

# MEASUREMENT AND CORRELATION OF PHASE EQUILIBRIA FOR THE CARBON DIOXIDE-ETHANOL-WATER SYSTEM

SEIYA HIROHAMA\* AND TORU TAKATSUKA

*Chiyoda Corp.,*

*13 Moriyacho 3-chome, Kanagawa-ku, Yokohama 221*

SHINJI MIYAMOTO AND TUNEHISA MUTO

*Idemitsu Petrochemical Co.,*

*1-1 Miyamae-cho, Tokuyama, Yamaguchi Prefecture 745*

**Key Words:** Equation of State, Extraction, Supercritical Fluid, Phase Equilibrium, Mixing Rule

Phase equilibria for the carbon dioxide-ethanol system and the carbon dioxide-ethanol-water system were measured to provide the thermodynamic base for the extraction of ethanol from its aqueous solutions using near-critical carbon dioxide as solvent. The experiments were carried out at 283K-298K and 5-7MPa, including extraction conditions and solvent-recovery conditions in a wide range of ethanol concentration.

An empirical mixing rule for the Helmholtz function with ternary as well as binary non-randomness parameters was proposed based on the density-dependent local composition concept. A correlation model was derived by a combination of the mixing rule with the Helmholtz function obtained from the Patel-Teja equation of state. The model successfully correlated the phase equilibria of the carbon dioxide-ethanol-water system.

## Introduction

Extraction using supercritical or near-critical fluids as solvent is a potential technology for separating ethanol from aqueous solution. Carbon dioxide can be used as the solvent due to its established non-toxicity for food uses. Optimization of the process requires a process simulator that can predict the physical properties, including the phase equilibria for the carbon dioxide-ethanol-water system.

Although some experimental data<sup>3, 7, 9, 18)</sup> have been reported for the phase equilibria above the critical temperature of carbon dioxide, only a few data<sup>6)</sup> are available below the critical temperature.

The extractor is supposed to be followed by a solvent recovery unit which is a distillation column that separates the solute from the extract. But experimental data of phase equilibria regarding solvent recovering conditions are scarce.

The conventional quadratic mixing rule cannot correlate the phase equilibria for highly non-ideal mixtures of polar components and supercritical fluids<sup>4)</sup>. The density-dependent local composition (DDLC) mixing rules proposed by Mollerup<sup>10, 11)</sup> and Whiting and Prausnitz<sup>19)</sup> increased the correlating capability. Skjold-Jørgensen<sup>16)</sup> derived a group contribution equation of state (GC-EOS) by combining a DDLC mixing rule with the Carnahan-Stirling-van der Waals equation of state (CS-vdW-EOS). Although the GC-EOS was not configured to estimate solvent density due to the poor accuracy of CS-vdW-EOS, it increased the predictive accuracy for the phase equilibria of the carbon dioxide-ethanol-water system<sup>2, 7)</sup>

In this paper, the Helmholtz function derived from the Patel-Teja<sup>12)</sup> equation of state is selected for combination with a newly developed mixing rule because of its predictive accuracy for solvent density<sup>18)</sup> and its simple form.

## 1. Experimental

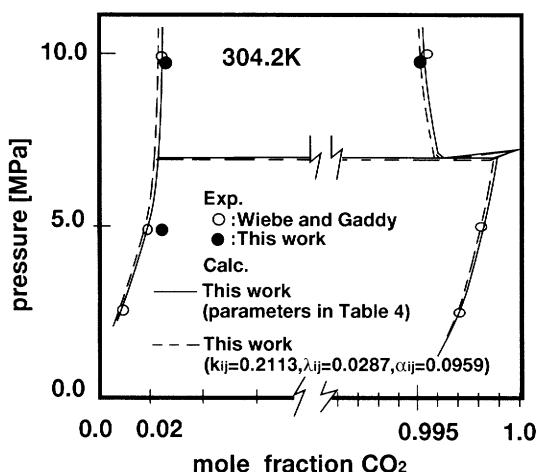
### 1.1 Apparatus and procedures

The experimental apparatus and methods were the same as those described in detail in a previous report<sup>5)</sup>. A static apparatus equipped with an equilibrium cell was employed. Mixtures of ethanol and water and carbon dioxide were pumped into the equilibrium cell. Coexisting phases were agitated by a magnetic stirrer to promote mass transfer between the phases. After separation and settling of the phases each coexisting phase was circulated through a sampling device where a small sample could be collected for composition analysis.

Ethanol supplied by Wako Pure Chemical Co. was of 99vol% purity and was used without further purification. Carbon dioxide supplied by Nippon Sanso Co. Ltd. was 99.9 vol% and was used without further purification.

To confirm the reliability of the experimental apparatus, vapor-liquid equilibria were measured for the carbon dioxide-water binary system, for which reliable experimental data were available. Good agreement was observed between the data obtained in the present work and those of Wiebe and Gaddy<sup>20, 21)</sup> as shown in Fig. 1 at 304.2K.

\* Received December 24, 1992. Correspondence concerning this article should be addressed to S. Hirohama.



**Fig. 1** Vapor-liquid and fluid-liquid equilibria for the carbon dioxide-ethanol system

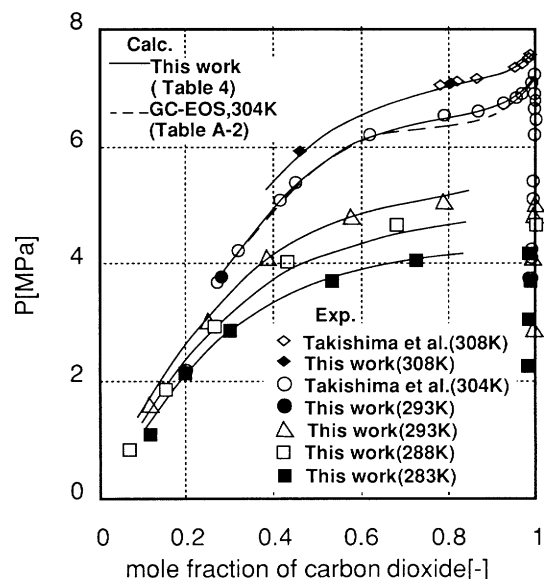
**Table 1.** Vapor-liquid equilibria for the carbon dioxide-ethanol system

