Solubility of Methane in Alcohols and Saturated Density at 280.15 K

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The solubilities of methane in methanol or ethanol and saturated densities were measured at 280.15 K. The experimental apparatus was equipped with two Anton Paar DMA 512P vibrating tube density meters, one for measuring the vapor density and the other for liquid densities. The apparatus could operate to a maximum temperature of 400 K and a maximum pressure of 20 MPa. The solubilities of methane in methanol or ethanol and their densities were successfully correlated with the three-parameter pseudocubic equation of state.

Introduction

High-pressure vapor−liquid equilibria are required in many industrial applications, such as in the design and operation of distillation columns and supercritical fluid extraction. The authors[1] previously proposed an apparatus for measurement of binary vapor−liquid equilibrium at high pressure, using two density meters. The vapor−liquid equilibrium compositions can be evaluated by combining measurements at the same temperature and pressure, without any analysis of phase compositions, based on mass balance and the phase rule. Applying the experimental apparatus presented in the previous work,[1] the authors proposed an experimental method for determination of gas solubilities in nonvolatile liquid mixtures.[2] The solubilities of gases in a liquid can be evaluated on the basis of mass balance. The solubilities of carbon dioxide in heavy hydrocarbons and their mixtures have been recently determined without any analysis of phase compositions.[2−4]

Methane hydrates are being considered as a natural gas resource. Gas hydrates are crystalline compounds that are formed by physically stable interactions between water and relatively small guest molecules that occupy the cavities built by water molecules. It is well-known that more than 120 guest species are able to stabilize the icelike clathrate hydrates.

Large amounts of natural gas hydrates consisting of primarily methane and other hydrocarbons are available in the deep ocean near the continent and further in the frozen soil in the polar region. Methane hydrates are therefore important in the future as a main energy supply resource. A clean energy cycle is possible using natural gas as the alternate energy source compared with fossil fuel.

A recovery technology of natural gases is proposed in the present study, by the injection of alcohol into the natural gas hydrates to dissociate the hydrate. The phase equilibrium properties are therefore important not only for the methane + water containing the hydrate but also for the methane + alcohol.

For methane + methanol, Takeuchi et al.[5] previously measured only liquid compositions at 273.15 K and 50 bar with a vapor recirculation apparatus. The liquid phase was analyzed by gas chromatography. Hong et al.[6] previously measured the vapor−liquid equilibrium relations and the saturated densities at 273.15 K and 290 K and up to 41.37 MPa with a vapor recirculation apparatus. The vapor and liquid phases were analyzed by gas chromatography. For methane + ethanol, Brunner et al.[7] measured the vapor−liquid equilibrium relations at 298.15 K and up to 31.38 MPa with an apparatus that included the vapor and liquid phases' recirculation. Two different methods were adopted for these measurements: (a) two high-pressure optical cells for moderate to high ethanol mole fractions and (b) gas chromatography determination of composition at low ethanol mole fractions. The equilibrium data reported by Takeuchi et al.[5] and Hong et al.,[6] however, have no density data.

Table 1. Normal Boiling Points, T_b, Densities, ρ, and Refractive Indexes, n_D, of the Alcohols Used

	T_b/K		ρ(298.15 K)/kg·m^{-3}		n_D/(298.15 K)	
material	exptl	lit.	exptl	lit.	exptl	lit.
methanol	337.65	337.651[a]	786.6	786.62[a]	1.3265	1.326 52[b]
ethanol	351.45	351.475[a]	785.1	785.10[a]	1.3594	1.359 41[b]

[a] Reference 13. [b] Reference 12.

In the present study, the solubilities of methane in methanol or ethanol and their saturated densities were measured at 280.15 K in the pressure range from 1 MPa to 12 MPa, which corresponds to a depth of sea from 100 m to 1200 m. The present experimental data obtained were correlated with the three-parameter pseudocubic equation of state.[2,8−10]

Experimental Section

Materials. Methane of 99.999% purity was supplied by Nippon Sanso Corp. Methanol and ethanol were the special grade reagents of Wako Pure Chemical Industries, Ltd., and were used without further purification. The physical properties of methanol and ethanol are listed in Table 1.

