Isothermal Vapor-Liquid Equilibrium Data for Binary Systems Containing Carbon Dioxide at High Pressures: Methanol–Carbon Dioxide, n-Hexane–Carbon Dioxide, and Benzene–Carbon Dioxide Systems

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Isothermal vapor-liquid equilibrium data for the systems methanol–carbon dioxide, n-hexane–carbon dioxide, and benzene–carbon dioxide were measured by a static method at 25° and 40°C. By use of the Lewis rule and the Redlich-Kwong equation of state for carbon dioxide in the vapor phase, the activity coefficients in the liquid phase and the fugacity coefficients in the vapor phase were evaluated from thermodynamic relationships.

The isothermal vapor-liquid equilibria at high pressures for binary systems containing carbon dioxide were reported in previous papers, in which methanol–carbon dioxide and acetone–carbon dioxide systems were measured by a vapor recirculation method (3), and ethyl ether–carbon dioxide and methyl acetate–carbon dioxide systems by a static method (4).

In this study the vapor-liquid equilibria for three binary systems of methanol–carbon dioxide, n-hexane–carbon dioxide, and benzene–carbon dioxide were measured at 25° and 40°C by the static method.

The activity coefficients in the liquid phase and fugacity coefficients in the vapor phase were determined by using the Lewis rule and the Redlich-Kwong equation of state for carbon dioxide in the vapor phase.

The liquid activity coefficients in the methanol–carbon dioxide system are the largest of the three systems, though those in n-hexane–carbon dioxide and benzene–carbon dioxide are also considerably large.

Experimental

The experimental apparatus and the operation procedure used in this work are the same as the case reported previously (4).

The equilibrium cell of about 300 cc had two windows for keeping the interface of liquid phase near the center of the cell. Equilibrium pressure was measured within an accuracy of 0.01 atm by use of a dead weight gauge manufactured by American Instrument Co. and a pressure transducer from Yokogawa Electric Works Ltd.

The sample of the gas phase was introduced into a container of variable volume and expanded to about 0.1 atm before the composition analysis. The sample of liquid phase was vaporized in an evaporator and introduced into a liquid-phase container controlled to about 0.1 atm. The ball valves at the sampling parts were used for avoiding the flashing phenomenon. The variable volume container for the vapor sample was the same as the evaporator for the liquid sample, and the possible working volume ranged from 10 to 1000 cc.

The composition analysis was made by gas chromatography, and compositions of the samples were determined by direct comparison of the peak area ratio of an unknown sample with the peak area of a known sample prepared at a total pressure of about 0.1 atm of similar concentration. The main parts of stainless tubes were covered with ribbon heaters to avoid vapor condensation.

The carbon dioxide used in this experiment was supplied by the Seitetu Kagaku Co., Ltd., and had a specified minimum purity of 99.99%. The solvents, methanol, n-hexane, and benzene, obtained from Wako Pure Chem. Ind., Merck Co., and J. T. Baker Chem. Co., respectively, were spectro grade. A small amount of impurities was detected for each material by gas chromatography (PEG 6000); the ratios of peak areas were 1:12000 for methanol, 1:50000 for n-hexane, and 1:15000 for benzene.

Discussion

Vapor-liquid equilibrium data (P-x-y) for the three binary systems are listed in Tables I–III. The method of data analysis was essentially the same as in the previous paper (4). The fugacity coefficients of carbon dioxide were calculated by the Redlich-Kwong equation of state (5) and the Lewis rule. The activity coefficients of carbon dioxide were determined with the following equation:

$$\gamma_2 = \frac{\varphi_2 y_2 P}{f_{2,pure}^{L(P0)} x_2 \exp \int_{P0}^{P} (\bar{v}_2 / RT) dP} \tag{1}$$

The partial molar volume of carbon dioxide, $\bar{v}_2$, in Equation 1 was assumed to be approximately equal to the partial molar volume at infinite dilution, $\bar{v}_2^{\infty}$ (2).

