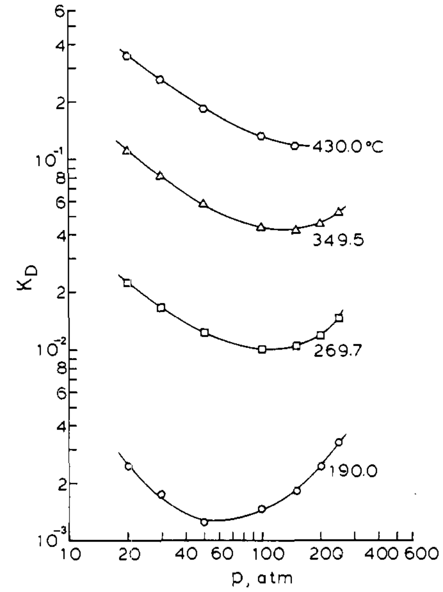

Figure 4. K values of 9,10-dihydrophenanthrene.

of the saturated compositions are reported in Table I. The mole fractions of NTDP at 430 °C include those of phenanthrene. The x and y values are used to calculate the vaporization equilibrium ratios for methane and 9,10-dihydrophenanthrene. The results are summarized in the table and are shown in Figures 3 and 4, respectively.

NTDP is the heaviest aromatic hydrocarbon and the only three-ringed compound which has been studied in this laboratory. The nature of the solvent is reflected in the relatively low methane solubility as compared to the lighter solvents.

Glossary

K	vaporization equilibrium ratio
p	pressure, atm
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscript

D	9,10-dihydrophenanthrene
M	methane

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Gas-Liquid Equilibrium of Carbon Dioxide plus *m*-Cresol and Carbon Dioxide plus Quinoline at Elevated Temperatures

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Compositions of coexisting vapor and liquid phases were experimentally determined for two binary systems: CO_2 plus *m*-cresol and CO_2 plus quinoline at pressures up to 50 atm. Temperatures were 189.5-391.5 °C for the former system and 188.6-430.2 °C for the latter. A flow apparatus was used for both.

Introduction

Recent development in high temperature refining processes has intensified interest in vapor-liquid equilibria of CO_2 in mixtures with heavy hydrocarbon solvents. An examination of the open literature shows that studies of phase equilibrium behavior of mixtures containing CO_2 and heavy nonparaffinic hydrocarbons at high temperatures are scarce. In this work, we observe the vapor and liquid equilibrium phase compositions for two binary systems: CO_2 plus *m*-cresol and CO_2 plus quinoline at temperatures up to 430 °C in the pressure range 20-50 atm. Vaporization equilibrium ratios for CO_2 and the solvents are

Table I. Carbon Dioxide plus *m*-Cresol Vapor-Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_{Cr}
		189.5 °C		
19.25	0.0391	0.9540	24.40	0.0479
30.10	0.0639	0.9679	15.15	0.0343
39.9	0.0851	0.9724	11.43	0.0302
51.1	0.1109	0.9756	8.80	0.0274
		269.3 °C		
20.10	0.0304	0.7312	24.05	0.2772
30.18	0.0516	0.8097	15.69	0.2007
40.3	0.0734	0.8457	11.52	0.1665
49.9	0.0930	0.8657	9.31	0.1481
		351.3 °C		
20.53	0.00895	0.1717	19.18	0.8358
29.87	0.0300	0.3634	12.11	0.6563
40.4	0.0532	0.4872	9.16	0.5416
50.2	0.0760	0.5519	7.26	0.4850
		391.5 °C		
40.5	0.0342	0.2219	6.49	0.8057
50.1	0.0592	0.3044	5.14	0.7394

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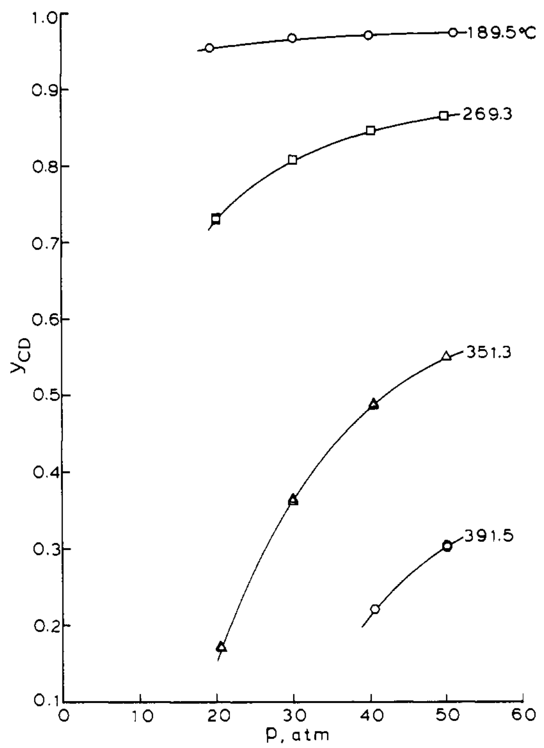

Figure 1. Mole fraction of CO_2 in the saturated vapor of CO_2 plus *m*-cresol system.

