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Solubilities of Heavy *n*-Paraffins in Subcritical and Supercritical Carbon Dioxide

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The solubilities of *n*-tetracosane, *n*-octacosane, *n*-dotriacontane, and *n*-hexatriacontane in carbon dioxide have been measured by using a semiflow phase equilibrium apparatus over the temperature range from 308.2 to 338.2 K at pressures up to 208.9 bar. The measured mole fractions of *n*-tetracosane, *n*-octacosane, *n*-dotriacontane, and *n*-hexatriacontane are correlated with the reduced density and reduced pressure of carbon dioxide and temperature.

Introduction

The phase behavior of low-volatile components in supercritical fluid is of great interest in the processing of petroleum products, food processing, special chemicals processing, and pharmaceutical industries (*1*). One of the significant advantages of supercritical fluid extraction is that the solvent can be easily separated from the accompanying solute, thereby significantly reducing the contamination of valuable compounds with a residual solvent. Compressed CO_2 has a high degree of solvency for many low-volatile components, and up to now it is one of the most important supercritical solvents for practical applications (*2*).

Limited fundamental studies on the solubilities of heavy *n*-paraffin in supercritical CO_2 are presented in the literature. Schmitt and Reid (*3*) have measured the solubilities of *n*-octadecane, *n*-nonadecane, *n*-eicosane, *n*-docosane, and *n*-tetracosane in supercritical CO_2 at 310 and 320 K. McHugh et al. (*4*) have reported the solubilities of *n*-octacosane in dense supercritical CO_2 over the temperature range from 307.9 to 325.2 K at pressures up to 276 bar. Swaid et al. (*5*) have presented the solubilities of *n*-octacosane in dense supercritical CO_2 at 323.7, 343.2, and 362.5 K. King et al. (*6*) have presented the solubilities of *n*-dotriacontane in supercritical CO_2 at 308.2 K over a pressure range from 91.9 to 161.0 bar. Spee and Schneider (*2*) have reported the solubilities of *n*-dotriacontane in supercritical CO_2 at 393.2 K and pressures up to 630 bar.

Although some solubility data for supercritical CO_2 + heavy *n*-paraffin systems have been reported, only Charoensombutamon et al. (*7*) have studied in detail both the subcritical and the supercritical states for the system CO_2 + *n*-hexadecane over the temperature range from 308.2 to 343.2 K and over a pressure range from 6.9 to 258.7 bar. Previously reported data also include the solubilities of 1-hexadecanol and 1-octadecanol (*8*) in subcritical and supercritical CO_2. In the present work, the solubilities of *n*-tetracosane, *n*-octacosane, *n*-dotriacontane, and *n*-hexatriacontane in CO_2 have been measured over the temperature range from 308.2 to 338.2 K at pressures ranging from 30.0 to 208.9 bar, and then the measured data are correlated by the proposed equations.

Table I. Solubility Data of *n*-Tetracosane (2) in Carbon Dioxide (1) and the Reduced Densities of Carbon Dioxide $\rho_{r,1}$ ($\rho_{c,1}$ = 0.4687 g cm^{-3}) (*15*)

T/K	P/bar	$10^2 y_2$	$\rho_{r,1}$
308.2	50.3	0.0486	0.238
	67.2	0.0503	0.398
	93.1	0.0629	1.500
	114.5	0.0813	1.640
	138.6	0.0917	1.725
	161.3	0.1195	1.773
	182.7	0.1520	1.830
	204.8	0.2050	1.860
313.2	50.3	0.0418	0.234
	67.9	0.0363	0.373
	93.1	0.0735	1.150
	113.4	0.1330	1.523
	139.3	0.1874	1.650
	160.7	0.2290	1.725
	182.0	0.3170	1.779
	207.2	0.4303	1.816
318.2	50.3	0.0482	0.228
	67.7	0.0394	0.361
	90.7	0.0483	0.723
	113.8	0.1160	1.309
	140.0	0.2380	1.527
	161.0	0.3210	1.612
	182.0	0.4770	1.688
	208.9	0.7670	1.740