T [K]	P [MPa]	mole fraction of carbon dioxide	
		vapor	liquid
283.1	1.14	0.996	0.105
283.8	2.16	0.997	0.199
238.1	2.91	0.998	0.299
283.1	3.83	0.998	0.535
283.4	4.14	0.998	0.725
288.2	0.86	0.993	0.066
287.9	1.90	0.997	0.155
288.2	2.96	0.997	0.261
288.7	4.06	0.998	0.430
288.9	4.67	0.997	0.676
292.5	1.63	0.995	0.119
292.3	3.08	0.997	0.253
292.5	4.12	0.997	0.385
292.0	4.82	0.997	0.577
292.2	5.08	0.997	0.789
308.2	5.83	0.989	0.478
308.2	7.14	0.989	0.820

## 1.2 Experimental results

**Table 1** and **Fig. 2** show vapor-liquid equilibria for the carbon dioxide-ethanol system measured at 283K-308K and 2-8MPa. The experimental data at 282K-284K, 287K-289K, 292K-294K and 308.2K are indicated by 283K, 288K, 293K and 308K respectively in Figs. 2 through 6. The results at 308K agreed well with the data of Takishima *et al.* as shown in Fig. 2.

**Table 2** shows the liquid-liquid equilibria for the carbon dioxide-ethanol-water system at 283K-293K and 5-7MPa. The pressure was set at a slightly higher value than the bubbling pressure of carbon dioxide. The sum of solubilities of ethanol and water into carbon dioxide and the separation factor of ethanol to water are compared with the literature data in **Figs. 3** and **4**, respectively. The results at 293K and 6-7MPa agreed well with the data of Inomata *et al.* in the low-concentration region of ethanol (0-15mol% carbon dioxide-free basis). As the conditions changed from 308K and 10MPa to 293K and



**Fig. 2** Vapor-liquid equilibria for the carbon dioxide-ethanol system

**Table 2.** Liquid-liquid equilibria for the carbon dioxide-ethanol-water system at extraction conditions

T [K]	P [MPa]	component	mole fraction	
			extract	raffinate
284.1	6.29	carbon dioxide	0.9952	0.0280
		ethanol	0.0031	0.0433
		water	0.0017	0.9287
282.5	6.02	carbon dioxide	0.9924	0.0324
		ethanol	0.0054	0.0635
		water	0.0022	0.9041
282.8	5.98	carbon dioxide	0.9926	0.0330
		ethanol	0.0054	0.0651
		water	0.0020	0.9019
283.1	6.05	carbon dioxide	0.9681	0.1096
		ethanol	0.0275	0.3083
		water	0.0044	0.5821
288.1	5.40	carbon dioxide	0.9912	0.0414
		ethanol	0.0061	0.0666
		water	0.0027	0.8920
287.6	6.18	carbon dioxide	0.9891	0.0421
		ethanol	0.0082	0.0932
		water	0.0027	0.8647
287.8	5.59	carbon dioxide	0.9694	0.0432
		ethanol	0.0240	0.1892
		water	0.0066	0.7676
287.5	5.79	carbon dioxide	0.9596	0.1087
		ethanol	0.0343	0.3162
		water	0.0061	0.5751
292.5	6.01	carbon dioxide	0.9907	0.0300
		ethanol	0.0064	0.0597
		water	0.0029	0.9103
293.5	6.72	carbon dioxide	0.9799	0.0433
		ethanol	0.0161	0.1248
		water	0.0040	0.8319
292.5	5.89	carbon dioxide	0.9510	0.1032
		ethanol	0.0373	0.2863
		water	0.0117	0.6105

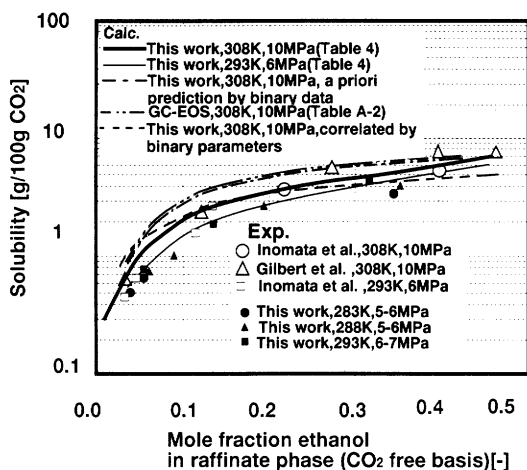


Fig. 3 The sum of solubilities of ethanol and water into carbon dioxide

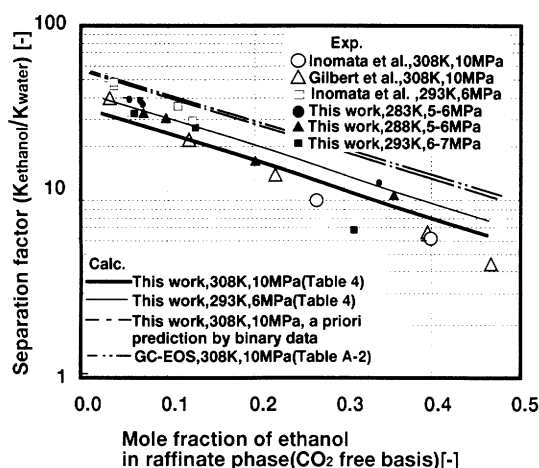


Fig. 4 Separation factor of ethanol to water

6-7MPa, the sum of solubilities decreased. The separation factor of ethanol to water did not show significant change, although an increasing tendency was observed within the fluctuation of the experimental data.

