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Solubilities of Long-Chain Hydrocarbons in Carbon Dioxide[1]

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Heavy hydrocarbons are becoming an increasingly important problem for the natural gas industry as it develops more costly gas reserves, such as those in the deep Gulf of Mexico. The waxy substances precipitate during natural gas processing, causing blockage of transmission pipelines. Knowledge of the solubility behavior of these hydrocarbon solids is therefore necessary to develop solutions to the solid deposition problem. This work reports solid–supercritical fluid equilibrum data for long-chain *n*-alkanes in carbon dioxide, a component of natural gas, over a range of temperatures and pressures that are typical of natural gas processing. A flow apparatus was used to measure the solubility, and the data were correlated by the Patel–Teja equation of state. Satisfactory agreement was obtained between calculated and experimental values, so the equation of state may be used to estimate the conditions for solid deposition and the amounts of solids formed at typical processing conditions.

KEY WORDS: equation of state; heavy hydrocarbons; natural gas; supercritical carbon dioxide; wax deposition.

1. INTRODUCTION

The natural gas industry is becoming increasingly concerned with heavy hydrocarbon solids that are obtained during natural gas production from associated gas and crude oil wells. These solids tend to deposit out of the natural gas stream onto pipeline walls leading to costly problems such as corrosion and plugging of the pipeline. The solubility behavior of the long-chain alkane solids in natural gas components is therefore of considerable practical interest. The prediction of solubility behavior also presents an

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interesting theoretical challenge, because of the difficulty in adequately describing the interactions between molecules with significant size differences.

The solubilities of long-chain alkanes in supercritical carbon dioxide have been measured by several researchers. Schmitt and Reid [1] measured the solubility of n-$C_{18}H_{38}$ (octadecane), n-$C_{19}H_{40}$ (nonadecane), n-$C_{20}H_{42}$ (eicosane), n-$C_{22}H_{46}$ (docosane), and n-$C_{24}H_{50}$ (tetracosane) in CO_2. Data were measured at 310 and 320 K over a range of pressures of from 11.0 to 28.0 MPa. Yau and Tsai [2] measured the solubility of n-$C_{24}H_{50}$, n-$C_{28}H_{58}$ (octacosane), n-$C_{32}H_{66}$ (dotriacontane), and n-$C_{36}H_{74}$ (hexatriacontane) in CO_2 at temperatures ranging from 308 to 338 K and pressures ranging from 3.0 to 20.9 MPa. The solubility of n-$C_{28}H_{58}$ in CO_2 in the temperature range 308 to 325 K and pressure range 8.2 to 32.7 MPa was measured by McHugh et al. [3], whereas Reverchon et al. [4] measured binary solubility data for n-$C_{28}H_{58}$ and n-$C_{30}H_{62}$ (triacontane) in CO_2 at experimental conditions ranging from 308 to 318 K and 8.0 to 25.0 MPa. All of the above studies employed a dynamic flow apparatus and obtained the amount of solid dissolved by gravimetric methods with the exception of the study by McHugh et al. [3], in which a calibrated high-pressure sampling loop was employed and the amount of solute obtained by gas chromatography. Spee and Schneider [5], on the other hand, measured the solubility of n-$C_{16}H_{34}$ (hexadecane) and n-$C_{32}H_{66}$ in CO_2 at 393 K and from 10.0 to 63.0 MPa using a vapor–liquid equilibrium (VLE) apparatus, in which samples were taken from both phases and analyzed by gas chromatography.

The solubilities of n-$C_{28}H_{58}$, n-$C_{29}H_{60}$, n-$C_{30}H_{62}$, n-$C_{32}H_{66}$, and n-$C_{33}H_{68}$ (tritiacontane) in a different solvent, C_2H_6 (ethane), were measured by Moradinia and Teja [6,7] using a flow system. Experimental conditions ranged from temperatures of 308 to 319 K and pressures of 6.57 to 20.02 MPa.

Most of the data reported in the work cited above cover a limited range of pressures and temperatures. Some of the data overlap in pressure and temperature but do not necessarily agree in concentrations. Therefore, there is a need for continued study of these systems to resolve some of the differences and to provide information for the development of better models for wax deposition.

