MEASUREMENT AND PREDICTION OF PHASE EQUILIBRIA FOR THE
CO_2-ETHANOL-WATER SYSTEM

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ABSTRACT

    In relation to the concentration of ethanol solution from fermentation using near- or super-critical CO_2 extraction, vapor-liquid equilibria for the CO_2-Ethanol-Water system were measured at 9.6, 17.2, 19.6, 25.0 and 32.0 °C up to 9 MPa in the wide range of ethanol concentration, including very dilute region (0.1-5wt%) , where no data have been reported. A flow type apparatus equipped with a back pressure regulator was adopted for measurements in order to maintain the feed composition. From our experimental results, we concluded that,
1) There are certain T and P conditions which give a maximum separation factor.
2) In the low concentration region of ethanol, the distribution coefficient of ethanol is about 2/3 of the value in the higher ethanol concentration region.
The measured data were compared with the results predicted by Patel-Teja equation and Group-Contribution equations of state (GC-EOS).

INTRODUCTION
    Supercritical fluid extraction of ethanol from the fermentation aqueous solutions has several attractive aspects as an ethanol recovery process and has been studied by many researchers in this decade. However, definite conclusion has not been made on its applicability. This is partly attributed to the scarcity of phase equilibrium data and the lack of reliable

prediction methods.

In a previous paper (Takishima et al. 1986), we reported phase equilibrium data for the CO_2-ethanol-water system at supercritical conditions of CO_2 in the relatively high ethanol concentration region. The results of other researchers [Kuk and Motagna(1983), Kreim(1983) and Moses et al. (1982)] were also reported for the high ethanol concentration region, while no data have been reported in the ethanol dilute region, which is necessary for designing or examining the extraction tower performance, especially of the stripping section.

In this work, vapor-liquid equilibria for the CO_2-ethanol-water system were measured at 9.6 - 32.0 °C up to 9 MPa in the wide range of ethanol concentration including the very dilute region.

EXPERIMENTAL APPARATUS AND PROCEDURE

In this work, a flow type apparatus, which had an overflow type liquid-level-control system equipped with a back pressure regulator as shown in Fig.1, was used to maintain the feed composition. The apparatus and experimental procedure are almost same as those discussed elsewhere (Inomata et al., 1986) except that a cooling jacket was added before the preheater zone and a gas chromatograph was used for composition analysis.

A ethanol-water mixture, which was prepared at a specified composition, was compressed and mixed with a gas stream of CO_2, and this heterogeneous mixture was heated or cooled to the desired temperature in the cooling jacket and preheater zone. A static mixer was used to attain equilibrium, and the equilibrated phases were separated in a cell. The liquid stream from the bottom of the cell was sampled and measured volumetrically for CO_2 and gravimetrically for ethanol-water mixture whose composition was analyzed by a gas chromatograph. Equilibrium compositions of the liquid phase were determined from these quantities. The vapor stream from the top of the cell was allowed to flow into a gas chromatograph for on-line composition analysis. Stainless steel columns (1.5m long x 3mm i.d.) packed with PEG6000 for liquid phase and with Porapak-Q for vapor phase were used and operated isothermally at 120°C.