Vapor-liquid equilibria were also measured under the conditions of the solvent recovery unit at 298K and 6MPa in the high-ethanol concentration region (75-95 mol% carbon dioxide-free basis). The results are shown in Table 3. Significantly large separation factors were observed in the separation of carbon dioxide from ethanol, as is shown in Fig. 5. The  $K$ -value of water was greater than that of ethanol, though it was always smaller than that of carbon dioxide under the solvent recovery conditions predicted by Brignole *et al.*<sup>2)</sup> with the GC-EOS.

## 2. Correlation Model

### 2.1 DDLC mixing rule for the Helmholtz function

The configurational Helmholtz energy for a single component can be written as Eq. (1) for the equation of state of van der Waals form:

$$A^{\text{conf}} = A^{\text{conf}}_{\text{rep}} + A^{\text{conf}}_{\text{att}} \quad (1)$$

Table 3. Vapor-liquid equilibria for the carbon dioxide-ethanol-water system at solvent recovering conditions

$T$ [K]	$P$ [MPa]	component	mole fractions	
			vapor	liquid
298.4	6.2	carbon dioxide	0.9973	0.9846
		ethanol	0.0017	0.0110
		water	0.0010	0.0044
298.3	6.1	carbon dioxide	0.9957	0.9543
		ethanol	0.0033	0.0369
		water	0.0010	0.0088
298.6	5.9	carbon dioxide	0.9948	0.8827
		ethanol	0.0045	0.1068
		water	0.0007	0.0105
298.5	6.1	carbon dioxide	0.9964	0.9628
		ethanol	0.0026	0.0296
		water	0.0010	0.0076

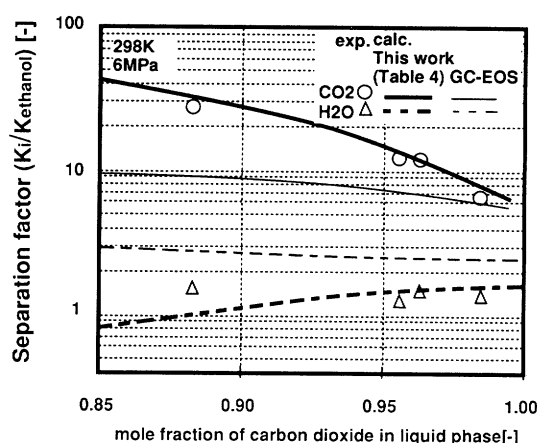


Fig. 5 Separation factors at solvent recovery conditions

The well-known van der Waals, Soave-Redlich-Kwong<sup>17)</sup>, Peng-Robinson<sup>15)</sup> and Patel-Teja<sup>12)</sup> equations of state commonly have an attractive part ( $A^{\text{conf}}_{\text{att}}$ ) which can be expressed by the following equation using an energy parameter ( $a$ ) and volumetric parameters ( $b$  and  $c$ ).

$$A^{\text{conf}}_{\text{att}} = n a f(v, b, c) \quad (2)$$

The  $f(v, b, c)$  represents the density dependence of the attractive part and is equivalent to  $(1/v)$  in the van der Waals equation. The configurational Helmholtz function for mixtures may be expressed in a similar form:

$$A^{\text{conf}}_m = A^{\text{conf}}_{\text{rep}, m} + A^{\text{conf}}_{\text{att}, m} \quad (3)$$

In the present work the attractive part ( $A^{\text{conf}}_{\text{att}, m}$ ) is assumed to be expressed by the following simple form, which is similar to Eq. (2):

$$A^{\text{conf}}_{\text{att}, m} = n a_m f(v, b_m, c_m) \quad (4)$$

The density-dependent local composition mixing rule is applied to the energy parameter ( $a_m$ ):

$$a_m = \sum_i x_i \sum_j x_j a_{ji} \quad (5)$$

The  $x_{ji}$  is the local mole fraction of component  $j$  around a central molecule of component  $i$  and can be estimated by following equation:

$$x_{ji} = \frac{x_i \eta_{ji}}{\sum_k x_k \eta_{ki}} \quad (6)$$

The  $\eta$  is the density-dependent availability factor and is approximated by a Boltzman factor as follows:

$$\eta_{ji} = \exp \left[ -\frac{E_{ji}}{RTv} \right] \quad (7)$$

Since some ternary data exist for the liquid-liquid and fluid-liquid equilibria for the carbon dioxide-ethanol-water system, the ternary data can be used to improve the calculated precision, which is essential in the design of the extraction process. Although binary parameters are often adjusted using the ternary data, it is difficult to correlate the ternary data with enough accuracy while keeping the correlative accuracy of each binary system. To increase the correlative precision for the ternary system, the present work attempts to introduce ternary parameters assuming that the availability factor for the molecule of component  $j$  around a central molecule of component  $i$  is affected by the mole fraction of component  $k$  ( $\neq i$  or  $j$ ) as expressed by the following empirical equation:

$$E_{ji} = E_{ji}^{\text{binary}} \left( 1 - \sum_{\substack{k \neq i \\ k \neq j}} x_k m_{jik} \right) \quad (8)$$

where  $m_{jik} = m_{ijk}$  is assumed and the ternary parameter  $m_{jik}$  represents the effect of the mole fraction of component- $k$  on  $E_{ji}$ . Although Eq. (8) is empirical,  $\eta_{ji}$  can be affected by the composition in the system studied in the present work due to the rearrangement of the solution structures induced by the addition of component  $k$  ( $\neq i$  or  $j$ ) into the binary solution of component  $i$  and component  $j$ . The  $E_{ji}^{\text{binary}}$  in Eq. (8) is assumed to be expressed as follows, using the binary non-randomness parameter ( $\alpha_{ji}$ ):

$$E_{ji}^{\text{binary}} = \alpha_{ji} \left( \frac{a_{ji}}{b_{ji}} - \frac{a_{ii}}{b_{ii}} \right) b_{ii} \quad (9)$$

where

$$a_{ji} = (a_i a_j)^{0.5} (1 - k_{ji}), k_{ji} = k_{ji} \quad (10)$$

$$b_{ji} = \frac{b_i + b_j}{2} (1 - \lambda_{ji}), \lambda_{ji} = \lambda_{ji} \quad (11)$$

The  $k_{ji}$  in Eq. (10) and  $\lambda_{ji}$  in Eq. (11) are the energetic and volumetric binary interaction parameters respectively. The thermodynamic properties can be readily derived analytically from Eq. (3) even if  $\alpha_{ji}$  has a different value for each binary system and/or  $m_{jik}$  has a different value for each ternary system.

