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Liquid–Liquid Mutual Solubilities of Binary Mixtures of Ammonia with *n*-Pentane, *n*-Hexane, and *n*-Octane up to Upper Critical Solution Temperature

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Liquid–liquid mutual solubilities for the binary mixtures of ammonia with *n*-pentane, *n*-hexane, and *n*-octane have been measured over a temperature range up to the upper critical solution temperature. The liquid–liquid equilibrium coexistence curves were expressed with the scaled equation of state.

Introduction

The separation of liquid mixtures with near-critical solvent has been of interest in recent years. The experimental data of the liquid–liquid mutual solubility under pressure are important for the design of the high-pressure liquid extraction process. While the liquid–liquid mutual solubility data at atmospheric pressure have been measured extensively, the data under pressure are scarce.

Liquid ammonia is useful solvent with physical properties and selectivity necessary for an effective separation of several hydrocarbon types (*1–3*). Ammonia is also expected to be a useful entrainer in the supercritical and near-critical fluid extraction process (*4–6*).

Fenske et al. proposed the extraction process using liquid ammonia as a solvent and separated petroleum fractions into different types of hydrocarbons (*1*). Ishida measured the mutual solubilities of ammonia and aromatic hydrocarbons at temperatures near the upper critical solution temperature, which were usually less than 320 K, and those of other hydrocarbons at 273.15 and 293.15 K (*2*). It was found that the mutual solubilities of ammonia and aromatic hydrocarbons are greater than those of ammonia and *n*-paraffins at 293.15 and 273.15 K. However the mutual solubility data for the ammonia–*n*-paraffin system up to the upper critical solution temperature have not been reported. In this study, we measured the mutual solubilities of the three ammonia–*n*-paraffin binary systems, ammonia–*n*-pentane ammonia–*n*-hexane, and ammonia–*n*-octane, up to the upper critical solution temperature.

Experimental Section

The miscibility temperature was determined by observing turbidity changes during heating and cooling of a sealed agitating solution. An experimental apparatus used in this study is shown in Figure 1. The details of the equilibrium cell are shown in Figure 2. The cell is an 18-mm-o.d., 11-mm-i.d., and 180-mm-length Pyrex glass cell of about 20 cm^3. The cell was pressure tested and proved to be reliable up to 10 MPa. Mixing of the sample was attained by movement of a small steel ball caused by a magnet held outside the cell. We used the same type of glass cell to measure the vapor pressure of the CO_2–C_6 hydrocarbon systems (*7*).

The *n*-paraffin was loaded into the cell and degassed by several freeze–pump–thaw cycles. The amount of the *n*-paraffin was determined by weighing. Then, the cell was connected to an apparatus for filling the cell with liquid ammonia. This apparatus is shown in Figure 3. The line connecting the cell and the ammonia reservoir was pumped down for 30 min to remove traces of adsorbed gases on its inner wall. The cell was cooled to about 0 °C, and then the valves attached the cell and the ammonia reservoir opened. The cell was kept at 0 °C until the desired amount of the ammonia was condensed into the cell. Then, the cell was disconnected from the line. The amount of ammonia was also determined by weighing. The weighing was performed with an analytical balance with an accuracy of ±0.1 mg. The experimental uncertainty in a composition determination was less than 0.01%. The cell was connected to a pressure delivery system, shown in Figure 1, and set in the thermostated bath. The cell was heated to a complete homogeneity of the sample and then cooled at a rate of about 0.01 °C/min until turbidity appeared. The temperature was noted when the turbidity appeared. Each determination was repeated several times. When the temperatures were within 0.02 °C, it seemed that the cloud-point temperature of the sample was determined with a desired precision. The pressure of the sample was adjusted to keep a constant value in a constant-pressure liquid–liquid equilibrium (LLE) measurement and to keep a small bubble in the top of the cell in a vapor–liquid–liquid equilibrium (VLLE) measurement. Mercury was used as a pressurized fluid. The temperature of the thermostated bath was measured with an accuracy of ±0.02 K with the thermister thermometer, which was calibrated by the Leeds-Northrup platinum resistance thermometer according to IPTS-68. The pressure of the cell was measured by the dead-weight gauge with an accuracy of ±10 kPa.

Material

The ammonia used in this study was furnished by the Seitetu Kagaku Co., Ltd., and the *n*-paraffins by the Wako Chemical Co., Ltd.

Purities were 99.99 mol % for ammonia, 99.9 mol % for *n*-pentane, 99.8 mol % for *n*-hexane, and 99.9 mol % for *n*-octane, and the chemicals were used without further purification. The water contents in the chemicals were measured with the Karl-Fischer titration apparatus and were found to be less than 0.01 mol % for ammonia and less than 0.005 mol % for the *n*-paraffins.