Table II. Carbon Dioxide plus Quinoline Vapor-Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_Q
		188.6 °C		
19.89	0.0466	0.9813	21.06	0.0196
29.83	0.0696	0.9856	14.16	0.0155
40.1	0.0926	0.9880	10.67	0.0129
50.0	0.1145	0.9892	8.64	0.0122
		269.5 °C		
20.30	0.0359	0.8882	24.74	0.1160
29.96	0.0548	0.9169	16.73	0.0879
39.8	0.0748	0.9315	12.45	0.0740
50.0	0.0934	0.9406	10.07	0.0655
		350.5 °C		
19.87	0.0240	0.5802	24.18	0.4301
29.92	0.0432	0.6960	16.11	0.3177
39.9	0.0622	0.7562	12.16	0.2600
49.9	0.0814	0.7907	9.71	0.2278
		430.2 °C		
30.20	0.0221	0.2699	12.21	0.7466
40.0	0.0439	0.3920	8.93	0.6359
50.3	0.0659	0.4740	7.19	0.5631

presented. No data have been previously reported in the literature for these two systems.

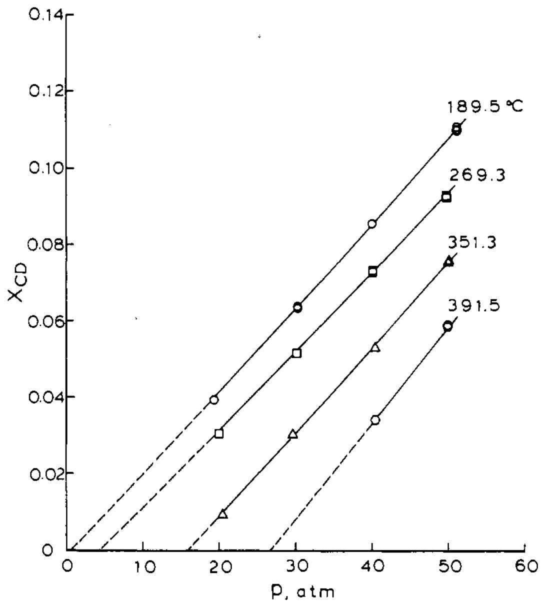

Figure 2. Solubility of CO_2 in *m*-cresol.

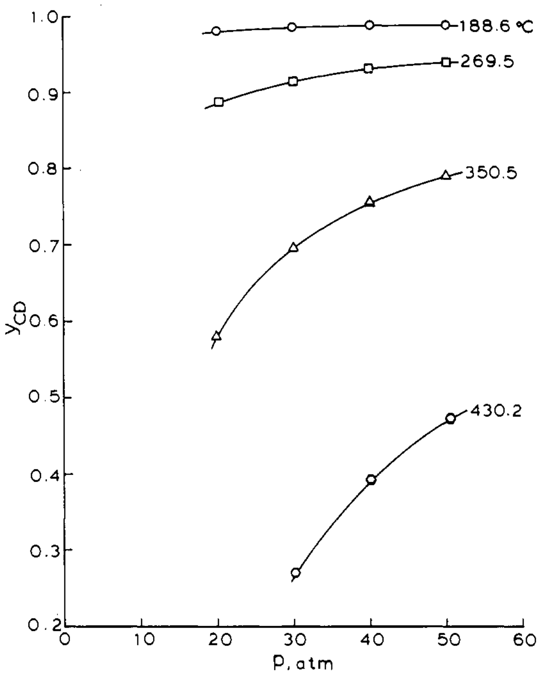

Figure 3. Mole fraction of CO_2 in the saturated vapor of CO_2 plus quinoline system.

Experimental Section

The experimental apparatus and method used in this work have been described by Simnick and co-workers (*2*). This work departed from the description given there in a minor way in that the gas compressor was bypassed. Carbon dioxide gas was supplied to the system directly from the cylinder as purchased. Carbon dioxide was supplied by Matheson with a minimum purity of 99.99% (Coleman Instrument grade). *m*-Cresol purchased from Aldrich Chemical Co. was Gold Label grade of 99+% purity. Quinoline was from Fisher Scientific Co. with a reported purity of 99+% (certified reagent grade) but showed a deep purple color. Further purification to remove the color was made by vacuum fractional distillation over zinc as described by Sebastian et al. (*1*). The purities of the hydrocarbon solvents were checked by gas chromatography with a FID detector and found to be as good as claimed.