Combination of the above equations yields the expression for the attractive part of the Helmholtz function ( $A_{\text{att},m}^{\text{conf}}$ ), differentiation of which with respect to volume gives the attractive contribution to pressure:

$$P_{\text{att}} = -na_m \left\{ \frac{\partial f(v, b_m, c_m)}{\partial V} \right\}_{T,ni} \dots - \left( \frac{\partial na_m}{\partial V} \right)_{T,ni} f(v, b_m, c_m) \quad (12)$$

where

$$\left( \frac{\partial na_m}{\partial V} \right)_{T,ni} = \sum_i x_i \sum_j x_j a_{ji} \dots \frac{\left( \frac{\partial \eta_{ji}}{\partial V} \right)_{T,ni} \sum_k x_k \eta_{ki} - \eta_{ji} \sum_k x_k \left( \frac{\partial \eta_{ki}}{\partial V} \right)_{T,ni}}{\left( \sum_k x_k \eta_{ki} \right)^2} \quad (13)$$

$$\left( \frac{\partial \eta_{ji}}{\partial V} \right)_{T,ni} = E_{ji} \eta_{ji} / RTv^2 \quad (14)$$

The first term on the right-hand side of Eq. (12) is identical in form with the attractive part of the original equation of state. The second term appears due to the density dependency of the mixing rule and vanishes when  $\alpha_{ji}$  approaches zero and/or in case of a pure component.

## 2.2 The model combined with Patel-Teja equation

The design of processes using supercritical fluid requires a good predictive accuracy of the PVT relationship in the supercritical region. The Patel-Teja<sup>12)</sup> equation of state shown in **Appendix 1** predicts the density of carbon dioxide including the supercritical region and the saturated liquid density of many pure substances, including polar components with practical accuracy. For the Patel-Teja equation of state,  $f(v)$  is derived as follows.

$$f(v, b_m, c_m) = \frac{1}{2d} \ln \left( \frac{Q-d}{Q+d} \right) \quad (15)$$

where

$$Q = \frac{b_m + c_m}{2} + V/n, d = \sqrt{b_m c_m + \frac{(b_m + c_m)^2}{4}} \quad (16)$$

The repulsive part of the configurational Helmholtz free energy ( $A_{\text{rep},m}^{\text{conf}}$ ) becomes:

$$A_{\text{rep},m}^{\text{conf}} = -nRT \ln(v - b_m) \quad (17)$$

The conventional quadratic mixing rule was applied to volumetric parameters  $b$  and  $c$ .

$$b_m = \sum_i x_i \sum_j x_j b_{ij}, b_{ij} = \frac{b_i + b_j}{2} (1 - \lambda_{ij}) \quad (18)$$

$$c_m = \sum_i x_i \sum_j x_j c_{ij}, c_{ij} = \frac{c_i + c_j}{2} (1 - \lambda_{ij}) \quad (19)$$

Substituting Eqs. (4), (15), (16), (17), (18) and (19) to Eq. (3), the configurational Helmholtz free energy ( $A_m^{\text{conf}}$ ) becomes:

$$\frac{A_m^{\text{conf}}}{n} = -RT \ln(v - b_m) + \frac{a_m}{2d} \ln \left[ \frac{Q-d}{Q+d} \right] \quad (20)$$

The  $A_m^{\text{conf}}$  differentiated with respect to volume gives the expression for pressure:

**Table 4.** Parameters of the model for the carbon dioxide(1)-ethanol(2)-water(3) system

Parameters for each single component				
i	$T_{ci}$	$P_{ci}$	$F_i$	$\zeta_{ci}$
1	304.2	7.34	0.7077	0.3090
2	516.2	6.37	1.2304	0.3000
3	647.3	22.04	0.6898	0.2690
Binary parameters				
i,j	$k_{ij}$	$\alpha_{ij}$	$\lambda_{ij}$	
12	0.0702	-0.0112	0.0493	
23	-0.0758	0.0056	-0.0404	
13	0.1797	0.0167	0.1373	
Ternary parameters				
i,j,k	$m_{ijk}$			
231	-13.2335			
132	1.4221			
123	-1.9147			

$$\begin{aligned}
 P &= - \left( \frac{\partial A_m^{conf}}{\partial V} \right)_{T, n_i} \\
 &= \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m) + c_m(v - b_m)} \cdots \\
 &\cdots - \frac{1}{2d} \left( \frac{\partial a_m}{\partial V} \right)_{T, n_i} \ln \left( \frac{Q - d}{Q + d} \right) \quad (21)
 \end{aligned}$$

The first and second terms on the right-hand side of Eq. (21) are identical with the original Patel-Teja equation of state. The third term appears due to the density dependency of the mixing rule. Since the third term becomes zero for a single substance, the parameters to compute  $a$ ,  $b$  and  $c$  for a pure component can be readily obtained by the conventional procedures shown in Appendix 1, using the critical properties and/or saturated properties. The fugacity coefficient, enthalpy departure and entropy departure are readily derived from Eq. (20). The fugacity coefficient is shown in Appendix 2.

### 3. Test of The Correlating Capability

The correlating capability of the model is tested for the phase equilibria of the mixtures studied in this work and is compared with that of the GC-EOS at 304K-308K, where experimental data from different sources are available. The parameter values of the GC-EOS used in the present work were determined as described in Appendix 3.

