J. Chem. Eng. Data **1996,** *41,* 6−10

Phase Equilibria of Alkanes in Natural Gas Systems. 3. Alkanes in Carbon Dioxide

Karen Chandler, Frederic L. L. Pouillot, and Charles A. Eckert*

School of Chemical Engineering and Center for Specialty Separations, Georgia Institute of Technology,
Atlanta, Georgia 30332-0100

A chromatographic technique was used to measure experimental capacity factors for the *n*-alkanes from C_9H_{20} to $C_{36}H_{74}$ in CO_2 from 308.2 to 348.2 K and from 100 to 240 bar. Infinite dilution activity coefficients, γ_i^{∞}, were calculated for the solid *n*-alkanes ($C_{24}H_{50}$ to $C_{36}H_{74}$) utilizing regular solution theory to characterize the stationary phase. This allowed the estimation of solubilities from capacity factors for the solid *n*-alkanes in CO_2.

Introduction

Conventional methods for measuring solid solubilities in supercritical fluids (SCFs), such as a single pass flow apparatus where a flowing SCF is equilibrated with a thermostated bed of solid (Johnston and Eckert, 1981; McHugh *et al.*, 1984; Reverchon *et al.*, 1993), are less accurate under conditions where the solubility is low. In previous papers, we have presented a reliable chromatographic method which is capable of providing phase equilibrium data at conditions where the conventional techniques fail (Suleiman *et al.*, 1993; Suleiman and Eckert, 1995a). Also, this method has several other advantages over conventional methods including rapid measurements, small sample requirements, and low purity requirements (because the impurities are separated in the chromatographic column). New experimental capacity factors and the corresponding estimated solubilities were reported for the *n*-alkanes from C_7H_{16} to $C_{36}H_{74}$ in CH_4 from 293.2 to 423.2 K and from 120 to 240 bar (Suleiman and Eckert, 1995a) and for the *n*-alkanes from $C_{24}H_{50}$ to $C_{36}H_{74}$ in C_2H_6 from 308.2 to 348.2 K and from 80 to 240 bar (Suleiman and Eckert, 1995b). Similarly, this paper reports capacity factors for the *n*-alkanes from C_9H_{20} to $C_{36}H_{74}$ in CO_2 from 308.2 to 348.2 K and from 100 to 240 bar, and the estimated solubilities for the solid *n*-alkanes ($C_{24}H_{50}$ to $C_{36}H_{74}$) in CO_2 were calculated from the capacity factors.

Because this chromatographic experiment gives information about the distribution of the solute between the stationary and fluid phases at infinite dilution, care must be taken in extracting the relevant phase equilibrium information. In order to determine solubilities for the solid *n*-alkanes, the actual physical state of the solute at the conditions of the experiment are required. Therefore, an estimate of melting point depression for the *n*-alkanes in CO_2 must be made. Correlations are also required for the vapor and sublimation pressures of the *n*-alkanes to compute the proper reference states, and we present a new and simple correlation for the vapor pressures as a function of temperature and alkane carbon number. Finally, a method of extrapolating data with the carbon number has been developed to determine capacity factors and solubilities for higher carbon number solutes with elution times too long to measure accurately with the chromatographic technique.

Experimental Section

Apparatus and Materials. The experimental apparatus described in detail elsewhere (Suleiman *et al.*, 1993; Suleiman and Eckert, 1995a) has been slightly modified for use with CO_2. A 5 μL injection loop was used to introduce small amounts of the solute dissolved in pentane. The column (100 mm in length and 4.6 mm in internal diameter) was packed with 3 μm particles of Hypersil ODS C_{18} (Alltech). Since chromatographic measurements are taken at infinite dilution, pure fluid densities were used for CO_2 (Ely *et al.*, 1989). Coleman Instrument grade CO_2 (99.99% purity) was obtained from Matheson Gas Products, and the *n*-alkanes from C_5H_{12} to $C_{36}H_{74}$ were obtained from Aldrich Chemical Co. with a stated purity of 98% or better.

