

# PHASE EQUILIBRIUM STUDY OF THE SEPARATION OF ETHANOL-WATER SOLUTION WITH SUPERCRITICAL CO<sub>2</sub>

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To provide a better theoretical basis for obtaining higher concentration of ethanol from a fermentation broth using near- or super-critical CO<sub>2</sub> extraction, the vapor-liquid equilibria for the quaternary system of CO<sub>2</sub>, ethanol, water and an entrainer were measured at 35.0°C and 10 MPa for various entrainer concentrations. Experiments were carried out for four entrainers: glycerol, ethylene glycol, 1,3-propanediol and propylene glycol. The experimental results demonstrated that the upper limit of ethanol composition for the CO<sub>2</sub>-ethanol-water ternary system could be raised by the addition of the above entrainers other than propylene glycol. It was also found that this effect of the entrainer could be estimated qualitatively from its solubility parameter value. The group parameter values of the GC-EOS by Jørgensen were redetermined using binary vapor-liquid equilibrium (VLE) data in order to improve the accuracy of prediction of the VLE of the CO<sub>2</sub>-ethanol-water and the CO<sub>2</sub>-ethanol-water-entrainer mixtures.

## Introduction

Supercritical fluid extraction of ethanol from aqueous fermentation solutions has several attractive aspects as an ethanol recovery process. Although a number of workers have reported experimental data for the carbon dioxide-ethanol-water system (Paulaitis *et al.*<sup>1,4</sup>); Moses *et al.*<sup>1,2</sup>); Kuk and Montagna<sup>10</sup>), no definite conclusions have been reached as to its applicability. This is partly attributable to the scarcity of phase equilibrium data and the lack of reliable prediction methods.

In a previous paper<sup>17</sup>) we reported on phase equilibrium data for the CO<sub>2</sub>-ethanol-water system at 31° and 35°C. Our results, like those of other researchers, indicated that it was not possible to exceed the ethanol-water azeotropic composition (89.4 mol%) for atmospheric distillation with a simple CO<sub>2</sub> extraction around room temperature. The reason for this may be that the distribution coefficient of ethanol between the CO<sub>2</sub> and water phases has a low value around room temperature because ethanol has a high degree of affinity for water despite its high solubility in CO<sub>2</sub>.

There are two possible methods of breaking the azeotropic limit. One is the change of extraction temperature and pressure. Furuta *et al.*<sup>5</sup>) investigated experimentally and reported that an ethanol solution of more than 90 mol% could be obtained by extraction

with CO<sub>2</sub> at 60°C and 10 MPa. Another method is the use of an entrainer or cosolvent to bring about greater separation than can a single solvent (CO<sub>2</sub>). Moses *et al.*<sup>1,2</sup>) of Arthur D. Little Inc. tested the entrainer effect of several alcohols and reported an evident increase in the distribution coefficient of ethanol but not breaking the azeotropic point, while Fukuzato *et al.*<sup>4</sup>) pointed out that an ethanol solution above azeotropic concentration could be obtained by the use of glycerol as an entrainer in CO<sub>2</sub> extraction.

In this work, we measured vapor-liquid equilibria for CO<sub>2</sub>-ethanol-water-entrainer systems at 35°C and 10 MPa and investigated the effects of entrainers on ethanol-water separation with supercritical CO<sub>2</sub>. Furthermore, the applicability of a group-contribution equation of state (GC-EOS) proposed by Jørgensen<sup>1,15</sup>) to the phase equilibrium calculation was examined.

## 1. Experimental Section

### 1.1 Materials

As entrainers, we used polyols such as glycerol, ethylene glycol, propylene glycol and 1,3-propanediol which are considered to have a strong affinity for water.

Ethanol of a purity of 99.5 vol% supplied by Wako Pure Chemical Ind. Co., Ltd. and liquefied CO<sub>2</sub> of a purity of 99.9 vol% supplied by Nippon Sanso K.K. were used without further purification. Water was ion-exchanged and purified by distillation. The glycerol, ethylene glycol, propylene glycol and

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1,3-propanediol, supplied by Wako Pure Chemical Ind. Co., Ltd., were of 98.0 vol% purity and were used without further purification.

## 1.2 Apparatus and procedure

For the phase equilibrium measurements, this work adopted a flow-type apparatus. As shown in Fig. 1, the apparatus has an overflow type liquid level-control system equipped with a back-pressure regulator. The apparatus and experimental procedure are almost the same as those discussed elsewhere<sup>7)</sup> except for employing a cooling jacket in the preheater zone and a gas chromatograph for composition analysis.

An ethanol-water-entrainer mixture of a desired composition was compressed and mixed with a stream of CO<sub>2</sub> by a pump, and this heterogeneous mixture was heated or cooled to the experimental temperature in the cooling jacket and preheater zone. Then it was allowed to flow into a static mixer which was used to ascertain the attainment of equilibrium, and the equilibrated phases were separated in a cell. The liquid-phase stream from the bottom of the cell was decompressed through a metering valve and the liquid portion (ethanol-water-entrainer solution) was trapped in a sampler, while the gas portion (mainly CO<sub>2</sub>) flowed into a gas cylinder. The trapped amounts were determined gravimetrically and volumetrically and the compositions were analyzed by a gas chromatograph with TCD. The equilibrium composition of the liquid phase was determined from these quantities. The equilibrium composition of the vapor-phase stream from the top of the cell was determined in the same way as that of the liquid phase.

