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Solubility of Carbon Dioxide in 1-Tetradecanol, 1-Hexadecanol, and 1-Octadecanol

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The solubility of carbon dioxide in three 1-alkanols (C_{14}, C_{16}, and C_{18}) has been measured in a semiflow apparatus under temperatures ranging from 100 to 300 °C at pressures up to 50.7 bar. Henry's constant and the partial molar volume at infinite dilution are evaluated from the solubility data.

Introduction

Vapor–liquid equilibria (VLE) of carbon dioxide with hydrocarbons are of interest in some industrial processes, including processing of petroleum products, production of coal liquids, and enhanced oil recovery. Limited data are available on systems involving carbon dioxide and those heavy hydrocarbons which exist as solids at room temperature. Robinson et al. (*1–3*) have determined the solubility of carbon dioxide in several heavy *n*-paraffins, cycloparaffins, and aromatic solvents at temperatures to 160 °C. Chao et al. (*4–6*) have reported the solubility of carbon dioxide in several heavy *n*-paraffins over the temperature range from 100 to 300 °C and at pressures to 50 atm. Tsai et al. (*7–9*) have measured the VLE data of carbon dioxide with aromatic hydrocarbons at temperatures of 50–300 °C and pressures to 50 atm.

The heavy alcohols are of significant interest in their pure form because of their extensive use in the cosmetic, pharmaceutical, and surfactant industries. The VLE data of carbon dioxide with heavy alcohols are required for a promising process to obtain these alcohols in a very pure form. In the present study, the solubility of carbon dioxide in 1-tetradecanol, 1-hexadecanol, and 1-octadecanol at temperatures from 100 to 300 °C and at pressures from 10.1 to 50.7 bar has been measured. Henry's constant and the partial molar volume of carbon dioxide at infinite dilution are obtained by fitting the Krichevsky–Kasarnovsky equation (*10*) to the data.

Experimental Section

A semiflow VLE apparatus was used for the measurement of gas solubility. A detailed description of the equipment and sampling procedure has been reported (*11*). Briefly, carbon dioxide gas supplied from a high-pressure cylinder was bubbled through a presaturator and an equilibrium cell in series while both were filled with the 1-alkanol solvents. To promote mixing and equilibration, the cells were packed with raschig rings. Equilibration required about 20–40 min, at the end of which the liquid composition reached a constant value. Attainment of VLE was tested by varying the gas flow rate. The vapor and liquid compositions were found to be independent of the gas flow rate when equilibrium was achieved.

Saturated liquid in the equilibrium cell was sampled by withdrawing the liquid through a tube, releasing the pressure, and collecting the liquid in a trap which was immersed in an ice bath. The trap with the solidified sample was weighed to determine the sample mass. The liberated gas from the solidified sample was determined volumetrically in a buret. The sampling procedure for the gas phase was similar to that of the liquid phase, except that a wet test meter was used in place of a buret to measure the gas. The temperature of the equilibrium cell was measured to an accuracy of 0.2 K with a type J thermocouple inserted in the equilibrium cell. The pressure was measured with a Heise gauge to ±0.1 bar.

Table 1. Solubility Data of Carbon Dioxide in 1-Tetradecanol for Temperature *T*, Pressure *P*, Liquid (*x*) and Vapor (*y*) Mole Fraction of Carbon Dioxide, and *K* = *y*/*x* Values

T/°C	P/bar	x_{CO_2}	y_{CO_2}	K_{CO_2}
100	10.1	0.0618	0.9952	16.10
	20.3	0.1185	0.9960	8.41
	30.4	0.1715	0.9971	5.81
	40.5	0.2258	0.9976	4.42
	50.7	0.2704	0.9984	3.69
150	10.1	0.0589	0.9890	16.79
	20.3	0.1091	0.9901	9.08
	30.4	0.1590	0.9927	6.24
	40.5	0.2067	0.9934	4.81
	50.7	0.2542	0.9954	3.92
200	10.1	0.0474	0.9838	20.76
	20.3	0.0923	0.9892	10.72
	30.4	0.1324	0.9924	7.50
	40.5	0.1698	0.9932	5.85
	50.7	0.2063	0.9950	4.82

Table 2. Solubility Data of Carbon Dioxide in 1-Hexadecanol for Temperature *T*, Pressure *P*, Liquid (*x*) and Vapor (*y*) Mole Fraction of Carbon Dioxide, and *K* = *y*/*x* Values

