pacity of the solvent increases. This is also evident from the data reported in Table III.

Figure 4 shows the tie line correlation curve on the Othmer-Tobias (*6*) coordinates for the system at 25° and 50°C. Since the data do not exhibit much scatter from straight line, they are judged acceptable on the empirical basis, indicating internal consistency of the experimental data.

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Nomenclature

x = liquid-phase composition (wt fraction)

Subscripts

1 = *n*-heptane
2 = sulfolane
3 = toluene
11, 31 = composition (wt fraction) of components 1 and 3, respectively, in phase 1 (*n*-heptane-rich phase)
22, 32 = composition (wt fraction) of components 2 and 3, respectively, in phase 2 (sulfolane-rich phase)

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Isothermal Vapor-Liquid Equilibria for Systems Ethyl Ether–Carbon Dioxide and Methyl Acetate–Carbon Dioxide at High Pressures

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The isothermal vapor-liquid equilibrium data for the systems ethyl ether–carbon dioxide and methyl acetate–carbon dioxide were measured by a static method over a pressure range from 5 to 80 atm at 25° and 40°C. By use of the Lewis rule and the Redlich-Kwong equation of state for only carbon dioxide in the vapor phase, the activity coefficients of both components in the liquid phase and the fugacity coefficient of the solvent component in the vapor phase were evaluated with the thermodynamic relationships.

Carbon dioxide is one of the most important industrial gases, and the data on phase equilibria of systems containing carbon dioxide have been reported abundantly. However, vapor-liquid equilibrium data of carbon dioxide with one of the heavy components having normal boiling points at about 50°C are scarce.

In this study, the vapor-liquid equilibria for the systems ethyl ether–carbon dioxide and methyl acetate–carbon dioxide were measured at 25° and 40°C by a static method with a new apparatus.

The thermodynamic procedures were applied for determining the nonidealities of vapor and liquid phases of these systems. Thereafter, the nonidealities were compared and discussed between these two systems.

Apparatus and Operations

The schematic diagram of the experimental apparatus is shown in Figure 1. The solvent was fed from a solvent vessel H, and carbon dioxide from a gas cylinder I flowed through valves 1, 2, and 3 into an equilibrium cell A. The contents of the equilibrium cell were agitated by a magnetic stirrer operated by a separated solenoid M. At the center of the equilibrium cell, two windows, pyrex glass disk 3.5 cm in diameter and 2.5 cm thick each, were set, and the vapor-liquid interface was controlled to be at the center of the windows with a needle valve 8. The equilibrium cell was a stainless-steel cylinder, approximately 300 cm^3 in volume, and the operating maximum pressure was about 150 atm.

The liquid-phase sampler K was a small steel tube approximately 0.15 cm^3 in volume with a ball valve 4, and a needle valve 5 was approximately 2 cm^3. The ball valves 4, 6, and 7 were used with the sampling valves for avoiding the flushing phenomenon. The sample of gas phase was introduced to a container B of variable volume and expanded to about 0.1 atm. The sample of liquid phase was vaporized in an evaporator C and introduced to a liquid-phase container D, constantly maintained at about 0.1 atm. The variable volume container B was the same as the evaporator C, and the possible working volume ranged from 10 to 1000 cm^3.

The compositions of each phase sample were determined by direct comparison of the peak area ratio of the

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unknown sample to one of a known sample prepared separately at a total pressure of about 0.1 atm of similar concentration in other equipment. The samples were analyzed with a Shimadzu GC 4B-PT gas chromatograph using PEG 1500 columns. The peak areas were counted by a Shimadzu ITG-2A electronic integrator.

The equilibrium pressure was measured with the combination of a dead weight gage G manufactured by American Instrument Co. and a differential pressure transducer E from Yokogawa Electric Works Ltd. The accuracy of the equilibrium pressure was within ±0.01 atm.