Determination of Solubilities. In chromatography, the degree of retention of a solute depends on its distribution between the mobile and stationary phases, and information is obtained at infinite dilution. The relationship between the mole fraction solubility of a solute *i*, y_i, in a SCF and the experimentally determined capacity factor, k_i, can be derived from the phase equilibrium between the stationary and mobile phases, and the phase equilibrium between the solute and the mobile phase (Suleiman and Eckert, 1995a).

$$y_i = |\frac{P_{i,\mathrm{sat}}V^{\mathrm{s}}}{k^{\mathrm{o}}_{\mathrm{H},i}V^{\mathrm{m}}V^{\mathrm{s}}_{\mathrm{m}}}\exp\left(\frac{V_i(P^{\mathrm{o}} - P_{i,\mathrm{sat}})}{RT}\right)|\frac{V^{\mathrm{m}}_{\mathrm{m}}}{k_i} = |C_i(T)|\frac{V^{\mathrm{m}}_{\mathrm{m}}}{k_i} \qquad (1)$$

where $P_{i,\mathrm{sat}}$ is the saturation pressure (sublimation pressure for a solid solute), and $k^{\mathrm{o}}_{\mathrm{H},i}$ is the Henry's law constant of solute *i* in the stationary phase at the reference pressure P^{o}. The molar volumes of the stationary and mobile phases in the chromatographic column are represented as $V^{\mathrm{s}}_{\mathrm{m}}$ and $V^{\mathrm{m}}_{\mathrm{m}}$, while V^{s} and V^{m} are the physical volumes of the stationary and mobile phases, respectively. The $C_i(T)$ term, which is a constant for a particular chromatographic column, temperature, and solute *i*, must be determined at each temperature in order to obtain solubilities from this relationship. Therefore, it is necessary either to measure at least one solubility value for each solute at a given temperature with an independent technique or to calculate it. Once $C_i(T)$ is known, the entire solubility isotherm can be determined rapidly from the experimentally determined capacity factors. For solid solutes, $C_i(T)$ reduces to

$$C_i(T) = |\frac{V^{\mathrm{s}}}{V^{\mathrm{m}}V^{\mathrm{s}}_{\mathrm{m}}}|\frac{1}{\gamma_i^{\infty}}\frac{P_{i,\mathrm{sub}}}{P_{i,\mathrm{vap}}} \qquad (2)$$

where γ_i^{∞} is the activity coefficient at infinite dilution

0021-9568/96/1741-0006$12.00/0 © 1996 American Chemical Society

between solute i and the stationary phase and the $P_{i,\mathrm{sub}}$ and $P_{i,\mathrm{vap}}$ are chosen to represent the reference fugacities of the solid solute and the hypothetical subcooled liquid solute, respectively.

An important assumption made in the derivation of eq 1 is that the pure solute as a condensed phase does not absorb the mobile phase. Therefore, this paper presents solubilities for *n*-alkanes in CO_2 only at conditions where the solute is a solid in the presence of the mobile phase. An estimate of melting point depression is required for *n*-alkanes in CO_2 to determine the physical state of the solute at the conditions of the experiment. Solid−liquid−vapor equilibria for CO_2 and several heavy *n*-alkanes ($C_{20}H_{42}$ to $C_{28}H_{58}$) have been reported in the literature (McHugh *et al.*, 1984; Fall *et al.*, 1985) and show a melting point depression of around 10 K for each case. Therefore, a solute is assumed to be a solid in the presence of CO_2 if the temperature of the experiment is at least 10 K below the known melting point of the pure solute.

The infinite dilution activity coefficient between the solute and the stationary phase, γ_i^∞, is obtained from regular solution theory (Prausnitz *et al.*, 1986). The stationary phase is an ODS-bonded phase to a silica support, and since no solubility parameter for this material was available, several experimental solubilities for $C_{28}H_{58}$ in CO_2 were used to regress the constant $C_i(T)$, which provided γ_i^∞, and therefore the solubility parameter of the stationary phase. Four solubilities were obtained from Reverchon *et al.* (1993) at 308.2 K over a range of pressures, and one was obtained at 318.2 K and 200 bar. Solubility data presented by McHugh *et al.* (1984) were also used at 318.6 K for three pressures. The temperature of the solubility data from McHugh *et al.* (1984) is slightly different from the temperature of our capacity factor data (318.2 K); however, both values are within our experimental control of temperature. The regressed solubility parameters for the stationary phase show no trends with temperature or pressure and were averaged to 19.5 $(\mathrm{J/cm^3})^{0.5}$ with a standard deviation of 0.2 $(\mathrm{J/cm^3})^{0.5}$. The assumption that the solubility parameter for the stationary phase is not a function of temperature and pressure should be adequate if the CO_2 does not swell the stationary phase. This is often not the case if the stationary phase is cross-linked, but the ODS-bonded phase used in this work is not cross-linked and the assumption should be valid (Bartle *et al.*, 1990). The solubility parameters and molar volumes for the *n*-alkanes are also required, and these values, along with their temperature dependence, were calculated using a group contribution method proposed by Fedors (1974). The isobaric thermal expansion coefficients of the *n*-alkanes from C_5H_{12} to $C_{17}H_{36}$, which are required to account for the temperature dependence, were obtained from Nikolic (1993), and these values were extrapolated with the carbon number to provide the isobaric thermal expansion coefficients for the heavier *n*-alkanes ($C_{18}H_{38}$ to $C_{36}H_{74}$).