2. EXPERIMENTS

A flow technique similar in principle to those used by Schmitt and Reid [1] and Moradinia and Teja [6, 7] was used in this work to obtain solid–fluid phase equilibrium data. In the flow method, a gas under pressure (the solvent) is brought into intimate contact with the solid solute and the amount of dissolved solid is obtained gravimetrically after depressurization. Two flow apparatuses were used in this work and are described below.

The first flow apparatus is shown in Fig. 1. Briefly, the solvent (carbon dioxide) was compressed into the reservoir of a syringe pump (ISCO 500D) and delivered at the desired pressure to the equilibrium vessel described below. The solvent stream from the pump was preheated to the desired temperature in a stainless-steel coil submerged in a liquid bath. The temperature of the bath was controlled to ±0.02 K by a liquid heater/circulator (Haake Model E3). The temperatures inside the vessel and the bath were monitored with type T thermocouples calibrated with a NIST-certified standard platinum resistance thermometer (Chino Corporation Model R800-3). The pressure in the system was monitored by means of an analog gauge (Heise Model CM-51917) calibrated with a dead weight tester (Budenberg Model 380H) accurate to ±0.05%. A Grove Industries back-pressure regulator, controlled by compressed nitrogen, was used to maintain a constant pressure in the system.

A Jerguson view cell (Model 17-T-40) of 40 ml internal volume served as the equilibrium vessel. A view cell, rather than the more conventional blind cell, is preferred because it is important to monitor the formation of any liquid phases in the system. Contact between the gas and the solute in the equilibrium vessel was achieved by means of alternating layers of solute and glass beads. We have found that equilibrium can be achieved rapidly in such an arrangement [6,7]. The loaded stream exiting the equilibrium chamber was then depressurized across a heated micrometering valve

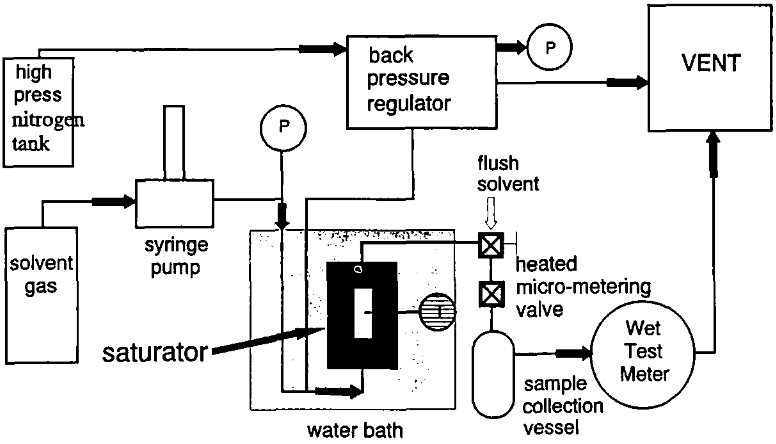

Fig. 1. Flow apparatus 1.

(Whitey Model SS-21RS2) and the solute collected in a separation vessel for further analysis. The separation vessel was immersed in a low-temperature bath and packed with glass wool at the outlet to ensure that all the solute was collected. The exiting gas stream from the separator passed through a wet test meter (Precision Scientific Model 63111), for the measurement of the total amount of gas. The mass of the solute was obtained gravimetrically. The wet test meter was factory-calibrated and certified accurate to within 0.5%.

The second apparatus consisted of a similar liquid delivery system including a ISCO 260D syringe pump. The equilibrium cell was a 10-ml stainless-steel cartridge housed in an ISCO SFX 2-10 extractor unit. The loaded stream exiting the extractor unit was depressurized across a heated micrometering valve, and the solute dropped out of solution into a sample collection vessel immersed in a low temperature bath. The mass of solute was obtained gravimetrically, whereas the total amount of solvent used was obtained by flow totalization using a wet test meter.

2.1. Materials

Carbon dioxide was obtained from Holox with a stated purity of 99.99+%. The *n*-alkanes *n*-$C_{25}H_{52}$ and *n*-$C_{29}H_{60}$ were obtained from Aldrich Chemical Company, *n*-$C_{24}H_{50}$ was obtained from Wiley, and *n*-$C_{28}H_{58}$ was obtained from Sigma. All chemicals were supplied at a stated purity of 99%. Purities were checked by the measuring the melting temperatures on a Mel-Temp melting point apparatus and are presented in Table I. The chemicals were used without further purification.