In determining the equilibrium composition, small corrections were made for the amount of CO_2 dissolved in the ethanol solution. Each sample was analyzed at lease three times and the reproducibility was within 3%.
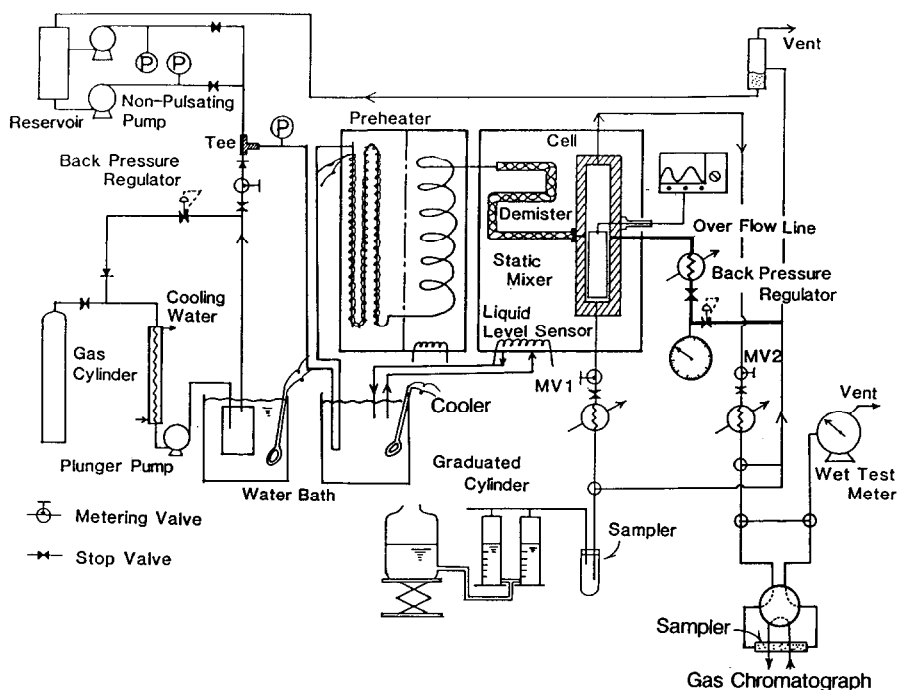
Fig.1 Schematic diagram of experimental apparatus

MATERIALS AND EXPERIMENTAL CONDITIONS

Ethanol with purity 99.5 vol% supplied by Wako Pure Chemical Ind. Co., Ltd. and liquefied CO_2 with purity 99.9 vol% supplied by Nippon Sanso K.K. were used without further purification. Water was ion-exchanged and purified by distillation.

We measured vapor-liquid equilibria for various temperatures, pressures and the concentrations of feed ethanol solution. Table 1 shows the experimental conditions.

Table 1 Experimental Conditions

System	Temp. (°C)	Press. (atm)
CO_2-ethanol	17.9, 31.0	20 – 63
CO_2-Water	24.7	6 – 73
CO_2-ethanol-water	9.6, 17.2, 19.6	45 – 88
"	25.0, 32.0	"

Table 2 Vapor-liquid equilibria for carbon dioxide-ethanol-water system

Pressure	Equilibrium Composition (mole fraction)						Separation Factor
	Liquid Phase			Vapor Phase			
[atm]	CO2	Ethanol	Water	CO2	Ethanol	Water	
temp = 9.6 °C							
45.6	0.0275	0.0173	0.9552	0.9993	0.0002	0.0005	19.8
59.3	0.0271	0.0178	0.9552	0.9964	0.0019	0.0017	60.6
73.6	0.0283	0.0176	0.9541	0.9964	0.0018	0.0019	51.7
87.6	0.0287	0.0174	0.9540	0.9961	0.0019	0.0020	52.4
temp = 17.2 °C							
45.1	0.0226	0.0156	0.9618	0.9992	0.0003	0.0006	30.8
60.0	0.0250	0.0186	0.9564	0.9957	0.0031	0.0012	132.8
73.6	0.0288	0.0181	0.9531	0.9952	0.0024	0.0024	52.7
88.1	0.0270	0.0180	0.9550	0.9955	0.0022	0.0024	48.6
temp = 19.6 °C							
45.9	0.0226	0.0148	0.9626	0.9990	0.0003	0.0007	25.8
59.7	0.0255	0.0172	0.9573	0.9961	0.0024	0.0016	84.4
74.0	0.0248	0.0173	0.9579	0.9952	0.0025	0.0023	61.0
87.6	0.0272	0.0168	0.9561	0.9950	0.0026	0.0025	59.1
temp = 25.0 °C							
45.2	0.0206	0.0149	0.9645	0.9987	0.0004	0.0009	28.1
59.5	0.0243	0.0130	0.9627	0.9984	0.0006	0.0010	40.6
73.7	0.0252	0.0158	0.9591	0.9953	0.0021	0.0026	49.8
87.1	0.0258	0.0157	0.9586	0.9946	0.0026	0.0028	57.7
temp = 32.0 °C							
45.4	0.0186	0.0121	0.9692	0.9985	0.0005	0.0009	44.2
59.3	0.0203	0.0116	0.9681	0.9983	0.0006	0.0010	52.1
74.5	0.0239	0.0166	0.9595	0.9957	0.0020	0.0024	48.7
88.6	0.0250	0.0151	0.9599	0.9949	0.0022	0.0028	50.0