The expression, $V^s/V^m V^s_m$, was calculated from experimental retention times and physical information provided by the manufacturer of the chromatographic column (Alltech). The physical volume of the mobile phase, V^m, was determined by multiplying the measured volumetric flow rates and retention times of an unretained solute (pentane). The total volume of the column was calculated from the physical dimensions of the column, and from these two values the total volume of the packing material could be calculated. The manufacturer reported that the packing was 10% by mass carbon phase which was determined to be 24.9% by volume. Therefore, the physical volume of the stationary phase, V^s, is 24.9% of the total volume of the packing material. The manufacturer also reported that 1.2 g of total packing was used in each column, and 10% of this value divided by V^s gives the density of the stationary phase. By assuming the molecular weight of the stationary phase to be the same as that of an octadecane molecule, the molar volume of the stationary phase, V^s_m, can be calculated. The constant, $V^s/V^m V^s_m$, calculated in this manner for the chromatographic column used for these experiments was estimated to be 0.36 mol/L.

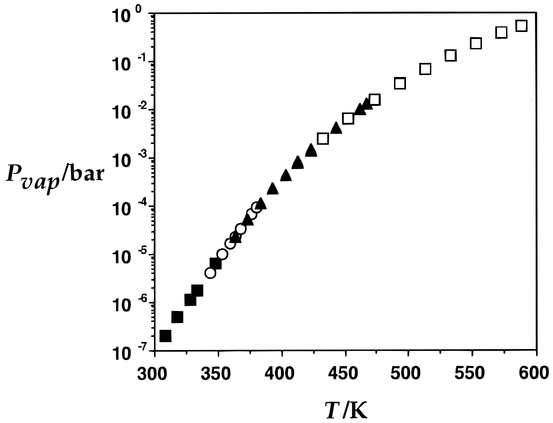

Figure 1. Vapor pressure, P_{vap}, versus temperature, T, for $C_{20}H_{42}$: (■) correlation from this investigation; (○) Macknick and Prausnitz (1979); (▲) Sasse *et al.* (1988); (□) Morgan and Kobayashi (1994).

Correlations are required for vapor and sublimation pressures of the *n*-alkanes to compute the proper reference states, and we developed a simple correlation for the vapor pressure as a function of temperature and carbon number. A large set of vapor pressure data has been experimentally determined by Morgan and Kobayashi (1994) for the *n*-alkanes from $C_{10}H_{22}$ to $C_{28}H_{58}$ and from 323 to 588 K. These data were plotted as the log of vapor pressure versus the carbon number and were fit exponentially for each isotherm as shown by eq 3, where N is the carbon number

$$P_{i,\mathrm{vap}} = a \times 10^{[b(N-c)]} \qquad (3)$$

and $P_{i,\mathrm{vap}}$ is in bar. The coefficients were regressed to be

$$a = 39.29 + 9.811 \times 10^{-2}T - 2.045 \times 10^{-4}T^2 \qquad (4)$$

$$b = -1.415 + 4.140 \times 10^{-3}T - 3.353 \times 10^{-6}T^2 \qquad (5)$$

$$c = 5.412 - 2.776 \times 10^{-2}T + 4.911 \times 10^{-5}T^2 \qquad (6)$$

where T is temperature (K). The vapor pressures obtained with our correlation at the temperatures of our experiments (308.2−348.2 K) compared well with the experimental data of Morgan and Kobayashi (1994), as well as data measured experimentally at intermediate temperatures by Macknick and Prausnitz (1979) and Sasse *et al.* (1988) for several of the *n*-alkanes ($C_{19}H_{40}$ to $C_{22}H_{46}$). A comparison of vapor pressures produced by our correlation and experimentally determined vapor pressures is shown for $C_{20}H_{42}$ in Figure 1.