Results and Discussion

The mutual solubilities of the ammonia–*n*-pentane, ammonia–*n*-hexane, and ammonia–*n*-octane systems at the vapor–liquid–liquid (VLL) equilibrium pressure and under pressure at the liquid–liquid (LL) equilibrium pressure are reported in Tables I–III, respectively. The VLL equilibrium pressure was almost the same as the vapor pressure of ammonia. Figure 4 shows the liquid–liquid equilibrium coexistence curves at the VLL equilibrium pressures. As can be seen from Figure 4, the direct method to determine the upper critical solution point is very difficult because of the flatness of the curve near the critical point. Therefore, we determined the upper critical solution point

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Table I. Liquid–Liquid Mutual Solubility Data for the Ammonia–*n*-Pentane System

	VLL equilibrium		T at LL equilibrium/K		
X	P/MPa	T/K	P = 2.03 MPa	P = 2.53 MPa	P = 3.04 MPa
0.0902	0.973	296.75	297.25	297.46	297.72
0.1612	1.459	309.93	310.30	310.47	310.74
0.3285	1.859	318.65		318.93	319.11
0.3636	1.910	319.29	319.37	319.52	319.73
0.4600	1.915	319.35		319.65	319.82
0.4635	1.920	319.42	319.47	319.68	319.90
0.5352	1.915	319.35		319.62	319.80
0.6853	1.869	318.43	318.60	318.71	319.96
0.7934	1.667	314.58	314.75	314.86	316.15
0.9104	1.469	300.75	300.99	301.18	301.28

Table II. Liquid–Liquid Mutual Solubility Data for the Ammonia–*n*-Hexane System

	VLL equilibrium		T at LL equilibrium/K	
X	P/MPa	T/K	P = 304 MPa	P = 4.05 MPa
0.0742	1.059	300.01	300.83	301.00
0.1769	1.829	319.36	319.70	320.11
0.3798	2.224	326.94	327.33	327.78
0.4634	2.265	327.10	327.52	327.98
0.5322	2.249	327.11	327.49	327.98
0.6169	2.229	326.85	327.27	327.76
0.8285	1.844	319.74	320.14	320.54
0.8357	1.809	319.16	319.54	319.94
0.8868	1.520	313.16	313.60	313.92

Table III. Liquid–Liquid Mutual Solubility Data for the Ammonia–*n*-Octane System

	VLL equilibrium		T at LL equilibrium/K
X	P/MPa	T/K	P = 4.05 MPa
0.0933	1.728	318.24	319.16
0.1649	2.462	331.69	332.40
0.2683	2.943	338.60	339.12
0.3606	3.065	340.36	341.26
0.4177	3.085	340.75	341.26
0.4820	3.106	340.77	341.19
0.5812	3.070	340.61	341.09
0.6587	3.025	339.95	340.46
0.8214	2.604	333.84	334.46
0.8710	2.295	328.86	329.55

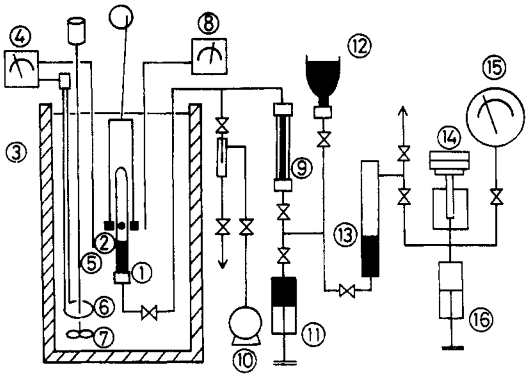

Figure 1. Flow diagram of apparatus: 1, equilibrium cell; 2, magnetic stirrer; 3, water thermostat; 4, temperature controller; 5, regulater; 6, heater; 7, stirrer; 8, thermometer; 9, Pyrex glass tube; 10, vacuum pump; 11, mercury pump; 12, mercury reservoir; 13, mercury-oil separator; 14, dead-weight gauge; 15, Bourdon gauge; 16, pump.

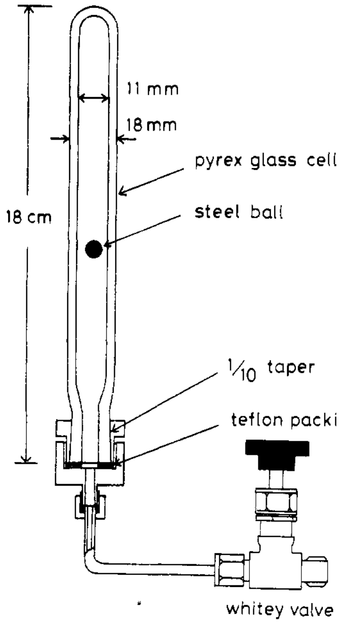

Figure 2. Details of Pyrex glass equilibrium cell.

by numerical anlysis of the data.