Experimental Section

A semiflow phase equilibrium apparatus has been used for the measurement of solubilities for heavy *n*-paraffins in CO_2 from the subcritical to the supercritical state. The experimental equipment and sampling procedure have been described elsewhere (*8*). Briefly, in the course of an experiment, the solid heavy *n*-paraffin was introduced into the equilibrium cell at three evenly spaced points separated with 0.2-cm-diameter stainless steel balls. The cell was inserted in a constant-temperature stirred water bath. Liquid CO_2 was compressed into the cell by a positive-displacement liquid pump from a cylinder. After the flow had passed the equilibrium cell for about 1 h, the saturated CO_2 was withdrawn, reduced in pressure, and raised in temperature about 150–200 K above the bath temperature in order to avoid precipitation of the heavy *n*-paraffin on the line (*9*), and then the *n*-paraffin was collected in a cold trap that was packed with cotton in order to catch the small particles of the heavy *n*-paraffin. The collected *n*-paraffin was weighed with an analytical balance, and the liberated gas from the trap was measured volumetrically in a wet test meter. The temperature uniformity across the equilibrium cell was measured to an accuracy of 0.2 K by a type J thermocouple. The pressure was measured by a Heise gauge to ±0.28 bar.

Materials. The carbon dioxide used in this work had a minimum purity of 99.5 mol %. The *n*-tetracosane was purchased from Merck, *n*-octacosane from Aldrich, and

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Table II. Solubility Data of n-Octacosane (2) in Carbon Dioxide (1) and the Reduced Densities of Carbon Dioxide $\rho_{r,1}$ ($\rho_{c,1}$ = 0.4687 g cm^{-3}) (15)

T/K	P/bar	$10^2 y_2$	$\rho_{r,1}$
308.2	50.3	0.0499	0.238
	63.8	0.0387	0.375
	91.0	0.0388	1.475
	111.2	0.0410	1.612
	133.8	0.0447	1.716
	157.2	0.0565	1.768
	188.9	0.0761	1.837
	204.1	0.0870	1.858
318.2	48.6	0.0380	0.219
	64.1	0.0387	0.330
	90.7	0.0422	0.723
	111.7	0.0473	1.279
	132.9	0.0552	1.474
	155.1	0.0697	1.591
	178.2	0.0830	1.675
	205.1	0.0948	1.734
328.2	49.3	0.0383	0.204
	64.2	0.0410	0.300
	89.4	0.0426	0.523
	110.0	0.0391	0.930
	130.0	0.0618	1.236
	151.0	0.0975	1.394
	178.6	0.1233	1.553
	203.4	0.1570	1.633

Table III. Solubility Data of n-Dotriacontane (2) in Carbon Dioxide (1) and the Reduced Densities of Carbon Dioxide $\rho_{r,1}$ ($\rho_{c,1}$ = 0.4687 g cm^{-3}) (15)

T/K	P/bar	$10^2 y_2$	$\rho_{r,1}$
318.2	46.9	0.0390	0.210
	60.8	0.0334	0.308
	87.9	0.0314	0.650
	112.0	0.0305	1.290
	134.8	0.0328	1.486
	155.5	0.0363	1.593
	181.0	0.0520	1.680
	203.1	0.0628	1.730
328.2	48.3	0.0300	0.200
	61.2	0.0252	0.290
	87.4	0.0269	0.506
	108.8	0.0306	0.900
	131.2	0.0316	1.245
	153.5	0.0430	1.408
	177.9	0.0538	1.550
	205.8	0.0659	1.638
338.2	47.2	0.0372	0.185
	61.0	0.0318	0.270
	85.5	0.0256	0.420
	108.2	0.0294	0.656
	131.7	0.0362	0.962
	153.8	0.0494	1.191
	178.6	0.0668	1.391
	205.5	0.1162	1.509

2n-dotriacontane from Tokyo Kasei Kogyo Co., Ltd., with a minimum purity of 99 mol %. The n-hexatriacontane was purchased from Aldrich with a minimum purity of 98 mol %. The chemicals were used without further purification.

