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Solubility of Carbon Dioxide in Pentadecane, Hexadecane, and Pentadecane + Hexadecane

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Solubilities and saturated densities of carbon dioxide in pentadecane, hexadecane, and an equimolar mixture of pentadecane + hexadecane were measured at 313.15 K without analysis of the phase compositions. The measured solubilities and saturated liquid densities were correlated with an equation of state.

Introduction

In the conventional experimental methods for phase equilibria, both vapor and liquid compositions are analytically determined after attainment of the equilibrium state.

A new experimental method for measuring binary vapor–liquid equilibria at high pressures was presented previously (*1*), based on mass balance and the phase rule, almost similar to that of Hall et al. (*2*). An apparatus with a variable-volume cell was built previously (*1*); the saturated densities and vapor–liquid equilibria were measured for the carbon dioxide + acetone system at 298.15 K (*1*).

A new experimental method for measuring the solubility of a gas in a liquid was proposed in the previous study (*3*), based on mass balance; the saturated densities and the gas solubilities of carbon dioxide in tridecane, tetradecane, and their equimolar mixture at 313.15 K were measured (*3*). The experimental method does not require any analysis of the phase compositions, and the densities of each phase can be measured with density meters.

In the present study, the solubilities and saturated densities of carbon dioxide in pentadecane, hexadecane, and an equimolar mixture of pentadecane + hexadecane were measured at 313.15 K. The experimental values obtained were correlated with the equation of state previously proposed (*3–6*).

Experimental Section

The experimental method previously proposed requires a high-pressure cell equipped with two density meters (*1, 3*). This method is based on mass balance (*3*).

Assuming that the liquid component is nonvolatile, the mass fraction of gas solubility, w_A, can be obtained by

$$w_A = 1 - \frac{m_B}{\rho_L V_L} \qquad (1)$$

where

$$V_L = \frac{(m_A + m_B) - \rho_V V_T}{\rho_L - \rho_V} \qquad (2)$$

The mass fraction of gas solubility w_A can be obtained from the feed masses, m_A and m_B, 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, and the experimental saturated vapor and liquid volumes, V_V and V_L, are not required.

The experimental apparatus and procedures are described in the previous study (*3*). Carbon dioxide with 99.999% purity was supplied by Nihon Sanso Co., Ltd. Special grade reagents of pentadecane and hexadecane were supplied by Tokyo Kasei Co., with the guarantee of 99% and 98% purity, respectively. The physical properties of the materials used are listed in Table I.

Table I. Densities ρ and Refractive Indexes n_D of the Materials Used

	ρ(298.15K)/(kg·m^{-3})		n_D(298.15K)	
	exptl	lit. (*7*)	exptl	lit. (*7*)
pentadecane	765.7	764.88	1.430 65	1.429 79
hexadecane	770.1	770.3	1.433 00	1.432 50

Table II. Equilibrium Pressure *P*, Solubility *x*, Saturated Liquid Density ρ_L, and Saturated Vapor Density ρ_V at 313.15 K

P/MPa	x_1	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
Carbon Dioxide (1) + Pentadecane (2)			
1.703	0.183	761.0	31.4
2.084	0.218	762.3	39.7
3.068	0.312	766.2	60.6
3.617	0.360	768.5	74.5
5.031	0.474	775.1	114.8
5.541	0.514	777.7	132.4
6.002	0.550	780.4	150.0
6.415	0.584	782.6	167.8
Carbon Dioxide (1) + Hexadecane (2)			
1.726	0.189	765.0	31.8
2.133	0.227	766.4	40.7
3.103	0.319	770.1	61.5
3.768	0.375	772.8	78.3
4.733	0.453	777.0	105.5
5.257	0.494	779.5	122.5
6.040	0.553	783.7	152.1
6.473	0.587	785.9	170.9

Results and Discussions

The solubilities and liquid densities of carbon dioxide in pentadecane, hexadecane, and an equimolar mixture of pentadecane + hexadecane were measured at 313.15 K. The accuracy of the calculated solubilities is estimated to be $\delta x = \pm 0.001$, considering the accuracies of the present apparatus and meters used.

The experimental gas solubility and liquid density values at 313.15 K for carbon dioxide + pentadecane and carbon dioxide + hexadecane are given in Table II and shown in Figures 1 and 2. The values obtained for the solubilities of carbon dioxide in an equimolar mixture of pentadecane + hexadecane are given in Table III and shown in Figure 3.

The gas solubility and the saturated liquid density values were correlated with the equation of state previously proposed (*3–6*).