Apparatus and Procedures. The experimental apparatus is the same as that in the previous study.[1−4] The apparatus is a static-circulation type with a maximum temperature 400 K and a pressure 20 MPa. Pressure was measured with the Ruska 2465-752 air dead weight gauge and the Ruska 2480-700 oil dead weight gauge, using Ruska 2413-705 and 2439-702 pressure transducers. The

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temperatures were measured with a Hewlett-Packard 2804 A quartz thermometer. The main parts of the apparatus were placed in a constant-temperature liquid bath controlled to within an accuracy of ±0.01 K. The volume of the cell was determined by means of a digital counter connected to the piston. The volume of the cell could be varied from 78×10^{-6} m^3 to 134×10^{-6} m^3 by the displacement of the piston with a sensitivity in the range $\pm 0.01 \times 10^{-6}$ m^3. The present apparatus is equipped with two density meters with the accuracies of ± 0.01 $kg{\cdot}m^{-3}$ and ± 0.1 $kg{\cdot}m^{-3}$, respectively, in the density range less than and greater than ± 100.0 $kg{\cdot}m^{-3}$. The vapor and liquid phases are continuously recirculated through the density meters with the two magnetic circulation pumps. The experimental accuracies of temperature and pressure, respectively, seem to be about ±0.01 K and ±1 kPa.

The experimental method is based on mass balance.[2] Assuming that the liquid component is nonvolatile, the mass fraction of gas in the liquid, w_1, can be obtained by

$$w_1 = 1 - \frac{m_2}{\rho_L V_L} \tag{1}$$

where

$$V_L = \frac{(m_1 + m_2) - \rho_V V_T}{\rho_L - \rho_V} \tag{2}$$

The mass fraction of gas in the liquid w_1 can be obtained from the feed masses, m_1 and m_2, the total volume, V_T, and the densities of the vapor and liquid phases, ρ_V and ρ_L.

This experimental method does not require analysis of the phase compositions. In the determination, only the total volume, V_T, is measured. The experimental saturated vapor and liquid volume, V_V and V_L, are not required.

At the start of an experiment, the variable volume cell is evacuated and then charged with the component gas. The amount of charged gas was obtained from the volume and density of gas. Next, the nonvolatile liquid was charged with a hand syringe pump to the variable volume cell. The amount of the nonvolatile liquid charged was measured by the turns of the hand syringe pump. The vapor and liquid phases were then circulated with circulation pumps. After attainment of equilibrium, the densities of the vapor and liquid phases, pressure, and temperature were measured, observing the coexistence of vapor and liquid phases through the visual glass window. The total volume was also determined from the movement of the piston.

Results and Discussion

The experimental gas solubility and saturated density data obtained at 280.15 K for the methane + methanol system and the methane + ethanol system are given in Table 2 and shown in Figures 1 and 2. The reliability of the present solubility data is estimated to be within ±0.001 mole fraction, considering the accuracies of the present apparatus and the meters used.

The volumetric properties were measured at high pressures for the pure substances methane, methanol, and ethanol and are given in Table 3. The average deviation between experimental and literature values[11] for methane was 0.35 $kg{\cdot}m^{-3}$. For methanol and ethanol, the average deviations between experimental and literature values[12] were 0.6 $kg{\cdot}m^{-3}$and 0.5 $kg{\cdot}m^{-3}$, respectively.

The present experimental temperature was given by the average temperature of seawater as 280.15 K. It is lower than the room temperature. The vapor pressures of methanol and ethanol are small at 280.15 K, such as 0.0062 MPa and 0.0026 MPa, respectively, compared with the present experimental pressures from 2 MPa to 11 MPa. The volatilities of the alcohols were therefore neglected in the present experiment at high pressures.

Table 2. Equilibrium Pressure, P, Solubility Mole Fraction, x_1, Saturated Liquid Density, ρ_L, and Saturated Vapor Density, ρ_V, at 280.15 K

P / MPa	x_1	ρ_L / $kg{\cdot}m^{-3}$	ρ_V / $kg{\cdot}m^{-3}$	P / MPa	x_1	ρ_L / $kg{\cdot}m^{-3}$	ρ_V / $kg{\cdot}m^{-3}$
			Methane (1) + Methanol (2)				
2.112	0.017	792.3	15.50	7.002	0.058	769.8	57.23
3.078	0.025	788.0	22.81	8.538	0.068	763.7	71.63
4.100	0.034	783.2	30.98	10.004	0.079	758.1	86.17
4.848	0.041	779.8	37.35	11.408	0.088	753.0	100.4
6.027	0.051	774.1	48.31				
			Methane (1) + Ethanol (2)				
1.575	0.018	791.0	11.31	6.967	0.085	764.2	56.83
2.107	0.025	788.4	15.28	8.026	0.094	761.2	66.86
3.051	0.038	783.6	22.55	9.002	0.105	756.3	76.27
4.282	0.053	777.6	32.33	9.988	0.114	751.9	86.29
5.683	0.070	770.9	44.25	11.371	0.126	745.2	100.3