The temperature of the cell was measured by a chromel-alumel thermocouple calibrated against IPTS-68. The cell was maintained at a constant pressure by the back-pressure regulator and measured by a Nagano Keiki precise bourdon gauge. The chromatographic peaks were analyzed with a commercial electronic integrator. The column arrangements of gas chromatography are listed in Table 1.

## 1.3 Experimental conditions

We measured vapor-liquid equilibria for the CO<sub>2</sub>-ethanol-water-entrainer quaternary systems at 35°C and 10 MPa for comparison with the CO<sub>2</sub>-ethanol-water ternary system. Measurement was performed at various concentrations of entrainer in the feed ethanol-water-entrainer solution, as shown in Table 2.

## 1.4 Experimental results

To test the reliability of the experimental apparatus and procedure, we first measured vapor-liquid equilibria for the CO<sub>2</sub>-ethanol-water ternary system, for which reliable experimental data are readily available. The measured data are listed in Table 3. Agreement between our data and those of Paulaitis *et al.*<sup>14)</sup> and Takishima *et al.*<sup>17)</sup> is good to within 0.002

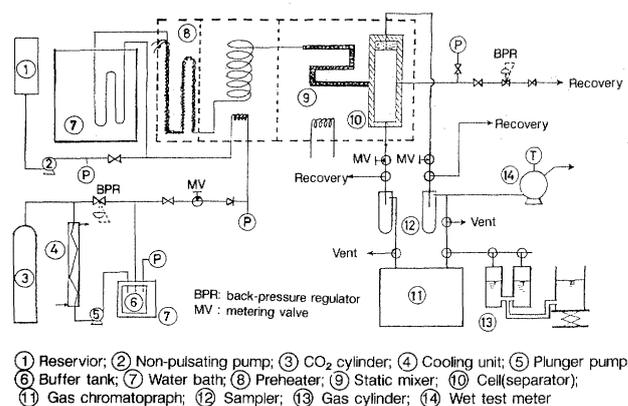


Fig. 1. Schematic diagram of experimental apparatus  
 ① Reservoir; ② Non-pulsating pump; ③ CO<sub>2</sub> cylinder; ④ Cooling unit; ⑤ Plunger pump; ⑥ Buffer tank; ⑦ Water bath; ⑧ Preheater; ⑨ Static mixer; ⑩ Cell(separator); ⑪ Gas chromatograph; ⑫ Sampler; ⑬ Gas cylinder; ⑭ Wet test meter

Fig. 1. Schematic diagram of experimental apparatus

Table 1. Column arrangement for gas chromatograph analysis

Carrier Gas: Helium		
Column		
1) PEG600	<SUS φ3 mm × 2.5 m>	(CO <sub>2</sub> , ethanol, water)
	Column 120°C	Detection 150°C Injection 150°C
2) Porapak Q	<SUS φ3 mm × 2.5 m>	(propylene glycol, 1,3-propanediol)
	Column 120°C	Detection 150°C Injection 150°C
3) Porapak P	<Glass φ3 mm × 2 m>	(glycerol, ethylene glycol)
	Column 200°C	Detection 260°C Injection 260°C

Table 2. Experimental conditions

	Temperature: 308 K	Pressure: 10 MPa
System	Entrainer concentration of feed solution (mol%)	
CO <sub>2</sub> -ethanol-water	0	
CO <sub>2</sub> -ethanol-water-glycerol	5, 15, 25	
CO <sub>2</sub> -ethanol-water-ethylene glycol	5, 15, 25	
CO <sub>2</sub> -ethanol-water-propylene glycol	5, 25	
CO <sub>2</sub> -ethanol-water-1,3-propanediol	25	

Table 3. Vapor-liquid equilibrium data for the CO<sub>2</sub>-ethanol-water system

Temp. (K)	Pres. (MPa)	Mole fraction			Phase
		CO <sub>2</sub>	EtOH	H <sub>2</sub> O	
107.8	10.2	0.9816	0.0140	0.0044	vap
		0.0225	0.0365	0.9410	liq
307.6	10.1	0.9547	0.0365	0.0089	vap
		0.0548	0.2108	0.7344	liq
308.0	10.2	0.9368	0.0510	0.0121	vap
		0.1406	0.3431	0.5162	liq
308.1	10.2	0.9042	0.0760	0.0198	vap
		0.2890	0.3846	0.3264	liq
308.0	10.2	0.8647	0.1047	0.0307	vap
		0.3816	0.4008	0.2175	liq

