volume of the solutes investigated either in crystal form or in aqueous solution occupies about one fourth of their total volume. These results are close to those given previously for relatively polar molecules (*19*). For such molecules, the empty volume around them in the crystal is small due to the strong forces holding them together. Such molecules also have a small empty volume associated with them in aqueous solution because of their strong attraction to the polar water molecules, which results in a shrinkage of the empty volume.

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Solubility of Carbon Dioxide in *n*-Tetracosane and in *n*-Dotriacontane

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The solubility of carbon dioxide in *n*-tetracosane and *n*-dotriacontane has been measured in a semiflow apparatus over the temperature range from 100 to 300 °C at pressures up to 50 atm. Henry's constant and the partial molar volume at infinite dilution are determined from the solubility data.

Introduction

The solubility of carbon dioxide in heavy paraffins is of interest in some industrial processes, notably Fischer–Tropsch syntheses. Robinson et al. (*1–3*) have measured the solubility of carbon dioxide in several heavy *n*-paraffins, in the cycloparaffins cyclohexane and *trans*-decalin, and in several aromatic solvents at temperatures to 160 °C. Chao et al. (*4–6*) have reported the solubility of carbon dioxide in *n*-hexatriacontane, *n*-octacosane, and *n*-eicosane over the temperature range of 100–300 °C and at pressures from 10 to 50 atm. In the present study, the solubility of carbon dioxide in *n*-tetracosane (n-C_{24}) and *n*-dotriacontane (n-C_{32}) at temperatures up to 300 °C and pressures to 50 atm has been determined. Henry's constant and the partial molar volume at infinite dilution of the dissolved gas are obtained from the data.

Experimental Section

The experimental apparatus used for the measurement of gas solubility was a semiflow vapor–liquid equilibrium apparatus. Detailed description of the equipment and sampling procedure has been reported (*7*). Briefly, a gas stream from a high-pressure cylinder is passed through two cells in series containing the hydrocarbon liquid. The first cell is the presaturator and the second the equilibrium cell. Upon saturation, the sample from the latter is withdrawn, reduced in pressure, and collected in a trap. The collected hydrocarbon is weighed with an analytical balance, and the liberated gas from the trap is measured volumetrically in a buret for the liquid phase and in a wet test meter for the gas phase. Temperature of the

Table I. Solubility Data of Carbon Dioxide in *n*-Tetracosane

T, °C	*P*, atm	*x*	*y*	*K*
100.0	10.0	0.0819	1.0000	12.22
	20.0	0.1720	1.0000	5.814
	30.0	0.2437	1.0000	4.103
	40.0	0.3004	1.0000	3.329
	50.0	0.3531	1.0000	2.832
200.0	10.0	0.0646	0.9996	15.47
	20.0	0.1228	0.9997	8.141
	30.0	0.1762	0.9998	5.674
	40.0	0.2284	0.9998	4.377
	50.0	0.2705	0.9999	3.696
300.0	10.0	0.0595	0.9889	16.62
	20.0	0.1127	0.9937	8.817
	30.0	0.1612	0.9951	6.173
	40.0	0.2060	0.9957	4.833
	50.0	0.2533	0.9961	3.932

Table II. Solubility Data of Carbon Dioxide in *n*-Dotriacontane

T, °C	*P*, atm	*x*	*y*	*K*
100.0	10.0	0.1008	1.0000	9.921
	20.0	0.1971	1.0000	5.074
	30.0	0.2701	1.0000	3.702
	40.0	0.3371	1.0000	2.966
	50.0	0.3962	1.0000	2.524
200.0	10.0	0.0714	1.0000	14.01
	20.0	0.1465	1.0000	6.826
	30.0	0.2010	1.0000	4.975
	40.0	0.2582	1.0000	3.873
	50.0	0.3074	1.0000	3.253
300.0	10.0	0.0649	0.9989	15.39
	20.0	0.1260	0.9994	7.932
	30.0	0.1868	0.9995	5.351
	40.0	0.2367	0.9995	4.223
	50.0	0.2839	0.9996	3.521

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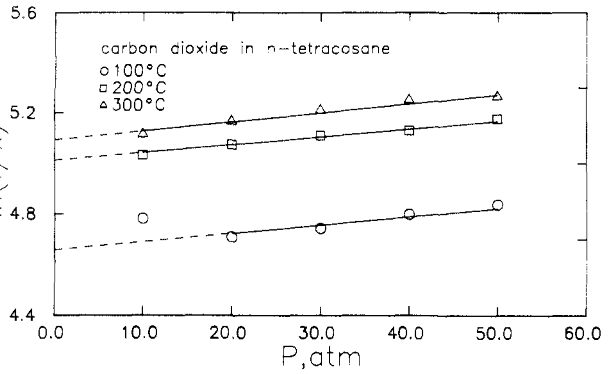

Figure 1. Plot of ln (f/x) versus pressure for system CO_2 + n-tetracosane.