#### 3.1 Binary systems

The values of the binary parameters  $k_{ij}$ ,  $\alpha_{ij}$  and  $\lambda_{ij}$  for the carbon dioxide-ethanol system were determined by the data shown in Table 1 and the data obtained by Takishima *et al.*<sup>18)</sup> The parameters are shown in Table 4. Good agreement was observed between the experimental data and the correlation with the model even in the vicinity of the critical point of carbon dioxide as shown in Fig. 1. The correlating capability of the model was better than that of the GC-EOS at 304K.

The GC-EOS as well as the present model corre-

**Table 5.** Comparison of predictive accuracies for ethanol-water binary system

Exp.			Calc.					
Obtained by Pemberton and Mash			GC-EOS	This work (1)		This work (2)		
			values listed in Table A-2	$k_{ji} = 0.1869$ $\alpha_{ji} = 0.0785$ $\lambda_{ji} = 0.2389$ (determined by binary data)		values listed in Table 4		
$x$	$P$	$y$	$P$	$y$	$P$	$y$	$P$	$y$
[-]	[kPa]	[-]	[kPa]	[-]	[kPa]	[-]	[kPa]	[-]
0.05	5.8	0.31	6.0	0.31	5.8	0.28	6.1	0.32
0.11	7.3	0.47	7.9	0.51	7.2	0.45	7.6	0.48
0.25	8.7	0.59	9.7	0.62	8.8	0.59	8.7	0.57
0.32	9.1	0.62	10.0	0.65	9.2	0.62	8.9	0.59
0.50	9.7	0.68	10.7	0.70	9.7	0.68	0.94	0.65
0.58	9.9	0.71	11.0	0.73	9.9	0.70	9.6	0.68
0.72	10.2	0.78	11.5	0.80	10.1	0.76	9.8	0.77
0.81	10.3	0.83	11.7	0.86	10.2	0.82	9.9	0.83
0.90	10.4	0.91	12.0	0.92	10.2	0.89	10.0	0.90
0.95	10.5	0.95	12.1	0.96	10.1	0.95	10.0	0.95
0.97	10.5	0.97	12.2	0.98	10.1	0.97	10.0	0.97
					7.37	1.80	3.02	

lates the phase equilibria for the carbon dioxide-water system and the ethanol-water system as shown in Table 5 and Fig. 1 at 298K-308K, with good agreement with the experimental data for each binary system<sup>13, 20, 21)</sup>. The values of the binary parameters for carbon dioxide-water system and the ethanol-water system are listed in Fig. 1 and Table 5 respectively.

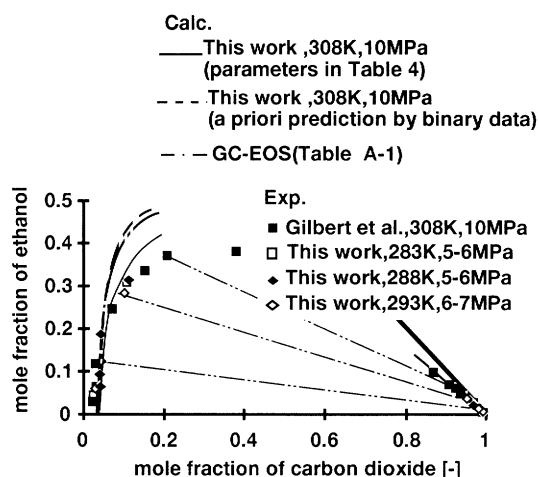
#### 3.2 Ternary system

1) A priori prediction by binary data alone Setting the values of  $m_{jik}$  at zero, the predictive accuracy of the model was tested with the values only of binary parameters determined by each binary datum. Both the model and the GC-EOS predict the solubility of carbon dioxide into ethanol aqueous solution with fairly good agreement with the experimental data as shown in Fig. 6.

But the model as well as the GC-EOS overestimated the sum of solubilities of ethanol and water into carbon dioxide in the low ethanol concentration region (0-15 mol% carbon dioxide-free basis) as shown in Fig. 3. The model and the GC-EOS overestimated the separation factor of ethanol to water also as shown in Fig. 4.

2) Correlation of ternary data The values of the binary parameters for the ethanol-water system and carbon dioxide-water system were optimized simultaneously using the experimental data for each binary system as well as the carbon dioxide-ethanol-water ternary system. Although the correlative accuracy was improved as shown in Fig. 3, it was difficult to calculate the solubility with sufficient precision when the parameter values were constrained to maintain correlative accuracy for each binary system.

The values of ternary parameters ( $m_{jik}$ ) and the



**Fig. 6** Liquid-liquid and fluid-liquid equilibria for the carbon dioxide-ethanol-water system

binary parameters ( $k_{ji}$ ,  $\lambda_{ji}$ ,  $\alpha_{ji}$ ) for the ethanol-water system and the carbon dioxide-water system were optimized simultaneously to increase the correlative precision. Optimized values of the parameters, listed in Table 4, enabled use of the model to calculate solubility and the separation factors with good agreement with the experimental data as shown in Figs. 3 and 4 respectively at 293K and 6MPa as well as 308K and 10MPa. The average absolute deviation for the carbon dioxide-water system and the ethanol-water system stayed within 5% after the above adjustment of parameter values. The model also predicts the separation factors at solvent recovery conditions with better agreement with the experimental data than that of the *a priori* prediction by the GC-EOS as shown in Fig. 5 with the values of parameters listed in Table 4.

## Conclusions

The phase equilibria for the carbon dioxide-ethanol system and the carbon dioxide-ethanol-water system were measured to provide the thermodynamic base for the design of an extraction system that separates ethanol from aqueous solution by using liquid or supercritical carbon dioxide as solvent.

Liquid-liquid equilibria were measured at 283K-292K and 5-7MPa in a wide range of ethanol concentration, including the region of 20-50 mol% (carbon dioxide-free basis) where few experimental data have been reported.