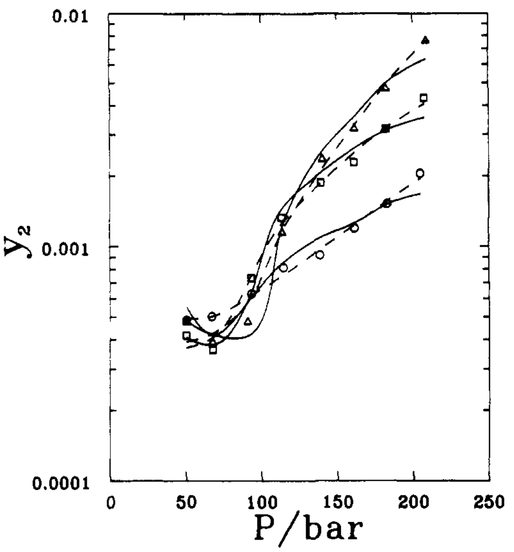

Figure 1. Comparison of the calculated mole fraction y_2 of n-tetracosane in carbon dioxide with experimental data at different temperatures: ○, 308.2 K; □, 313.2 K; △, 318.2 K; —, calculated with eq 2; - - -, calculated with eq 3.

Table IV. Solubility Data of n-Hexatriacontane (2) in Carbon Dioxide (1) and the Reduced Densities of Carbon Dioxide $\rho_{r,1}$ ($\rho_{c,1}$ = 0.4687 g cm^{-3}) (15)

T/K	P/bar	$10^2 y_2$	$\rho_{r,1}$
318.2	35.2	0.0262	0.149
	57.7	0.0265	0.282
	86.5	0.0259	0.640
	107.6	0.0269	1.180
	131.4	0.0277	1.463
	155.1	0.0303	1.591
	180.3	0.0404	1.678
	206.5	0.0527	1.736
328.2	35.9	0.0254	0.140
	58.1	0.0257	0.265
	86.4	0.0260	0.489
	109.3	0.0255	0.912
	132.7	0.0269	1.260
	155.1	0.0289	1.420
	180.0	0.0423	1.550
	202.7	0.0518	1.630
338.2	30.0	0.0246	0.110
	58.1	0.0244	0.255
	85.0	0.0259	0.414
	107.4	0.0248	0.654
	130.3	0.0319	0.949
	156.5	0.0392	1.227
	180.0	0.0601	1.394
	203.4	0.0997	1.502

Results

Tables I–IV present the experimental solubility data for n-tetracosane, n-octacosane, n-dotriacontane, and n-hexatriacontane with CO_2, respectively, from the subcritical to the supercritical state. These data are also presented in Figures 1–4. Each reported data is the average value of at least two replicate samples. The sample compositions were generally reproducible within 2% in the mole fractions of n-paraffins for the fluid phase. It can be seen that the solubilities of the solute increase with pressure in the supercritical state, but in the subcritical state, the solubilities decrease with increasing pressure. From the effect of temperature on the solubilities, we find that retrograde solubility (crossover pressure) behavior (10–12) exists in all systems.

Comparing our data with those reported by Schmitt and Reid (3) for CO_2 + n-tetracosane, McHugh et al. (4) for CO_2 + n-octacosane, and King et al. (6) and Spee and Schneider (2) for CO_2 + n-dotriacontane, we find that the solubilities of this work are systematically higher than those of the literature. We think the discrepancy may be a result of solute impurity, raise in temperature on the line after the equilibrium cell, and packing with cotton in the cold trap in our work. The solubilities of 1-octadecanol in the supercritical CO_2 measured by Kramer and Thodos (13) are higher than those of Schmitt and Reid (3), and we find that the trap was packed with glass wool in the work of Kramer and Thodos.

Most of the experimental data can be plotted in a format which compares the solubilities of compounds forming

Table V. Correlation of Solubility Data with Two Approaches[a]