**Table 4.** Vapor-liquid equilibrium data for the CO<sub>2</sub>-ethanol-water-glycerol (GLY) system

Temp. (K)	Pres. (MPa)	Conc. of entrainer in feed	Mole fraction				Phase
			CO <sub>2</sub>	EtOH	H <sub>2</sub> O	GLY	
308.0	10.2		0.9667	0.0260	0.0072	0.0072	vap
			0.0259	0.0908	0.8292	0.0541	liq
307.8	10.2		0.9452	0.0444	0.0103	0.0001	vap
			0.0412	0.1851	0.7194	0.0544	liq
307.6	10.2		0.9375	0.0501	0.0123	0.0001	vap
			0.0149	0.2660	0.6667	0.0523	liq
307.6	10.2	5 mol%	0.9092	0.0680	0.0220	0.0008	vap
			0.1727	0.3670	0.4134	0.0469	liq
307.6	10.2		0.9301	0.0592	0.0103	0.0004	vap
			0.1536	0.3446	0.4519	0.0499	liq
308.4	10.2		0.4378	0.3737	0.1593	0.0292	vap
			0.1779	0.4040	0.3852	0.0330	liq
308.1	10.2		0.6145	0.2653	0.1026	0.0176	vap
			0.3595	0.4342	0.1702	0.0360	liq
308.1	10.2		0.8908	0.0877	0.0212	0.0004	vap
			0.3211	0.4112	0.2231	0.0447	liq
307.7	10.2		0.9734	0.0164	0.0100	0.0002	vap
			0.0287	0.0703	0.7504	0.1507	liq
308.4	10.1		0.9613	0.0313	0.0692	0.0004	vap
			0.0412	0.1531	0.6496	0.1561	liq
308.0	10.1	15 mol%	0.9259	0.0594	0.0128	0.0019	vap
			0.0966	0.2815	0.4470	0.1750	liq
307.7	10.2		0.9130	0.0726	0.0135	0.0010	vap
			0.1404	0.3398	0.3415	0.1784	liq
308.1	10.2		0.8837	0.0985	0.0162	0.0017	vap
			0.1812	0.3904	0.2494	0.1790	liq
308.0	10.2		0.8348	0.1426	0.0209	0.0016	vap
			0.3310	0.4485	0.0799	0.1406	liq
308.7	10.2		0.9842	0.0094	0.0054	0.0010	vap
			0.0448	0.0432	0.6544	0.2576	liq
308.1	10.1		0.9798	0.0153	0.0049	0.0000	vap
			0.0264	0.0661	0.6871	0.2204	liq
308.0	10.1		0.9605	0.0349	0.0044	0.0002	vap
			0.0532	0.1834	0.5218	0.2416	liq
307.8	10.2		0.9646	0.0306	0.0047	0.0001	vap
			0.0461	0.1704	0.5510	0.2325	liq
307.8	10.2	25 mol%	0.9410	0.0520	0.0065	0.0005	vap
			0.0826	0.2604	0.4081	0.2490	liq
308.0	10.3		0.9378	0.0561	0.0057	0.0004	vap
			0.1161	0.3235	0.3233	0.2371	liq
307.6	10.2		0.9117	0.0811	0.0054	0.0017	vap
			0.1337	0.3520	0.2079	0.3063	liq
307.9	10.3		0.8979	0.0956	0.0059	0.0007	vap
			0.2123	0.4225	0.1147	0.2505	liq
307.9	10.1		0.8999	0.0923	0.0047	0.0031	vap
			0.1770	0.3994	0.1458	0.2778	liq
308.3	10.1		0.8794	0.1134	0.0037	0.0034	vap
			0.2714	0.4177	0.0655	0.2455	liq

mole fraction in vapor and liquid phases.

We then measured the CO<sub>2</sub>-ethanol-water-entrainer quaternary system at 35°C and 10 MPa while maintaining constant feed entrainer concentration. The raw experimental data are listed in **Tables 4 to 7**. It is noted that the entrainer exists mostly in liquid phase because of its very low vapor pressures. **Figure 2** shows vapor-liquid equilibria for the CO<sub>2</sub>-ethanol-water-glycerol system at 308 K and 10 MPa on a

glycerol-free basis. For comparison, the binodal line for the CO<sub>2</sub>-ethanol-water ternary system is also shown. The binodal region of the quaternary system is larger than that of the ternary system and its plait point seems to vanish with the addition of over 15 mol% glycerol. This additive effect is probably in proportion to the amount of glycerol present. For ethylene glycol and 1,3-propanediol, similar results were obtained. However, as shown in **Fig. 3**, a small

