$\tilde{T}$	reduced temperature; $\tilde{T}_A = (\tilde{v}_A^{1/3} - 1)\tilde{v}_A^{-4/3}$
V^E	excess volume
V^E_{Flory}	Flory's excess volume, $=(x_A V_A^* + x_B V_B^*)(\tilde{T} - \tilde{T}^0)(\tilde{v}^0)^{7/3}/[^4/_3 - (\tilde{v}^0)^{1/3}]$
V	molar volume
$\tilde{v}$	reduced volume, $=[(1 + 4\alpha T/3)/(1 + \alpha T)]^3$
V^*	characteristic volume, $= V/\tilde{v}$
V_0, V_1, V_2	coefficients in eq 1
X_{AB}	interaction parameter, $=p_A^*[1 - (V_B^*/V_A^*)^{1/6}\cdot(p_B^*/p_A^*)^{1/2}]^2$
$X_{AB}(H^E)$	interaction parameter calculated from excess enthalpy
x_i	mole fraction of component i
α	thermal expansivity
σ	standard deviation

Registry No. Methyl ethyl ketone, 78-93-3; benzene, 71-43-2; toluene, 108-88-3; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; nitrobenzene, 98-95-3.

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Solubilities of Carbon Dioxide in Heavy Normal Paraffins (C_{20}–C_{44}) at Pressures to 9.6 MPa and Temperatures from 323 to 423 K

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Solubility data have been obtained for carbon dioxide in the heavy normal paraffin solvents *n*-eicosane, *n*-octacosane, *n*-hexatriacontane, and *n*-tetratetracontane. Measurements were made over the temperature range from 323 to 423 K (122 to 302 °F) at pressures up to 9.6 MPa (1400 psia). At carbon dioxide mole fractions below 0.45, the solubility data are described by the Krichevsky–Kasarnovsky equation with average deviations of 0.002 in mole fraction.

Introduction

Vapor–liquid phase equilibrium data are an essential element in the rational design and development of many industrial processes as well as for the enhancement of our understanding of fluid-phase behavior. CO_2 + hydrocarbon vapor–liquid equilibria data, in particular, are of interest in a number of industrial processes, including processing of petroleum products, production of coal liquids, and enhanced oil recovery.

Limited data are available on systems involving CO_2 and those heavy normal paraffin solvents which are solid at room temperature. Only two studies have been found in the literature dealing with such systems. The first system is CO_2 + *n*-eicosane reported by Huie et al. (*1*), and the second is CO_2 with traces of *n*-octacosane presented recently by McHugh et al. (*2*).

The purpose of the investigation reported here was to obtain solubility data for CO_2 in the following members of the normal paraffin homologous series: *n*-eicosane (*n*-C_{20}), *n*-octacosane (*n*-C_{28}), *n*-hexatriacontane (*n*-C_{36}), *n*-tetratetracontane (*n*-C_{44}). These studies were designed to provide useful information for the further development of generalized predictive methods, which thus far have necessarily been based on insufficient data for heavy paraffin molecules (see, e.g., ref *3*).

Experimental Method

The experimental apparatus and procedures used in this work are described in detail by Gasem (*4*) and are summarized briefly below. The general arrangement of the apparatus is illustrated in Figure 1. It employs a static-type equilibrium cell. One distinct feature of the apparatus is its capability for handling solvents which are solid at room temperature. Solvent solidification presents significant problems in conventional equilibrium apparatuses; this may explain, in part, the lack of data for such systems.

The central part of the apparatus is a high-pressure, variable-volume, rocking cell housed in a constant-temperature bath. The equilibrium cell (EC) is a 90-cm^3 high-pressure stainless steel cylinder held in an aluminum block rocking assembly. The effective volume of the cell can be varied by the introduction or withdrawal of mercury. The apparatus is designed specifically to accommodate heavy solvents (solids at room temperature) by placing the solvent reservoir (SV) inside the high-temperature air oven (TB). The reservoir is a 125-cm^3 commercial reactor bomb with screw-top closure, which may be filled with the solid solvent by removing the top of the bomb.