The correlation used for sublimation pressure was developed by Drake (1993) from the corresponding states theory based on the triple point. In this correlation, the triple point of the *n*-alkanes was assumed to be equal to the melting point, and the triple point correlations which we used were developed as a function of carbon number by Morgan and Kobayashi (1991). The critical temperature and pressure of the *n*-alkanes were also required for this correlation, and they were also estimated from correlations

Table 1. Capacity factors, k_i, for the *n*-Alkanes in CO_2[a]

T/K	240 bar	200 bar	180 bar	160 bar	140 bar	120 bar	100 bar	T/K	240 bar	200 bar	180 bar	160 bar	140 bar	120 bar	100 bar
C_9H_{20}															
348.2	0.06	0.18	0.29	0.37	0.83	1.6	2.8	318.2	0.14	0.12	0.09	0.12	0.19	0.28	0.50
333.2	0.14	0.22	0.19	0.32	0.45	1.1	2.9	308.2	0.11	0.14	0.14	0.17	0.18	0.19	0.21
328.2	0.11	0.14	0.15	0.21	0.29	0.76	2.2								
$C_{10}H_{22}$															
348.2	0.12	0.24	0.40	0.53	1.2	2.5	4.7	318.2	0.17	0.17	0.17	0.28	0.27	0.39	0.87
333.2	0.22	0.23	0.22	0.41	0.60	1.5	4.6	308.2	0.16	0.17	0.18	0.20	0.20	0.28	0.33
328.2	0.23	0.27	0.28	0.31	0.48	1.0	3.4								
$C_{11}H_{24}$															
348.2	0.21	0.28	0.50	0.69	1.7	3.8	7.4	318.2	0.24	0.24	0.22	0.34	0.39	0.49	1.7
333.2	0.23	0.29	0.39	0.43	0.84	2.0	6.8	308.2	0.18	0.25	0.21	0.32	0.40	0.36	0.54
328.2	0.27	0.34	0.30	0.41	0.75	1.4	4.9								
$C_{12}H_{26}$															
348.2	0.28	0.45	0.63	0.97	2.3	5.7	11*	318.2	0.25	0.29	0.25	0.42	0.47	0.65	2.1
333.2	0.31	0.30	0.46	0.45	1.1	2.8	10	308.2	0.23	0.32	0.40	0.40	0.50	0.54	0.74
328.2	0.33	0.38	0.41	0.52	0.88	2.0	7.3								
$C_{13}H_{28}$															
348.2	0.35	0.50	0.87	1.3	3.3	7.7	16*	318.2	0.30	0.34	0.42	0.55	0.58	0.89	2.7
333.2	0.45	0.33	0.57	0.59	1.3	4.0	15	308.2	0.29	0.39	0.50	0.49	0.67	0.66	0.88
328.2	0.38	0.46	0.52	0.65	1.1	2.6	11								
$C_{14}H_{30}$															
348.2	0.38	0.75	1.0	1.7	4.2	11	24*	318.2	0.36	0.45	0.63	0.70	0.82	1.1	3.4
333.2	0.46	0.44	0.68	0.75	1.5	5.1	21	308.2	0.41	0.48	0.68	0.67	0.82	0.79	1.0
328.2	0.44	0.49	0.58	0.71	1.3	3.3	15								
$C_{15}H_{32}$															
348.2	0.48	1.0	1.4	2.0	5.4	13	36*	318.2	0.42	0.46	0.77	0.78	1.0	1.4	4.7
333.2	0.59	0.58	0.95	0.93	2.3	6.7	30*	308.2	0.63	0.75	0.75	0.79	0.94	0.93	1.2
328.2	0.67	0.76	0.67	0.99	1.7	4.3	21*								
$C_{16}H_{34}$															