**Table 5.** Vapor-liquid equilibrium data for the CO<sub>2</sub>-ethanol-water-ethylene glycol (EG) system

Temp. (K)	Pres. (MPa)	Conc. of entrainer in feed	Mole fraction				Phase	
			CO <sub>2</sub>	EtOH	H <sub>2</sub> O	EG		
308.1	10.2	5 mol%	0.9778	0.0167	0.0053	0.0000	vap	
			0.0321	0.0774	0.8464	0.0441	liq	
308.2	10.0		0.9495	0.0406	0.0098	0.0001	vap	
			0.0751	0.2387	0.6408	0.0453	liq	
308.4	10.0		0.9506	0.0401	0.0088	0.0005	vap	
			0.1680	0.3458	0.4441	0.0422	liq	
308.5	10.0		0.9058	0.0734	0.0185	0.0023	vap	
			0.3552	0.3859	0.2060	0.0330	liq	
308.2	10.1		0.6946	0.2570	0.0317	0.0168	vap	
			0.6675	0.2840	0.0334	0.0152	liq	
307.3	10.1	15 mol%	0.9832	0.0127	0.0040	0.0001	vap	
			0.0322	0.0750	0.7560	0.1360	liq	
308.3	10.0		0.9634	0.0300	0.0062	0.0004	vap	
			0.0715	0.2157	0.5830	0.1298	liq	
308.4	10.0		0.9527	0.0385	0.0075	0.0014	vap	
			0.1650	0.3292	0.3775	0.1284	liq	
308.9	10.0		0.9229	0.0634	0.0099	0.0039	vap	
			0.2947	0.4009	0.2022	0.1022	liq	
308.2	10.2		25 mol%	0.9903	0.0058	0.0038	0.0001	vap
				0.0370	0.0644	0.6704	0.2283	liq
309.2	10.0	0.9778		0.0183	0.0034	0.0006	vap	
		0.0832		0.2085	0.4979	0.2105	liq	
308.3	10.1	0.9617		0.0308	0.0051	0.0024	vap	
		0.1726		0.3234	0.3025	0.2016	liq	
308.6	10.2	0.9349		0.0434	0.0116	0.0101	vap	
		0.3058		0.3681	0.1368	0.1893	liq	
307.2	10.2	0.9453		0.0470	0.0044	0.0034	vap	
		0.2688		0.3702	0.1457	0.2154	liq	

**Table 6.** Vapor-liquid equilibrium data for the CO<sub>2</sub>-ethanol-water-propylene glycol (PG) system

Temp. (K)	Pres. (MPa)	Conc. of entrainer in feed	Mole fraction				Phase	
			CO <sub>2</sub>	EtOH	H <sub>2</sub> O	PG		
306.3	9.9	5 mol%	0.9519	0.0386	0.0095	0.0001	vap	
			0.2081	0.3439	0.4114	0.0367	liq	
306.2	10.2		0.8892	0.0848	0.0224	0.0036	vap	
			0.3668	0.3426	0.2412	0.0494	liq	
306.2	10.3		0.9375	0.0501	0.0122	0.0002	vap	
			0.0720	0.2180	0.6688	0.0412	liq	
306.3	9.9		25 mol%	0.9519	0.0386	0.0095	0.0001	vap
				0.2081	0.3439	0.4114	0.0367	liq
306.2	10.2			0.8892	0.0848	0.0224	0.0036	vap
				0.3668	0.3426	0.2412	0.0494	liq
306.2	10.3	0.9375		0.0501	0.0122	0.0002	vap	
		0.0720		0.2180	0.6688	0.0412	liq	

reduction of the binodal region is seen for the propylene glycol system. **Figure 4** shows the ethanol concentrations in the liquid and vapor phases of four quaternary systems on a CO<sub>2</sub>- and entrainer-free basis. This figure indicates that it is glycerol that gives the highest concentration of ethanol among these four entrainers. The order is as follows:

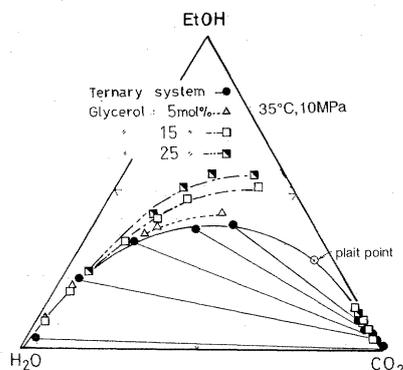
glycerol > ethylene glycol ≈ 1,3-propanediol  
> propylene glycol

The separation factor  $\alpha$  of ethanol against water, the selectivity of extraction, is defined by the ratio of the distribution coefficient of ethanol to that of water:

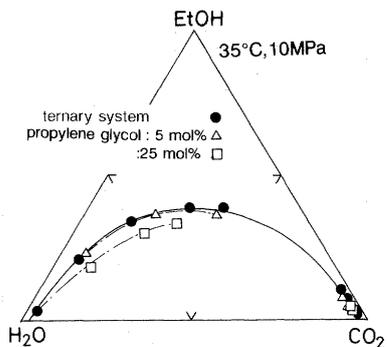
$$\alpha = (y_{ethanol}/x_{ethanol}) / (y_{water}/x_{water})$$

