hexane below the solid–liquid equilibrium temperature, two liquid phases appeared at a temperature of about 290 K (*24*).

The possibility of describing the properties of investigated systems by the monomer–dimer model is consistent with the results of our previous papers (*3*, *4*, *6*), where the suggestion is made that the polar compounds incapable of forming intermolecular hydrogen bonds dimerize as a result of dipole interactions. The presented results confirm also that the effect of association on the thermodynamic properties of the solutions of polar compounds in inert solvent is very important. The model taking self-association explicitly into account leads to a satisfactory representation of experimental data with adjustable parameters with defined physicochemical meaning. The model parameters $K$ and $D$ can be predicted on the basis of the properties of pure substances using the homomorph concept (*6*, *7*).

## Acknowledgment

We thank Professor A. Bylicki for his comments.

## Glossary

| | |
|---|---|
| $B$ | second molar virial coefficient of cyclohexane, $cm^3\ mol^{-1}$ |
| $D$ | parameter in eq 3, $MPa^{1/2}$ |
| $K$ | thermodynamic association constant |
| $p$ | total vapor pressure over the solution, kPa |
| $p_B$ | bubble point pressure |
| $p_D$ | dew point pressure |
| $p^\circ$ | vapor pressure of pure cyclohexane, kPa |
| $R$ | molar gas constant (=8314.31), $cm^3\ kPa\ K^{-1}\ mol^{-1}$ |
| $T$ | equilibrium temperature, K |
| $V_A$ | molar volume of solute, $cm^3\ mol^{-1}$ |
| $V_B$ | liquid molar volume of cyclohexane, $cm^3\ mol^{-1}$ |
| $x_A$ | mole fraction of solute in the liquid phase |
| $x_B$ | mole fraction of cyclohexane in the liquid phase |
| $\gamma_B$ | activity coefficient of cyclohexane in the liquid phase |
| $\Delta p$ | difference between the vapor pressures of pure cyclohexane and mixture |

**Registry No.** 2-Methoxyphenol, 90-05-1; 2-iodophenol, 533-58-4; 2-benzoyl-1-naphthol, 21009-99-4; 2-chloronitrobenzene, 88-73-3; 4-nitrotoluene, 99-99-0; 5-methyl-2-nitrophenol, 700-38-9; cyclohexane, 110-82-7.

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# Liquid–Liquid Mutual Solubilities of Binary Mixtures of Ammonia with *n*-Heptane, *n*-Decane, *n*-Undecane, and *n*-Dodecane up to Upper Critical Solution Temperature

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**Liquid–liquid mutual solubilities for binary mixtures of ammonia with *n*-heptane, *n*-decane, *n*-undecane, and *n*-dodecane have been measured between 317 K and the upper critical solution temperatures. The liquid–liquid equilibrium curves were expressed with the scaled equation of state. The upper critical solution temperature is a linear function of the number of carbon atoms in the *n*-alkane.**

## Introduction

Accurate liquid–liquid equilibrium data in the critical region are important not only for the theoretical study of critical phenomena but also for the development of semiempirical correlations near the critical region. In our previous study (*1*), we reported liquid–liquid mutual solubility data for binary mixtures of ammonia with *n*-pentane, *n*-hexane, and *n*-octane up to the upper critical solution temperatures. In this study, we report similar data for ammonia with *n*-heptane, *n*-decane, *n*-undecane, and *n*-dodecane.

## Experimental Section

***Apparatus and Procedure*.** The experimental measurements were performed in a pressurized Pyrex-glass cell. Miscibility temperature was determined by observing turbidity changes during heating and cooling of solutions. The apparatus and the procedures were essentially the same as those described in our previous study (*1*). We measured the mutual solubility both at the vapor–liquid–liquid equilibrium (VLLE) pressure and under pressure at the liquid–liquid equilibrium (LLE) pressure in the previous study. Figure 1 shows the comparison between the VLLE pressures reported in the previous study with the vapor pressure of pure ammonia. It can be seen that the VLLE

