined using a HP 5890 gas chromatograph with a thermal conductivity detector.

Experimental Apparatus. Details of this apparatus are given in our previous studies.[16] 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. The air bath temperature was controlled by a PID temperature controller to the desired temperature within ±0.1 K. And then, the fine control of the cell temperature within ±0.006 K was allowed by the flow rate of circulating-liquids with the circulating minipump. The cell temperature was measured using a platinum resistance thermometer (1502A by Hart Scientific, Inc). Its uncertainty was estimated to

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

	methylcyclopentane rich phase, x_{11}			NFM rich phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
300.27	0.9835	0.9829	0.9828	0.0673	0.0687	0.0689
311.55	0.9751	0.9771	0.9771	0.0806	0.0773	0.0772
319.28	0.9712	0.9721	0.9722	0.0880	0.0848	0.0847
328.84	0.9669	0.9646	0.9647	0.0942	0.0965	0.0964
338.80	0.9561	0.9548	0.9549	0.1057	0.1122	0.1122
348.93	0.9447	0.9419	0.9420	0.1329	0.1330	0.1331
358.33	0.9253	0.9264	0.9264	0.1539	0.1581	0.1583
368.06	0.8991	0.9051	0.9051	0.1903	0.1923	0.1925
373.19	0.8896	0.8908	0.8907	0.2217	0.2149	0.2151
378.18	0.8751	0.8741	0.8740	0.2544	0.2409	0.2410
383.12	0.8562	0.8538	0.8536	0.2789	0.2717	0.2717
387.07	0.8323	0.8337	0.8336	0.3073	0.3012	0.3010
390.95	0.8114	0.8094	0.8094	0.3340	0.3358	0.3355
395.44	0.7693	0.7720	0.7721	0.3816	0.3866	0.3866
398.73	0.7344	0.7332	0.7327	0.4210	0.4363	0.4363

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

	methylcyclohexane rich phase, x_{11}			NFM rich phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
301.24	0.9784	0.9782	0.9784	0.0626	0.0609	0.0629
309.04	0.9787	0.9776	0.9778	0.0672	0.0677	0.0686
323.96	0.9758	0.9744	0.9744	0.0797	0.0831	0.0822
335.97	0.9679	0.9712	0.9693	0.0984	0.0984	0.0966
345.80	0.9590	0.9631	0.9628	0.1086	0.1137	0.1115
352.48	0.9521	0.9572	0.9568	0.1268	0.1261	0.1237
362.06	0.9484	0.9453	0.9447	0.1511	0.1477	0.1456
372.11	0.9362	0.9262	0.9256	0.1850	0.1776	0.1765
376.82	0.9247	0.9136	0.9131	0.2083	0.1955	0.1951
381.88	0.9067	0.8962	0.8958	0.2292	0.2189	0.2193
387.54	0.8713	0.8697	0.8698	0.2539	0.2519	0.2537
392.81	0.8285	0.8345	0.8354	0.2860	0.2933	0.2965
398.53	0.7584	0.7743	0.7771	0.3382	0.3597	0.3650
401.17	0.7096	0.7304	0.7347	0.3978	0.4065	0.4127
402.28	0.6905	0.7054	0.7104	0.4205	0.4319	0.4387

be within ±0.006 K. The cell and the quartz window were sealed with PTFE (Teflon) gaskets. The magnetic stirrer promoted the mixing. The cell temperature is controlled using the two methods. The thermometer was calibrated at the ice point and by comparison to standard platinum thermometers (SPRTs) calibrated on the basis of the international temperature scale of 1990 (ITS-90). The sampling system was connected to a gas chromatograph (Hewlett-Packard 5890 Series II) with a thermal conductivity detector (TCD) and a 1.828 m × 0.003 175 m column packed with Chromosorb WHP 100/120 coated with OV-101.

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. Each phase was circulated with recirculation pumps for 1 h. The sampling was made when the cell temperature change was within ±0.02 K for 10 min. The samples were analyzed by gas chromatography. The temperatures of the injector and the detector were maintained at 523.15 K. After 1 min holding at 353.15 K, the column temperature was raised to the final temperature of 423.15 K at the rate of 25 K·min^{-1}. Helium was used as the carrier gas at the rate of 23 cm^3·min^{-1}. Single-phase samples of known composition were used to calibrate the gas chromatograph in the composition range of interest. The samples of each phase at the same temperature were analyzed at least three times, and the average values were used. The average error of duplicating sample analysis is 0.1%.