T/°C	P/bar	x_{CO_2}	y_{CO_2}	K_{CO_2}
100	10.1	0.0635	0.9938	15.65
	20.3	0.1253	0.9950	7.94
	30.4	0.1905	0.9958	5.23
	40.5	0.2488	0.9965	4.01
	50.7	0.3041	0.9975	3.28
200	10.1	0.0525	0.9925	18.90
	20.3	0.0989	0.9932	10.04
	30.4	0.1452	0.9947	6.85
	40.5	0.1977	0.9955	5.04
	50.7	0.2371	0.9969	4.21
300	10.1	0.0425	0.9481	22.31
	20.3	0.0879	0.9690	11.02
	30.4	0.1299	0.9794	7.54
	40.5	0.1701	0.9808	5.77
	50.7	0.2017	0.9822	4.87

The carbon dioxide used in this work had a minimum purity of 99.8 mol %. The 1-tetradecanol was purchased from Merck with a minimum purity of 98 mol %. The 1-hexadecanol and 1-octadecanol from Sigma had a minimum purity of 99 mol %. The chemicals were used without further purification.

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Table 3. Solubility Data of Carbon Dioxide in 1-Octadecanol for Temperature *T*, Pressure *P*, Liquid (*x*) and Vapor (*y*) Mole Fraction of Carbon Dioxide, and *K* = *y*/*x* Values

T/°C	P/bar	x_{CO_2}	y_{CO_2}	K_{CO_2}
100	10.1	0.0720	0.9980	13.86
	20.3	0.1385	0.9983	7.21
	30.4	0.1967	0.9990	5.08
	40.5	0.2540	0.9996	3.94
	50.7	0.2923	0.9997	3.42
200	10.1	0.0528	0.9953	18.85
	20.3	0.1040	0.9960	9.58
	30.4	0.1448	0.9977	6.89
	40.5	0.1837	0.9980	5.43
	50.7	0.2268	0.9987	4.40
300	10.1	0.0473	0.9760	20.63
	20.3	0.0931	0.9839	10.57
	30.4	0.1436	0.9851	6.86
	40.5	0.1723	0.9879	5.73
	50.7	0.2135	0.9906	4.64

Table 4. Critical Properties and Acentric Factor

substance	T_c/°C	P_c/bar	ω
carbon dioxide	30.1	73.8	0.239
1-tetradecanol	429.5	17.6	1.131
1-hexadecanol	451.2	15.7	1.181
1-octadecanol	473.9	14.1	1.234

Table 5. Correlation of VLE Data with Modified Soave Equation: Temperature *T*, Pressure *P* Range, Average Relative Percent Deviation in Pressure 100Δ*P*/*P*, and Average Absolute Deviation in the Vapor-Phase Mole Fraction of Carbon Dioxide Δ*y*

solvent	T/°C	P range/ bar	data points	k_{12}	$100\Delta P/P$[a]	Δy[b] $\times 10^4$
1-tetradecanol	100	10.1–50.7	5	0.0868	0.68	31
	150	10.1–50.7	5	0.0201	1.63	74
	200	10.1–50.7	5	0.0346	2.12	48
1-hexadecanol	100	10.1–50.7	5	0.0713	3.57	43
	200	10.1–50.7	5	−0.0100	1.85	34
	300	10.1–50.7	5	0.266	1.37	230
1-octadecanol	100	10.1–50.7	5	0.0667	2.06	11
	200	10.1–50.7	5	0.0074	3.00	20
	300	10.1–50.7	5	−0.0170	2.90	119

[a] $\Delta P/P = (1/n)\sum_{i=1}^{n}|(P_{i,\mathrm{calcd}} - P_{i,\mathrm{exptl}})/P_{i,\mathrm{exptl}}|$. [b] $\Delta y = (1/n)\sum_{i=1}^{n}|y_{i,\mathrm{calcd}} - y_{i,\mathrm{exptl}}|$.

Results

Table 1 presents VLE data for carbon dioxide with 1-tetradecanol at three temperatures: 100, 150, and 200 °C. Tables 2 and 3 present VLE data for carbon dioxide with 1-hexadecanol and 1-octadecanol, respectively, at three temperatures: 100, 200, and 300 °C. At each temperature, five pressures (10.1, 20.3, 30.4, 40.5, and 50.7 bar) were investigated for all systems. The reported data were the average values of at least four replicate samples at each experimental condition. The sample compositions were generally reproducible within 2% in the mole fraction of carbon dioxide for the liquid phase and 0.1% for the vapor phase. The *K* values of carbon dioxide listed in Tables 1–3 were calculated from the average values of mole fractions in the liquid phase *x* and mole fractions in the vapor phase *y* according to the definition $K = y/x$. It can be seen that the solubility of carbon dioxide increases with pressure *P* and decreases with rising temperature *T* under the conditions of this work.