Samples of the solvents were collected from the equilibrium cell effluents on both gas and liquid streams of all the runs and analyzed by gas chromatography to check for thermal stability. No products from chemical reactions were detected at any of the conditions studied.

The temperature of the equilibrium cell fluctuated no more than 0.2 °C for CO_2 plus *m*-cresol and 0.1 °C for CO_2 plus quinoline during a complete isothermal run.

Solubilities of CO_2 in *m*-cresol and in quinoline at ambient conditions, which are required for making a minor correction to the directly observed volume of CO_2, were determined in this laboratory. The method used was to bubble the gas through the solvent at atmospheric pressure and to analyze the content of dissolved gas in the saturated solution by gas chromatography.

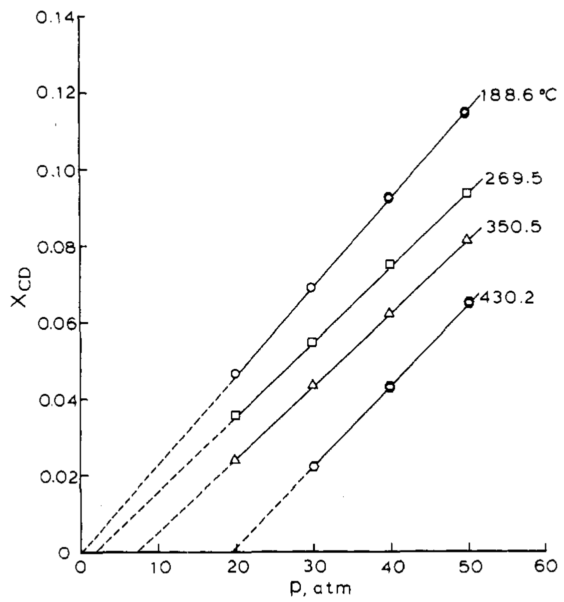

Figure 4. Solubility of CO_2 in quinoline.

Results

Table I presents compositions of the coexistent vapor and liquid phases in CO_2 plus *m*-cresol mixtures at the temperatures 189.5, 269.3, 351.3, and 391.5 °C. The pressures are from 20 to 50 atm for each of the three lower temperatures. However, at the highest temperature, only two pressures at 40 and 50 atm were measured because of the high vapor pressure of *m*-cresol.

Figures 1 and 2 show the saturated compositions of the vapor and the liquid phases, respectively, for mixtures of CO_2 plus *m*-cresol as a function of the total pressure. Individual samples are plotted in the figures as separate points where they can be differentiated. The end points at $X_{CD} = 0$ in Figure 2 correspond to the vapor pressures of *m*-cresol, which are available from Simnick and co-workers (*3*).

Table II presents the results for the CO_2 plus quinoline system at the temperatures 188.6, 269.5, 350.5, and 430.2 °C and pressures up to 50 atm. The equilibrium compositions are shown in Figure 3 for the vapor phase and Figure 4 for the liquid. The vapor pressure data indicated in Figure 4 were taken from Sebastian et al. (*1*).

The reported phase compositions are the averages of at least two observations at a fixed *T* and *p*. The deviations of the direct observations from the average are generally within 0.5% in mole fraction of CO_2. The average values of *x* and *y* are used to calculate the *K* values.

Acknowledgment

Mark J. Horvath assisted in measuring the solubilities of CO_2 in *m*-cresol and in quinoline at ambient conditions.

Glossary

K	vaporization equilibrium ratio
p	pressure, atm
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

CD	carbon dioxide
Cr	*m*-cresol
Q	quinoline

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(1) Sebastian, H. M.; Simnick, J. J.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1978**, *23*, 305.
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Solubility of Benzoic Acid in Aqueous Polyethylene Glycol Solutions

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Solubility of benzoic acid in aqueous solutions of polyethylene glycols (PEG) (mol wt = 4000, 6000, and 20 000) containing 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0% polymers by weight are reported in the temperature range 30–55 °C. The solubility in the polymer solutions at a given temperature is higher than that in water, increases with increasing polymer concentration and decreasing polymer molecular weight, and seems to approach a constant value at higher polymer concentrations.

Introduction

Increasing occurrence of non-Newtonian fluids in many process industries and our other day-to-day activities as well as in biological systems has generated interest in the study of transport characteristics of these complex fluids. Fundamental mass-transfer studies with such fluids are often made by using a sparingly soluble solid solute such as benzoic acid. Analysis of raw experimental data in all such cases needs accurate values of system properties.

This communication reports the solubility of benzoic acid in aqueous solutions of polyethylene glycols (PEG). These results will also be useful to the pharmaceutical industry. The results reported here have been obtained adjunct with the mass-transfer investigations conducted with aqueous polyethylene glycol solutions and benzoic acid.

Experimental Section

Conductivity-grade distilled water used for making solutions was prepared in the laboratory. Polyethylene glycols (PEG) used

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