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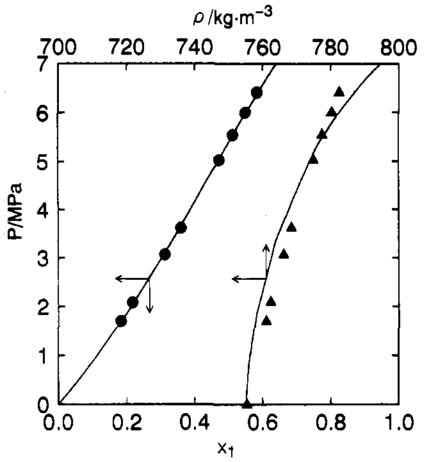

Figure 1. Experimental solubilities and liquid densities of carbon dioxide (1) in pentadecane (2) at 313.15 K: (●) solubilities; (▲) liquid densities; (—) calculated by the equation of state.

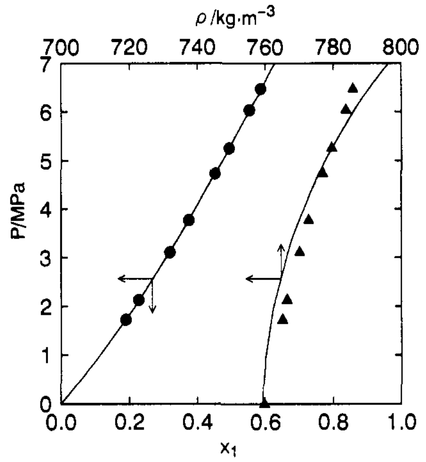

Figure 2. Experimental solubilities and liquid densities of carbon dioxide (1) in hexadecane (2) at 313.15 K: (●) solubilities; (▲) liquid densities; (—) calculated by the equation of state.

Table III. Equilibrium Pressure P, Mole Fractions x, Saturated Liquid Density ρ_L, and Saturated Vapor Density ρ_V for the Ternary System at 313.15 K

P/MPa	x_1	x_2, x_3	ρ_L/(kg·m^{-3})	ρ_V/(kg·m^{-3})
Carbon Dioxide (1) + Pentadecane (2) + Hexadecane (3)				
1.714	0.184	0.408	762.9	31.7
2.116	0.222	0.389	764.3	40.5
3.089	0.316	0.342	768.1	61.2
3.743	0.370	0.315	770.7	77.7
4.708	0.450	0.275	775.2	104.8
5.257	0.494	0.253	777.7	122.7
6.009	0.552	0.224	781.8	150.7
6.405	0.582	0.209	784.0	168.1

The pseudocubic equation of state used in the present study is given as follows (*3–6*):

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

where

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

$$a_c = 27(RT_c)^2/64P_c, \quad b_c = RT_c/8P_c \tag{5}$$

$$\epsilon = (1 - \theta)(\xi - 2), \quad \sigma = (1 - \theta)(\xi + 2) \tag{6}$$

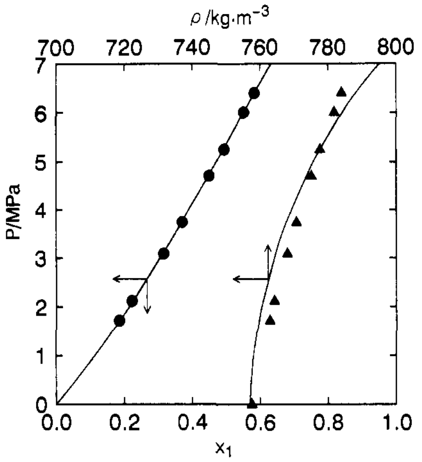

Figure 3. Experimental solubilities and liquid densities of carbon dioxide (1) in an equimolar mixture of pentadecane (2) + hexadecane (3) at 313.15 K: (●) solubilities; (▲) liquid densities; (—) calculated by the equation of state.

Table IV. Parameters Used in the Equation of State, K_a and K_b, for Pentadecane and Hexadecane at 313.15 K

substance	ρ_L/(kg·m^{-3})	P/kPa	K_a	K_b
pentadecane	755.4[a]	0.0028[b]	2.769 56	0.933 02
hexadecane	759.8[a]	0.0011[b]	2.842 49	0.918 24

[a] ρ_L: experimental values. [b] P: calculated by the Antoine equation with constants from Reid et al. (*8*).

$$\xi = \left(\frac{4 - \theta}{1 - \theta}\right)^{1/2} \tag{7}$$

$$\theta = 8Z_c/3, \quad Z_c = P_cV_c/RT_c \tag{8}$$

in which P, V, T, R, and Z_c denote the pressure, molar volume, temperature, gas constant, and critical compressibility factor, respectively. V^* means the apparent volume. The parameters a_c, b_c, and θ can be evaluated solely from the critical pressure P_c, critical volume V_c, and 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:

$$a = K_a a_c, \quad b = K_b b_c \tag{9}$$

$$\ln K_a = S\{1 - (T/T_c)^{1/2}\}, \quad S = 1.1746 + 3.4539\omega \tag{10}$$

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

The parameter K_a of carbon dioxide was calculated from eq 10, and the parameter K_b of carbon dioxide was taken to be unity. The parameters K_a and K_b of pentadecane and hexadecane computed from the vapor pressures and the densities at 313.15 K are given in Table IV.