Correlation

The solubility of carbon dioxide in 1-alkanol solvents is correlated by the modified Soave equation (*12*). For the modified Soave equation with one interaction parameter, k_{ij}, the specific relations are

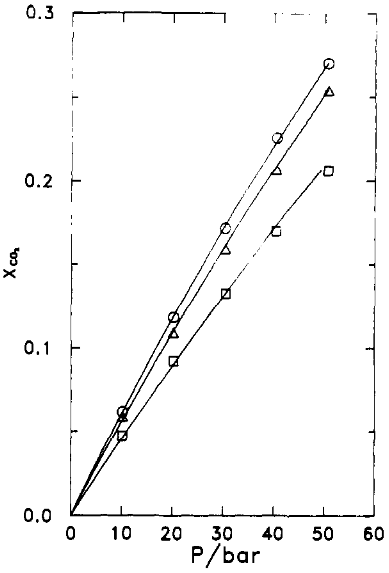

Figure 1. Comparison of the calculated solubility of carbon dioxide in 1-tetradecanol with experimental data: ○, 100 °C; △, 150 °C; □, 200 °C; —, calculated with eq 1.

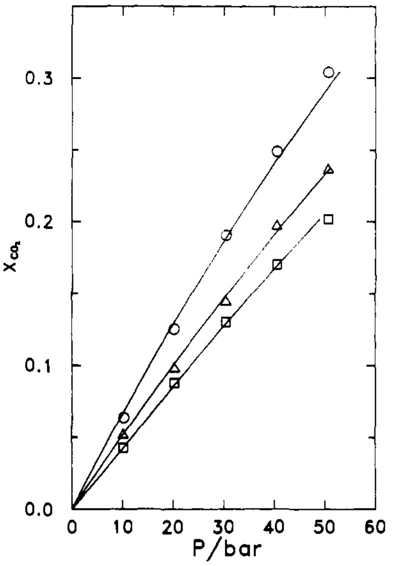

Figure 2. Comparison of the calculated solubility of carbon dioxide in 1-hexadecanol with experimental data: ○, 100 °C; △, 200 °C; □, 300 °C; —, calculated with eq 1.

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{1}$$

where *v* is the molar volume and

$$a = \sum_i \sum_j z_i z_j a_{ij} \tag{2}$$

$$b = \sum_i z_i b_i \tag{3}$$

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - k_{ij}) \tag{4}$$

$$a_{ii} = 0.42748\alpha_i R^2 T_{ci}^{\ 2}/P_{ci} \tag{5}$$

$$b_i = 0.08664RT_{ci}/P_{ci} \tag{6}$$

$$\alpha_i = [1 + m_i(1 - T_{r,i}^{\ 0.5})]^2 \tag{7}$$

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^{\ 2} \tag{8}$$

T_{ci}, P_{ci}, $T_{r,i}$, and ω_i are, respectively, the critical temperature, critical pressure, reduced temperature, and acentric factor of

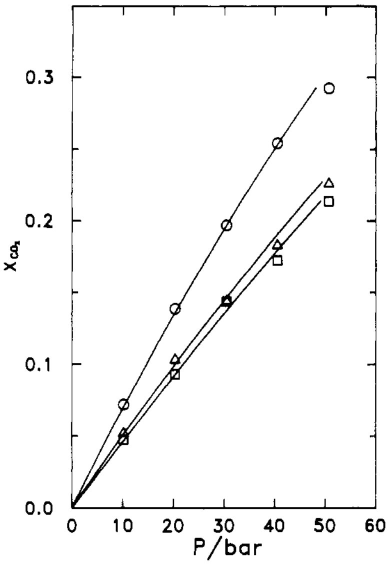

Figure 3. Comparison of the calculated solubility of carbon dioxide in 1-octadecanol with experimental data: ○, 100 °C; △, 200 °C; □, 300 °C; —, calculated with eq 1.

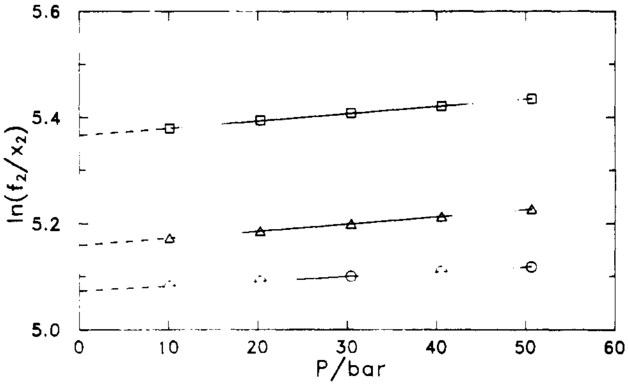

Figure 4. ln(*f*/*x*) versus pressure for the carbon dioxide + 1-tetradecanol system: ○, 100 °C; △, 150 °C; □, 200 °C.