Injections of solvent (liquid at the operating temperatures) into the equilibrium cell are done volumetrically by injecting mercury at the bottom of the solvent cylinder, thus displacing an equal quantity of solvent into the rocking cell. Sequential injections of solute are then made in like fashion from the solute storage cylinder (SU). The solute is housed in an external constant-temperature bath (TR), so it may be injected as gas or liquid as desired. The injected volumes are metered from a precision screw pump (SP) maintained at room temperature.

After each injection of solute into the solvent in the rocking cell, the bubble point pressure of the mixture is determined. This is done by injecting known amounts of mercury into the cell to alter the system volume. After each mercury injection, the cell is rocked to bring the system to equilibrium and the pressure is recorded. The bubble point pressure is located by observing the break point in a pressure–volume curve as the system passes from a two-phase to an all-liquid condition; example plots are shown in Figure 2.

Prior to an experiment, the hydrocarbon solvent is thoroughly degassed by applying a vacuum to the solvent. This degassing procedure is initiated at room temperature while the solvent is

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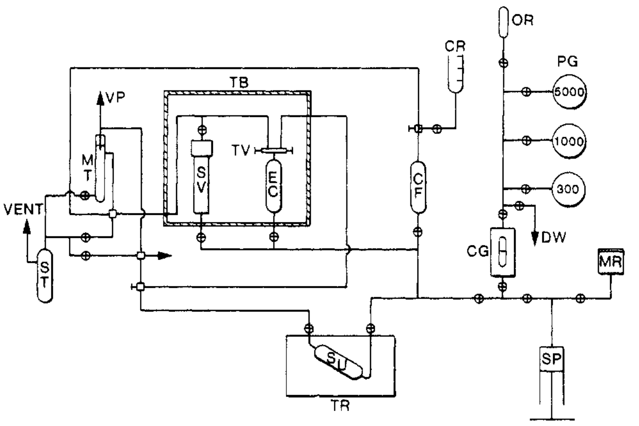

CF - CLEANING FLUID CYLINDER
CG - MERCURY-OIL CONTACT GAUGE
CR - CLEANING FLUID RESERVOIR
DW - TO DEAD-WT. GAUGE
EC - EQUILIBRIUM CELL
MT - MERCURY TRAP
MR - MERCURY RESERVOIR
OR - OIL RESERVOIR
PG - PRESSURE GAUGES

SP - SCREW PUMP
ST - SOLVENT TRAP
SU - SOLUTE STORAGE CYLINDER
SV - SOLVENT STORAGE CYLINDER
TB - CONSTANT TEMPERATURE BATH
TR - REFRIGERATED TEMPERATURE BATH
TV - THREE-WAY VALVE
VP - TO VACUUM PUMP

Figure 1. Gas solubility apparatus.

still in the solid state and continued at the desired equilibrium temperature prior to solvent injection.

Temperature is controlled by a commercial proportional-integral controller and measured within 0.1 K with a calibrated platinum resistance thermometer. Pressures are measured on precision Bourdon-tube gauges (PG), which are calibrated periodically against a dead-weight tester (not shown). Pressures are transmitted directly from the equilibrium cell to the gauges through the mercury-filled lines. The pressure gauges are oil filled and are connected to the mercury system through mercury–oil contact in a Jerguson sight gauge (CG); suitable head corrections are applied for the mercury. Compositions of the bubble point liquids are determined from the precisely known volumes of pure solvent and solute injected into the cell; thus, no compositional analyses are required. The densities of the solvent liquids were taken from the literature (*5*), as were the CO_2 densities (*6*).