				eq 2				eq 3			
solute	T/K	P/bar range	data pts	A	10^2B	10^4C	$10^2\Delta y_2/y_2$	A	10^4B	D	$10^2\Delta y_2/y_2$
n-tetracosane	308.2	50.3–204.8	8	−2.9945	−3.5754	6.0073	10.41	−3.3070	1.6605	43.080	3.42
	313.2	50.3–207.2	8	−3.2844	−1.4350	3.5544	9.07	−3.4535	1.0324	5.3380	6.10
	318.2	50.3–208.9	8	−3.1434	−2.1082	4.2331	8.38	−3.4167	1.2757	11.639	7.84
	overall	50.3–208.9	24	−3.1242	−2.4561	4.6522	11.93	−3.3867	1.3126	13.130	10.72
n-octacosane	308.2	50.3–204.1	8	−3.0349	−3.5977	5.3404	8.03	−3.3920	3.7557	2289.0	5.84
	318.2	48.6–205.1	8	−3.3349	−0.7593	1.4281	6.26	−3.4179	0.6214	38.600	2.17
	328.2	49.3–203.4	8	−3.2793	−1.0493	1.7524	7.46	−3.4176	0.7781	66.910	7.53
	overall	48.6–205.1	24	−3.2825	−1.0551	1.7706	10.00	−3.4026	0.8334	82.100	7.46
n-dotriacontane	318.2	46.9–203.1	8	−3.2566	−1.7062	2.1659	9.42	−3.4908	4.0532	20011	7.10
	328.2	48.3–205.8	8	−3.4663	−0.7731	1.1788	6.11	−3.5759	0.5057	84.30	4.76
	338.2	47.2–205.5	8	−3.3254	−1.2434	1.6331	6.65	−3.5149	1.8441	2936	7.63
	overall	46.9–205.8	24	−3.3582	−1.1543	1.5474	10.55	−3.5177	1.8141	2928	8.66
n-hexatriacontane	318.2	35.2–206.5	8	−3.4978	−0.8662	1.3205	9.89	−3.5817	6.7105	80420	1.70
	328.2	35.9–202.7	8	−3.5069	−0.7582	1.0496	9.24	−3.5967	3.7888	40610	3.01
	338.2	30.0–203.4	8	−3.5284	−0.7263	1.2218	8.62	−3.6033	2.1595	3761	2.66
	overall	30.0–206.5	24	−3.5052	−0.8183	1.2281	11.19	−3.5881	5.9729	78900	5.40

[a] $\Delta y_2/y_2 = (1/n)\sum_{i=1}^{n}|(y_{2,\mathrm{calcd},i} - y_{2,\mathrm{exptl},i})/y_{2,\mathrm{exptl},i}|$.

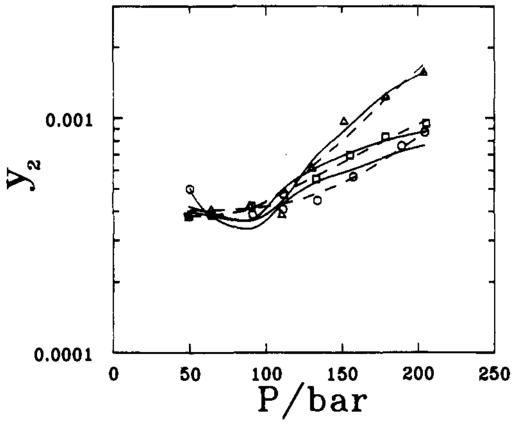

Figure 2. Comparison of the calculated mole fraction y_2 of n-octadecane in carbon dioxide with experimental data at different temperatures: ○, 308.2 K; □, 318.2 K; △, 328.2 K; —, calculated with eq 2; - - -, calculated with eq 3.

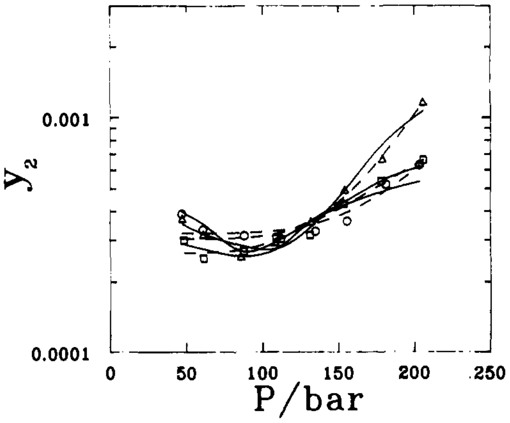

Figure 3. Comparison of the calculated mole fraction y_2 of n-dotriacontane in carbon dioxide with experimental data at different temperatures: ○, 318.2 K; □, 328.2 K; △, 338.2 K; —, calculated with eq 2; - - -, calculated with eq 3.

homologous groups that have similar chemical properties in the saturated alkanes. For example, in Figure 5, the solubilities of the four heavy n-paraffins n-tetracosane, n-octacosane, n-dotriacontane, and n-hexatriacontane at 318.2 K are plotted. It indicates that the solubilities of these systems decrease with increasing molecular weight of n-paraffins.