Vapor-liquid equilibria at the solvent-recovery conditions were measured at 298K, 6MPa in the high-concentration region of ethanol (70-95 mol% carbon dioxide-free basis).

An empirical DDLC mixing rule for the Helmholtz function with ternary as well as binary non-randomness parameters was proposed. The combination of the mixing rule with the Helmholtz function derived from the Patel-Teja<sup>12)</sup> equation of state successfully correlates the phase equilibria of the carbon dioxide-ethanol-water

**Table A-1.** Comparison of the correlative accuracy of saturated properties of carbon dioxide

Exp.				Patel-Teja				GC-EOS			
$T$	$P^{sat}$	dens.		$P^{sat}$	dens.			$P^{sat}$	dens.		
[K]	[MPa]	[mol/L]		[MPa]	[mol/L]			[MPa]	[mol/L]		
		Liq.	Gas.		Liq.	Gas.			Liq.	Gas.	
276.0	3.76	20.7	2.43	3.75	20.0	2.44		3.80	16.2	2.34	
280.0	4.16	20.1	2.76	4.16	19.2	2.78		4.21	15.6	2.66	
284.0	4.60	19.4	3.16	4.60	18.3	3.19		4.66	14.9	3.03	
288.0	5.07	18.7	3.63	5.08	17.3	3.68		5.15	14.1	3.48	
292.0	5.57	17.9	4.21	5.59	16.2	4.27		5.67	13.2	4.02	
294.0	5.84	17.4	4.56	5.85	15.6	4.63		5.94	12.7	4.34	
296.0	6.12	16.8	4.97	6.13	14.9	5.05		6.22	12.2	4.71	
298.0	6.41	16.2	5.47	6.42	14.2	5.54		6.52	11.6	5.16	
300.0	6.71	15.5	6.10	6.72	13.3	6.15		6.82	10.8	5.71	
<hr/>											
$\frac{1}{ND} \sum \left  \frac{\text{Exp.} - \text{Calc.}}{\text{Exp.}} \right  \times 100$				0.2	8.7	1.1		1.5	25.7	4.7	

system and sustains the correlative accuracy for each binary system.

## Acknowledgment

We wish to thank the Ministry of International Trade and Industry (MITI) of Japan and the Japan Alcohol Association for their support and approval for the publication of this paper.

## Appendix 1 Patel-Teja equation of state<sup>12)</sup>

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+c(v-b)} \quad (\text{A1})$$

$$a(T) = \Omega_a (R^2 T_c^2 / P_c) \{1 + F(1 - T_r^{0.5})\}^2, \quad T_r = T / T_c \quad (\text{A2})$$

$$b = \Omega_b (RT_c / P_c) \quad (\text{A3})$$

$$c = \Omega_c (RT_c / P_c) \quad (\text{A4})$$

where

$$\Omega_c = 1 - \zeta_c \quad (\text{A5})$$

$$\Omega_a = 3 \zeta_c^2 + 3(1 - 2 \zeta_c) \Omega_b + \Omega_b^2 + 1 - 3 \zeta_c \quad (\text{A6})$$

and  $\Omega_b$  is the smallest positive root of the following equation.

$$\Omega_b^3 + (2 - 3 \zeta_c) \Omega_b^2 + 3 \zeta_c^2 \Omega_b - \zeta_c^3 = 0 \quad (\text{A7})$$

The present work used the values of the  $F$  and  $\zeta_c$  determined by Patel and Teja<sup>12)</sup> from the data for vapor pressure and for the density of saturated gas and liquid. For carbon dioxide, the Patel and Teja<sup>12)</sup> equation gives higher accuracy than Jfrgensen's GC-EOS in the calculation both of saturated liquid density and of vapor pressure as shown in **Table A-1**.

## Appendix 2 Expressions for the fugacity coefficient

The fugacity coefficient can be derived from the expressions for the configurational Helmholtz function at constant volume.

$$RT \ln \phi_i = \left( \frac{\partial [A_m^{\text{conf}} - A_m^{\text{conf, ideal}}]_{T, v}}{\partial n_i} \right)_{T, v, n_j \neq i} - RT \ln Z \quad (\text{A8})$$

where

$$A_m^{\text{conf, ideal}} = -RTn \ln(v) \quad (\text{A9})$$

Substitution of Eq.(10) to Eq. (A8) yields

**Table A-2.** Parameters for Jørgensen's GC-EOS

group-group interaction parameters  
( $k'_{ji}k_{ji}^*$ )

	–CH <sub>3</sub>	–CH <sub>2</sub> OH	CO <sub>2</sub>	H <sub>2</sub> O
–CH <sub>3</sub>	—	0.9200	0.8930	0.5760
–CH <sub>2</sub> OH	–0.1620	—	1.3424	1.1368
CO <sub>2</sub>	0.0000	0.0000	—	0.9178
H <sub>2</sub> O	0.0000	0.0000	0.0000	—

non-random parameters  
( $\alpha_{ij}$ )

ij	–CH <sub>3</sub>	–CH <sub>2</sub> OH	CO <sub>2</sub>	H <sub>2</sub> O
–CH <sub>3</sub>	—	2.5850	8.2210	0.4000
–CH <sub>2</sub> OH	–15.0000	—	–5.8376	–1.7694
CO <sub>2</sub>	–0.7430	2.4823	—	0.2078
H <sub>2</sub> O	–3.0980	–1.0416	–0.9449	—

$$RT \ln \phi_i = -RT \ln \left( \frac{v - b_m}{v} \right) + \frac{RT}{v - b_m} - RT \ln Z \dots$$

$$\dots + \left[ \frac{1}{2d} \left\{ a_m + \left( \frac{\partial a_m}{\partial n_i} \right)_{T, V, nj \neq i} \right\} - \frac{a_m}{2d^2} \right] \ln \left( \frac{Q - d}{Q + d} \right) \dots$$