The following mixing rule is used in the present study, almost similar to the one in the previous works (*3, 4*).

Parameter a is expressed as

$$\frac{a}{b} = \sum x_i \frac{a_i}{b_i} - F \tag{11}$$

where

$$\frac{F}{RT} = -\mathrm{C}\sum x_i \ln\left(\sum x_i \Lambda_{ij}\right) \tag{12}$$

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.

Table V. Wilson Parameters, C, Λ_{12}, and Λ_{21}, the Parameter in the Equation of State, $B_{12}°$, Obtained from Two Binary Mixtures at 313.15 K

system	C	Λ_{12}	Λ_{21}	$B_{12}°$
carbon dioxide (1) + pentadecane (2)	3.0	0.6077	0.0320	−58.1177
carbon dioxide (1) + hexadecane (2)	3.0	0.5038	0.0150	−73.9501

Table VI. Mean Absolute Deviations in Solubility $|\Delta x_1|_{av}$, Liquid Density $|\Delta\rho_L|_{av}$, and Vapor Density $|\Delta\rho_V|_{av}$ for Three Systems at 313.15 K with the Equation of State

system	$\lvert\Delta x_1\rvert_{av}$	$\lvert\Delta\rho_L\rvert_{av}$/ (kg·m^{-3})	$\lvert\Delta\rho_V\rvert_{av}$/ (kg·m^{-3})
carbon dioxide (1) + pentadecane (2)	0.002	2.9	6.1
carbon dioxide (1) + hexadecane (2)	0.001	2.7	5.6
carbon dioxide (1) + pentadecane (2) + hexadecane (3)[a]	0.002	2.6	5.6

[a] $\Lambda_{23} = \Lambda_{32} = 1$, $B_{23}° = 0$, $|\Delta x_1|_{av} = \sum|(x_{1,calcd} - x_{1,exptl})|/I$, $|\Delta\rho_L|_{av} = \sum|(\rho_{L,calcd} - \rho_{L,exptl})|/I$, and $|\Delta\rho_V|_{av} = \sum|(\rho_{V,calcd} - \rho_{V,exptl})|/I$ (I is the number of experimental points).

Parameter b is expressed as

$$b = \sum x_i b_i + \Delta b \qquad (13)$$

For carbon dioxide (1) + pentadecane (2) and carbon dioxide (1) + hexadecane (2), the excess value Δb is given by

$$\Delta b = x_1 x_2 B_{12}° \qquad (14)$$

where $B_{12}°$ denotes the 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, comparing with the previous study (*3*).

For carbon dioxide (1) + pentadecane (2) + hexadecane (3), Δb is given by

$$\Delta b = x_1 x_2 B_{12}° + x_1 x_3 B_{13}° + x_2 x_3 B_{23}° \qquad (15)$$

In eqs 14 and 15, subscript 1 denotes the gas and subscripts 2 and 3 denote the liquid components. The parameter $B_{23}°$ between the liquid components 2 and 3 is taken to be zero.

Parameter θ is expressed as

$$\theta = \sum x_i \theta_i \qquad (16)$$

The parameters Λ_{12}, Λ_{21}, C, and $B_{12}°$ evaluated from the liquid densities and the solubilities at 313.15 K for binary mixtures are given in Table V. For carbon dioxide + pentadecane + hexadecane, the parameters obtained in the binary systems were used in the calculation, and the interactions between pentadecane and hexadecane were neglected.

The calculation results of gas solubilities in nonvolatile liquid mixtures and saturated liquid densities with the equation of state are shown in Figures 1–3 for the two binary systems and the ternary system. The calculation deviations are presented in Table VI.

Conclusions

The solubilities and saturated densities for the systems of carbon dioxide with pentadecane, hexadecane, and an equimolar mixture of pentadecane + hexadecane were measured at 313.15 K. The gas solubility data and saturated liquid densities obtained in the present study were correlated with the equation of state.

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Symbols

a = parameter in eq 3 (kPa·m^6·mol^{-2})
b = parameter in eq 3 (m^3·mol^{-1})
$B°$ = parameters in eqs 14 and 15 (m^3·mol^{-1})
C = Wilson parameter in eq 12
F = function in eq 11 (kPa·m^3·mol^{-1})
I = number of data
K_a, K_b = correction factors given by eq 9
m = mass (kg)
P = pressure (kPa)
R = gas constant (kPa·m^3·mol^{-1}·K^{-1})
S = parameter in eq 10
T = temperature (K)
V = volume (m^3·mol^{-1})
V^* = apparent volume (m^3·mol^{-1})
w = mass fraction
x = mole fraction
Z_c = critical compressibility factor

Greek Letters

Δ = excess value
ρ = density (kg·m^{-3})
ϵ, θ, σ, ξ = parameters in eqs 6–8
Λ = Wilson parameter in eq 12

Subscripts

A = gas component
B = liquid component
c = critical property
1, 2, 3, i, j = components
L = liquid phase
V = vapor phase
T = total amount

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