Table I. Vapor-Liquid Equilibria of Methanol(1)– Carbon Dioxide(2) System at 25° and 40°C

P, atm	x_2	y_2	$\log \gamma_1$	$\log \gamma_2$	φ_1	φ_2
			25°C			
7.792	0.0596	0.9761	0.0015	0.4808	0.8321	0.9660
18.814	0.1548	0.9907	0.0085	0.4249	0.7161	0.9183
30.246	0.2601	0.9920	0.0219	0.3735	0.5482	0.8694
39.503	0.3495	0.9929	0.0399	0.3340	0.4402	0.8298
48.664	0.4886	0.9930	0.0918	0.2509	0.3260	0.7905
55.013	0.6451	0.9931	0.2195	0.1631	0.2753	0.7629
57.509	0.7685	0.9930	0.4122	0.0980	0.2650	0.7519
58.749	0.9002	0.9930	0.7590	0.0344	0.2491	0.7464
			40°C			
5.697	0.0285	0.9363	0.0003	0.6121	0.9137	0.9783
17.469	0.1023	0.9774	0.0038	0.5340	0.7939	0.9340
29.654	0.1641	0.9847	0.0101	0.5269	0.6517	0.8886
40.337	0.2339	0.9868	0.0261	0.4757	0.5430	0.8492
56.313	0.3655	0.9882	0.0607	0.3747	0.4046	0.7903
61.903	0.4201	0.9880	0.0862	0.3359	0.3540	0.7696
70.006	0.5429	0.9866	0.1727	0.2429	0.2732	0.7391
76.021	0.6892	0.9840	0.3507	0.1438	0.2179	0.7158
79.530	0.8970	0.9748	0.8234	0.0185	0.1309	0.7018

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By use of the Redlich-Kister equation, the activity coefficients of each solvent component were evaluated with the relation of the Gibbs-Duhem equation.

The fugacity coefficients in the vapor phase of solvent components were calculated by Equation 2:

$$\varphi_1 = \frac{\gamma_1 x_1 f_{1,pure}^{L(P0)} \exp \int_{P0}^{P} (\bar{v}_1/RT)dP}{y_1 P}$$ (2)

The partial molar volume of the solvent component, $\bar{v}_1$, was assumed to be the molar volume of pure liquid, $v_{1,pure}$, and pressure independent.

The activity coefficients of the three systems at 25°C are shown in Figure 1, and the fugacity coefficients are shown in Figure 2.

The activity coefficients of carbon dioxide in the methanol-carbon dioxide system were considerably large. This fact was also recognized in the previous result (3) measured with a vapor recirculation method. The difference in liquid composition between the two methods is less than ±0.2 mol % at equivalent conditions. The nonidealities in the liquid phase of this system were explained mainly with the methanol self-association. Methanol molecule has one electron donor atom which causes the self-association, but it seems that the molecule does not act as an electron donor for carbon dioxide. In other words, the hydrogen bonding of methanol is too strong to recognize the effects of forces between unlike intermolecules.

In the systems of n-hexane–carbon dioxide and benzene–carbon dioxide, the nonidealities in the liquid phase are also considerable. There is a specific interaction between ben-
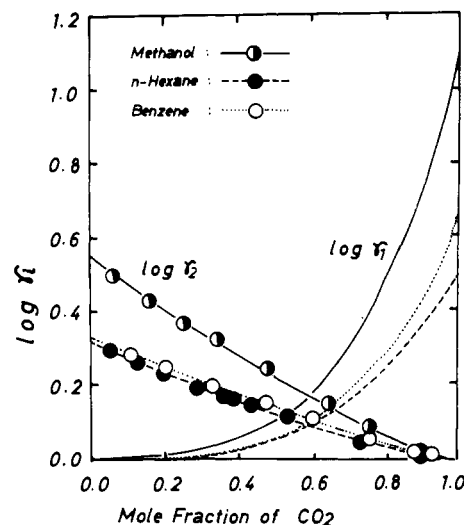
Table II. Vapor-Liquid Equilibria of n-Hexane(1)–Carbon Dioxide(2) System at 25° and 40°C