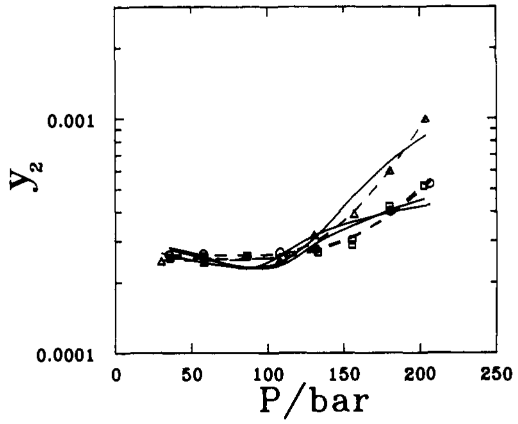

Figure 4. Comparison of the calculated mole fraction y_2 of n-hexatriacontane in carbon dioxide with experimental data at different temperatures: ○, 318.2 K; □, 328.2 K; △, 338.2 K; —, calculated with eq 2; - - -, calculated with eq 3.

Correlation

In our earlier study (*8*), we found the simple approach (*13, 14*)

$$\log y_2 = A + B\rho_{r,1} \tag{1}$$

does not describe adequately the relationship between y_2 and $\rho_{r,1}$ from the subcritical to the supercritical state.

In this study, we correlate the solubilities of n-tetracosane, n-octacosane, n-dotriacontane, and n-hexatriacontane in CO_2 by two approaches. In the first approach, the relation can be expressed by

$$\log y_2 = A + B\rho_{r,1}(T/\mathrm{K} - 273.2) + C[\rho_{r,1}(T/\mathrm{K} - 273.2)]^2 \tag{2}$$

The reduced densities of CO_2 used in the present study were obtained from the work of Kennedy and Thodos (*15*). These reduced densities are listed in Tables I–IV. The calculated results with optimum values of A, B, and C for each isotherm and for all temperature ranges are listed in Table V.

Because the solubilities decrease with increasing pressure in the subcritical state, the total pressure of the system may be introduced in the second approach. We express the

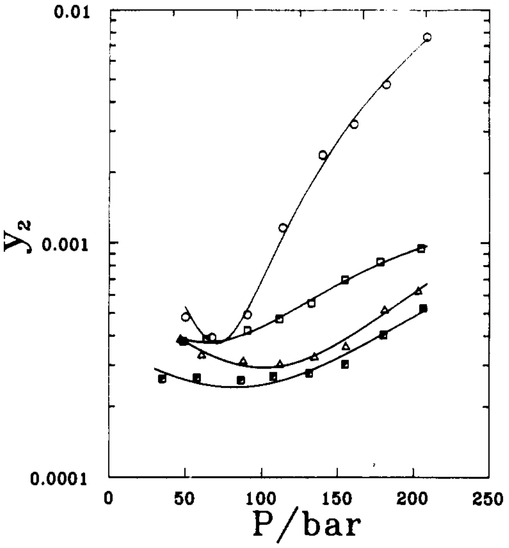

Figure 5. Fluid phase mole fraction y_2 of the four heavy n-paraffins in carbon dioxide at 318.2 K: ○, n-tetracosane; □, n-octacosane; △, n-dotriacontane; ▣, n-hexatriacontane.

approach as follows:

$$\log y_2 = A + B\left[\frac{\rho_{r,1}(T/\mathrm{K} - 273.2)^{2.5}}{D^{1/P_{r,1}}}\right] \qquad (3)$$

where $P_{r,1}$ is the reduced pressure of CO_2.

The calculated results with optimum values of A, B, and D for each isotherm and for all temperature ranges are listed in Table V.

The calculated results using eqs 2 and 3 for systems CO_2 + n-tetracosane, CO_2 + n-octacosane, CO_2 + n-dotriacontane, and CO_2 + n-hexatriacontane are shown in Figures 1–4, respectively. It can be seen that eq 2 gives qualitative agreement between calculated results and experimental data while eq 3 gives quantitative agreement.

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