348.2	0.64	1.1	1.6	2.4	6.9	18	52*	318.2	0.73	0.67	0.86	0.99	1.1	1.7	6.2
333.2	0.64	0.73	1.1	1.1	2.8	8.9	42*	308.2	0.71	0.87	0.87	0.97	1.1	1.2	1.5
328.2	0.71	0.84	0.98	1.1	1.9	5.1	29*								
$C_{17}H_{36}$															
348.2	0.74	1.3	1.9	3.1	8.8	26	77*	318.2	0.80	0.76	1.0	1.2	1.5	2.1	7.8
333.2	0.71	0.84	1.2	1.3	3.0	11	60*	308.2	0.75	0.97	0.97	1.1	1.3	1.3	1.7
328.2	0.79	0.92	1.2	1.4	2.3	6.4	40*								
$C_{18}H_{38}$															
348.2	0.78	1.5	2.2	3.8	11	35	110*	318.2	0.83	0.81	1.1	1.3	1.6	2.4	10
333.2	0.75	0.98	1.4	1.4	3.5	15	85*	308.2	0.89	1.1	1.1	1.3	1.5	1.5	1.9
328.2	0.83	1.0	1.3	1.6	2.7	8.0	56*								
$C_{20}H_{42}$															
348.2	0.92	1.9	3.0	5.4	18	62*	240*	318.2	0.92	1.1	1.3	1.6	2.1	3.4	16
333.2	0.93	1.1	1.7	2.2	5.2	25	170*	308.2	1.0	1.3	1.3	1.6	1.9	2.1	2.7
328.2	0.92	1.3	1.7	2.1	3.5	12	110*								
$C_{24}H_{50}$															
348.2	1.5	3.0	5.3	11	59*	200*	1100*	318.2	1.4	1.6	1.9	2.4	3.3	5.9	37*
333.2	1.3	1.8	2.9	3.8	9.8	56*	660*	308.2	1.5	1.9	1.9	2.1	2.8	3.1	4.8
328.2	1.4	1.8	2.4	3.4	6.4	25*	390*								
$C_{25}H_{52}$															
348.2	1.6	3.5	6.1	13	73*	260*	1600*	318.2	1.5	1.8	2.2	2.7	3.8	6.9	45*
333.2	1.4	2.0	3.3	4.3	12	70*	930*	308.2	1.7	2.1	2.2	2.5	3.2	3.5	5.7
328.2	1.6	2.0	2.7	3.9	7.5	30*	540*								
$C_{28}H_{58}$															
348.2	2.2	5.1	9.3	22	130*	630*	4800*	318.2	2.0	2.4	3.0	3.9	5.6	11	86*
333.2	1.8	2.8	4.7	6.7	20	140*	2600*	308.2	2.2	2.7	3.0	3.5	4.3	5.3	9.3
328.2	2.0	2.8	3.7	5.7	12	52*	1400*								
$C_{29}H_{60}$															
348.2	2.5	5.8	11	26	170*	830*	6900*	318.2	2.2	2.7	3.4	4.4	6.4	13	110*
333.2	2.2	3.4	5.3	7.6	24	170*	3700*	308.2	2.4	3.1	3.4	4.0	4.9	6.1	11
328.2	2.3	3.1	4.2	6.6	14	62*	1900*								
$C_{32}H_{66}$															
348.2	3.3	8.3	17	37*	310*	2000*	21000*	318.2	2.9	3.7	4.6	6.4	9.2	21	200*
333.2	2.9	4.5	7.5	12	33*	330*	10000*	308.2	3.3	4.1	4.5	5.4	7.2	8.8	13*
328.2	3.0	4.2	6.0	9.7	22	110*	5100*								
$C_{33}H_{68}$															
348.2	3.6	9.3	19	43*	380*	2600*	31000*	318.2	3.1	4.1	5.2	7.0	11	20*	240*
333.2	3.3	5.1	8.4	16	38*	410*	14000*	308.2	3.6	4.7	5.4	5.9	8.6	10	15*
328.2	3.4	4.9	6.8	11	25	130*	7000*								
$C_{36}H_{74}$															
348.2	4.1*	11*	24*	67*	710*	6200*	95000*	318.2	4.0	5.5	6.1*	8.3*	13*	29*	460*
333.2	3.5*	9.6	10*	21	58*	790*	40000*	308.2	4.2*	5.4*	6.1*	7.1*	9.8*	12*	21*
328.2	3.8*	5.5*	8.0*	13*	33*	220*	18000*								