Error Analysis

The expected uncertainties in the measured variables are estimated to be as follows:

$$\epsilon_T = 0.1 \text{ K}$$

$$\epsilon_V = 0.006V$$

$$\epsilon_P = 0.0007P \text{ (1000 psi gauge); } 0.001P \text{ (5000 psi gauge)}$$

By error propagation, the expected error in the mole fraction is found to be given by the relation

$$\epsilon_x = 0.01x(1 - x)$$

During the course of the experiments, repeated bubble point determinations were made on each of several fluid mixtures (at fixed temperature and composition). This was done by repeating the pressure–volume traverse (such as those shown in Figure 2) several times for a specific mixture and comparing the pressures at which the "breaks" occurred in the plots. The results revealed a correlation between the pressure level and the observed imprecision of the measured bubble point pressure (P_b). This correlation can be expressed as follows:

$$\epsilon_{P_b} = 0.003P_b \qquad (1)$$

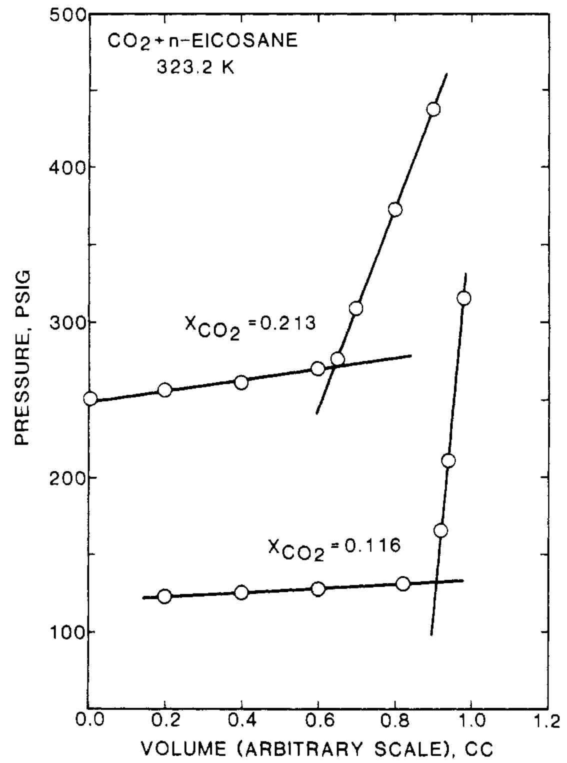

Figure 2. Typical pressure–volume plot for the determination of bubble point pressures.

Equation 1 reflects an increased uncertainty in the determined bubble point (in excess of the uncertainties contributed by the pressure and temperature measuring equipment) due, in part, to the effect of room-temperature variations on the exposed mercury in the screw pump (SP) and connecting lines. Thus, the total expected uncertainty in the reported bubble point pressures (including the gauge calibration errors) may be approximated as

$$\epsilon_{P_b} = 0.004P_b$$

Materials

The carbon dioxide used in this study had a stated purity of 99.99 mol % and was supplied by Linde Specialty Gases. The normal paraffins were of a reported purity of 99 mol % as supplied by Alfa Products. No further purification of the chemicals was attempted.

Results

To test the validity of the apparatus and procedures used in this study, several preliminary measurements were made. First, vapor pressures of pure propane and ammonia were determined at several temperatures. These data agreed well with literature sources, and the results were taken as a confirmation of the temperature and pressure measurement systems. Next, solubility data were measured on three systems for which literature data exist: ethane + *n*-dodecane, carbon dioxide + benzene, and carbon dioxide + *n*-eicosane. Data comparisons appear in Figure 3, where the data from the various sources are shown in terms of their deviations from simple polynomial functions fitted to the present data. Among the various data for ethane + *n*-dodecane (*7–9*), our results are in best agreement with those of Legret et. al. (*7*); the results shown in Figure 3 are equivalent to differences in bubble point pressures of about 4 psi. The carbon dioxide + benzene data show similarly good agreement with the bubble point data of Gupta et al. (*10*).