The air bath was controlled within ±0.1°C of a set point, and the equilibrium cell was placed in a low viscosity oil bath J controlled within ±0.02°C. A set of platinum resistance and a potentiometer was used for the temperature measurement of the oil bath. The main part of the stainless tube was covered with ribbon heaters to avoid vapor condensation.

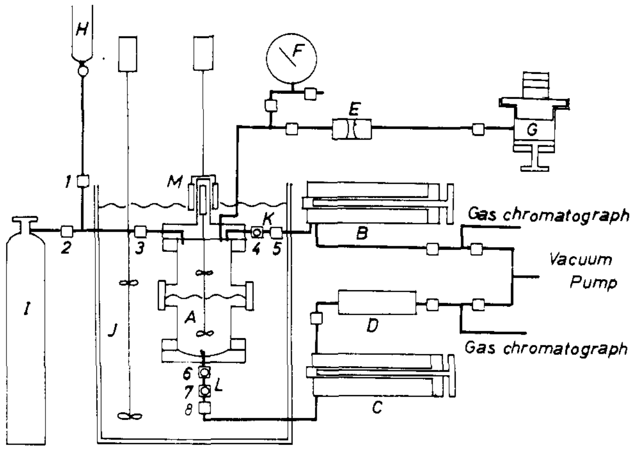

Figure 1. Schematic diagram of experimental apparatus

A: Equilibrium cell	H: Solvent vessel
B: Container for vapor sampling	I: Gas cylinder
C: Evaporator	J: Oil bath
D: Container for liquid sampling	K: Vapor sampling part
E: Pressure transducer	L: Liquid sampling part
F: Bourdon tube gage	M: Separated solenoid
G: Dead weight gage	

Materials

The carbon dioxide used in this experiment was obtained from Seitetsu Kagaku Co., Ltd., having a specified minimum purity of 99.99%. The solvents were supplied by Merck Co. and were spectro grade with a specified minimum purity of 99% and had lot analyses well above minimum specification.

Results and Analysis

The isothermal vapor-liquid equilibrium data (P-x-y) are listed in Tables I and II and are shown in Figures 2 and 3.

Details of the data analysis were presented elsewhere (*3*), and the method of data analysis was summarized as a flow diagram in Figure 4.

Since the mole fraction of carbon dioxide in the vapor phase is almost unity in this experimental condition, the Lewis rule can be applicable to carbon dioxide in the vapor phase. Therefore, the fugacity in the vapor phase for carbon dioxide is written by:

$$f_2^V = \varphi_{2,\text{pure}} y_2 P \tag{1}$$

The fugacity coefficient of carbon dioxide, $\varphi_{2,\text{pure}}$, is calculated from the modified Redlich-Kwong equation of state (*4*).

The fugacity of carbon dioxide in the liquid phase is written:

$$f_2^L = \gamma_2 x_2 f_2^{L(P0)} \exp \int \bar{v}_2/RTdP \tag{2}$$

At 25°C, the fugacity of pure liquid carbon dioxide at a reference pressure of 0 atm, $f_2^{L(P0)}$, was calculated from Canjar and Manning's data (*1*).

At 40°C, however, either the hypothetical liquid state or unsymmetrical convention method must be used for carbon dioxide because 40°C is above the critical temperature of carbon dioxide. In this study, the former method has been adopted. The hypothetical value of $f_2^{L(P0)}$ was evaluated from the results of the acetone–carbon dioxide system (*3*) as the product of Henry's constant and the activity coefficient extrapolated at pure carbon dioxide in unsymmetric convention.