[a] Asterisks denote extrapolated values.

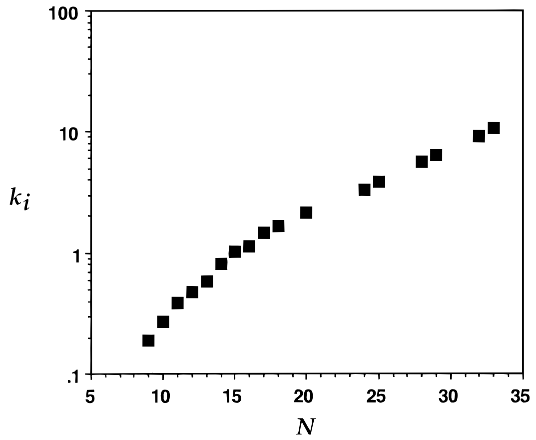

Figure 2. Capacity factors, k_i, versus the carbon number, N, for the n-alkanes in CO_2 at 140 bar and 318.2 K.

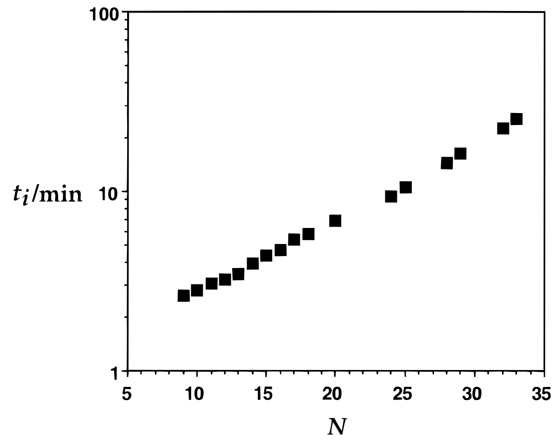

Figure 3. Retention times, t_i, versus the carbon number, N, for the n-alkanes in CO_2 at 140 bar and 318.2 K.

of Morgan and Kobayashi (1991) based on an equation form derived by Kreglewski and Zwolinski (1961).

Results and Discussion

Table 1 presents experimental capacity factors for the n-alkanes from C_9H_{20} to $C_{36}H_{74}$ in CO_2 from 308.2 to 348.2 K and from 100 to 240 bar. The capacity factors measured with the chromatographic technique proved to be very reproducible, with the standard deviations for the capacity factors ranging from approximately 2% to 5%. The reported pressures are the inlet pressures, and there is a small uncertainty in the pressure of the measurements due to the pressure drop across the column, which was found to be from 1% to 7% of the inlet pressure. The overall estimated experimental error of the measured capacity factors was determined to be approximately 15%. The largest contributions to the error included the pressure drop across the column, the flow variations from the constant pressure control, and determination of the maxima of retention times.

At certain conditions (high temperatures and low pressures), the elution times of the higher carbon number solutes were too long to measure accurately with the chromatographic technique, and a method of extrapolating data with the carbon number was developed. Because both the lower and higher carbon number solutes were investigated, the relationship between the log of the capacity factors versus the carbon number was not found to be linear. Instead, all of the plots showed a steeper slope in log k_i at the lower carbon numbers as shown in Figure 2. It does appear that the higher number n-alkanes display a linear relationship with log k_i; however, if extrapolation is required, not many data for these compounds are generally available. Therefore, the extrapolated capacity factors reported here were extrapolated from the log of the retention times versus the carbon number which is more nearly linear, as shown in Figure 3.

Table 2. Mole Fraction Solubilities, y_i, for the n-Alkanes in CO_2[a]

T/K		240 bar	200 bar	180 bar	160 bar	140 bar	120 bar	100 bar
				$C_{24}H_{50}$				
308.2	10^4y_i	4.3	3.5	3.6	3.3	2.6	2.4	1.7
				$C_{25}H_{52}$				
308.2	10^4y_i	3.0	2.5	2.5	2.2	1.8	1.7	1.1
				$C_{28}H_{58}$				
318.2	10^4y_i	4.7	4.1	3.4	2.7	2.0	1.1	0.19*
308.2	10^4y_i	1.3	1.1	1.0	0.87	0.73	0.62	0.38
				$C_{29}H_{60}$				
318.2	10^4y_i	3.6	3.1	2.5	2.0	1.5	0.80	0.12*
308.2	10^5y_i	9.8	7.9	7.3	6.4	5.4	4.5	2.7
				$C_{32}H_{66}$				
328.2	10^5y_i	56	42	31	20	9.9	2.4*	0.08*
318.2	10^5y_i	18	15	12	9.0	6.6	3.2	0.44*
308.2	10^5y_i	4.3	3.6	3.4	2.9	2.2	1.9	1.4*
				$C_{33}H_{68}$				
333.2	10^5y_i	80	55	35	20	9.5*	1.1*	0.05*
328.2	10^5y_i	44	32	24	16	7.7	1.8*	0.05*
318.2	10^5y_i	15	12	9.3	7.2	4.8	2.9*	0.32*
308.2	10^5y_i	3.4	2.7	2.4	2.3	1.6	1.4	1.0*
				$C_{36}H_{74}$				
333.2	10^5y_i	56*	22	22*	11	4.6*	0.44*	0.01*
328.2	10^5y_i	29*	21*	15*	9.8*	4.2*	0.78*	0.02*
318.2	10^5y_i	7.8	5.9	5.5*	4.2*	2.8*	1.4*	0.12*
308.2	10^5y_i	1.9*	1.5*	1.4*	1.2*	0.92*	0.78*	0.48*

[a] Asterisks denote extrapolated values.