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

	ethylcyclohexane rich phase, x_{11}			NFM rich phase, x_{12}		
T/K	exp	NRTL	UNIQUAC	exp	NRTL	UNIQUAC
297.85	0.9797	0.9773	0.9776	0.0274	0.0263	0.0273
311.01	0.9756	0.9760	0.9764	0.0347	0.0357	0.0358
319.70	0.9714	0.9742	0.9745	0.0417	0.0432	0.0428
329.05	0.9679	0.9712	0.9714	0.0494	0.0528	0.0519
338.63	0.9655	0.9669	0.9668	0.0628	0.0644	0.0632
348.67	0.9619	0.9605	0.9601	0.0802	0.0791	0.0777
358.01	0.9537	0.9521	0.9514	0.1031	0.0957	0.0944
362.87	0.9502	0.9464	0.9456	0.1123	0.1058	0.1047
368.63	0.9390	0.9383	0.9373	0.1299	0.1194	0.1186
372.44	0.9316	0.9319	0.9308	0.1395	0.1295	0.1291
378.41	0.9210	0.9196	0.9184	0.1489	0.1477	0.1479
383.34	0.9078	0.9068	0.9057	0.1589	0.1655	0.1662
387.97	0.8937	0.8920	0.8910	0.1763	0.1851	0.1864
392.81	0.8716	0.8724	0.8719	0.1951	0.2096	0.2116
397.46	0.8518	0.8483	0.8485	0.2261	0.2383	0.2410
403.13	0.8220	0.8076	0.8097	0.2652	0.2842	0.2875
407.64	0.7737	0.7604	0.7651	0.3214	0.3357	0.3385
408.62	0.7306	0.7471	0.7527	0.3629	0.3497	0.3526
409.63	0.6944	0.7319	0.7385	0.3966	0.3658	0.3680

Results and Discussion

The measurement for the three systems methylcyclopentane (1) + *N*-formylmorpholine (2), methylcyclohexane (1) + *N*-formylmorpholine (2), and ethylcyclohexane (1) + *N*-formylmorpholine (2) were performed within the range of about 300 K to the vicinity of the upper critical solution temperature (UCST). The experimental data are given in Tables 2−4.

The binary liquid−liquid equilibrium data were correlated using the NRTL and UNIQUAC models. NRTL and UNIQUAC models could not correlate the binary LLE data in the vicinity of the critical temperature because of the nonanalytical behavior with the flat slopes of the two branches of the coexistence curve near the critical region. Therefore, these models were modified to use the binary interaction parameters with temperature dependency. Different expressions for describing the temperature dependency of the binary interaction parameter of these models are found in the literature and commercial software.[17−21] In this work, temperature-dependent binary interaction parameters suggested by Aspen Technology Inc. were chosen.[21] The excess Gibbs energy for the binary systems of NRTL and UNIQUAC models is expressed by the following equations

NRTL model:

$$\frac{g^{\mathrm{E}}}{RT} = x_1 x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right) \tag{1}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), \quad \alpha_{12} = \alpha_{21} \tag{2}$$

$$\tau_{12} = a_{12} + b_{12}/T + c_{12}\ln T \tag{3}$$

where x is the mole fraction, α_{12} ($=\alpha_{21}$) is the nonrandomness parameter, and τ_{12} ($\neq\tau_{21}$) is the interaction parameter. For a binary mixture, the NRTL model contains seven parameters. In this work, the nonrandomness parameter is fixed as 0.3 and the six binary interaction parameters are optimized.

Table 5. Temperature Dependence of the Parameters of the NRTL Equation with $\alpha_{12} = 0.3$ for the Branched Cycloalkanes (1) + *N*-Formylmorpholine (2) Binary Systems

	binary interaction parameters					
system	a_{12}	a_{21}	b_{12}/K	b_{21}/K	c_{12}	c_{21}
methylcyclopentane + NFM	−14.616	82.929	2413.9	−3071.7	1.7193	−12.407
methylcyclohexane + NFM	254.71	29.701	−11370	−371.47	−37.485	−4.6313
ethylcyclohexane + NFM	194.08	−8.3869	−8527.4	2036.1	−28.539	0.75341

