Table VIII. Smoothed Values of B_{12} Extracted from Experimental Phase Equilibrium Data

T, K	B_{12}, cm³/g-mol	T, K	B_{12}, cm³/g-mol
	CF_4-H_2 System		
94.94	−118.0 ± 4.0	135.01	−49.4 ± 4.0
105.01	−88.3 ± 4.0	149.98	−34.9 ± 4.0
119.94	−64.8 ± 4.0	164.99	−26.7 ± 4.0
	$CClF_3$-H_2 System		
134.97	−69.9 ± 3.0	189.97	−32.5 ± 3.0
145.02	−60.2 ± 3.0	205.03	−22.7 ± 3.0
160.02	−50.7 ± 3.0	219.99	−16.8 ± 3.0
175.02	−42.2 ± 3.0		

of a gas–liquid equilibrium, then eq 9 may be rearranged and solved for B_{12} to give

$$B_{12} = \frac{V_m}{2y_2}\left[2\frac{B_{11}}{V_{01}} + \frac{3}{2}\frac{C_{111}}{V_{01}^2} - \ln\frac{P_{01}V_{01}}{RT} - \frac{3}{2V_m^2}(y_1C_{111} + 2y_1y_2C_{112} + y_2^2C_{122}) + \frac{1}{RT}\int_{P_{01}}^{P} V_1^c\,dP - \frac{2y_1B_{11}}{V_m} + \ln\frac{PV_m}{RT} + \ln x_1 - \ln\phi_1\right] \quad (20)$$

Along a given experimental isotherm eq 20 is solved for B_{12} for each pressure by making use of experimental values for y_i, x_i, and v_i^c from eq 5 and P_{01} for the saturated phase and B_{11} and B_{22}, and by assuming a model from which the third interaction coefficients C_{112} and C_{122} as well as C_{111} and C_{222} may be estimated. The volume V_m is also calculated by using these third virial coefficients together with an estimated value of B_{12}. The values of B_{12} so found from eq 20 are then plotted vs. the quantity $(P - P_{01})$ and the curve extrapolated to $(P - P_{01}) = 0$ to obtain the values of B_{12} shown in Table VIII. The values of B_{12} so obtained are only slightly dependent upon the model used to estimate the third virial coefficients and V_m. The uncertainty listed for each value is based primarily upon the effects on B_{12} of the uncertainty in the experimental values of y_1 and x_1 on the calculation of B_{12} from eq 20.

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Gas–Liquid Equilibrium in Mixtures of Carbon Dioxide + Toluene and Carbon Dioxide + *m*-Xylene

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Gas–liquid equilibrium data are determined for mixtures of CO_2 + toluene at five temperatures from 120 to 270 °C and for mixtures of CO_2 + *m*-xylene at four temperatures from 190 to 310 °C. The pressures were up to 50 atm for both systems.

Introduction

The phase behavior of carbon dioxide mixtures is of technological interest because of the occurrence of carbon dioxide in natural gas, crude oil, and numerous chemical processes. A number of phase equilibrium studies have been made on mixtures of carbon dioxide and hydrocarbons, mostly paraffins. In this work we report the phase behavior of carbon dioxide in mixtures with two aromatic hydrocarbons.

Battino and co-workers reported solubility data of CO_2 in toluene (*2*) and in *m*-xylene (*1*) in the temperature range 10–40 °C. The vapor-phase solubility of toluene in compressed CO_2 was studied by Prausnitz and Benson (*5*) at 50–75 °C in the pressure range of 20–90 atm. Recently Ng and Robinson (*4*) presented the experimental results for CO_2 + toluene mixtures at temperatures from 38 to 204 °C and pressures up to 150 atm. We report in this study vapor–liquid equilibrium data for mixtures of carbon dioxide + toluene up to 270 °C and for carbon dioxide + *m*-xylene to 310 °C. The pressure range studied is 10–50 atm.

Experimental Section

The experimental apparatus and procedure used in this work are essentially the same as those described by Simnick and co-workers (*6*). Carbon dioxide was supplied by Matheson with a minimum purity of 99.99%. *m*-Xylene was purchased from Aldrich Chemical Co. with a claimed purity of 99+%. Toluene obtained from Mallinckrodt Co. is analytical reagent grade. The

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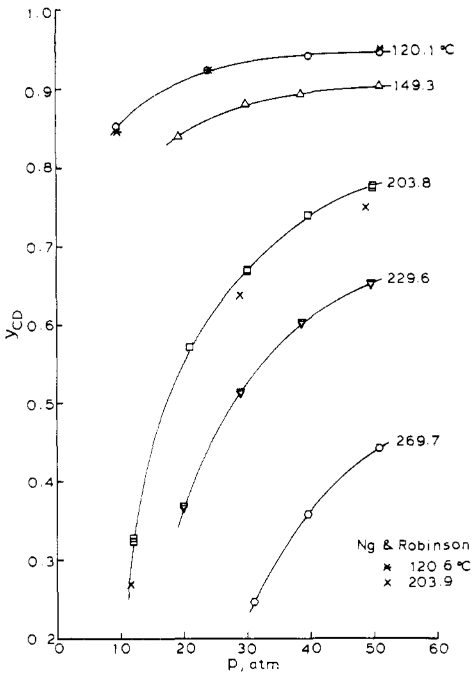