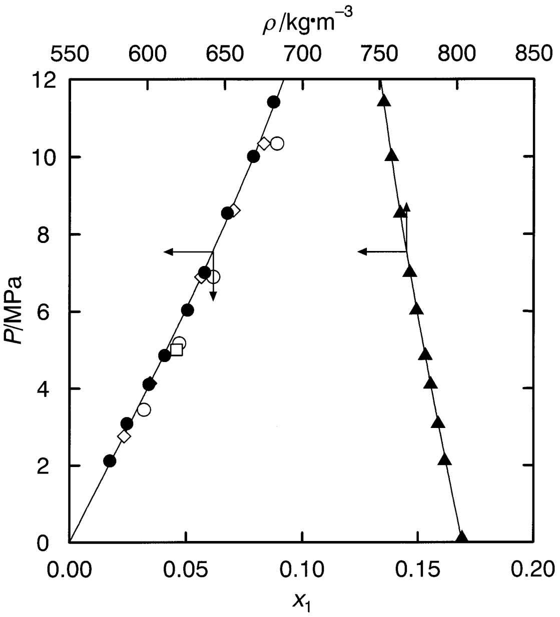

Figure 1. Experimental solubility of methane (1) in methanol (2) and saturated liquid density at 280.15 K: ●, solubility; ▲, saturated liquid density; ○, literature data at 273.15 K;[6] ◇, literature data at 290 K;[6] □, literature data at 273.15 K;[5] —, correlated with a pseudocubic equation of state.

Correlations

The gas solubility and saturated density data were correlated with the three-parameter pseudocubic equation of state previously proposed.[2,8–10] The fugacity of methane in the liquid mixture is equal to the fugacity of pure methane vapor, assuming the liquid component is nonvolatile.

$$P = \frac{RT}{V^* - b} - \frac{a}{V^{*2}} \tag{3}$$

where

$$V^* = \frac{(V - \epsilon b)(V + \sigma b)}{V} \tag{4}$$

$$\epsilon = (1 - \theta)(\xi - 2), \quad \sigma = (1 - \theta)(\xi + 2) \tag{5}$$

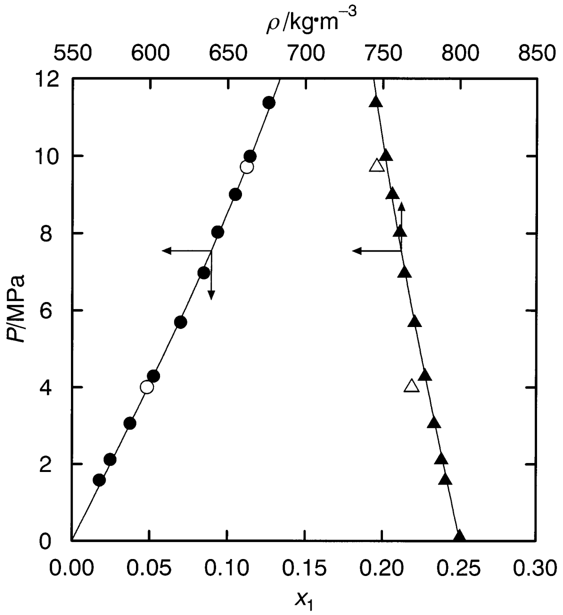

Figure 2. Experimental solubility of methane (1) in ethanol (2) and saturated liquid density at 280.15 K: ●, solubility; ▲, saturated liquid density; ○, △, literature data at 298.15 K;[7] —, correlated with a pseudocubic equation of state.

Table 3. Pressure, *P*, and Densities, *ρ*, for Pure Substances at 280.15 K

P	*ρ*/kg·m^{-3}		
MPa	methane	methanol	ethanol
0.1013		803.5	800.5
1.000	7.04	804.2	801.1
2.000	14.27	805.0	801.7
3.000	21.84	805.7	802.5
4.000	29.73	806.6	803.1
5.000	38.01	807.2	803.8
6.000	46.67	808.0	804.4
6.500	51.12	808.3	804.7
7.000	56.54	808.7	805.4
8.000	65.85	809.4	806.0
9.000	75.45	810.0	806.7
10.000	85.26	810.7	807.3
11.000	95.21	811.4	807.9

$$\xi = \sqrt{\frac{4-\theta}{1-\theta}} \tag{6}$$

$$\theta = \frac{Z_c}{Z_{cs}}, \quad Z_{cs} = \frac{3}{8} \tag{7}$$

in which P, V, T, R, and Z_c denote the pressure, molar volume, temperature, gas constant, and critical compressibility factor, respectively. V^* is the pseudovolume. The parameters a_c, b_c, and θ can be evaluated solely from the critical pressure, P_c, the critical volume, V_c, and the critical temperature, T_c. The equation of state has three parameters, a, b, and θ. The temperature dependences on the parameters a and b were introduced as follows:

$$a = K_a a_c, \quad b = K_b b_c \tag{8}$$

$$a_c = \Omega_a \frac{(RT_c)^2}{P_c}, \quad b_c = \Omega_b \frac{RT_c}{P_c} \tag{9}$$

$$\Omega_a = \frac{27}{64}, \quad \Omega_b = \frac{1}{8} \tag{10}$$

Table 4. Parameters Used in the Equation of State, K_a and K_b, for Methanol and Ethanol at 280.15 K