The partial molar volume of carbon dioxide, $\bar{v}_2$, was assumed to be equal to the partial molar volume at infinitely

Table I. Vapor-Liquid Equilibria for System Ethyl Ether(1)-Carbon Dioxide(2) at 25° and 40°C

	Compn		Activity coeff		Fugacity coeff	
Press, atm, P	x_2	y_2	log γ_1	log γ_2	φ_1	φ_2
			25°C			
6.925	0.1190	0.8878	0.0021	0.1209	0.7963	0.9757
12.411	0.2201	0.9354	0.0060	0.1001	0.7051	0.9459
17.243	0.3068	0.9564	0.0106	0.0883	0.6885	0.9251
20.398	0.3602	0.9613	0.0143	0.0831	0.6188	0.9115
29.652	0.5086	0.9709	0.0301	0.0697	0.4688	0.8719
38.975	0.6478	0.9776	0.0594	0.0556	0.3686	0.8320
44.690	0.7338	0.9783	0.0896	0.0426	0.2758	0.8076
52.801	0.8449	0.9860	0.1491	0.0260	0.2491	0.7725
56.320	0.9002	0.9899	0.1899	0.0177	0.2328	0.7571
			40°C			
12.731	0.1802	0.8837	0.0014	0.0990	0.7350	0.9518
17.684	0.2508	0.9177	0.0040	0.0895	0.6327	0.9332
33.269	0.4637	0.9404	0.0244	0.0603	0.4653	0.8753
38.237	0.5419	0.9505	0.0378	0.0402	0.3854	0.8570
48.240	0.6653	0.9556	0.0658	0.0250	0.2766	0.8201
51.234	0.7043	0.9601	0.0764	0.0180	0.2658	0.8091
57.501	0.7748	0.9667	0.0975	0.0088	0.2318	0.7859
64.619	0.8398	0.9645	0.1190	0.0038	0.1489	0.7594
71.283	0.9003	0.9662	0.1406	−0.0045	0.0952	0.7342

dilute solution, $\bar{v}_2^{\infty}$ (2) and was assumed to be independent of pressure and composition. From Equations 1 and 2, the activity coefficient of carbon dioxide is evaluated with the following equilibrium equation:

$$\gamma_2 = \frac{\varphi_2 y_2 P}{x_2 f_2^{L(P0)} \exp (P\bar{v}_2^{\infty}/RT)} \tag{3}$$

Constants in the Redlich-Kister equation are evaluated by fitting the equation to the activity coefficient of carbon dioxide. The evaluated constants give the value of γ_1 from the Gibbs-Duhem equation. Then the fugacity coefficient of solvent in the vapor phase, φ_1, is calculated by Equation 4,

$$\varphi_1 = \frac{\gamma_1 x_1 f_1^{L(P0)} \exp \int \bar{v}_1/RTdP}{y_1 P} \tag{4}$$

where $\bar{v}_1$ was assumed to be approximately equal to the molar volume of pure solvent and to be independent of pressure and composition.

Table II. Vapor-Liquid Equilibria for System Methyl Acetate(1)-Carbon Dioxide(2) at 25° and 40°C

	Compn		Activity coeff		Fugacity coeff	
Press, atm, P	x_1	y_2	log γ_1	log γ_2	φ_1	φ_2
			25°C			
6.380	0.1418	0.9574	0.0019	0.0143	0.8910	0.9721
11.003	0.2501	0.9725	0.0064	−0.0041	0.7158	0.9520
14.962	0.3442	0.9805	0.0118	−0.0169	0.6675	0.9349
19.515	0.4512	0.9857	0.0176	−0.0258	0.6007	0.9153
24.103	0.5439	0.9876	0.0195	−0.0279	0.4753	0.8956
33.248	0.6816	0.9892	0.0099	−0.0224	0.2784	0.8565
37.678	0.7546	0.9912	−0.0053	−0.0165	0.2277	0.8376
44.483	0.8373	0.9926	−0.0351	−0.0090	0.1452	0.8085
49.524	0.8791	0.9935	−0.0565	−0.0055	0.1068	0.7868
53.657	0.9222	0.9942	−0.0837	−0.0025	0.0677	0.7688
56.856	0.9496	0.9961	−0.1041	−0.0011	0.0593	0.7548
			40°C			
7.254	0.1336	0.9353	0.0032	0.0071	0.9709	0.9724
9.165	0.1706	0.9497	0.0048	0.0016	0.9555	0.9652
12.695	0.2401	0.9563	0.0079	−0.0119	0.7410	0.9519
22.035	0.4074	0.9696	0.0126	−0.0216	0.4985	0.9170
24.813	0.4553	0.9728	0.0124	−0.0246	0.4587	0.9066
31.203	0.5489	0.9788	0.0092	−0.0241	0.3927	0.8829
41.153	0.6624	0.9809	−0.0007	−0.0104	0.2496	0.8462
51.088	0.7621	0.9828	−0.0157	−0.0056	0.1569	0.8097
59.897	0.8397	0.9831	−0.0316	−0.0051	0.0910	0.7771
74.961	0.9308	0.9855	−0.0552	0.0004	0.0364	0.7200
78.704	0.9496	0.9852	−0.0607	0.0000	0.0247	0.7052