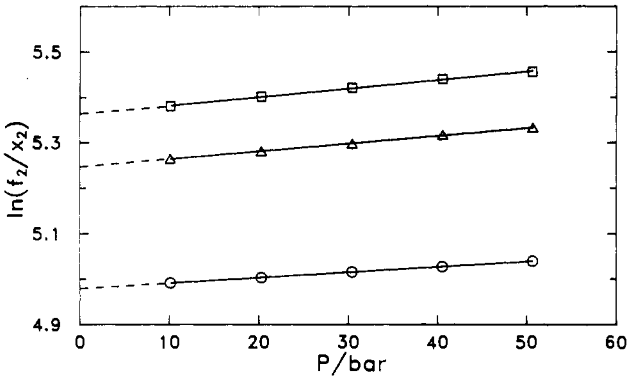

Figure 5. ln(*f*/*x*) versus pressure for the carbon dioxide + 1-hexadecanol system: ○, 100 °C; △, 200 °C; □, 300 °C.

component *i*. z_i is the mole fraction of component *i* in the liquid or vapor phase.

The critical temperatures T_c of 1-tetradecanol and 1-hexadecanol required in the equations are calculated by means of the Joback method (*13*), whereas the critical pressures P_c of the two components are obtained from the Teja et al. method (*14*). The critical data of 1-octadecanol are taken from the property data bank of Reid et al. (*15*). The acentric factors ω of 1-alkanols are estimated by the Lee–Kesler correlations (*16*). In Table 4 T_c, P_c, and ω are listed for all the substances used in this work.

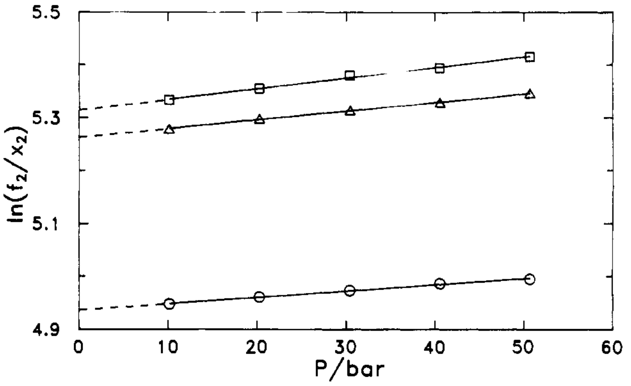

Figure 6. ln(*f*/*x*) versus pressure for the carbon dioxide + 1-octadecanol system: ○, 100 °C; △, 200 °C; □, 300 °C.

Table 6. Henry's Constant H_2 and Partial Molar Volume at Infinite Dilution $\bar{v}_2^\infty$

solvent	T/°C	H_2/bar	$\bar{v}_2^\infty$/(cm^3·mol^{-1})
1-tetradecanol	100	160	27.5
	150	174	48.0
	200	214	56.9
1-hexadecanol	100	146	34.1
	200	190	65.7
	300	213	92.5
1-octadecanol	100	139	38.8
	200	193	67.9
	300	203	99.7

The calculated results with the optimum value of k_{12} for each isotherm are summarized in Table 5. In the calculation, the optimum values of k_{12} are determined by minimizing the bubble pressure variance. For the majority of isotherms the calculated bubble pressures agree with experimental data within 3% on the average. Figures 1–3 show the comparisons of calculated and experimental solubilities of carbon dioxide in the three 1-alkanol solvents. It indicates that the calculated results are in agreement with experimental data over the entire temperature and pressure range of data.

Henry's constant H_2 and the partial molar volume $\bar{v}_2^\infty$ of carbon dioxide at infinite dilution are obtained from the solubility data by plotting $\ln(f_2/x_2)$ of the solute carbon dioxide at a temperature T as a function of pressure P. The solute fugacity f_2 is evaluated by the modified Soave equation coupled with the determined interaction parameters. Figures 4–6 show the linear result that is obtained. By the Krichevsky–Kasarnovsky equation,

$$\ln(f_2/x_2) = \ln H_2 + \bar{v}_2^\infty(P - P_1^s)/RT \tag{9}$$

where P_1^s is the saturated vapor pressure of the solvents, the intercept at the vapor pressure of the solvent determines Henry's constant, and the slope gives the partial molar volume of the solute at infinite dilution. The resulting values are reported in Table 6. The values of all the parameters increase with temperature.

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