	ρ_L	P		
material	kg·m^{-3}	kPa	K_a	K_b
methanol	803.5[a]	6.2045[b]	2.111 70	0.965 46
ethanol	800.5[a]	2.5649[b]	2.231 81	0.984 43

[a] Experimental value. [b] Calculated by the Antoine equation with constants from ref 14.

$$\ln K_a = S\left(1 - \sqrt{\frac{T}{T_c}}\right), \quad S = 1.1746 + 3.4539\omega \tag{11}$$

where S and ω denote the coefficient on the correction parameter K_a and the acentric factor, respectively.

The parameter K_a of methane was calculated from eq 11, and the parameter K_b of methane was taken to be unity. The parameters K_a and K_b of methanol and ethanol, computed from the vapor pressures and the densities at 280.15 K, are listed in Table 4.

The following mixing rule is used in the present study, almost similar to the one in the previous works.[2,8]

The parameter a is expressed as

$$\frac{a}{b} = \sum_i^N x_i \frac{a_i}{b_i} - F \tag{12}$$

where

$$\frac{F}{RT} = -C\sum_i^N x_i \ln\left(\sum_i^N x_j \Lambda_{ij}\right) \tag{13}$$

in which F and x denote the function and mole fraction, respectively; C and Λ_{ij} are the Wilson parameters. Subscripts i and j represent the components.

The parameter b is expressed as

$$b = \sum_i^N x_i b_i + \Delta b \tag{14}$$

For methane (1) + methanol (2) and methane (1) + ethanol (2), the excess value Δb is given by

$$\Delta b = x_1 x_2 B_{12}^{\circ} \tag{15}$$

where B_{12}° denotes a parameter between the gas component and the liquid. The equation form of Δb was simplified to reduce the number of the parameters from two to one, compared with the case of the previous study.[2]

In eq 15, subscript 1 denotes the methane and subscript 2 denotes the nonvolatile component.

The parameter θ is expressed as

$$\theta = \sum_i^N x_i \theta_i \tag{16}$$

The parameters Λ_{12}, Λ_{21}, C, and B_{12}° evaluated from the gas solubilities and liquid densities at 280.15 K for binary mixtures are given in Table 5. The correlated results of gas solubilities in nonvolatile liquid mixtures and saturated liquid densities with the equation of state are shown in Figures 1 and 2 for the two binary systems.

Table 5. Parameters for Methane + Alcohol Mixtures at 280.15 K

system	C	B°_{12} $\mathrm{m^3 \cdot kmol^{-1}}$	Λ_{12}	Λ_{21}
methane (1) + methanol (2)	3.0	14.52	0.3061	0.3983
methane (1) + ethanol (2)	3.0	12.02	0.4306	0.4778

Table 6. Mean Absolute Deviations in Solubility, $|\Delta x_1|_{av}$, Liquid Density, $|\Delta \rho_L|_{av}$, and Vapor Density, $|\Delta \rho_V|_{av}$, for Two Binary Systems at 280.15 K with a Pseudocubic Equation of State[a]

system	$|\Delta x_1|_{av}$	$|\Delta \rho_L|_{av}$ $\mathrm{kg \cdot m^{-3}}$	$|\Delta \rho_V|_{av}$ $\mathrm{kg \cdot m^{-3}}$
methane (1) + methanol (2)	0.001	0.2	3.1
methane (1) + ethanol (2)	0.001	0.6	3.1

[a] $|\Delta x_1|_{av} = \sum|x_{1,calcd} - x_{1,exptl}|/I$. $|\Delta \rho_L|_{av} = \sum|\rho_{L,calcd} - \rho_{L,exptl}|/I$. $|\Delta \rho_V|_{av} = \sum|\rho_{V,calcd} - \rho_{V,exptl}|/I$. I is the number of experimental data points.

The calculated deviations between experimental and correlated values are presented in Table 6.

Conclusions

The solubilities of methane in methanol or ethanol and saturated densities were measured at 280.15 K, without analysis of the phase compositions. The experimental data were successfully correlated with the three-parameter pseudocubic equation of state.

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