Table 6. Temperature Dependence of the Parameters of the UNIQUAC Equation for the Branched Cycloalkanes (1) + *N*-Formylmorpholine (2) Binary Systems

	binary interaction parameters					
system	a_{12}	a_{21}	b_{12}/K	b_{21}/K	c_{12}	c_{21}
methylcyclopentane + NFM	19.367	−42.600	−1388.3	1985.5	−2.6934	6.2238
methylcyclohexane + NFM	−86.992	23.740	4063.3	−1376.3	12.760	−3.4167
ethylcyclohexane + NFM	−70.549	27.740	3435.6	−1770.8	10.256	−3.9047

UNIQUAC model:

$$g^{E} = g^{E}_{\text{combinatorial}} + g^{E}_{\text{residual}} \tag{4}$$

$$\frac{g^{E}_{\text{combinatorial}}}{RT} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln\frac{\theta_1}{\Phi_1} + q_2 x_2 \ln\frac{\theta_2}{\Phi_2}\right) \tag{5}$$

$$\frac{g^{E}_{\text{residual}}}{RT} = -q_1 x_1 \ln[\theta_1 + \theta_2\tau_{21}] - q_2 x_2 \ln[\theta_2 + \theta_1\tau_{12}] \tag{6}$$

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \tag{7}$$

$$\tau_{12} = \exp(a_{12} + b_{12}/T + c_{12} \ln T) \tag{8}$$

where Φ is the segment fraction, θ is the area fraction, r and q are pure component relative volume and surface area parameters, respectively, and τ_{12} ($\neq \tau_{21}$) is the interaction parameter. The r and q values of *N*-formylmorpholine, methylcylopentane, methylcyclohexane, and ethylcyclohexane were estimated by the Bondi method. These values are (4.8642, 4.052), (3.9664, 3008), (4.6447, 3.548), and (5.3191, 4.088), respectively. The coordination number, z, was set to 10.

The parameters in both models were found by minimizing the objective function

$$\text{OF} = \sum_{k=1}^{N}\left\{\left(\frac{T_k^{\text{calc}} - T_k^{\text{exp}}}{\sigma_{T_k}}\right)^2 + \sum_{i=1}^{2}\sum_{j=1}^{2}\left(\frac{x_{ij}^{\text{calc}} - x_{ij}^{\text{exp}}}{\sigma_{x_{ijk}}}\right)^2\right\} \tag{9}$$

where N is the number of experimental data in each group k and σ_k is the standard deviation of group k. The superscripts calc and exp present calculated properties and experimental properties, respectively. The binary parameters for these models were evaluated by a nonlinear regression method based on the maximum likelihood. The temperature-dependent binary parameters of these models are given in Tables 5 and 6.

Figures 1−3 show graphical representations of the experimental data and the calculated data in the form of T, x', x'' diagrams, whereby the calculated values have been obtained by means of the NRTL equation. The NRTL and UNIQUAC models predict similar coexistence curves over a wide temperature range. The UCSTs and critical compositions calculated by these models were reported in Table 8.

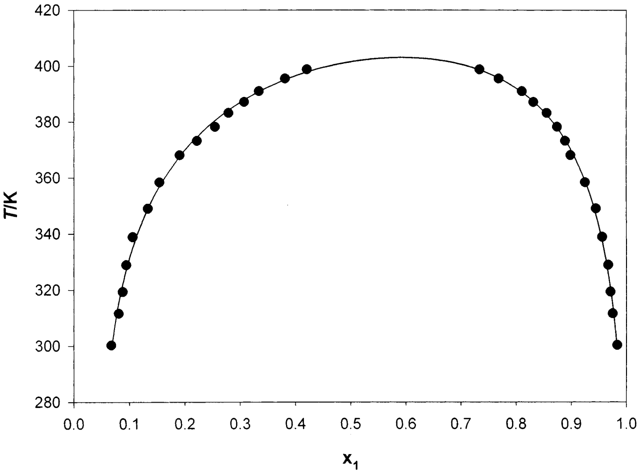

Figure 1. Experimental and calculated liquid−liquid equilibrium data for the methylcyclopentane (1) + *N*-formylmorpholine (2) mixture: points, experimental results; black solid line, NRTL with $\alpha = 0.3$.

