

zene and carbon dioxide (7), 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.

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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
(P_0) = 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 $\pm 0.01^\circ\text{C}$ 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

systems was obtained from Takachiho Kagakukogyo Co. Ltd., and was more than 99.7 mol % pure. Spectro grade chemicals were used for all liquid solvents. Methanol and acetone were obtained from Wako Pure Chem. Ind., methyl acetate, ethyl ether, and *n*-hexane from Merck Co., and benzene was obtained from J. T. Baker Chem. Co. 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, 1:10000 for acetone and methyl acetate, 1:5000 for *n*-hexane, and 1:15000 for ethyl ether and benzene.

Experimental Results

Isothermal vapor-liquid equilibrium data (*P*-*x*-*y*) for six binary systems are listed in Table I, and the relations for the ace-

tone-ethane and *n*-hexane-ethane systems at 25°C are shown in Figure 1.

Data Analysis

The method of data analysis was essentially the same as in the previous paper (6).

Fugacity coefficients of ethane. The fugacity coefficients of pure ethane were calculated by the Redlich-Kwong equation of state (8) similar to the method used in previous papers (3, 6). Since the mole fraction of ethane in the vapor phase is almost unity in this experiment, the Lewis rule can be applicable to ethane in the vapor phase. Therefore, the fugacity coefficients of ethane are written by:

$$\varphi_2 = \varphi_{2,pure} \quad (1)$$

Table I. Isothermal Vapor-Liquid Equilibrium Data at 25°C

<i>P</i> , atm	<i>x</i> ₂	<i>y</i> ₂	log ₁₀ γ_1	log ₁₀ γ_2	φ_1	φ_2
Methanol(1)-ethane(2)						
10.795	0.0403	0.9822	0.0021	0.9745	0.828	0.9181
20.746	0.0880	0.9887	0.0096	0.8733	0.667	0.8442
31.021	0.1755	0.9914	0.0347	0.6962	0.572	0.7681
38.059	0.2728	0.9921	0.0774	0.5538	0.499	0.7145
40.705	0.3511 ^a	0.9922	0.1223	0.4587	0.470	0.6933
Acetone(1)-ethane(2)						
4.741	0.0427	0.9371	0.0006	0.5973	0.851	0.9638
9.709	0.0916	0.9648	0.0030	0.5679	0.719	0.9263
17.465	0.1721	0.9769	0.0114	0.5166	0.579	0.8684
26.044	0.2826	0.9809	0.0349	0.4334	0.441	0.8050
33.179	0.4485	0.9819	0.1093	0.3001	0.341	0.7519
35.156	0.5770	0.9817	0.2150	0.2057	0.313	0.7369
35.768	0.6919	0.9821	0.3605	0.1310	0.321	0.7323
38.850	0.9268	0.9841	0.8731	0.0216	0.260	0.7083
Methyl acetate(1)-ethane(2)						
4.742	0.0487	0.9320	0.0008	0.5429	0.826	0.9638
9.804	0.1072	0.9648	0.0039	0.5046	0.742	0.9256
16.656	0.1895	0.9762	0.0125	0.4594	0.612	0.8744
24.952	0.3047	0.9816	0.0357	0.3893	0.491	0.8131
31.801	0.4489	0.9832	0.0935	0.2907	0.391	0.7623
32.844	0.4601	0.9834	0.0998	0.2883	0.382	0.7544
33.662	0.5214	0.9837	0.1407	0.2403	0.371	0.7483
34.017	0.5784	0.9838	0.1895	0.1978	0.364	0.7456
36.033	0.7921	0.9840	0.5023	0.0749	0.355	0.7302
37.992	0.9085	0.9846	0.7942	0.0271	0.304	0.7151
Ethyl ether(1)-ethane(2)						
9.434	0.2529	0.9244	0.0056	0.0982	0.749	0.9283
14.880	0.4010	0.9545	0.0131	0.0837	0.658	0.8876
17.501	0.4732	0.9630	0.0199	0.0732	0.621	0.8682
29.916	0.7840	0.9782	0.1182	0.0281	0.334	0.7763
34.760	0.8879	0.9788	0.1998	0.0141	0.189	0.7400
38.063	0.9588	0.9798	0.2782	0.0012	0.081	0.7145
Benzene(1)-ethane(2)						
7.658	0.1201	0.9801	0.0047	0.3652	0.741	0.9417
13.314	0.2202	0.9876	0.0158	0.3187	0.635	0.8993
20.116	0.3747	0.9910	0.0491	0.2353	0.514	0.8488
24.913	0.5355	0.9920	0.1165	0.1494	0.412	0.8134
28.418	0.6494	0.9927	0.1962	0.1049	0.364	0.7874
33.961	0.8602	0.9933	0.4559	0.0304	0.245	0.7460
37.510	0.9299	0.9937	0.5863	0.0195	0.162	0.7188
<i>n</i> -Hexane(1)-ethane(2)						
5.012	0.1497	0.9544	0.0025	0.0859	0.753	0.9617
8.897	0.2698	0.9722	0.0071	0.0691	0.616	0.9324
10.965	0.3306	0.9776	0.0101	0.0642	0.580	0.9168
14.993	0.4502	0.9825	0.0184	0.0487	0.464	0.8868
19.714	0.5833	0.9854	0.0339	0.0331	0.390	0.8518
29.310	0.8097	0.9869	0.0929	0.0140	0.141	0.7808
35.030	0.9135	0.9886	0.1437	0.0082	0.071	0.7379