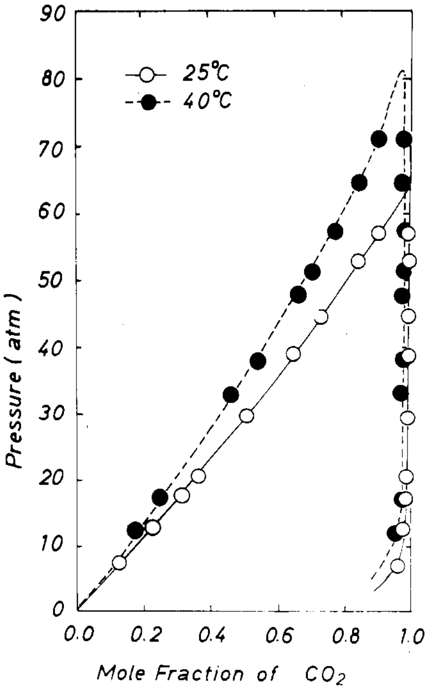

Figure 2. Vapor-liquid equilibrium data of ethyl ether(1)-carbon dioxide(2) system at 25° and 40°C

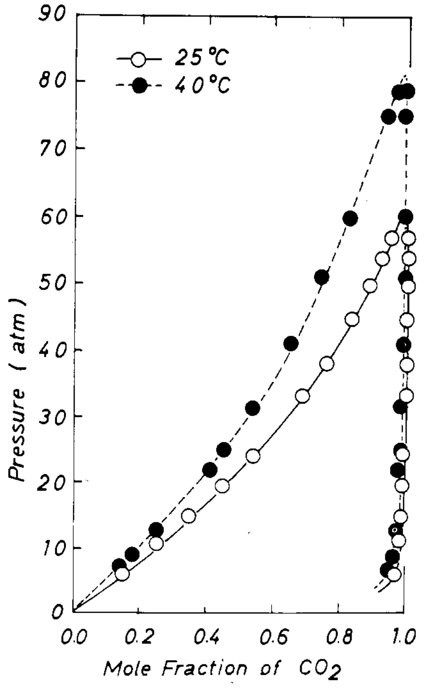

Figure 3. Vapor-liquid equilibrium data of methyl acetate(1)-carbon dioxide(2) system at 25° and 40°C