$$\dots - \frac{a_m}{d} \times \frac{1}{Q^2 - d^2} \left\{ \left( \frac{\partial Qn}{\partial n_i} \right)_{T, V, nj \neq i} d - \left( \frac{\partial nd}{\partial n_i} \right)_{T, V, nj \neq i} Q \right\}$$
(A10)

where

$$\left( \frac{\partial Qn}{\partial n_i} \right)_{T, V, nj \neq i} = \frac{1}{2} \left\{ \left( \frac{\partial b_m n}{\partial n_i} \right)_{T, V, nj \neq i} + \left( \frac{\partial c_m n}{\partial n_i} \right)_{T, V, nj \neq i} \right\}$$
(A11)

$$\left( \frac{\partial nd}{\partial n_i} \right)_{T, V, nj \neq i} = \frac{1}{2d} \left\{ b_m \left( \frac{\partial c_m n}{\partial n_i} \right)_{T, V, nj \neq i} \dots \right.$$

$$\dots + c_m \left( \frac{\partial b_m n}{\partial n_i} \right)_{T, V, nj \neq i} \left. \right\} + \frac{1}{2d} (b_m + c_m) \left( \frac{\partial Qn}{\partial n_i} \right)_{T, V, nj \neq i}$$
(A12)

$$\left( \frac{\partial a_m}{\partial n_i} \right)_{T, V, nj \neq i} = \frac{\sum_j^{NC} a_{ji} x_j \eta_{ji}}{\sum_l^{NC} x_l \eta_{li}} + \sum_k^{NC} x_k \dots$$

$$\dots \frac{\sum_l^{NC} x_l \eta_{lk} \sum_j^{NC} a_{ki} \left( \frac{\partial n_j \eta_{jk}}{\partial n_i} \right)_{T, V, nl \neq i}}{\left( \sum_l^{NC} x_l \eta_{lk} \right)^2} \dots$$

$$\dots \frac{\sum_j^{NC} a_{jk} x_j \eta_{jk} \sum_l^{NC} \left( \frac{\partial n_l \eta_{lk}}{\partial n_i} \right)_{T, V, nj \neq i}}{\left( \sum_l^{NC} x_l \eta_{lk} \right)^2}$$
(A13)

$$\left( \frac{\partial n_j \eta_{jk}}{\partial n_i} \right)_{T, V, nl \neq i} = \delta_{ji} \eta_{jk} + x_j \frac{\eta_{jk} E_{jk}^{binary}}{RTv} (m_{jki} - 1)$$

( $m_{jki} = 0$  when  $j = i$  or  $k = i$ )

(A14)

$$\left( \frac{\partial b_m}{\partial n_i} \right)_{T, V, nj \neq i} = 2 \sum_j^{NC} b_{ji} x_j - b_m$$
(A15)

$$\left( \frac{\partial c_m}{\partial n_i} \right)_{T, V, nj \neq i} = 2 \sum_j^{NC} c_{ji} x_j - c_m$$
(A16)

### Appendix 3 The GC-EOS proposed by Skjold-Jørgensen<sup>13)</sup>

The repulsive part of the configurational Helmholtz energy of the GC-EOS is expressed by the Carnahan-Starling equation for hard-sphere mixtures proposed by Mansoori and Leland<sup>7)</sup>:

$$\frac{A_{rep, m}^{conf} - A_m^{conf, ideal}}{RT} = 3 \frac{\lambda_1 \lambda_2}{\lambda_3} (Y - 1) \dots$$

$$\dots + \left( \frac{\lambda_2^3}{\lambda_3^2} \right) (Y^2 - Y - \ln Y) + \ln Y$$
(A17)

$$\lambda_k = \sum_j^{NC} n_j d_j^{hs, k}, Y = (1 - \pi \lambda_3 / 6V)^{-1}$$

The attractive part is the density-dependent NRTL-type expression based on a group contribution model as shown in Eq. (A18).

$$\frac{A_{att, m}^{conf}}{RT} = -\frac{z}{2} \sum_i^{NC} n_i \sum_j^{NG} v_j \sum_k^{NG} (\bar{q} \tau_{ki} / RT) / \sum_i^{NG} \theta_i \tau_{ij}$$
(A18)

where

$$\theta_j = n_j q_j / \bar{q}, \bar{q} = \sum_i^{NC} n_i \sum_j^{NG} v_j q_j$$
(A19)

$$\tau_{ji} = \exp [\alpha_{ji} \Delta g_{ji} \bar{q} / RTv]$$

$$\Delta g_{ji} = g_{ji} - g_{ii}$$

$$g_{ji} = k_{ji} \sqrt{g_{ii} g_{jj}}$$

$$g_{ji} = g_{ji}^* \{ 1 + g_{ji}' (T / T_i^* - 1) + g_{ji}'' \ln (T / T_i^*) \}$$

$$k_{ji} = k_{ji}^* \{ 1 + k_{ji}' \ln (T / T_{ji}^*) \}$$

$$T_{ji}^* = \frac{1}{2} (T_i^* + T_j^*)$$

The temperature dependence of the hard-sphere diameter,  $d$ , is given as follows:

$$d^{hs} = 1.065655 d_c^{hs} \{ 1 - 0.12 \exp (-2 T_c / 3T) \}$$
(A20)

The reference temperature ( $T^*$ ), the attractive interaction energy parameters ( $g^*$ ,  $g'$ ,  $g''$ ) and the number of surface segments ( $q$ ) are the parameters characteristic for each group (group parameters). In the present work, the values of the group parameters, group-group interaction parameters for (–CH<sub>3</sub>) / (CO<sub>2</sub>), (–CH<sub>3</sub>) / (H<sub>2</sub>O) and (–CH<sub>3</sub>) / (–CH<sub>2</sub>OH) pairs and  $d_c^{hs}$  proposed by Skjold-Jørgensen<sup>16)</sup> were used. The values of  $k_{ij}^*$ ,  $\alpha_{ij}$  and  $\alpha_{ji}$  for (–CH<sub>2</sub>OH) / (H<sub>2</sub>O), (–CH<sub>2</sub>OH) / (CO<sub>2</sub>) and (CO<sub>2</sub>) / (H<sub>2</sub>O) pairs were optimized to correlate the experimental data of vapor-liquid equilibria for the ethanol-water system obtained by Pemberton and Mash<sup>13)</sup> at 303K, the carbon dioxide-ethanol data at 293-304K shown in Fig. 2 and those for the carbon dioxide-water system obtained by Wiebe and Gaddy<sup>20)</sup> at 304K respectively. The values of  $k_{ij}'$  for these three pairs were set at zero. The value of each parameter is listed in Table A-2.