^a Composition of methanol-rich phase at consolute point.

Activity coefficients of ethane. The activity coefficients of ethane were determined with:

$$\gamma_2 = \frac{\varphi_2 \gamma_2^L P}{f_{2,pure}^{L(P_0)} x_2 \exp \int_{P_0}^P (\bar{v}_2/RT) dP} \quad (2)$$

In the calculation the partial molar volume of ethane, \bar{v}_2 , in Equation 2 was assumed to be approximately equal to the partial molar volume at infinite dilution, \bar{v}_2^∞ , which is obtained or estimated from the literature (2).

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

$$\log \gamma_1 = x_2^2 [B + C(3x_1 - x_2) + D(x_1 - x_2)(5x_1 - x_2)] \quad (3)$$

Fugacity coefficients of solvent components. The fugacity coefficients of solvent components were calculated by:

$$\varphi_1 = \frac{\gamma_1 x_1 f_{1,pure}^{L(P_0)} \exp \int_{P_0}^P (\bar{v}_1/RT) dP}{y_1 P} \quad (4)$$

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

Henry's constants. Henry's constants for six binary systems are calculated by:

$$H_{2,(1)}^{(P_1^s)} = \lim_{P \rightarrow P_1^s} (f_2/x_2) \quad (5)$$

The activity coefficients for the benzene-ethane and methyl acetate-ethane systems are shown in Figure 2. The fugacity coefficients for the methanol-ethane and ethyl ether-ethane systems are shown in Figure 3. Henry's constants for all systems are listed in Table II with the three parameters of the Redlich-Kister equation and the activity coefficients of ethane at infinite dilution.

Discussion

The vapor-liquid equilibrium data for the benzene-ethane system were reported by Kay (4), but the compositions in the vapor phase were not measured at 25°C. The equilibrium data (P - x) for the benzene-ethane system in this study is in good agreement with Kay's data.