The calculated solubilities for the solid n-alkanes from $C_{24}H_{50}$ to $C_{36}H_{74}$ are presented in Table 2. Solubilities are reported only for solutes assumed to be in the solid state at the conditions of the experiment. In previous papers we reported solubilities for liquid n-alkanes based on the assumption that the liquid solute did not absorb the mobile phase. Due to this limitation we do not report solubilities for the liquid solutes here. The error in the estimated solubilities was determined to be approximately 70−100%, with the largest contribution to the error resulting from the inability to describe accurately the stationary phase using regular solution theory. Although the error seems large, it is not unreasonable considering the low solubilities of the systems. Even published solubility data measured using conventional methods often differ by a factor of 2−10 for these systems. In order to verify the reliability of this approach for solid n-alkanes, calculated solubilities for $C_{28}H_{58}$ in CO_2 at 308.2 and 318.2 K are compared with those of Reverchon *et al.* (1993) (Figure 4).

The solubilities of $C_{33}H_{68}$ in CO_2 over a range of temperatures (308.2−333.2 K) are shown in Figure 5 to show the effect of temperature on solubility. This graph for $C_{33}H_{68}$, as well as graphs for the other solid n-alkanes, shows a crossover region in the low pressure range. As expected, the solubility increases with temperature at pressures higher than the crossover region and decreases with temperature at pressures lower than the crossover region.

In conclusion, experimental chromatographic capacity factors for the n-alkanes from C_9H_{20} to $C_{36}H_{74}$ in CO_2 were reported. Also, the estimation of solubilities from capacity factors was described, and solubilities for the solid n-alkanes in CO_2 from $C_{24}H_{50}$ to $C_{36}H_{74}$ were reported.

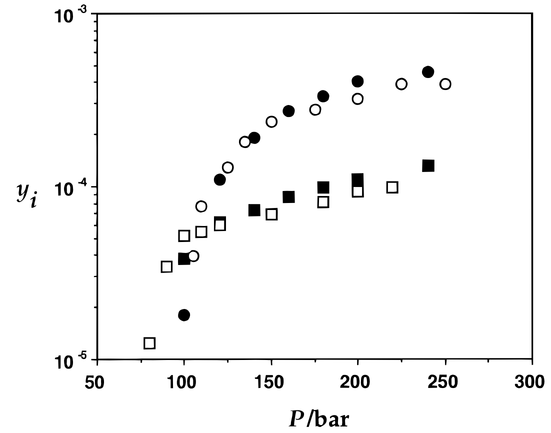

Figure 4. Mole fraction solubility, y_i, versus pressure, P, for $C_{28}H_{58}$ in CO_2: (■) this investigation at 308.2 K; (□) Reverchon *et al.* (1993) at 308.2 K; (●) this investigation at 318.2 K; (○) Reverchon *et al.* (1993) at 318.2 K.

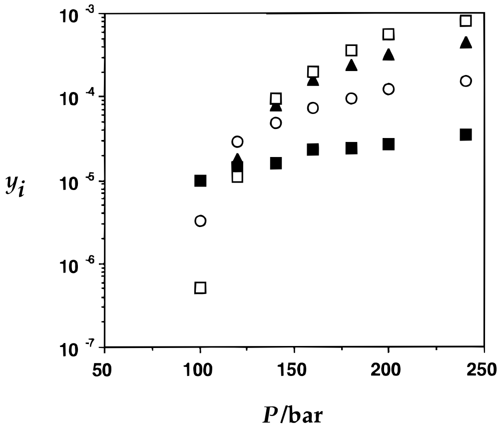

Figure 5. Mole fraction solubility, y_i, versus pressure, P, for $C_{33}H_{68}$ in CO_2 at various temperatures: (■) 308.2 K; (○) 318.2 K; (▲) 328.2 K; (□) 333.2 K.