The general prediction for the LL equilibrium coexistence curve involves a power law near the upper critical solution temperature, T_{ucs}, with the exponent β, plus nonanalytical corrections far from T_{ucs} (*8*, *9*). The composition difference of ammonia between the upper and lower phases and the diameter of the coexistence curve are expressed as follows

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

$$0.5(X_+ - X_-) = X_{ucs} + A_1\epsilon + A_2\epsilon^{1-\alpha} + ... \tag{2}$$

where X is the equilibrium composition of ammonia and $\epsilon = 1 - T/T_{ucs}$. The X_{ucs} is the critical composition. Compositions are expressed in weight fraction because then the coexistence curves become more symmetrical. The subscripts + and − represent the upper and lower phases, respectively. α is the critical exponent of the specific heat. From eq 1 and 2, the coexistence curve can be described by eq 3. The upper sign,

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

"+", of the third term in eq 3 corresponds to the upper liquid phase, while the lower one, "−", corresponds to the lower liquid phase. Equation 3 was used to analyze our data. The values for the critical exponents, β and α, were imposed to the theoretical ones, 0.325 and 0.1, recommended by Levelt Sengers

Table IV. Constants of the Scaled Equation of State for the Ammonia–*n*-Paraffin System

n-paraffin	P/MPa	T_{ucs}/K	X_{ucs}	A_1	A_2	B	b_1	dev[a]/K
n-pentane	VLLE	319.41	0.4976	−1.079 46	0.924 39	2.508 11	−0.795 89	0.06
	2.03	319.47	0.4880	−3.412 98	2.744 90	2.604 67	−0.912 48	0.13
	2.53	319.69	0.4979	−0.763 08	0.626 28	2.512 92	−0.791 69	0.06
	3.04	319.92	0.5090	−1.175 38	0.828 48	2.661 81	−0.979 78	0.10
n-hexane	VLLE	327.10	0.4908	−2.479 10	2.060 35	2.509 98	−0.766 65	0.06
	3.04	327.52	0.4920	−2.284 24	1.894 45	2.505 67	−0.760 18	0.05
	4.05	327.99	0.4921	−2.349 94	1.941 31	2.502 17	−0.763 16	0.06
n-octane	VLLE	340.76	0.4814	−3.156 75	2.743 77	2.473 04	−0.670 56	0.13
	4.05	341.32	0.4757	−3.466 40	3.039 53	2.471 83	−0.640 51	0.17

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

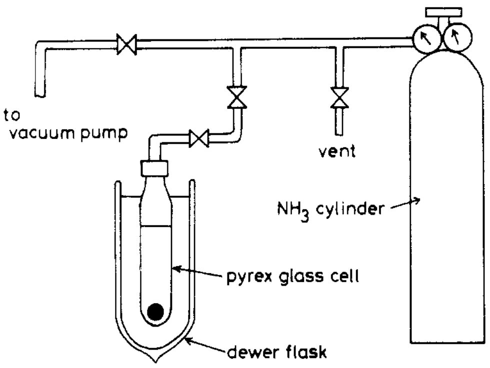

Figure 3. Apparatus for filling cell with liquid ammonia.

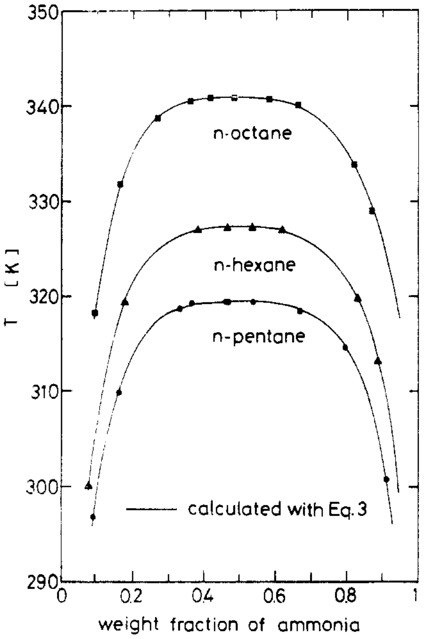

Figure 4. Mutual solubility curves at vapor-liquid-liquid equilibrium pressure for the systems of ammonia-*n*-pentane, ammonia-*n*-hexane, and ammonia-*n*-octane.

and Sengers (*10*). The T_{ucs}, X_{ucs}, and the constants A_1, A_2, B, and b_1 were determined by the least-squares fit to the experimental data. The values and the deviation between the experimental values and the calculated values from eq 3 are shown in Table IV. Equation 3 can fit the experimental temperature within 0.17 K.

Glossary

A_1, A_2	constants of the coexistence curve equation
B	constant of the coexistence curve equation
b_1	constant of the coexistence curve equation
P	pressure
T	temperature
T_{ucs}	upper critical solution temperature
X_{ucs}	concentration of ammonia at the upper critical solution temperature
X_+, X_-	equilibrium composition of ammonia

Greek Letters

α	critical exponent for specific heat
β	critical exponent for coexistence curve
ϵ	reduced temperature

Subscripts

ucs	upper critical solution

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