P, atm	x_2	y_2	$\log \gamma_1$	$\log \gamma_2$	φ_1	φ_2
			25°C			
4.379	0.0495	0.9423	0.0006	0.2993	0.7550	0.9808
9.586	0.1185	0.9685	0.0032	0.2596	0.6061	0.9582
14.524	0.1893	0.9777	0.0086	0.2265	0.5402	0.9368
18.952	0.2683	0.9793	0.0179	0.1798	0.4211	0.9177
24.978	0.3506	0.9830	0.0320	0.1679	0.3741	0.8919
26.414	0.3675	0.9828	0.0355	0.1674	0.3407	0.8857
30.112	0.4251	0.9843	0.0494	0.1508	0.3134	0.8699
36.016	0.5263	0.9852	0.0816	0.1182	0.2546	0.8447
44.001	0.7255	0.9872	0.1860	0.0419	0.1853	0.8105
51.376	0.8856	0.9904	0.3362	0.0003	0.1296	0.7787
			40°C			
6.237	0.0653	0.9253	0.0009	0.2783	0.7370	0.9763
11.609	0.1281	0.9523	0.0035	0.2559	0.5988	0.9559
20.449	0.2439	0.9681	0.0135	0.2045	0.4723	0.9228
29.527	0.3651	0.9740	0.0331	0.1628	0.3696	0.8893
39.148	0.4856	0.9792	0.0647	0.1308	0.3192	0.8535
45.813	0.5671	0.9821	0.0952	0.1052	0.2962	0.8289
53.734	0.7056	0.9841	0.1708	0.0510	0.2398	0.8000
60.630	0.8022	0.9872	0.2494	0.0198	0.2203	0.7742
66.490	0.8587	0.9875	0.3096	0.0054	0.1740	0.7522
75.573	0.9240	0.9875	0.3973	-0.0105	0.1057	0.7174

Table III. Vapor-Liquid Equilibria of Benzene(1)–Carbon Dioxide(2) System at 25° and 40°C

P, atm	x_2	y_2	$\log \gamma_1$	$\log \gamma_2$	φ_1	φ_2
			25°C			
8.821	0.1063	0.9815	0.0030	0.2772	0.7033	0.9615
16.306	0.2038	0.9885	0.0097	0.2469	0.5691	0.9291
25.011	0.3316	0.9906	0.0245	0.1980	0.4070	0.8917
34.887	0.4775	0.9918	0.0566	0.1556	0.2919	0.8495
41.039	0.5901	0.9931	0.1028	0.1158	0.2632	0.8232
47.362	0.7510	0.9934	0.2280	0.0535	0.1977	0.7961
53.514	0.8714	0.9946	0.3932	0.0225	0.1653	0.7694
56.979	0.9130	0.9959	0.4697	0.0184	0.1671	0.7542
			40°C			
14.697	0.1489	0.9754	-0.0004	0.2474	0.5793	0.9444
25.013	0.2501	0.9838	0.0035	0.2319	0.4766	0.9059
37.511	0.3859	0.9845	0.0229	0.1876	0.2974	0.8596
46.348	0.4823	0.9862	0.0518	0.1590	0.2513	0.8271
52.667	0.5803	0.9861	0.0985	0.1164	0.2027	0.8038
60.272	0.7291	0.9863	0.2115	0.0539	0.1546	0.7756
64.388	0.8057	0.9859	0.2933	0.0269	0.1235	0.7603
71.503	0.8903	0.9853	0.4054	0.0070	0.0780	0.7334
76.487	0.9327	0.9847	0.4708	-0.0008	0.0521	0.7140