**Table 7.** Vapor-liquid equilibrium data for the CO<sub>2</sub>-ethanol-water-1,3-propanediol (13-PD) system

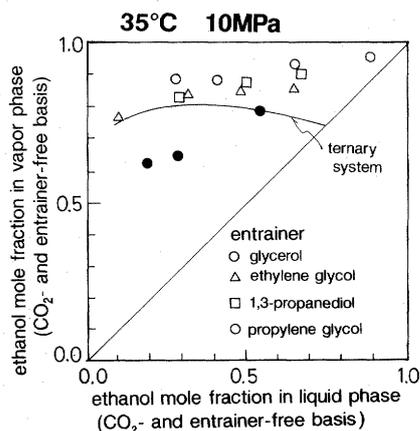
Temp. (K)	Pres. (MPa)	Conc. of entrainer in feed	Mole fraction				Phase
			CO <sub>2</sub>	EtOH	H <sub>2</sub> O	13-PD	
304.1	10.1		0.9832	0.0133	0.0034	0.0001	vap
			0.0939	0.1959	0.4911	0.2191	liq
304.1	10.1	25 mol%	0.9480	0.0465	0.0044	0.0011	vap
			0.2414	0.3724	0.1871	0.1991	liq
304.1	10.1		0.9669	0.0289	0.0040	0.0001	vap
			0.1593	0.3084	0.3292	0.2031	liq



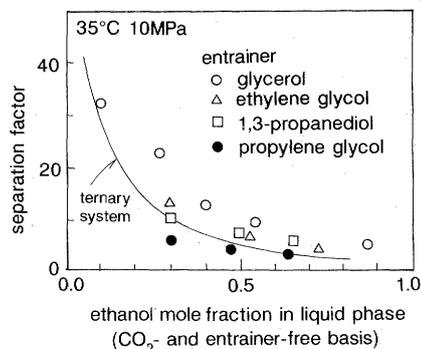
**Fig. 2.** Vapor-liquid equilibria for CO<sub>2</sub>-ethanol-water-glycerol system at 35°C and 10 MPa (compositions are on glycerol-free basis)



**Fig. 3.** Vapor-liquid equilibria for CO<sub>2</sub>-ethanol-water-propylene glycol system at 35°C and 10 MPa (compositions are on propylene glycol-free basis)



**Fig. 4.** Ethanol concentrations in vapor and liquid phases for CO<sub>2</sub>-ethanol-water-entrainer systems



**Fig. 5.** Separation factor of ethanol

where  $y_i$  and  $x_i$  are the mole fractions of component  $i$  in the vapor and liquid phases respectively. **Figure 5** shows the separation factor evaluated from the experimental data. The order given above for entrainers is confirmed by this figure. As a result, among the four entrainers used in this study, glycerol provides the highest selectivity for the separation of ethanol from aqueous solutions. It can be considered that the number and the bonded position of hydroxyl group in an entrainer molecule play a very important role in the interaction between the entrainer and water. Therefore the three hydroxyl groups of glycerol may contribute to its strong affinity for water.

A well-known physical property characterizing affinity is the solubility parameter " $\delta$ ". It can be said that a good solvent for a certain solute has a solubility parameter value close to that of the solute. The values of solubility parameters of CO<sub>2</sub>, ethanol, water and entrainers are listed in **Table 8**. Glycerol, ethylene glycol and 1,3-propanediol have intermediate values between those of water and ethanol, while propylene glycol has a  $\delta$ -value similar to that of ethanol. So glycerol has the highest affinity with water in liquid phase and propylene glycol the lowest. Then the order of  $\delta$ -values of the entrainers is the same as that based on the separation factor as mentioned above.

## 2. VLE Calculation with an Equation of State

Vapor-liquid equilibria for the CO<sub>2</sub>-ethanol-water and CO<sub>2</sub>-ethanol-water-entrainer systems were predicted using a group contribution equation of state

**Table 8.** Values of solubility parameter ( $\delta$ )

Substance	$\delta$ -value
Carbon dioxide	13.3
Ethanol	26.0
Water	47.9
Glycerol	33.8
Ethylene Glycol	29.9
1,3-Propanediol*	28.2
Propylene Glycol	25.8

\* Estimated by Van Krevelen method.

(GC-EOS) proposed by Jørgensen *et al.*<sup>1,15)</sup>

### 2.1 Group contribution equation of state (GC-EOS)

In the derivation of GC-EOS, the residual Helmholtz free energy is expressed by the sum of two contributions:

$$A^R = A_{rep}^R + A_{att}^R \quad (1)$$

where the repulsive term is described by the Carnahan-Starling equation for hard sphere mixtures proposed by Mansoori and Leland.<sup>11)</sup>

$$(A^R/RT)_{rep} = 3(\lambda_1\lambda_2/\lambda_3)(Y-1) + (\lambda_2^3/\lambda_3^2)(Y^2 - Y - \ln Y) + n \ln Y \quad (2)$$

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

The attractive term is the density-dependent NRTL-type expression based on a group contribution model as shown in Eq. (3).

$$(A^R/RT)_{att} = -Z/2 \sum_i^{NC} n_i \sum_j^{NG} v_j^i q_j \sum_k^{NG} \theta_k (q_{kj} \tilde{q}_{kj} / RTV) \left/ \sum_i^{NG} \theta_i \tau_{ij} \right. \quad (3)$$

where

$$\theta_j = n_j q_j / \tilde{q}, \quad \tilde{q} = \sum_i^{NC} n_i \sum_j^{NG} v_j^i q_j$$