3. RESULTS AND DISCUSSION

The experimental solubilities of *n*-$C_{24}H_{50}$ in carbon dioxide are presented in Table II. The data are also plotted in Fig. 2 together with the data of Schmitt and Reid [1] and Yau and Tsai [2] for comparison. The data of Schmitt and Reid [1] exhibit considerable scatter, whereas the data

Table I. Experimental Melting Temperatures of the Alkanes

Substance	T_m (K)	Literature T_m (K) [15]
n-$C_{24}H_{50}$	323.25–324.05	323.75
n-$C_{25}H_{52}$	326.55–327.25	326.65
n-$C_{28}H_{58}$	334.25–335.15	334.35
n-$C_{29}H_{60}$	337.15–337.45	336.55

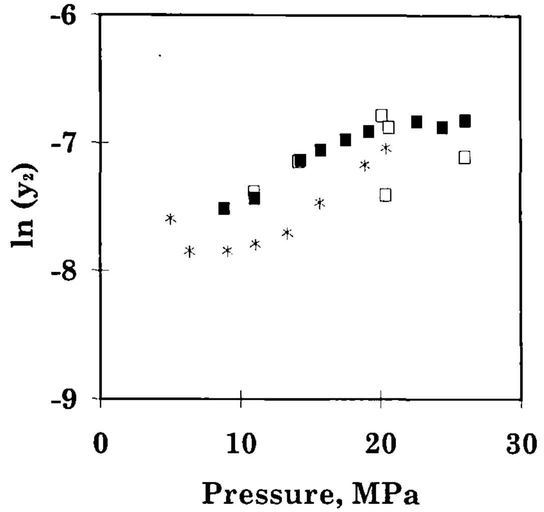

Fig. 2. Comparison of solubilities of n-C_{24} in CO_2. (■) This work (310 K); (□) Schmitt and Reid [1] (310 K); (∗) Yau and Tsai [2] (308 K).

of Yau and Tsai [2] show a different trend in the pressure region of interest. Yau and Tsai attribute this difference to impurities in their sample. The trends observed in the data obtained by each of the flow methods used in the present study, however, are consistent with each other and generally agree with the data of Schmitt and Reid.

Table II. Experimental Solubility of n-$C_{24}H_{50}$ in Carbon Dioxide at 310 K

P (MPa)	$y \times 10^4$	Solvent density ($mol \cdot L^{-1}$)
8.85	5.44[a]	13.57
11.03	5.72	16.47
14.31	8.06	18.02
15.74	8.63[a]	18.47
17.53	9.26	18.94
19.18	9.99[a]	19.31
22.62	10.8[a]	19.95
24.41	9.96	20.24
26.06	10.9[a]	20.47

[a] Denotes data obtained using flow apparatus 2.

Solubility data are presented for the other three binary systems of hydrocarbons with carbon dioxide in Tables III–V, and plotted against the reduced density of the solvent in Fig. 3. Solvent densities were obtained from Angus et al. [10]. Each reported solubility data point in Tables III–V represents the average of three measurements. In general, the three replicates agreed to within ±5%. Figure 3 shows that the solubilities of the heavy hydrocarbons in supercritical carbon dioxide increase with density and decrease with molecular weight as expected. However, the decrease is not uniform with carbon number as was also observed with C_2H_6–hydrocarbon systems by Moradinia and Teja [6,7]. Alkanes with an odd number of carbon atoms exhibit a higher solubility than would be expected from an interpolation of the solubilities of adjacent even-carbon number alkanes. This is due to differences in packing arrangements between the odd and the even alkanes [7]. In the solid-phase region, the even alkanes pack at a lower energy and have a lower sublimation pressure than the adjacent odd alkanes, leading to lower than expected solubilities. Also, the interactions between the solvent and even-alkane solute appear to be less than those between the solvent and an odd-alkane solute, as can be seen from an examination of their enhancement factors.