Figure 1. Activity coefficients for binary systems of methanol(1), n-hexane(1), and benzene(1) with carbon dioxide(2) at 25°C
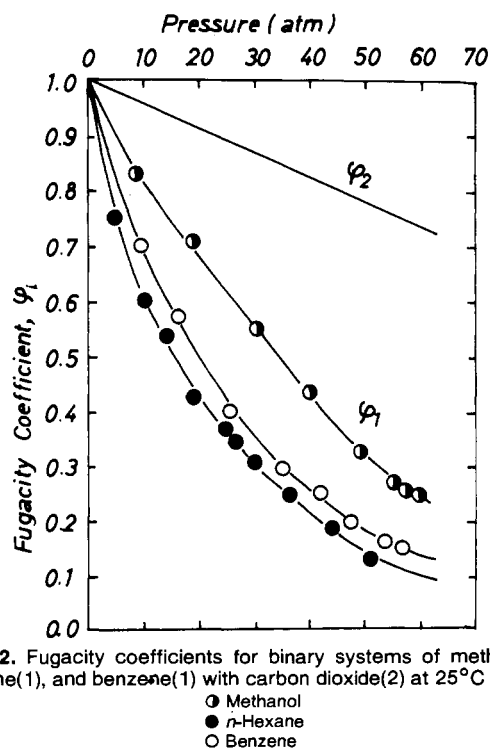

Figure 2. Fugacity coefficients for binary systems of methanol(1), n-hexane(1), and benzene(1) with carbon dioxide(2) at 25°C
○ Methanol
● n-Hexane
○ Benzene

zene and carbon dioxide (1), but the activity coefficient of carbon dioxide in benzene is relatively large.

The vapor-phase behavior of each system departs a great deal from that of an ideal gas as shown in Figure 2. The deviation from the ideal gas law is smallest for the methanol–carbon dioxide system and largest for the n-hexane–carbon dioxide system.

Acknowledgment

Nomenclature

P = total pressure, atm
R = gas constant, atm cc/mol K
T = temperature, K
f = fugacity, atm
v = molar volume, cc/mol
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = activity coefficient
φ = fugacity coefficient

Superscripts

∞ = infinite dilution
$(P0)$ = reference pressure of 0 atm
L = liquid phase
V = vapor phase
$-$ = partial molar quantity

Subscripts

1 = solvent component
2 = carbon dioxide
pure = pure component

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Isothermal Vapor-Liquid Equilibrium Data for Binary Systems Containing Ethane at High Pressures

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Isothermal vapor-liquid equilibrium data for six binary systems of ethane with methanol, acetone, methyl acetate, ethyl ether, n-hexane, and benzene were measured by a static method at 25°C in a pressure range from 4 to 40 atm. By use of the Redlich-Kwong equation of state and the Lewis rule for ethane in the vapor phase, the activity coefficients in the liquid phase and the fugacity coefficients in the vapor phase were evaluated. The nonidealities of vapor and liquid phases obtained were compared with the corresponding systems containing carbon dioxide rather than ethane.

Isothermal vapor-liquid equilibrium data for binary systems containing carbon dioxide at high pressures were reported previously (3, 6, 7). In the studies methanol, acetone, methyl acetate, ethyl ether, n-hexane, and benzene were chosen as the solvent components.

In this study the same solvent components were used, and carbon dioxide was replaced with ethane having a similar critical temperature to that of carbon dioxide.

The nonidealities of vapor and liquid phases of the ethane systems were determined with the thermodynamic procedures and were compared between these six systems.

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Experimental

The experimental apparatus and operation procedure used in this study are essentially the same as the case reported previously (6).

The equilibrium pressure was measured within an accuracy of 0.01 atm by use of a dead weight gage and a pressure transducer.

The samples of vapor and liquid phases were expanded to about 0.1 atm before composition analysis. Composition analysis was made by use of gas chromatography, and compositions of the samples were determined by direct comparison of the peak area ratio of an unknown sample with the peak area ratio of a known sample prepared at a similar concentration. Reproducibility in the composition analysis was within 1% for the component with less concentration.

The main parts of stainless tubes were covered with ribbon heaters to avoid vapor condensation. The main parts of the apparatus were set in a water bath controlled within ±0.01°C of a set point. The water bath and accessory parts were put in an air bath kept 0.1°C higher than the temperature of the water bath.

Materials

The ethane used for the methanol, acetone, and methyl acetate systems was supplied by Phillips Petroleum Co. and had a specified minimum purity of 99.96 mol % of research grade. The ethane in the n-hexane, ethyl ether, and benzene