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

$$\tau_{ji} = \exp[\alpha_{ij} \Delta g_{ji} \tilde{q} / RTV]$$

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

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

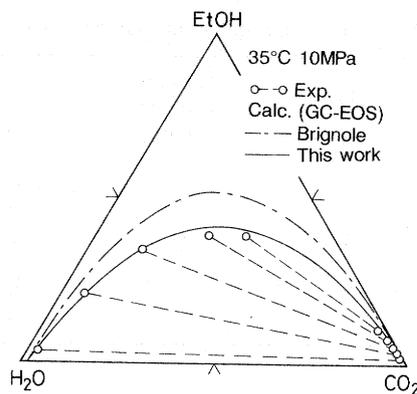
$$k_{ji} = k_{ji}^* \{1 + k_{ji}' \ln(T/T_{ji}^*)\}$$

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

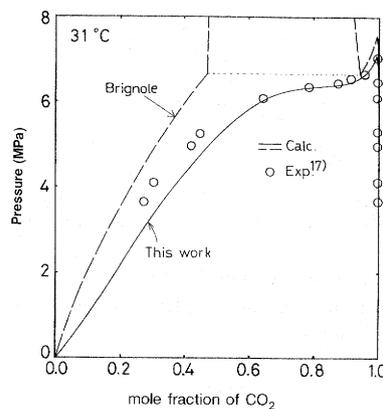
The temperature dependence of hard sphere diameter,  $d$ , is given as follows:

$$d = 1.065655 d_c \{1 - 0.12 \exp(-2T_c/3T)\} \quad (4)$$

The hard sphere diameter at critical temperature ( $T_c$ ),



**Fig. 6.** Comparison between calculated and experimental vapor-liquid equilibria for CO<sub>2</sub>-ethanol-water system



**Fig. 7.** Comparison between calculated and experimental vapor-liquid equilibria for CO<sub>2</sub>-ethanol system

$d_c$ , is usually given by the following equation:

$$d_c = (0.08943 RT_c / P_c)^{1/3} \quad (5)$$

The group parameters of GC-EOS are the reference temperature ( $T^*$ ), the attractive interaction energy parameters ( $g^*$ ,  $g'$ ,  $g''$ ), the number of surface segments ( $q$ ), the binary nonrandomness parameter ( $\alpha_{ij}$ ), and the  $i$ - $j$  group pair interaction parameter ( $k_{ij}$ ). In this study, we used the values of group parameters proposed by Brignole *et al.*<sup>2)</sup>

### 2.2. Calculation results of GC-EOS

**Figure 6** shows the predicted result and experimental vapor-liquid equilibria for the CO<sub>2</sub>-ethanol-water system at 35°C and 10 MPa. The result predicted from Brignole's original parameters is shown as a dashed line. The deviation between predicted and experimental compositions is quite considerable. To find the reason for this disagreement we then predicted vapor-liquid equilibria for binary systems composed of CO<sub>2</sub>, ethanol and water. Although the deviations for the CO<sub>2</sub>-water and the water-ethanol systems are fairly small, that for the CO<sub>2</sub>-ethanol system is larger, as shown in **Fig. 7**. It was also found that the calculated phase diagram showed a three-phase equilibrium (vapor-liquid-liquid) whereas experimental observa-

tion did not. This may be due to the choice of data used in determining the group parameters. Therefore, in the present work we redetermined the parameter set of GC-EOS to improve the prediction accuracy of the mixtures of CO<sub>2</sub>, ethanol, water and entrainer.

**Table 9.** Group parameters of GC-EOS

Group		$T^*$	$q$	$g^*$	$g_1$	$g_2$
1	-CH <sub>3</sub>	600.0	0.848	316910	-0.9274	0.0
2	-CH <sub>2</sub>	600.0	0.540	356080	-0.8755	0.0
3	CH <sub>3</sub> OH	512.6	1.432	1109600	-0.9474	0.0
4	-CH <sub>2</sub> OH	512.6	1.124	1207500	-0.6502	0.0
5	-CHOH	512.6	0.908	1207500	-0.6502	0.0
6	CO <sub>2</sub>	304.2	1.261	531890	-0.5780	0.0
7	H <sub>2</sub> O	647.3	0.866	1689200	-0.6925	0.0

