N-Formylmorpholine과 탄화수소와의 이성분계 액-액 상평형

고민수, 나상엽, 권소영, 김화용
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Liquid-Liquid Equilibria for the Binary Systems of *N*-Formylmorpholine with Hydrocarbons

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Introduction

There have been ever-increasing demands for high purity aromatic compounds as a feedstock for chemical synthesis. Many solvents such as sulfolane, *N*-methylpyrrolidone, glycol, and *N*-formylmorpholine 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 PRO Ⅱ (SimSci), HYSYS (Hyprotech) and ASPEN-PLUS (Aspentech) have been used to determine the optimum solvent rate. However, LLE data are not available for these mixtures.

Liquid-liquid equlilibria (LLE) data were measured for binary systems containing alkanes (pentane, hexane, heptane, and octane), cycloalkanes (cyclopentane, cyclohexane, and cyclooctane), isoalkanes (isopentane and isohexane), and branched cycloalkanes (methylcyclopentane, methylcyclohexane, and ethylcyclohexane) with *N*-formylmorpholine over the wide temperature range using a circulation type equipment with an equilibrium view cell.

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 and hydrocarbons systems at the operating temperature range of the NFM extractive distillation process. The compositions of both light and heavy phases were analyzed by on-line gas chromatography. Experimental data were correlated with the NRTL and UNIQUAC models with the function of temperature dependent parameters. Both of models correlate the experimental data well. The mutual solubility increased as the temperature increased at all these systems. The solubility in the *N*-formylmorpholine increased in the following order at the same temperature; cycloalkanes, branched-cycloalkanes, isoalkanes, and alkanes.

Experiment

Experimental Apparatus. The sampling parts of the recirculation type apparatus used in the previous studies were modified and used in this study. 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, constant temperature air bath, magnetic stirrer, charge-discharge device, temperature and pressure measurement devices and an analysis system. The volume of the equilibrium cell was 240 cm³. 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 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 were connected to a gas chromatography (Hewlett Packard 5890 Series Ⅱ) 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%.
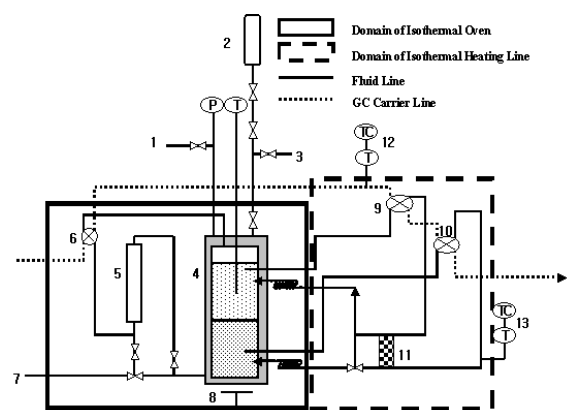

Figure 1. Flow diagram of the apparatus: 1. vacuum line for the removal of air with vacuum pump, 2. bottle for charge a reagent, 3. air line for the leak test, 4. equilibrium cell with the view window (quartz), 5. magnetic pump (chromium plating), 6. 6-way valve for vapor, 7. discharge line with vacuum,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