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**Table I. Liquid–Liquid Mutual Solubility Data (Mass Fraction $X$ of Ammonia and Temperature $T$) for the Ammonia + $n$-Alkane Systems at the Vapor–Liquid–Liquid Equilibrium Pressures**

| $X$ | $T$/K | $X$ | $T$/K | $X$ | $T$/K |
|---|---|---|---|---|---|
| | | *n*-Heptane | | | |
| 0.1087 | 316.36 | 0.3833 | 334.21 | 0.6667 | 333.25 |
| 0.1814 | 326.97 | 0.5234 | 334.50 | 0.8962 | 319.06 |
| | | *n*-Decane | | | |
| 0.06682 | 317.10 | 0.3654 | 353.67 | 0.7152 | 350.88 |
| 0.1228 | 336.32 | 0.4977 | 353.49 | 0.8652 | 341.59 |
| 0.1775 | 334.93 | 0.5354 | 353.37 | | |
| | | *n*-Undecane | | | |
| 0.07087 | 324.93 | 0.3113 | 358.08 | 0.6683 | 357.82 |
| 0.1276 | 342.22 | 0.3675 | 358.90 | 0.8560 | 347.90 |
| 0.1931 | 351.65 | 0.4874 | 359.18 | | |
| | | *n*-Dodecane | | | |
| 0.05003 | 317.17 | 0.3432 | 363.76 | 0.6797 | 362.50 |
| 0.1123 | 342.53 | 0.4111 | 364.36 | 0.8466 | 353.10 |
| 0.1469 | 350.35 | 0.5187 | 364.42 | | |

pressure was almost the same as the vapor pressure of pure ammonia. Therefore we did not measure the VLLE pressure in this study. The temperature of the thermostated bath was measured with an accuracy of ±0.02 K with a thermistor thermometer, which was calibrated by means of a Leeds-Northrup platinum resistance thermometer according to IPTS-68. The accuracy of the temperature measurements was estimated to be 0.05 K. The composition of the ammonia + *n*-alkane mixture was determined by weighing with an analytical balance with an accuracy of 0.1 mg. The experimental uncertainty of the composition, expressed in mass fraction, was less than 0.01%.

***Materials.*** The ammonia used in this study was provided by Seitetu Kagaku Co., Ltd., and it has a purity of 99.99 mol %. *n*-Heptane and *n*-decane were supplied by Wako Pure Chemical Co., Ltd. *n*-Undecane and *n*-dodecane were supplied by Tokyo Kasei Kogyo Co., Ltd. Stated purities of these alkanes were 99+%, but a chromatographic scan indicated these to be better than 99.8+%. These chemicals were used without further purification.

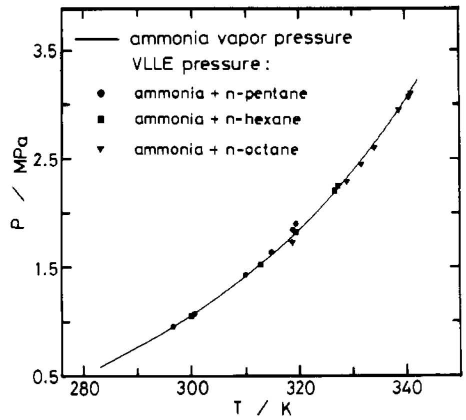

**Figure 1.** Comparison between the vapor–liquid–liquid equilibrium (VLLE) pressures of ammonia + *n*-alkane systems and the pure ammonia vapor pressures $P$ as a function of temperature $T$.

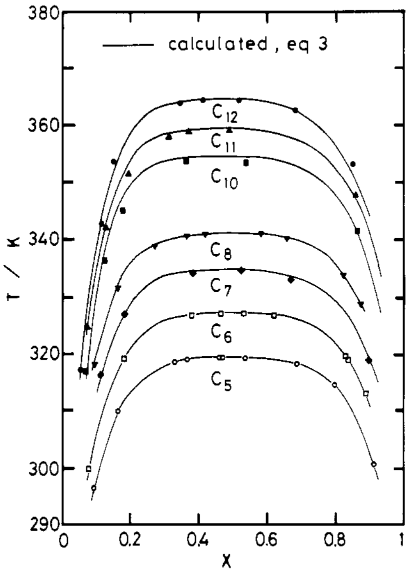

**Figure 2.** Mutual solubility curves (temperature $T$ versus mass fraction $X$ of ammonia) at the vapor–liquid–liquid equilibrium pressures for ammonia + *n*-alkane ($C_n$) systems.