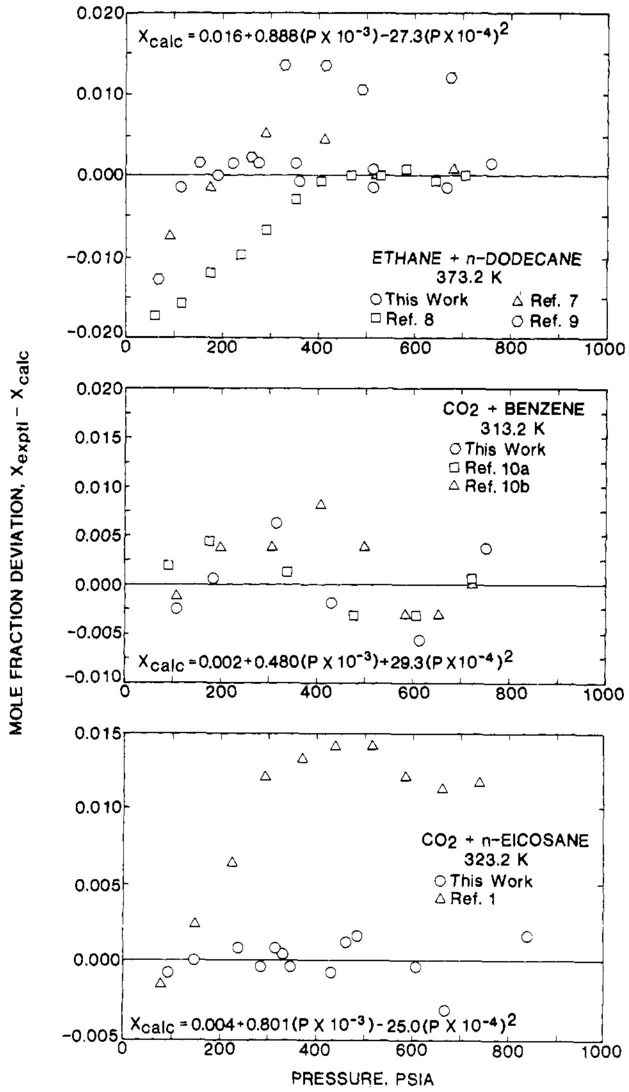

Figure 3. Comparisons of phase behavior data.

The present data for carbon dioxide + *n*-eicosane are in substantial disagreement with those of Huie et al. (*1*). Deviations shown in the figure represent differences in bubble point pressures as large as 28 psi for the 122 °F isotherm (Figure 3); deviations of up to 0.014 mole fraction (49 psi) were obtained for the 212 °F isotherm. Recent unpublished data by Fall and Luks (*11*), however, confirm the present measurements at 122 °F within the combined uncertainties in the two data sets.

The combined comparisons described above were taken as confirmation of the proper operation of the present apparatus and procedures. Measurements were then performed on the heavier paraffin solvents. Complete data for the test systems and for the CO_2 + paraffin systems of the present study are given in Table I.

Krichevsky–Kasarnovsky Analysis

At mole fractions below 0.45, CO_2 solubility in the normal paraffins can be represented excellently by the Krichevsky–Kasarnovsky (KK) equation (*12*):

$$\ln (f_{CO_2}/x_{CO_2}) = \ln (H_{CO_2,hc}) + (\bar{V}^{\infty}_{CO_2}/RT)(P_b - P_{hc}^{0}) \quad (2)$$

In eq 2 the fugacity of pure CO_2 was substituted for the fugacity of CO_2 in the vapor-phase mixture since the vapor phase is essentially pure CO_2. The pure CO_2 fugacity data were taken from the literature (*6*). Figure 4 presents the data in the form suggested by the KK equation. The model fits the solubility data with average errors of less than 0.002 in CO_2 mole fraction; these errors represent average deviations of less than 0.5% of the measured values of the solubilities.