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 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 cm³·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 of each compositions. 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, alkanes (pentane, hexane, heptane, and octane), cycloalkanes (cyclopentane, cyclohexane, and cyclooctane), isoalkanes (isopentane and isohexane), and branched cycloalkanes (methylcyclopentane, methylcyclohexane, and ethylcyclohexane) with *N*-formylmorpholine are shown in Figure 2. Concentrations of components, *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 by the NRTL and UNIQUAC equations.
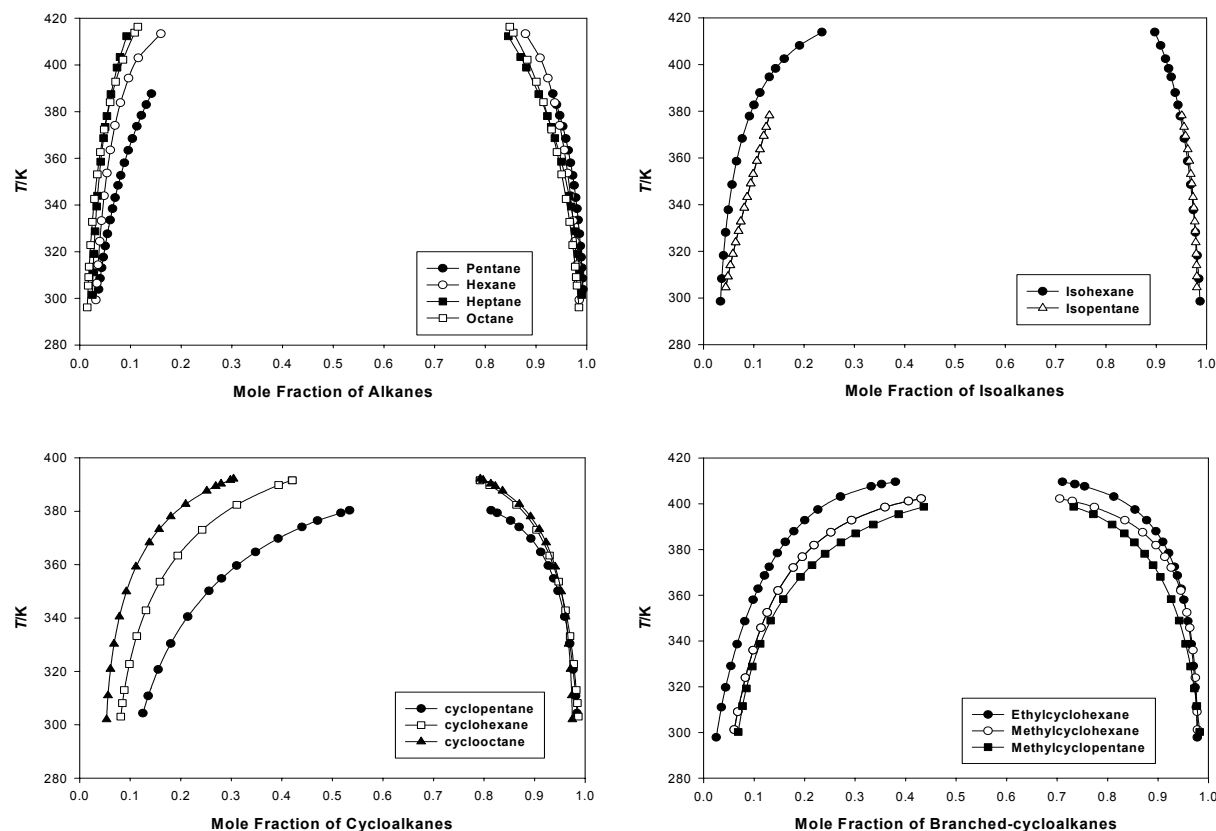

Figure 2. Mutual solubility for the *N*-formylmorpholine and non-aromatic mixtures

The binary parameters have the temperature dependence function,

    for NRTL model:

$$\tau_{ij} = a_{ij} + b_{ij}/T + e_{ij}\ln T \quad \text{and} \quad \alpha_{ij} = c_{ij} + d_{ij}(T - 273.15K) \tag{1}$$

for UNIQUAC model:

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T + c_{ij}\ln T) \tag{2}$$

where τ_{ij} is in dimensionless and T is in K.

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:

$$OF = \sum_{k=1}^{N} \left\{ \left(\frac{T_k^{cal} - T_k^{\exp}}{\sigma_{T_k}} \right)^2 + \sum_{i=1}^{2}\sum_{j=1}^{2} \left(\frac{x_{ij}^{cal} - x_{ij}^{\exp}}{\sigma_{x_{ijk}}} \right)^2 \right\} \tag{3}$$

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

The NRTL model showed slightly smaller deviations than UNIQUAC model in the bottom phase of all systems, however in the top phase, the have similar deviations. The mutual solubility increase as the temperature increased at all these systems. The solubility of n-paraffin in the *N*-formylmorpholine, i.e. bottom phase, increased in the following order at the same temperature; cycloalkanes, branched-cycloalkanes, isoalkanes, and alkanes.

Conclusions

In this work, we have determined the interaction parameters of the NRTL and UNIQUAC equations for the *N*-formylmorpholine + hydrocarbon systems from experimental binary liquid-liquid equilibrium data. The temperature dependency of the parameters of NRTL and UNIQUAC models can be expressed by eqs 1 and 2, 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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