## Results and Discussion

The mutual solubilities of the ammonia + *n*-heptane, ammonia + *n*-decane, ammonia + *n*-undecane, and ammonia + *n*-dodecane systems at the VLLE pressure are reported in Table I. Figure 2 shows the liquid–liquid equilibrium coexistence curves. The previous results of the ammonia + *n*-pentane, + *n*-hexane, and + *n*-octane systems (*1*) are also represented for comparison. Compositions are expressed in mass fractions to obtain more symmetrical coexistence curves.

The difference in mass fractions $X$ of ammonia between the upper, $X_+$, and lower, $X_-$, liquid phases and the diameter of the coexistence curve are properly expressed in terms of the scaled equation of state (*2*, *3*), as follows:

$$|X_+ - X_-| = B\epsilon^{\beta}(1 + b_1\epsilon^{0.5} + ...) \qquad (1)$$

$$0.5(X_+ + X_-) = X_{UCS} + A_1\epsilon + A_2\epsilon^{1-\alpha} \qquad (2)$$

where $\epsilon = 1 - T/T_{UCS}$ and $X_{UCS}$ and $T_{UCS}$ are respectively the mass fraction of ammonia and the temperature at the upper critical solution point. $\alpha$ is the critical exponent of the specific heat, and $\beta$, the critical exponent for the coexistence curve. From eqs 1 and 2, the coexistence curve can be described by

$$X_{\pm} - X_{UCS} = A_1\epsilon + A_2\epsilon^{1-\alpha} \pm 0.5B\epsilon^{\beta}(1 + b_1\epsilon^{0.5}) \qquad (3)$$

The plus sign of the third term in eq 3 corresponds to the upper liquid phase, while the minus sign corresponds to the lower liquid phase. Equation 3 was used to determine the upper critical solution point. The values for the critical exponents, $\beta$ and $\alpha$, were set to the theoretical ones, 0.325 and 0.1, recommended by Levelt-Sengers and Sengers (*4*). $T_{UCS}$, $X_{UCS}$, and the constants $A_1$, $A_2$, $B$, and $b_1$ were determined by the least-squares method. Values calculated with eq 3 are shown by solid lines in Figure 2. The values of the parameters in eq

**Table II. Temperature $T_{UCS}$ and Mass Fraction of Ammonia $X_{UCS}$ at the Critical Solution Point and Constants of the Scaled Equation of State, Equations 1–3, and Deviations $\Delta T$ for the Ammonia + $n$-Alkane Systems**

| *n*-alkane | $T_{UCS}$/K | $X_{UCS}$ | $A_1$ | $A_2$ | $B$ | $b_1$ | $\Delta T^a$/K |
|---|---|---|---|---|---|---|---|
| *n*-heptane | 334.75 | 0.4786 | −7.161 77 | 5.834 93 | 2.509 75 | −0.738 667 | 0.48 |
| *n*-decane | 354.60 | 0.4602 | −4.905 66 | 4.296 02 | 2.507 95 | −0.808 469 | 1.09 |
| *n*-undecane | 359.21 | 0.4507 | −8.087 24 | 6.900 36 | 2.492 84 | −0.788 643 | 0.47 |
| *n*-dodecane | 364.48 | 0.4603 | −3.670 64 | 3.273 96 | 2.367 53 | −0.702 323 | 0.88 |

[a] Mean deviation of the experimental values of miscibility temperature from the values calculated with eq 3.

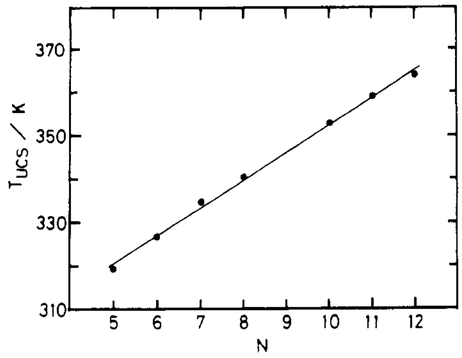

**Figure 3.** Relationship between the upper critical solution temperature $T_{UCS}$ of ammonia + *n*-alkane systems and the number *N* of carbon atoms in the *n*-alkane.