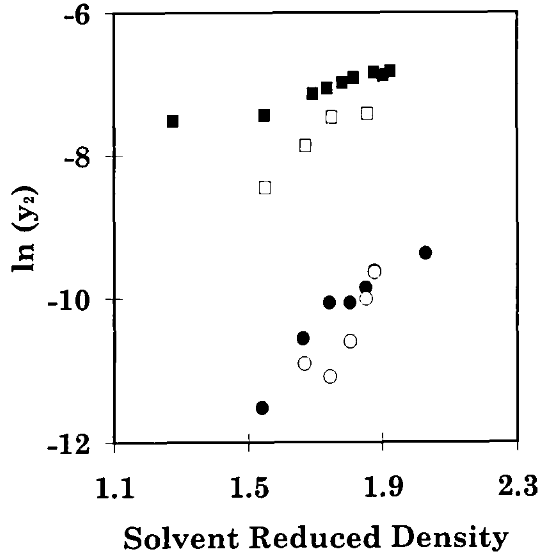

Fig. 3. Solubility versus solvent reduced density for alkanes in CO_2 at 308 K. (■) C_{24} (310 K); (□) C_{25}; (●) C_{28}; (○) C_{29}.

Table III. Experimental Solubility of n-$C_{25}H_{52}$ in Carbon Dioxide at 308 K

P (MPa)	$y \times 10^4$	Solvent density ($mol \cdot L^{-1}$)
10.36	2.15	16.49
12.68	3.83[a]	17.77
15.20	5.74[a]	18.62
20.23	6.02[a]	19.75

[a] Denotes data obtained using flow apparatus 2.

Table IV. Experimental Solubility of n-$C_{28}H_{58}$ in Carbon Dioxide at 308 K

P (MPa)	$y \times 10^5$	Solvent density ($mol \cdot L^{-1}$)
10.00	3.90	16.21
14.98	5.32	18.53
17.51	6.47	19.18
19.98	6.89	19.69
21.51	7.24	19.96
34.03	8.58[a]	21.57

[a] Denotes data obtained using flow apparatus 2.

Table V. Experimental Solubility of n-$C_{29}H_{60}$ in Carbon Dioxide at 308 K

P (MPa)	$y \times 10^5$	Solvent density ($mol \cdot L^{-1}$)
12.65	3.14	17.73
17.51	3.81	19.18
20.03	4.55	19.70
21.51	6.62	19.96

The enhancement factor is a measure of solubility enhancements due to intermolecular interactions between the solute and the solvent molecules. It is defined by

$$E = y_2 \frac{P}{P_2^{\text{sat}}} \tag{1}$$

where y_2 is the solubility of the solute in mole fraction, P is the system pressure, and P_2^{sat} is the saturation pressure of the solute.

The calculated enhancement factors in the four systems studied in this work were found to be greater for the higher molecular weight solutes because the sublimation pressures of the heavier substances are lower, as are their fugacity coefficients in the supercritical phase.

Enhancement factors for n-$C_{28}H_{58}$ and n-$C_{29}H_{60}$ in carbon dioxide and ethane are plotted versus solvent reduced density in Fig. 4. All trends are linear, and the enhancement effect of ethane is greater than the enhancement effect of carbon dioxide on hydrocarbon solubilities. This indicates that solute–solvent interactions are higher when ethane is the solvent; thus, ethane is a better solvent for the substances in this study.

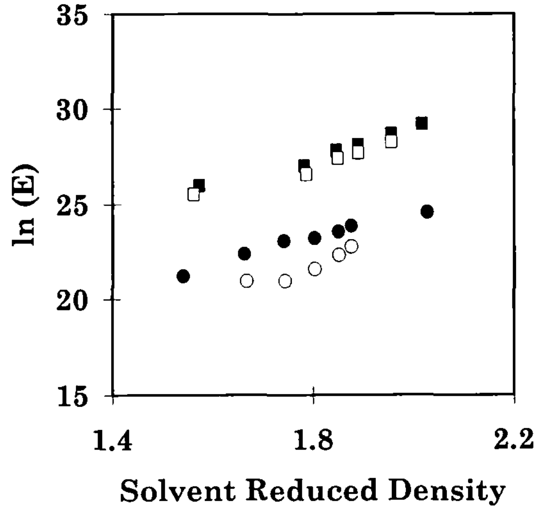

Fig. 4. Enhancement factor versus solvent reduced density for C_{28} and C_{29} in CO_2 and C_2. (■) C_2-C_{28}; (□) C_2-C_{29}; (●) CO_2-C_{28}; (○) CO_2-C_{29}.