Figure 1. Mole fraction of CO_2 in the saturated vapor of carbon dioxide + toluene mixtures.

purities of these chemicals were checked with a gas chromatograph and were found to be above 99.9% for both. Samples of the solvents were collected from cell effluents of both gas and liquid streams of all experiments and analyzed by gas chromatography to check for thermal stability. No decomposition products were detected at any of the conditions studied.

Pressures below 34 atm were measured by a precision Bourdon tube pressure gauge (Heise Model CMM) with an uncertainty of ±0.03 atm. Another Heise gauge with a full range of 340 atm was used for the higher pressures with an uncertainty of ±0.1% or 0.3 atm, whichever is the greater. The temperature of the equilibrium cell was measured by a calibrated type K chromel-alumel thermocouple inserted in the thermowell in the wall of the cell. This thermocouple was calibrated with a NBS-certified platinum resistance thermometer. The accuracy of the reported temperature is believed to be ±0.1 °C. Saturated fluid phase compositions were determined by sampling the effluents from the equilibrium cell; the quantity of the gas in the sample was measured volumetrically and the liquid gravimetrically. The volumetric measurement is accurate to within 1%, while the accuracy of the gravimetric measurement is better than 0.01%.

Fluctuations in the temperature of the equilibrium cell during the course of measurement of all the points on an isotherm were within 0.1 °C.

To verify the attainment of equilibrium in the flow apparatus of this study, we took samples at 30.58 atm and 270 °C for carbon dioxide + *m*-xylene mixtures at two different liquid feed flow rates, 22 and 31 cm^3/min. Figures 3 and 4 show that there are no appreciable effects of flow rate on the equilibrium compositions. A similar test was made at 19.63 atm and 149.4 °C for the carbon dioxide + toluene system. The slightly different sample compositions that were obtained cannot be differentiated in Figures 1 and 2.

Results and Discussion

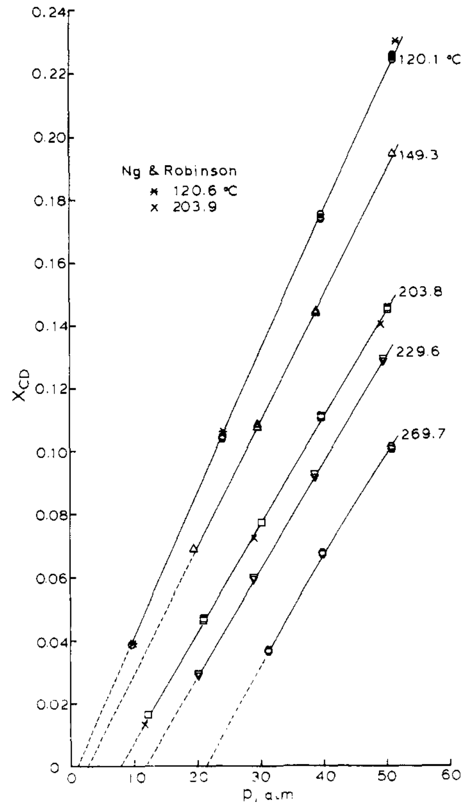

Figure 2. Solubility of CO_2 in liquid toluene.

Table I. Carbon Dioxide + Toluene Gas-Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_T
		120.1 °C		
9.63	0.0385	0.8558	22.22	0.1500
23.86	0.1032	0.9258	8.97	0.0827
39.64	0.1742	0.9392	5.39	0.0736
51.3	0.2261	0.9485	4.20	0.0665
		149.3 °C		
19.53	0.0694	0.8419	12.13	0.1699
19.63	0.0693	0.8398	12.12	0.1721
30.03	0.1099	0.8824	8.03	0.1321
38.75	0.1445	0.8949	6.19	0.1229
51.2	0.1954	0.9047	4.63	0.1184
		203.8 °C		
12.21	0.0166	0.3349	20.17	0.6763
21.03	0.0474	0.5726	12.08	0.4487
30.25	0.0776	0.6718	8.66	0.3558
39.98	0.1122	0.7406	6.60	0.2922
50.3	0.1461	0.7766	5.32	0.2616
		229.6 °C		
20.35	0.0299	0.3637	12.16	0.6528
29.40	0.0598	0.5153	8.62	0.5155
38.82	0.0919	0.5985	6.51	0.4421
49.7	0.1291	0.6557	5.08	0.3953
		269.7 °C		
31.25	0.0364	0.2474	6.80	0.7810
39.96	0.0679	0.3589	5.29	0.6878
50.9	0.1000	0.4436	4.44	0.6182