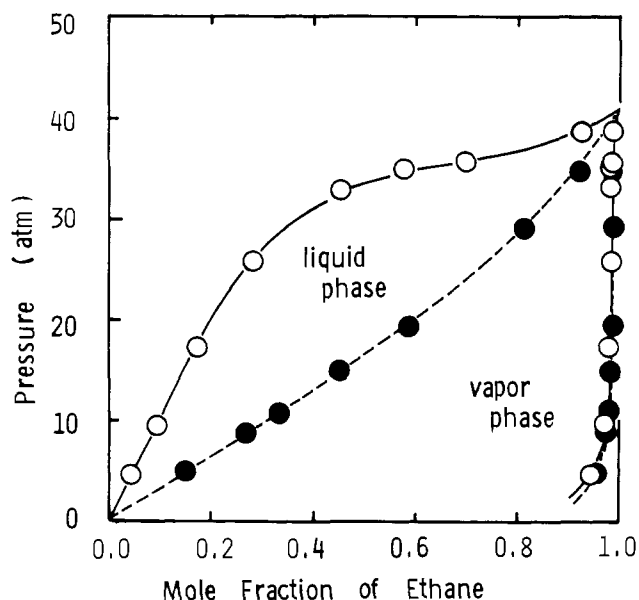


Figure 1. Vapor-liquid equilibria for binary systems of acetone(1)-ethane(2) (—○—) and *n*-hexane(1)-ethane(2) (-●-) at 25°C

The two liquid phases appeared in the methanol-ethane system at 25°C at 40.705 atm and $x_2 = 0.3511$ in the methanol-rich phase. Ma and Kohn (5) have already pointed out this phenomenon, and their corresponding values at 25°C are 40.74 atm and $x_2 = 0.3528$.

The nonidealities in the liquid phase among the systems are compared by activity coefficients. Values of γ_2^∞ obtained are in order of $\gamma_{2(\text{methanol})}^\infty > \gamma_{2(\text{acetone})}^\infty > \gamma_{2(\text{methyl acetate})}^\infty > \gamma_{2(\text{benzene})}^\infty > \gamma_{2(\text{ethyl ether})}^\infty > \gamma_{2(n\text{-hexane})}^\infty$ in the systems containing ethane.

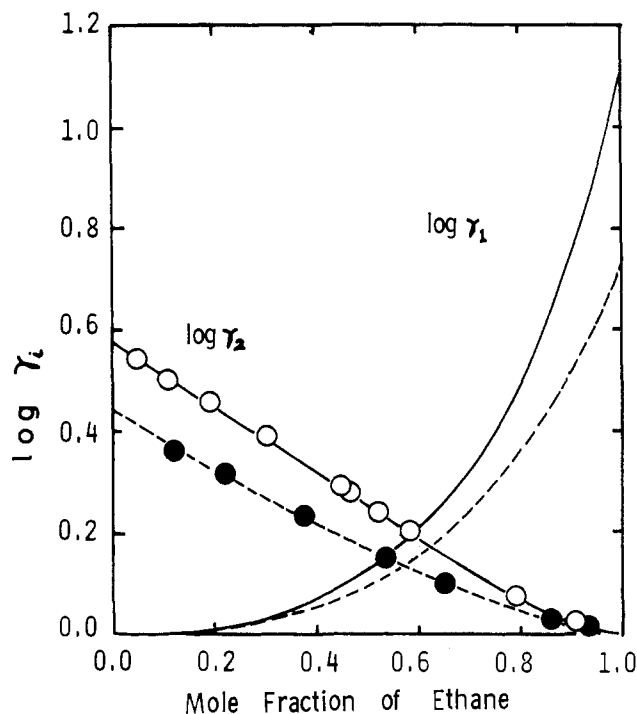


Figure 2. Activity coefficients for binary systems of methyl acetate(1)-ethane(2) (—○—) and benzene(1)-ethane(2) (-●-) at 25°C