**Table 10.** Binary systems used for parameter optimization

System	T-range [K]	P-range [MPa]	AAD* (%)		Ref
			Optimized	Brignole	
CO <sub>2</sub> -methanol	298.15-313.15	0.8-8.0	2.34	5.46	13)
CO <sub>2</sub> -ethanol	291.15-333.15	2.1-8.9	2.31	3.46	17)
CO <sub>2</sub> -water	297.80-323.15	0.6-20.0	0.25	0.10	19)
CO <sub>2</sub> -propanol	313.15	0.8-8.0	1.68	3.95	16)
CO <sub>2</sub> -2-propanol	308.75-333.15	1.6-8.3	12.1	10.7	*)
methanol-water	373.15-523.15	0.2-7.5	1.94	10.2	5)
methanol-2-propanol	340.60-352.53	0.1	0.60	30.5	18)
methanol-butanol	344.15-375.15	0.1	2.54	12.4	6)
ethanol-water	298.15-423.15	0.04-1.0	6.75	3.60	3)
propanol-water	360.77-367.90	0.1	13.56	3.85	20)
water-propylene glycol	373.15-414.15	0.1	1.88	5.19	8)

$$AAD = \frac{100}{N} \sum \{|x_i^{EXP} - x_i^{CALC}| + |y_i^{EXP} - y_i^{CALC}|\} / 2$$

\*) : See Appendix.

**Table 11.** Optimized group-group parameters of GC-EOS ( $K'_{ij} \setminus K^*_{ij}$ )

	-CH <sub>3</sub>	-CH <sub>2</sub>	CH <sub>3</sub> OH	-CH <sub>2</sub> OH	-CHOH	CO <sub>2</sub>	H <sub>2</sub> O
-CH <sub>3</sub>	—	0.8954	0.9544	0.6644	0.7453	0.3532	0.2901
-CH <sub>2</sub>	-0.6636	—	0.6414	0.7840	0.7463	0.7477	0.5609
CH <sub>3</sub> OH	0.5349	-0.0989	—	1.0971	1.1689	0.9850	0.9819
-CH <sub>2</sub> OH	-0.0229	0.4001	0.3201	—	1.0082	0.7658	0.9607
-CHOH	0.0844	0.6972	0.3994	0.0186	—	0.9850	0.5221
CO <sub>2</sub>	-0.0845	-0.3986	0.0000	0.2779	0.0000	—	0.8563
H <sub>2</sub> O	-1.0374	0.0000	-0.0592	-0.1456	-2.7920	-0.0477	—

( $\alpha_{ij}$ )	-CH <sub>3</sub>	-CH <sub>2</sub>	CH <sub>3</sub> OH	-CH <sub>2</sub> OH	-CHOH	CO <sub>2</sub>	H <sub>2</sub> O
-CH <sub>3</sub>	—	0.0000	1.4785	1.5400	1.4710	5.6431	6.4382
-CH <sub>2</sub>	0.0000	—	1.4227	1.4710	1.4710	3.3690	0.6370
CH <sub>3</sub> OH	4.8296	-1.4280	—	-4.0461	0.0000	-0.4276	1.3124
-CH <sub>2</sub> OH	14.3122	10.2200	-1.6699	—	-10.4766	8.0963	-1.7927
-CHOH	10.2200	10.2200	0.0000	5.0659	—	-0.3900	-1.9330
CO <sub>2</sub>	3.9855	3.3690	0.0741	0.8436	0.4680	—	0.2063
H <sub>2</sub> O	1.8927	0.6370	1.6760	-1.0684	-1.9330	0.7149	—

### 2.3 Redetermination of parameters

The present study considers only the seven groups, "CO<sub>2</sub>", "H<sub>2</sub>O", "-CH<sub>3</sub>", "-CH<sub>2</sub>", "-CHOH", "-CH<sub>2</sub>OH", and "CH<sub>2</sub>OH" necessary for the phase equilibrium prediction for the mixtures of CO<sub>2</sub>, ethanol, water and entrainer, and also reduces the number of parameters to be redetermined. That is, the pure group parameters ( $T^*$ ,  $q$ ,  $g^*$ ,  $g'$ ,  $g''$ ) were not revised, that is, the original values presented in **Table 9** were used. The binary nonrandomness parameters ( $\alpha_{ij}$ ) and the binary interaction parameters ( $k_{ij}^*$ ,  $k_{ij}'$ ) were optimized in this work by fitting the vapor-liquid equilibrium data of the eleven binary systems shown in **Table 10**. The parameter values determined are summarized in **Table 11**. The  $d_c$  values have been determined using normal boiling point and saturated

**Table 12.** Correlation results for saturated vapor pressure

Substance	<i>T</i> (K)	<i>P</i> (MPa)	<i>d<sub>c</sub></i>	No. of data	<i>AAD</i> * (%)
Carbon dioxide	216–304	0.05 – 7.3	3.1247	17	2.044
methanol	260–510	0.0016– 7.5	3.6462	26	0.826
ethanol	260–510	0.0006– 5.7	3.9062	26	3.075
1-propanol	290–530	0.0016– 4.6	4.2879	25	1.752
2-propanol	300–510	0.0063– 5.0	4.3185	22	5.718
1-butanol	290–550	0.0005– 3.6	4.6161	27	2.445
2-butanol	280–520	0.0005– 3.4	4.2849	25	0.610
water	273–647	0.0006–22.0	2.7721	25	1.522
ethylene glycol	326–470	0.0001– 0.1	4.2250	10	4.107
propylene glycol	319–461	0.0001– 0.1	3.6366	10	8.654
1,3-propanediol	333–446	0.0001– 0.03	4.5770	8	11.194
glycerol	399–563	0.0001– 0.1	4.8823	10	6.943

$$AAD = \frac{100}{N} \sum |P_i^{EXP} - P_i^{CALC}| / P_i^{EXP}$$

vapor pressure data for each pure component. The obtained  $d_c$  values are listed in **Table 12**, and are found to be very close to those from Eq. (5). The average absolute deviations for vapor pressures of each pure substance are also presented in Table 12.