3 and the deviation of the experimental values of the miscibility temperature from those calculated with eq 3 are shown in Table II. Equation 3 can fit the experimental temperature with a mean deviation of less than 1.1 K. There is a linear relationship between $T_{UCS}$ and the number of carbon atoms, *N*, in the *n*-alkane (Figure 3).

$$T_{UCS}/K = 6.4454N + 288.58 \qquad N = 5–12 \qquad (4)$$

### Glossary

| | |
|---|---|
| $A_1$, $A_2$, $B$, $b_1$ | constants in eqs 2 and 3 |
| $N$ | number of carbon atoms in *n*-alkane |
| $P$ | pressure, MPa |
| $T$ | temperature, K |
| $T_{UCS}$ | upper critical solution temperature, K |
| $X$ | mass fraction of ammonia |

*Subscripts*

| | |
|---|---|
| UCS | upper critical solution point |

**Registry No.** $NH_3$, 7664-41-7; $H_3C(CH_2)_5CH_3$, 142-82-5; $H_3C(CH_2)_8CH_3$, 124-18-5; $H_3C(CH_2)_9CH_3$, 1120-21-4; $H_3C(CH_2)_{10}CH_3$, 112-40-3.

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# Temperature and Concentration Dependence of Viscosity of the $NiCl_2$ + $CH_3OH$ System

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**Density and viscosity of the $NiCl_2$ + $CH_3OH$ system were measured as functions of temperature (288.15–323.15 K) and concentration (0.01817–5.3086 *m*). The temperature dependence of viscosity has been analyzed by using the Vogel–Tammann–Fulcher (VTF) equation. The concentration dependence of viscosity has been described by using a three-parameter isothermal equation.**

## Introduction

Extensive studies on the properties of aqueous solution has provided sufficient data to enable us to correlate the effects of variation in concentration on the physicochemical properties of aqueous electrolytic solutions. The study of nonaqueous electrolytic solutions to obtain the same type of information, however, has been quite limited.

Earlier we have reported an isothermal equation of the form

$$Y = a \exp(bm + cm^2) \qquad (1)$$

to describe the concentration dependence of *Y* (viscosity and conductivity) of 1–1, 1–2, and 2–1 valent aqueous electrolytic solutions (*1–3*) over a concentration range. In eq 1, *a*, *b*, and *c* are adjustable parameters and *m* is the molality.

In the present paper we have made use of eq 1 to describe the viscosity of the $NiCl_2$ + $CH_3OH$ system as function of concentration.

## Experimental Section

***Materials.*** Anhydrous nickel chloride (SD, AR grade) was prepared as described elsewhere (*4*) and was kept in a vacuum desiccator over silica gel until used. Methanol (SM, LR grade) was treated with quicklime and was distilled after refluxing for about 4 h. Finally anhydrous methanol was prepared by using a dry magnesium turnings and iodine mixture as described elsewhere (*5*). Only the middle fraction was used in our study. The molecular weights of nickel chloride and methanol used in the present study were 129.62 and 32.04, respectively, having an assay of more than 99.8%. The densities of anhydrous methanol as measured at 298 and 303 K were found to be 0.786 47 and 0.781 70 g $cm^{-3}$, which are in good agreement with the literature values 0.7864 and 0.7816 g $cm^{-3}$ (*6*) and 0.786 45 and 0.781 81 g $cm^{-3}$ (*7*), respectively.

***Preparation of Solutions.*** Solutions of the nickel chloride–methanol system of different concentration were prepared by weight.

***Density Measurements.*** Densities of all the solutions were measured with a single-stem graduated pycnometer provided with a well-fitted glass stopper to prevent evaporation. The pycnometer was calibrated by using conductivity water. The difference between the duplicate density values of all the solutions were found to be less than 0.01%.

***Viscosity Measurements.*** The viscosities of all the solutions were measured by using a Hoppler BH-2 falling-sphere viscometer. In this viscometer, since the solution is sealed, the condensation of the solvent vapor at low temperatures and the loss of solvent at high temperatures are prevented. The viscometer was calibrated by using conductivity water. The tem-

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