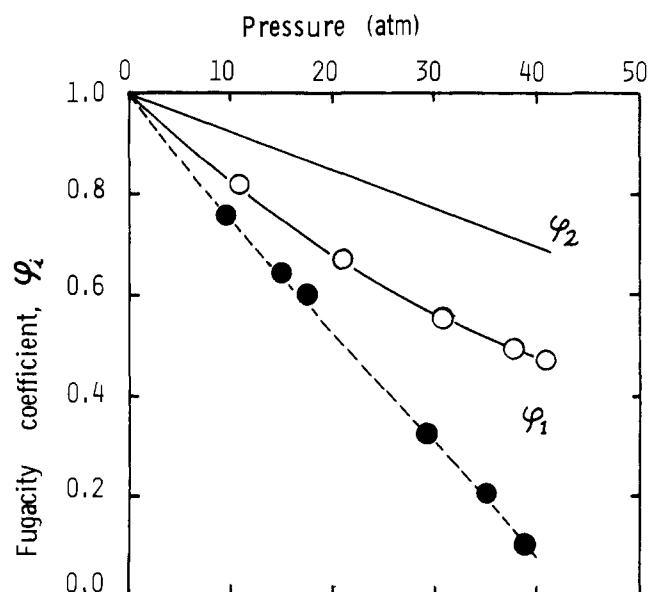


Figure 3. Fugacity coefficients for binary systems of methanol(1)-ethane(2) (—○—) and ethyl ether(1)-ethane(2) (-●-) at 25°C

Table II. Henry's Constants and Parameters of Redlich-Kister Equation

System		$H_{2,(1)}^{(P_1^s)}$, atm		Redlich-Kister equation				
Component 1	Component 2	Exptl	Lit	B	C	D	$\log_{10} \gamma_1^\infty$	$\log_{10} \gamma_2^\infty$
Methanol	Ethane	260	253.1 (1)	1.0701	-0.1174	0.1267	1.3140	1.0794
Acetone	Ethane	105	103 ^a	0.8239	-0.2418	0.0453	1.1108	0.6274
Methyl acetone	Ethane	93	94 ^a	0.7666	-0.2658	0.0740	1.1063	0.5748
Ethyl ether	Ethane	41	...	0.2027	-0.0891	0.1062	0.3980	0.2198
Benzene	Ethane	68	67 ^a	0.5432	-0.1522	0.0509	0.7463	0.4419
<i>n</i> -Hexane	Ethane	32	32 (10)	0.1342	-0.0414	0.0274	0.2030	0.1202

^a Interpolated value from Seidell and Linke's data (9).

For the systems containing carbon dioxide, the values are in order of $\gamma_{2(\text{methanol})}^\infty > \gamma_{2(\text{benzene})}^\infty > \gamma_{2(n\text{-hexane})}^\infty > \gamma_{2(\text{ethyl ether})}^\infty > \gamma_{2(\text{acetone})}^\infty > \gamma_{2(\text{methyl acetate})}^\infty$. The differences among these orders may be caused by specific interactions of unlike molecules and like molecules. The self-association of the solvent component may make the activity coefficient of solute gas in the system large; on the other hand, the interaction between solvent component and solute gas may make it small.

All activity coefficients of solute gas in the systems containing ethane are larger than those in the systems containing carbon dioxide except the *n*-hexane-ethane system. This behavior may be explained by the specific interactions between carbon dioxide and each solvent component. In the systems of acetone-ethane, methyl acetate-ethane, and ethyl ether-ethane, the nonidealities in the liquid phase especially are greater than the systems containing carbon dioxide.

The nonidealities in the vapor phase are represented by fugacity coefficients; fugacity coefficients of solvent components at high pressures are small in all systems. The deviation of the solvent component in the vapor phase from the ideal gas law is smallest for the methanol-ethane system and largest for the *n*-hexane-ethane system. This tendency is the same as in those systems containing carbon dioxide.

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Nomenclature

B, C, D = parameters of the Redlich-Kister equation
 H = Henry's constant, atm
 P = total pressure, atm
 R = gas constant, atm cc/mol K
 T = absolute 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
 (P_0) = reference pressure of 0 atm
 L = liquid phase
 V = vapor phase
 $-$ = partial molar quantity

Subscripts

1 = solvent component
2 = solute gas
pure = pure component

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