### Nomenclature

$A$	= Helmholtz free energy	[kJ/mol]
$a$	= energy parameter	[kJL/mol <sup>2</sup> ]
$b$	= volumetric parameter	[L/mol]
$c$	= volumetric parameter	[L/mol]
$d$	= parameter of eq. (15)	[L/mol]
$d^{hs}$	= hard sphere diameter	[cm/mol]
$E_{ji}$	= energy term in eq. (7)	[kJL/mol <sup>2</sup> ]
$F$	= Parameter of Patel-Teja equation	[-]
$f$	= function in eq. (2)	[mol/L]
$g$	= group interaction parameter	[kJL/mol <sup>2</sup> ]
$K_i$	= K-value	[-]
$k_{ij}$	= binary interaction parameter	[-]
$m_{ijk}$	= ternary non-randomness parameter	[-]
$NC$	= number of components	[-]
$ND$	= number of data	[-]
$NG$	= number of groups	[-]
$n$	= number of molecules	[mol]
$P$	= pressure	[MPa]

$Q$	= parameter of eq. (15)	[L/mol]
$q$	= surface area parameter	[-]
$R$	= gas constant	[kJ/molK]
$S$	= entropy	[kJ/K]
$T$	= temperature	[K]
$V$	= total volume	[L]
$v$	= molar volume	[L/mol]
$x$	= mole fraction in liquid phase	[-]
$y$	= mole fraction in vapor phase	[-]
$Z$	= compressibility coefficient	[-]
$z$	= coordination number	[-] ( $z = 10$ )

$\alpha_{ji}$	= non-randomness parameter	[-]
$\delta_{ji}$	= Kronecker's delta	[-]
$\zeta_c$	= parameter of Patel-Teja equation	[-]
$\eta_{ji}$	= availability factor	[-]
$\theta$	= surface fraction	[-]
$v_j$	= number of group-j in component-i	[-]
$\lambda_{ji}$	= volumetric binary interaction parameter	[-]
$\phi$	= fugacity coefficient	[-]

#### <Subscripts>

$att$	= attractive contribution
$c$	= critical property
$i, j, k$	= component identification number
$m$	= mixture
$r$	= reduced value
$rep$	= repulsive contribution

#### <Superscripts>

binary	= characteristic for binary system
conf	= configurational
ideal	= ideal gas
$\sim$	= total
*	= reference

#### Literature Cited

- Angus, B. Armstrong, K.M. de Reuck, V.V. Altunin, O.G. Gadetskin, G.A. Chapera, J.A. Rowlinson: "International Thermodynamic Tables of the Fluid State Carbon Dioxide", International Union of Pure and Applied Chemistry, pp.656-732, Pergamon Press New York (1987)
- Brignol, E.A., S. Skjold-Jørgensen and Aa. Fredenslund: *Ber. Bunsenges. Phys. Chem.*, **88**, 801-806 (1984)
- Gilbert, M.L., M.E. Paulaitis: *J. Chem. Eng. Data*, **31**, 296-298 (1986)
- Heidemann, R.A. and Aa. Fredenslund: *Chem. Eng. Res. Des.* **67**, 145-158 (1989)
- Hirohama, S., T. Takatuka, S. Miyamoto and T. Muto: *J. Chem. Eng. Japan*, **26**, 247-253 (1993)
- Inomata, H., K. Arai, S. Saito, S. Ohba and K. Takeuchi: *Fluid Phase Equilibria*, **53**, 23-30 (1989)
- Inomata, H., K. Arai, A. Kondo and S. Saito: *J. Chem. Eng. Japan*, **23**, 199-207 (1990)
- Mansoori, G.A., and T.W. Leland: *J. Chem. Soc., Faraday Trans. II*, **68**, 320-344 (1972)
- Martinez, E.O., V. Brandani and G.D. Cabriele: *Fluid Phase Equilibria*, **56**, 325-340 (1990)
- Mollerup, J.: *Fluid Phase Equilibria*, **7**, 121-138 (1981)?
- Mollerup, J. and W.M. Clark: *Fluid Phase Equilibria*, **51**, 257-268 (1989)
- Patel, N.C. and A.S. Teja: *Chem. Eng. Sci.*, **37**, 463-473 (1982)
- Pemberton and C.J. Mash: *J. Chem. Thermodynamics*, **10**, 867-888 (1978)
- Reid, C.R., J.M. Prausnitz and B.E. Poling: "The Properties of Gases and Liquids", 4th ed., pp.656-732, McGraw-Hill New York (1987)
- Peng, D. and D.B. Robinson: *Ind. Eng. Chem. Fundam.*, **15**, 59-64 (1975)
- Skjold-Jørgensen, S.: *Fluid Phase Equilibria*, **16**, 317-351 (1984)
- Soave, G.: *Chem. Eng. Sci.*, **27**, 1119-1203 (1972)
- Takishima, S., K. Saiki, K. Arai and S. Saito: *J. Chem. Eng. Japan*, **19**, 48-56 (1986)
- Whitting, W.B. and J.M. Prausnitz: *Fluid Phase Equilibria*, **9**, 119-147 (1982)
- Wiebe, R. and V.L. Gaddy: *J. Am. Chem. Soc.*, **62**, 815-817 (1940)
- Wiebe, R. and V.L. Gaddy: *J. Am. Chem. Soc.*, **63**, 475-477 (1941)