The solubilities of the solid solutes in supercritical CO_2 were also calculated from

$$y_2 = \left[P_2^{\text{sat}} \exp\left(\frac{v_2^{\text{sat}}(P - P_2^{\text{sat}})}{RT} \right) \right] \Big/ \phi_2^{\text{SCF}} P \qquad (2)$$

where v_2^{sat} is the molar volume of the solute, R is the universal gas constant, T is the system temperature, and ϕ_2^{SCF} is the fugacity coefficient of the solute in the supercritical solvent. This equation may be derived from the equality of fugacity condition at equilibrium with the assumption that the solid solute is incompressible, that it has a negligible vapor pressure, and that the supercritical fluid is not soluble in the solid. The solid molar volume v_2^{sat} was supplied by the manufacturer. The sublimation pressures P_2^{sat} for the long-chain alkanes in the solid phase, on the other hand, were not available and had to be obtained using estimation techniques from the literature [11,12]. The technique of Moradinia [11] was used in the present work because it was derived from the experimental sublimation pressures of lower alkanes.

The fugacity coefficient ϕ_2^{SCF} may be obtained from an equation through standard thermodynamic relationships. The Patel–Teja equation of state (EOS) [13] was used in this work to obtain ϕ_2^{SCF} and hence correlate experimental solubilities. The Patel–Teja equation is given by

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + c(V - b)} \qquad (3)$$

where the three equation of state constants may be obtained from a knowledge of T_c, P_c, and ω as shown [13]:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \left(1 + m \left(1 - \sqrt{\frac{T}{T_c}} \right) \right)^2 \qquad (4)$$

$$b = \Omega_b \frac{RT_c}{P_c} \qquad (5)$$

$$c = \Omega_c \frac{RT_c}{P_c} \qquad (6)$$

$$m = 0.452413 + 1.30982\omega - 0.295937\omega^2 \qquad (7)$$

where Ω_a, Ω_b, and Ω_c are constants whose values depend on the apparent critical compressibility factor of the substance, which is obtained from

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2 \qquad (8)$$

The critical properties of the long-chain alkanes have not been measured, because the *n*-alkanes decompose at temperatures below their critical points. Therefore, the correlations presented by Teja et al. [14] based on the measured critical properties of the alkanes up to *n*-$C_{18}H_{38}$ were used in the present work.

The equation-of-state constants for mixtures were calculated from the van der Waals one-fluid mixing rules, with the cross-term a_{ij} given by the following combining rule:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{9}$$

The single binary interaction parameter k_{ij} was found by a least-squares fit of the experimental data.

Satisfactory agreement between calculated and experimental data is obtained if one binary interaction parameter is used, as shown in Fig. 5. Agreement, however, is not within experimental error, altough it can be improved with better estimates of critical temperature, pressure, and sublimation pressure as well as using mixing rules that more adequately account for the size differences between the solute and the solvent molecules.

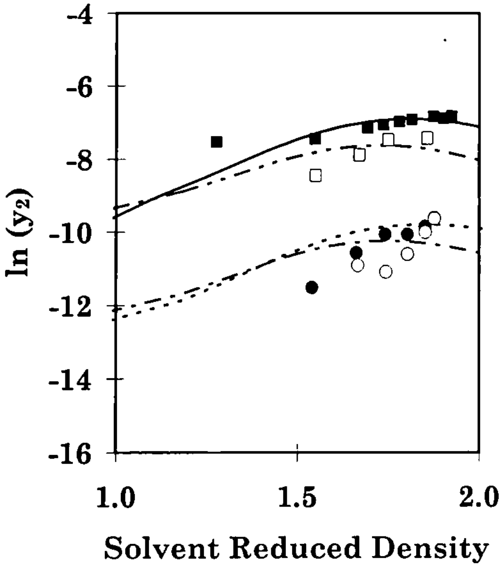

Fig. 5. Calculated and experimental solubilities for alkanes in CO_2. (■) C_{24} (310 K) and (——) PT EOS with $k_{ij} = -0.00007$; (□) C_{25} and (-----) PT EOS with $k_{ij} = 0.03819$; (●) C_{28} and (----) PT EOS with $k_{ij} = 0.00185$; (○) C_{29} and (----) PT EOS with $k_{ij} = 0.04089$.

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