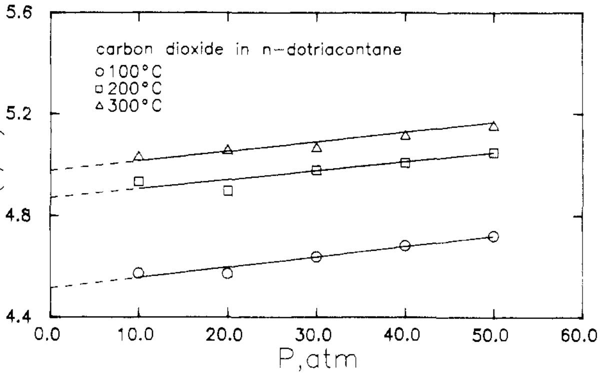

Figure 2. Plot of ln (f/x) versus pressure for system CO_2 + n-dotriacontane.

equilibrium cell is measured to an accuracy of 0.2 °C by a type J thermocouple inserted in the equilibrium cell. Pressure was measured by a Heise gauge to ±1.5 psi.

The n-tetracosane and n-dotriacontane was purchased from Tokyo Kasei Kogyo Co., Ltd., with a minimum purity of 99%. The purity of carbon dioxide used in this work is 99%.

Results

Tables I and II present vapor–liquid equilibrium data for carbon dioxide + n-tetracosane and carbon dioxide + n-dotriacontane, respectively, at three temperatures: 100, 200, and 300 °C. At each temperature, data are reported at five pressures: 10, 20, 30, 40, and 50 atm. Four replicate samples were taken at each experimental condition. Reproducibility of the replicates was within 2%. K values listed in Tables I and II were calculated from the averaged values of x and y according to the definition $K = y/x$. It can be seen that the solubility of carbon dioxide increases with pressure and decreases with increasing temperatures at the conditions of this work.

Henry's constant and the partial molar volume at infinite dilution are determined from the solubility data by plotting ln (f/x) of the solute at a temperature vs the pressure. The fugacity f is calculated for pure carbon dioxide by using the equation proposed by Huang et al. (*8*). Figures 1 and 2 show the linear result that is obtained. By the equation of Krichevsky and Kasamovsky (*9*), the intercept at the pressure equal to the vapor pressure of the solvent determines Henry's constant, and the slope gives the partial molar volume at infinite dilution. Table III lists the results.

Table III. Henry's Constant and the Partial Molar Volume at Infinite Dilution

solvent	temp, °C	Henry's const, atm	partial molar vol, mL/mol
n-$C_{24}H_{50}$	100	105	100
	200	150	120
	300	163	168
n-$C_{32}H_{66}$	100	91.5	125
	200	130	138
	300	145	179

Table IV. Soave Correlation of Solubility Data

solvent	T, °C	P range, atm	data pts	10^2k_{ij}	% AAD, $\Delta P/P^a$	AAD, $10^4\Delta y^b$
n-$C_{24}H_{50}$	100	10–50	5	9.21	3.48	0.45
	200	10–50	5	5.51	1.45	1.13
	300	10–50	5	6.20	1.92	18.99
n-$C_{32}H_{66}$	100	10–50	5	4.97	2.88	0.37
	200	10–50	5	−1.77	2.21	0.48
	300	10–50	5	−6.06	0.87	4.98

[a] Percent average absolute deviation: $\Delta P/P = (1/n)\sum_{i=1}^{n} |(P_{i,\mathrm{cal}} - P_{i,\mathrm{exp}})/P_{i,\mathrm{exp}}| \times 100\%$. [b] Average absolute deviation: $\Delta y = (1/n)\cdot\sum_{i=1}^{n} |y_{i,\mathrm{cal}} - y_{i,\mathrm{exp}}|$.

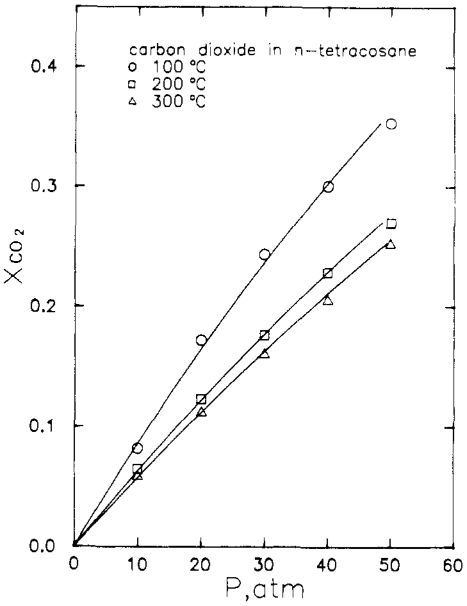

Figure 3. Comparison of calculated solubility of carbon dioxide in n-tetracosane with experimental data.