Table I. Solubility Data for Several Binary Systems

solute mole fraction	press., MPa (psia)
Ethane + *n*-Dodecane at 373.2 K (212 °F)	
0.111	0.776 (112.5)
0.179	1.348 (195.5)
0.204	1.558 (226.0)
0.244	1.927 (279.5)
0.297	2.437 (353.5)
0.300	2.489 (361.0)
0.399	3.551 (515.0)
0.403	3.571 (518.0)
0.487	4.626 (671.0)
0.534	5.233 (759.0)
CO_2 + Benzene at 313.2 K (40 °C)	
0.056	0.758 (110.0)
0.101	1.262 (183.0)
0.191	2.192 (318.0)
0.260	2.954 (428.5)
0.405	4.257 (617.5)
0.531	5.171 (750.0)
CO_2 + *n*-Eicosane at 323.2 K (122 °F)	
0.073	0.621 (90.0)
0.098	0.855 (124.0)
0.116	1.010 (146.5)
0.180	1.624 (235.5)
0.213	1.972 (286.0)
0.235	2.199 (319.0)
0.242	2.272 (329.5)
0.251	2.382 (345.5)
0.300	2.947 (427.5)
0.322	3.182 (461.5)
0.335	3.337 (484.0)
0.399	4.188 (607.5)
0.425	4.606 (668.0)
0.501	5.767 (836.5)
CO_2 + *n*-Eicosane at 373.2 K (212 °F)	
0.090	1.069 (155.0)
0.153	1.906 (276.5)
0.214	2.765 (401.0)
0.249	3.316 (481.0)
0.314	4.402 (638.5)
0.332	4.730 (686.0)
0.371	5.481 (795.0)
0.416	6.429 (932.5)
0.430	6.757 (980.0)
CO_2 + *n*-Octacosane at 348.2 K (167 °F)	
0.099	0.845 (122.5)
0.160	1.448 (210.0)
0.231	2.241 (325.0)
0.301	3.123 (453.0)
0.399	4.623 (670.5)
0.470	5.933 (860.5)
0.551	7.722 (1120.0)
0.617	9.604 (1393.0)
CO_2 + *n*-Octacosane at 373.2 K (212 °F)	
0.082	0.807 (117.0)
0.098	0.972 (141.0)
0.149	1.565 (227.0)
0.289	3.475 (504.0)
0.339	4.288 (622.0)
0.391	5.236 (759.5)
0.465	6.812 (988.0)
0.558	9.346 (1355.5)
CO_2 + *n*-Octacosane at 423.2 K (302 °F)	
0.070	0.841 (122.0)
0.107	1.338 (194.0)
0.155	2.024 (293.5)
0.226	2.934 (425.5)
0.301	4.537 (658.0)
0.397	6.681 (969.0)
0.490	9.253 (1342.0)
CO_2 + *n*-Hexatriacontane at 373.2 K (212 °F)	
0.062	0.524 (76.0)
0.101	0.872 (126.5)
0.172	1.579 (229.0)
0.178	1.662 (241.0)
0.206	1.948 (282.5)
0.280	2.868 (416.0)
0.335	3.644 (528.5)
0.375	4.282 (621.0)
0.390	4.382 (653.5)
0.459	5.878 (852.5)
CO_2 + *n*-Hexatriacontane at 423.2 K (302 °F)	
0.097	1.017 (147.5)
0.147	1.610 (233.5)
0.191	2.196 (318.5)
0.280	3.527 (511.5)
0.302	3.923 (569.0)
0.393	5.674 (823.0)
0.405	6.009 (871.5)
0.502	8.632 (1252.0)
CO_2 + *n*-Tetratetracontane at 373.2 K (212 °F)	
0.080	0.579 (84.0)
0.122	0.938 (136.0)
0.188	1.606 (233.0)
0.238	1.999 (290.0)
0.343	3.357 (486.0)
0.401	4.185 (607.0)
0.502	6.112 (886.5)
CO_2 + *n*-Tetratetracontane at 423.2 K (302 °F)	
0.091	0.814 (118.0)
0.152	1.441 (209.0)
0.193	1.924 (279.0)
0.270	2.930 (425.0)
0.319	3.654 (530.0)
0.398	5.092 (738.5)
0.485	7.081 (1027.0)