Table 3 Vapor-liquid equilibria for carbon dioxide-ethanol-water system

Feed EtOH	Equilibrium Composition (mole fraction)						Separation Factor
	Liquid Phase			Vapor Phase			
[wt%]	CO2	Ethanol	Water	CO2	Ethanol	Water	
temp = 16.6 °C press = 59.8 atm							
0.5	0.0258	0.0012	0.9730	0.9988	0.0002	0.0010	161.3
5.	0.0272	0.0196	0.9532	0.9963	0.0028	0.0010	141.3
10.	0.0256	0.0356	0.9388	0.9944	0.0046	0.0011	113.5
30.	0.0264	0.1061	0.8675	0.9757	0.0202	0.0041	40.7
30.	0.0316	0.1286	0.8398	0.9723	0.0229	0.0049	30.7
temp = 18.6 °C press = 59.3 atm							
5.	0.0241	0.0147	0.9612	0.9970	0.0019	0.0011	117.7
5.	0.0252	0.0161	0.9587	0.9962	0.0028	0.0010	158.6
10.	0.0253	0.0331	0.9416	0.9945	0.0045	0.0010	122.4
10.	0.0260	0.0356	0.9384	0.9951	0.0040	0.0010	108.4
temp = 19.6 °C press = 60.2 atm							
1.	0.0263	0.0042	0.9695	0.9984	0.0005	0.0011	110.5
5.	0.0255	0.0172	0.9573	0.9961	0.0024	0.0016	84.4
10.	0.0256	0.0353	0.9381	0.9932	0.0045	0.0023	51.2
10.	0.0256	0.0385	0.9359	0.9921	0.0052	0.0027	47.4
30.	0.0260	0.1040	0.8700	0.9815	0.0152	0.0033	38.5
30.	0.0310	0.1285	0.8405	0.9737	0.0219	0.0043	33.1
temp = 24.8 °C press = 73.9 atm							
0.5	0.0256	0.0012	0.9732	0.9973	0.0002	0.0025	66.2
1.	0.0250	0.0039	0.9711	0.9974	0.0005	0.0022	56.7
5.	0.0254	0.0195	0.9552	0.9949	0.0027	0.0024	55.1
5.	0.0256	0.0156	0.9588	0.9952	0.0022	0.0027	50.1
30.	0.0308	0.1184	0.8508	0.9718	0.0232	0.0050	33.7
30.	0.0300	0.1311	0.8389	0.9707	0.0242	0.0051	30.4

EXPERIMENTAL RESULTS

To test the reliability of the experimental apparatus and procedure, we first measured isothermal vapor-liquid equilibria for the CO_2-ethanol and the CO_2-water binary systems because reliable data have been reported for these systems. Figures 2 and 3 show the comparison between our data and those of Wiebe et al. (1940, 1941) and Takishima et al. (1986). Agreement is good within 0.001 in mole fraction.