Correlation

The solubility of carbon dioxide in n-paraffin solvents n-C_{24} and n-C_{32} are correlated by the modified Soave equation (*10*). For the modified Soave equation, the specific relations are

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)}$$

where

$$a = \sum_i \sum_j z_i z_j a_{ij}$$

$$b = \sum_i z_i b_i$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2}(1 - k_{ij})$$

$$a_{ii} = 0.42748\alpha_i R^2 T_{ci}^2 / P_{ci}$$

$$b_i = 0.08664RT_{ci}/P_{ci}$$

$$a_i = [1 + m_i(1 - T_{ri}^{0.5})]^2$$

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2$$

The critical temperature T_c and pressure P_c of n-paraffins required in the equations are calculated by means of Gasem

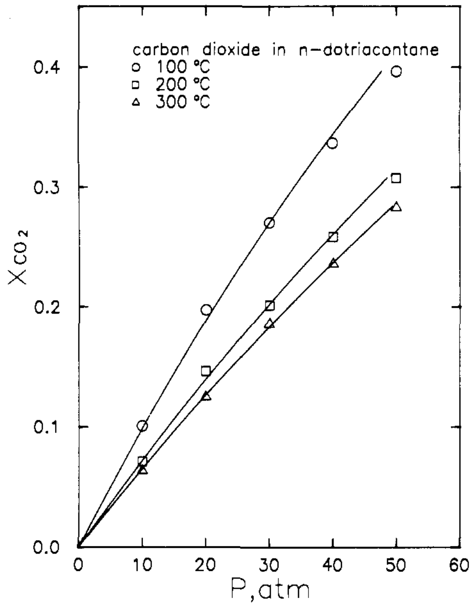

Figure 4. Comparison of calculated solubility of carbon dioxide in *n*-dotriacontane with experimental data.

and Robinson's correlation as described by Huang et al. (*7*). Values of normal boiling points needed in the calculations for T_c are taken from API-44 Tables (*11*).

The calculated results with the optimum values of k_{ij} for each isotherm are listed in Table IV. The average absolute deviations in P are not more than 4%. Figures 3 and 4 show the comparisons of calculated solubilities of carbon dioxide in n-$C_{24}H_{50}$ and in n-$C_{32}H_{66}$, respectively, with experimental data. It indicates that the modified Soave equation with one interaction parameter is adequate to correlate the solubility data.

Glossary

a,b	parameters in Soave equation of state
f	fugacity
k_{ij}	interaction parameters between components i and j in mixing rules for equation of state
K	vaporization equilibrium ratio, y/x
P	pressure
P_c	critical pressure
T	temperature
T_c	critical temperature
T_r	reduced temperature, T/T_c
v	molar volume
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
z	mole fraction (liquid or vapor phase)
ω	acentric factor

Registry No. CO_2, 124-38-9; *n*-tetracosane, 646-31-1; *n*-dotriacontane, 544-85-4.

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Limiting Interdiffusion Coefficients of Some Hydroxylic Compounds in Water from 265 to 433 K

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Interdiffusion coefficients of ethanol, 1-propanol, 1-butanol, 2-methyl-2-propanol, ethylene glycol, glycerol, and pentaerythritol have been measured in water at concentrations close to infinite dilution and temperatures between 265.2 and 433.2 K. Activation energies are not sensitive to the solutes, decrease with increasing temperature, and are close to that for the self-diffusion of pure water. At the lower temperatures, the quantity $D\eta/T$ decreases with decreasing temperature for 2-methyl-2-propanol. This effect is smaller for 1-butanol and 1-propanol. For ethanol and the polyols, the quantity $D\eta/T$ is insensitive to temperature.

Introduction

In earlier work, we determined the limiting interdiffusion coefficients of hydrophobic solutes such as aromatic hydrocarbons (*1*, *2*) and a neutral metal complex (*3*) in water. Because water is known to be a "structured" solvent (*4*), we attempted to discover if there is an effect of "water structure" itself, or of the enhanced water structure around hydrophobic solute molecules, on the diffusion of hydrophobic molecules. In one of these studies, we made measurements covering a wide temperature range—from the supercooled region to the region above the normal boiling point of water (*2*).

The present study was undertaken to make measurements on hydroxylic compounds over a wide temperature range and

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