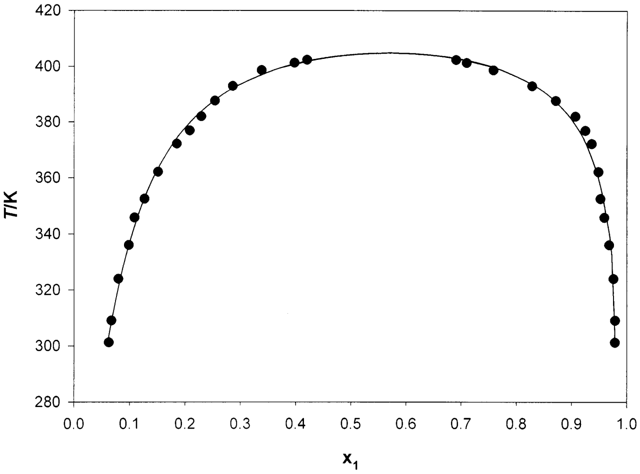

Figure 2. Experimental and calculated liquid−liquid equilibrium data for the methylcyclohexane (1) + *N*-formylmorpholine (2) mixture: points, experimental results; black solid line, NRTL with $\alpha = 0.3$.

The percent absolute average deviations (AAD%) of the composition in both phases over the considered temperature range for the NRTL and UNIQUAC equations are listed in Table 7. Both the NRTL and UNIQUAC models predict the experimental data for the branched cycloalkanes rich phase with an AAD of 0.8%, while the deviation is 3% for the *N*-formylmorpholine rich phase. The NRTL

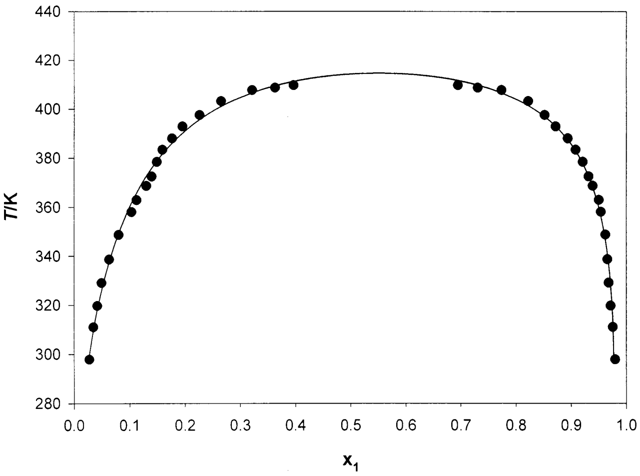

Figure 3. Experimental and calculated liquid−liquid equilibrium data for the ethylcyclohexane (1) + *N*-formylmorpholine (2) mixture: points, experimental results; black solid line, NRTL with $\alpha = 0.3$.

Table 7. Percent Absolute Average Deviations (AAD%)[a] of the NRTL and UNIQUAC Equations for the Branched Cycloalkanes (1) + *N*-Formylmorpholine (2) Binary Systems

	branched cycloalkanes rich phase		NFM rich phase	
system	NRTL	UNIQUAC	NRTL	UNIQUAC
methylcyclopentane + NFM	0.219	0.224	2.72	2.76
methylcyclohexane + NFM	0.897	1.01	2.97	3.40
ethylcyclohexane + NFM	0.736	0.816	5.03	5.07

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

Table 8. Calculated Values for the Upper Critical Solution Temperature (UCST) and the Critical Composition, x_c

	UCST		x_c	
system	NRTL	UNIQUAC	NRTL	UNIQUAC
methylcyclopentane + NFM	403.29	403.26	0.5933	0.5927
methylcyclohexane + NFM	404.78	404.90	0.5707	0.5772
ethylcyclohexane + NFM	414.73	414.99	0.5509	0.5574

model showed slightly smaller deviations in both phases. Both the NRTL and the UNIQUAC models give an excellent correlation of the experimental solubility data for both the liquid phases far from the critical region. The mutual solubility increases in the following order at the same temperature: cyclopentane, cyclohexane, and cyclooctane.

Conclusions

Liquid−liquid equilibrium data for three binary branched cycloalkanes + *N*-formylmorpholine systems were measured in the temperature range from around 300 K to the near upper critical solution temperature (UCST). The measured data were correlated with the temperature-dependent interaction parameters of the NRTL and UNIQUAC models.

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