#### 2.4 Calculation results with optimized parameters

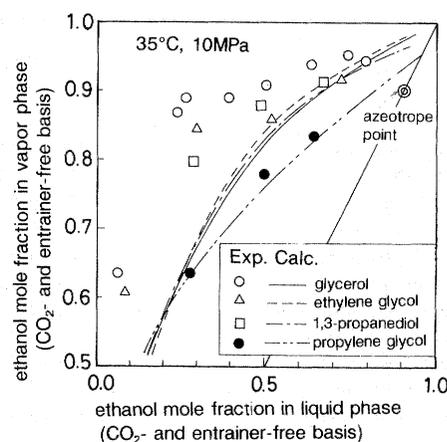
Table 10 compares the correlated results for binary systems using the optimized parameters with those of Brignole's original parameters.<sup>2)</sup> Using the optimized parameters the average absolute deviations are reduced to within 5 mol% for most of the systems examined. For the CO<sub>2</sub>-ethanol system, the GC-EOS with the optimized parameters correlate the experimental data well even at region near the critical point as shown in Fig. 7. For other systems presented in Table 10, similar results have been obtained.

Figure 6 shows a comparison between the GC-EOS predictions and experimental vapor-liquid equilibria for the CO<sub>2</sub>-ethanol-water ternary system. The prediction accuracy of the GC-EOS is also improved by the optimization of parameters.

We then calculated phase equilibria for the quaternary systems in order to examine the effect of the entrainers on supercritical CO<sub>2</sub> extraction of ethanol. **Figure 8** shows the predicted ethanol concentration in liquid and vapor phases on a CO<sub>2</sub>- and entrainer-free basis at 35°C and 10 MPa. Although prediction represents a qualitative behavior exceeding the azeotropic composition afforded by the use of entrainers, the agreement between the experimental and predicted results has still not been improved. This may result from the basic assumption of the group contribution model that the contribution by one group is independent of that by another group.

#### Conclusions

Vapor-liquid equilibria for quaternary systems of



**Fig. 8.** Comparison between calculated and experimental ethanol concentration in vapor and liquid phases for CO<sub>2</sub>-ethanol-water-entrainer systems

CO<sub>2</sub>, ethanol, water and entrainers (glycerol, ethylene glycol, 1,3-propanediol and propylene glycol) were measured at 35°C and 10 MPa. It was found that the addition of the entrainers except for propylene glycol could vanish the plait point observed for the CO<sub>2</sub>-ethanol-water ternary system and provide higher concentration of ethanol exceeding the azeotropic composition of ethanol-water.

The parameter tables for GC-EOS were revised for the prediction of supercritical CO<sub>2</sub> extraction of ethanol from aqueous solutions. Using the revised parameters, it is possible to predict and correlate the vapor-liquid equilibria for the CO<sub>2</sub>-ethanol-water system and its related binary mixtures at room temperatures. However, the prediction accuracy for the quaternary systems including a polyol as an entrainer is still unsatisfactory and needs improving.

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## Appendix

The raw VLE data for the CO<sub>2</sub>-2-propanol system are listed in Table A-1.

### Nomenclature

$A^R$	= residual Helmholtz free energy
$d$	= hard sphere diameter
$g$	= interaction parameter
$k_{ij}$	= binary interaction parameter of groups $i$ and $j$
$n$	= total number of moles
$NC$	= total number of components
$NG$	= total number of groups
$P$	= pressure
$q$	= surface area parameter
$R$	= gas constant
$T$	= temperature
$V$	= total volume
$x$	= mole fraction in liquid phase
$y$	= mole fraction in vapor phase
$z$	= coordination number ( $z=10$ )
$\alpha$	= separation factor
$\alpha_{ij}$	= nonrandomness parameter
$\theta$	= surface fraction
$v_j^i$	= number of group- $j$ in component $i$

### <Subscripts>

$att$	= contribution from attractive forces
$c$	= critical property
$rep$	= contribution from repulsive forces

### <Superscripts>

$\sim$	= total
*	= reference

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**Table A-1.** Vapor-liquid equilibrium data for the CO<sub>2</sub>-2-propanol system

Temp. (K)	Press. (MPa)	Mole fraction of CO <sub>2</sub>	
		Vapor	Liquid
309.95	4.94	0.9932	0.5954
308.95	3.73	0.9939	0.4519
308.75	2.39	0.9934	0.2812
333.15	6.06	0.9798	0.5523
332.55	3.73	0.9787	0.3727
332.65	1.60	0.9775	0.1366

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