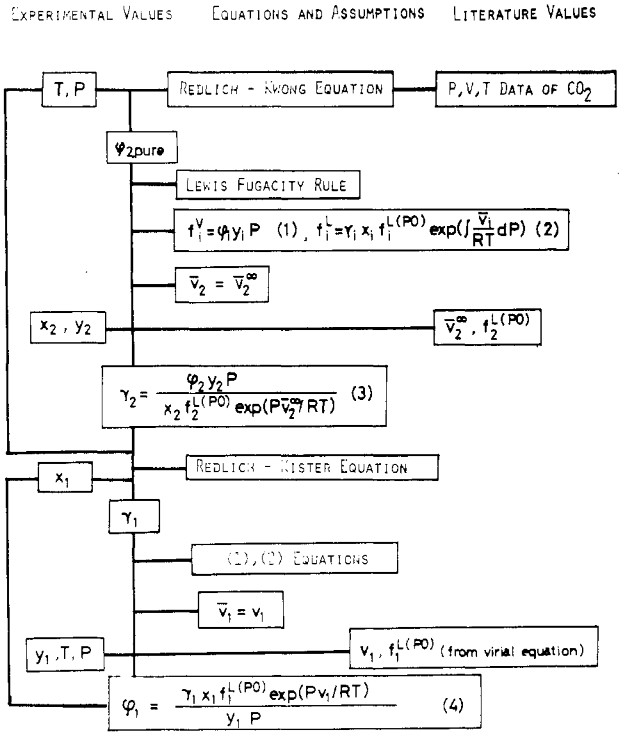

Figure 4. Flow diagram of data analysis

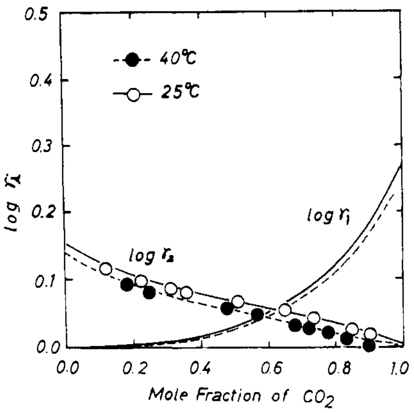

Figure 5. Activity coefficients of ethyl ether(1)-carbon dioxide(2) system at 25° and 40°C

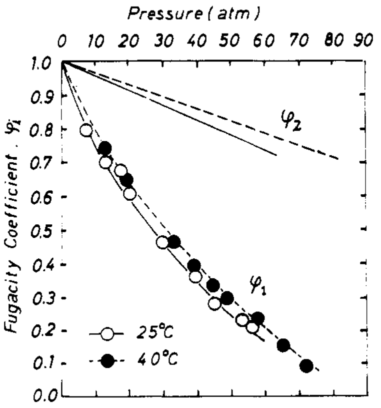

Figure 6. Fugacity coefficients of ethyl ether(1)-carbon dioxide(2) system at 25° and 40°C

Discussion

The activity coefficients in the liquid phase of the ethyl ether-carbon dioxide system are shown in Figure 5, and the fugacity coefficients in the vapor phase are in Figure 6.

Both ethyl ether and methyl acetate are slightly polar substances, but a methyl acetate molecule has two electron donor atoms, and an ethyl ether has one. Therefore, if carbon dioxide acts as the electron acceptor, it may be expected that carbon dioxide is more soluble in methyl acetate than in ethyl ether and that the activity coefficient of carbon dioxide in the system methyl acetate-carbon dioxide is smaller than that in the system ethyl ether-carbon dioxide. From the results of data analysis, the above assumption seems to be reasonable in these systems. The activity coefficients of carbon dioxide in the system methyl acetate-carbon dioxide are smaller than unity in the range between 0.2 and 1.0 mole fractions of carbon dioxide. This fact may be explained with the strong interaction between methyl acetate and carbon dioxide.

The nonidealities in the vapor phase, represented with the fugacity coefficients, are considerably large in both systems and are nearly equal from low to moderate pressures. However, the fugacity coefficients in the ethyl ether-carbon dioxide system become larger than those of the methyl acetate system at high pressures.

Acknowledgment

The authors acknowledge the valuable assistance of Yoshitaka Kugawa and Fumihiko Sano in performing the experimental measurements.

Nomenclature

H = Henry's constant, atm
P = total pressure, atm
R = gas constant, atm cm^3/mol K
T = temperature, K
f = fugacity, atm
v = molar volume, cm^3/mol
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = activity coefficient
φ = fugacity coefficient

Superscripts

∞ = infinitely dilute solution
(PO) = 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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