Nomenclature

γ_i^∞	infinite dilution activity coefficient of solute i in the stationary phase
$C_i(T)$	constant for a particular chromatographic column, temperature, and solute
k_i	chromatographic capacity factor
$k^o_{H,i}$	Henry's law constant for solute i in the stationary phase at the reference pressure
N	carbon number
P	pressure
P^o	reference pressure
$P_{i,sat}$	saturation (vapor/sublimation) pressure of solute i
$P_{i,sub}$	sublimation pressure of solute i
$P_{i,vap}$	vapor pressure of solute i
R	universal gas constant
T	temperature
t_i	chromatographic retention time
V^m	physical volume of the mobile phase
V^s	physical volume of the stationary phase
V_m^m	molar volume of the mobile phase
V_m^s	molar volume of the stationary phase
y_i	mole fraction of solute i in the mobile phase (solubility)

Literature Cited

Bartle, K. D.; Clifford, A. A.; Jafar, S. A. Relationship Between Retention of a Solid Solute in Liquid and Supercritical Fluid Chromatography and its Solubility in the Mobile Phase. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 855−860.

Drake, B. D. Prediction of Sublimation Pressures of Low Volatility Solids Ph.D. Thesis, University of South Carolina, Columbia, SC, 1993.

Ely, J. F.; Haynes, W. M.; Bain, B. C. Isochoric (p, V_m, T) measurements on CO_2 and on (0.982 CO_2 + 0.018 N_2) from 250 to 330 K at pressures to 35 MPa. *J. Chem. Thermodyn.* **1989**, *21*, 879−894.

Fall, D. J.; Fall, J. L.; Luks, K. D. Liquid−Liquid−Vapor Immiscibility Limits in Carbon Dioxide + *n*-Paraffin Mixtures. *J. Chem. Eng. Data* **1985**, *30*, 82−88.

Fedors, R. F. A Method for Estimating Both the Solubility Parameters and Molar Volumes of Liquids. *Polym. Eng. Sci.* **1974**, *14*, 147−154.

Johnston, K. P.; Eckert, C. A. An Analytical Carnahan-Starling-van der Waals Model for the Solubility of Hydrocarbon Solids in Supercritical Fluids. *AIChE J.* **1981**, *27*, 773−779.

Kreglewski, A.; Zwolinski, B. J. A New Relation for Physical Properties of *n*-Alkanes and *n*-Alkyl Compounds. *J. Phys. Chem.* **1961**, *65*, 1050−1052.

Macknick, A. B.; Prausnitz, J. M. Vapor Pressures of High-Molecular-Weight Hydrocarbons. *J. Chem. Eng. Data* **1979**, *24*, 175−178.

McHugh, M. A.; Seckner, A. J.; Yogan, T. J. High-Pressure Phase Behavior of Binary Mixtures of Octacosane and Carbon Dioxide. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 493−499.

Morgan, D. L.; Kobayashi, R. Direct Vapor Pressure Measurements of Ten *n*-Alkanes in the C_{10} - C_{28} Range. *Fluid Phase Equilib.* **1994**, *97*, 211−242.

Morgan, D. L.; Kobayashi, R. Triple Point Corresponding States in Long-Chain *n*-Alkanes. *Fluid Phase Equilib.* **1991**, *63*, 317−327.

Nikolic, A. D. Predictions of Solvation and Vaporization Enthalpies. 1. *n*-Alkane + *n*-Alkane Solutions. *J. Solution Chem.* **1993**, *22*, 253−262.

Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: New Jersey, 1986.

Reverchon, E.; Russo, P.; Stassi, A. Solubilities of Solid Octacosane and Triacontane in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1993**, *38*, 458−460.

Sasse, K.; Jose, J.; and Merlin, J. C. A Static Apparatus for Measurement of Low Vapor Pressures. Experimental Results on High Molecular-Weight Hydrocarbons. *Fluid Phase Equilib.* **1988**, *42*, 287−304.

Suleiman, D.; Eckert, C. A. Phase Equilibria of Alkanes in Natural Gas Systems. 1. Alkanes in Methane. *J. Chem. Eng. Data* **1995a**, *40*, 2−11.

Suleiman, D.; Eckert, C. A. Phase Equilibria of Alkanes in Natural Gas Systems. 2. Alkanes in Ethane. *J. Chem. Eng. Data* **1995b**, *40*, 572−577.

Suleiman, D.; Gurdial, G. S.; Eckert, C. A. An Apparatus for Phase Equilibria of Heavy Paraffins in Supercritical Fluids. *AIChE J.* **1993**, *39*, 1257−1260.

Received for review June 9, 1995. Accepted September 10, 1995.[⊗] We gratefully acknowledge financial support from the GRI (Gas Research Institute) and the GPA (Gas Processors Association).

JE950138A

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.