The experimental results are summarized in Table I for the carbon dioxide + toluene system. Each data point in the table is the average of at least two measurements, and the deviations from the average are in general within 0.5% of the mole fraction value of CO_2. The saturated vapor and liquid phase compositions are shown respectively in Figures 1 and 2. Individual data points are plotted in the figures as separate points when they can be distinguished. The dotted line shown in Figure 2 on the low-pressure side of each isotherm represents an extrapolation of the experimental solubility data to join the vapor pressure of toluene at $x_{CD} = 0$. The vapor pressure data are taken from Simnick et al. (*7*). Also shown in the figures are the experimental results reported by Ng and Robinson (*4*) at 120.6 and 203.9 °C,

Table II. Carbon Dioxide + *m*-Xylene Gas-Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_M
		189.0 °C		
21.14	0.0651	0.8120	12.47	0.2011
30.12	0.0984	0.8548	8.69	0.1611
39.78	0.1315	0.8770	6.67	0.1416
51.9	0.1735	0.8909	5.14	0.1320
		228.9 °C		
21.27	0.0501	0.6214	12.40	0.3986
30.05	0.0813	0.7102	8.74	0.3155
40.46	0.1143	0.7599	6.65	0.2711
51.4	0.1513	0.7899	5.22	0.2474
		270.2 °C		
20.48	0.0252	0.2928	11.62	0.7255
29.70	0.0582	0.4532	7.79	0.5806
30.58	0.0604	0.4647	7.69	0.5697
40.28	0.0931	0.5473	5.88	0.4992
50.9	0.1314	0.5985	4.56	0.4622
		309.4 °C		
31.09	0.0336	0.1777	5.29	0.8509
39.04	0.0639	0.2760	4.32	0.7734
50.8	0.1091	0.3611	3.31	0.7171

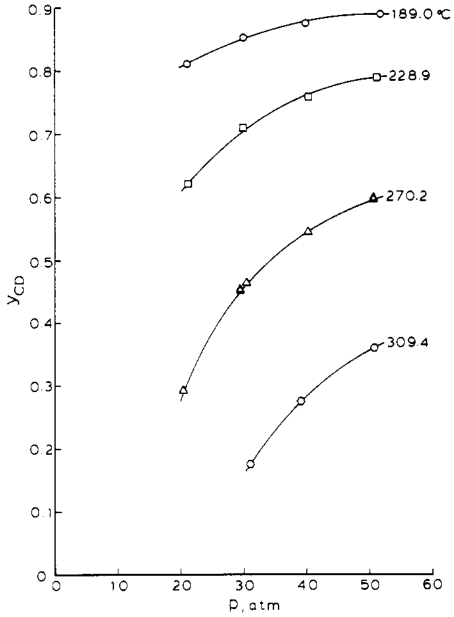

Figure 3. Mole fraction of CO_2 in the saturated vapor of carbon dioxide + *m*-xylene mixtures.

which were obtained by a static method. At 120.6 °C both sets of data agree closely. At 203.9 °C the liquid compositions also agree, but the vapor compositions differ appreciably. The difference increases with pressure, and amounts to about 3% in the mole fraction of CO_2 at 50 atm which is the highest pressure observed in this work.

Equilibrium saturated vapor and liquid compositions of the carbon dioxide + *m*-xylene system are reported in Table II and similarly shown in Figures 3 and 4. The vapor pressures of *m*-xylene were taken from Krase and Goodman (*3*). Phase equilibrium data are not available in the literature for this system at the temperatures of the present work. Thus no comparison can be made.

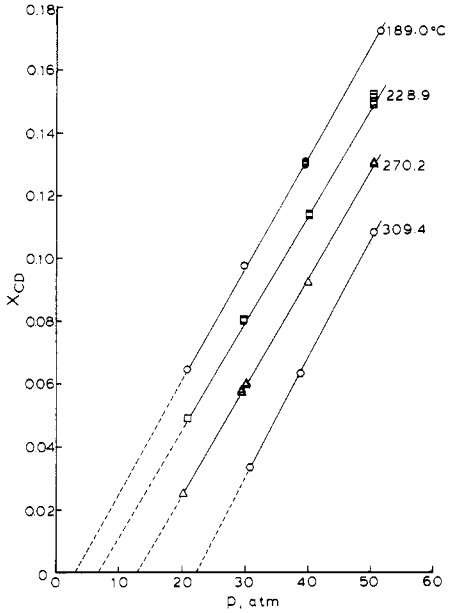

Figure 4. Solubility of CO_2 in liquid *m*-xylene.

Glossary

K	vaporization equilibrium ratio—y/x
p	pressure, atm
t	temperature, °C
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Subscript

CD	carbon dioxide
T	toluene
M	*m*-xylene

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