The experimental data were regressed according to eq 2 to obtain values for the Henry's constant and infinite-dilution partial molar volume of CO_2. The resulting parameters are in Table II. The Henry's constant at 323.2 K obtained for *n*-eicosane, 8.23 MPa, is in excellent agreement with the value of 8.26 MPa

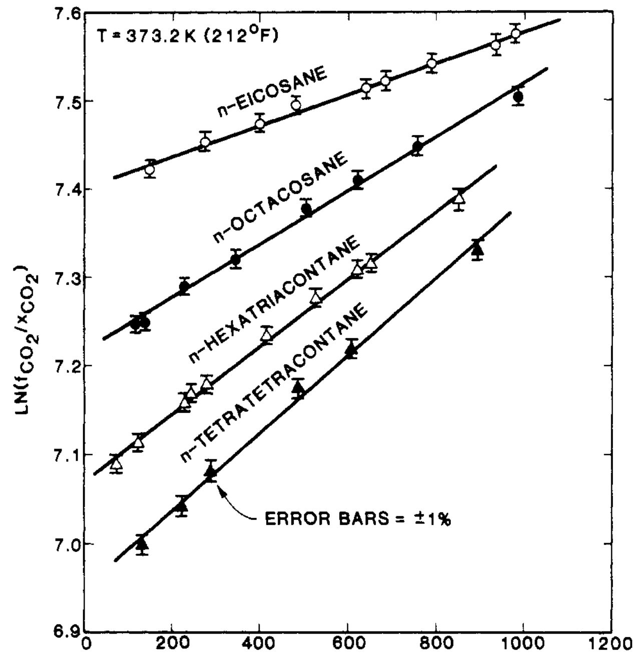

Figure 4. Krischevsky-Kasarnovsky analysis of CO_2 solubility data.

Table II. Henry's Constants and Infinite-Dilution Partial Molar Volumes for Carbon Dioxide in Heavy Normal Paraffins

temp, K (°F)	Henry's constant,[a] MPa	partial mol vol,[a] cm^3/g-mol
	n-C_{20}	
313.2 (122)	8.23 (0.03)	48 (3)
373.2 (212)	11.29 (0.03)	79 (1)
	n-C_{28}	
348.2 (167)	8.12 (0.12)	131 (8)
373.2 (212)	9.38 (0.09)	139 (6)
423.2 (302)	11.56 (0.17)	151 (11)
	n-C_{36}	
373.2 (212)	7.74 (0.03)	170 (4)
423.2 (302)	9.85 (0.07)	189 (5)
	n-C_{44}	
373.2 (212)	7.06 (0.08)	211 (11)
423.2 (302)	8.52 (0.08)	226 (8)

[a] Standard errors in the tabulated values are given in parentheses.

interpolated from the data of Chai et al. (*13*). However, care must be exercised in attributing physical significance to the values in Table II. Investigations using more complex models (*4*) have led us to believe that the Henry's constants in Table II are no more than a few percent from the true values. The reported partial volumes of CO_2, however, may be considerably less accurate.

Acknowledgment

McRay Anderson, Steven George, and Judy Couch Tiffin provided valuable assistance in the experimental measurements.

Glossary

f_{CO_2}	fugacity of CO_2 in the mixture
$H_{CO_2,hc}$	Henry's constant for CO_2 in the hydrocarbon (hc) solvent
P	system pressure
P_b	bubble point pressure
P_{hc}^0	hydrocarbon vapor pressure
R	gas constant
T	temperature
V	volume of injected fluid
$\bar{V}^\infty_{CO_2}$	partial molar volume at infinite dilution of CO_2 in the liquid phase
x	mole fraction of CO_2 in the liquid phase
ϵ	expected uncertainty

Registry No. CO_2, 124-38-9; *n*-eicosane, 112-95-8; *n*-octacosane, 630-02-4; *n*-hexatricontane, 630-06-8; *n*-tetratetracontane, 7098-22-8.

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