We measured the ternary system at several temperatures and pressures by maintaining the feed ethanol concentration of 5wt%. The raw experimental data are listed in Table 2. The separation factor α of ethanol and water between the liquid phase and the vapor phase is defined by the ratio of the distribution coefficient of ethanol and water;

$$\alpha = (Y_{ethanol}/X_{ethanol}) / (Y_{water}/X_{water})$$

where Y_i and X_i are the mole fractions of component i in the vapor and liquid phase, respectively.
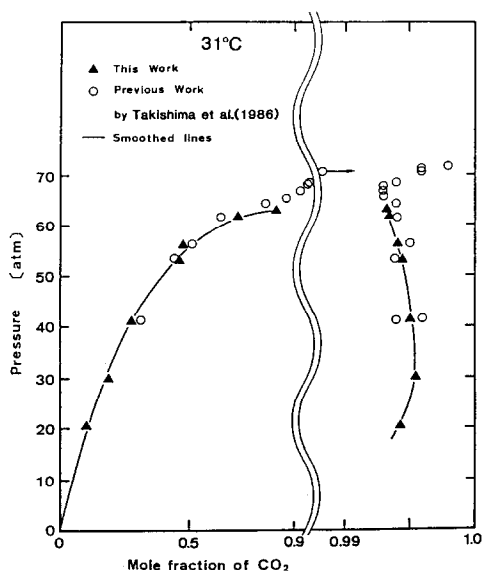
Fig.2 Vapor-liquid equilibria
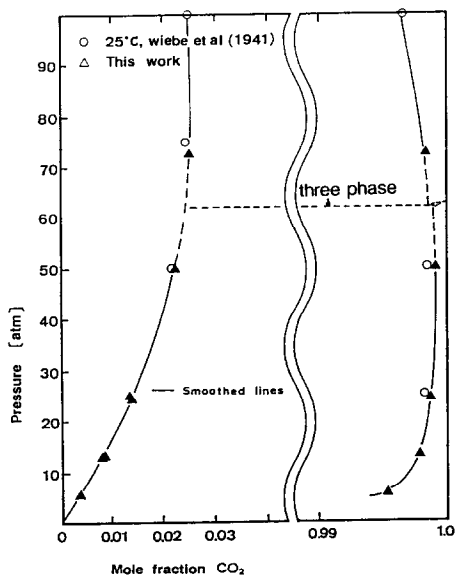for the CO_2-ethanol system

Fig.3 Vapor-liquid equilibria
for the CO_2water system

The value of separation factor has a great influence on the economic feasibility of the extraction tower. Figure 4 shows the value of separation factor evaluated from the experimental data. A condition around 17°C and 60 atm gives maximum separation factor. Then we measured vapor-liquid equilibria for the CO_2-ethanol-water system around 17°C and 60 atm for various feed ethanol concentration (0.1 to 30 wt%). Table 3 presents the raw data. The values of separation factor at 16.6, 18.6, 19.6°C were higher compared with those at 24.8 °C.

McHugh et al. (1986) concluded from their distribution plot (x-y) that the extraction condition did not influence the extractability and that the x-y relation of ethanol could be represented by a straight line with a gradient of about 0.09 at the conditions examined [20-50°C, 70-200 atm]. However, as shown in Fig. 5, our results supported their conclusion only in the higher ethanol concentration region, but in the very dilute region (less than 10wt% ethanol), the gradient decreased to about 0.06.
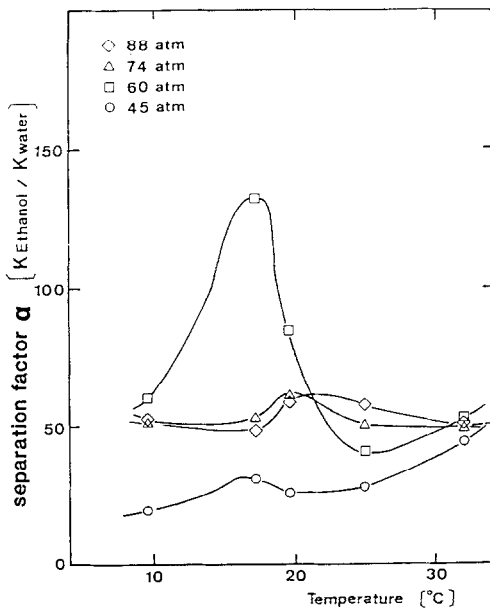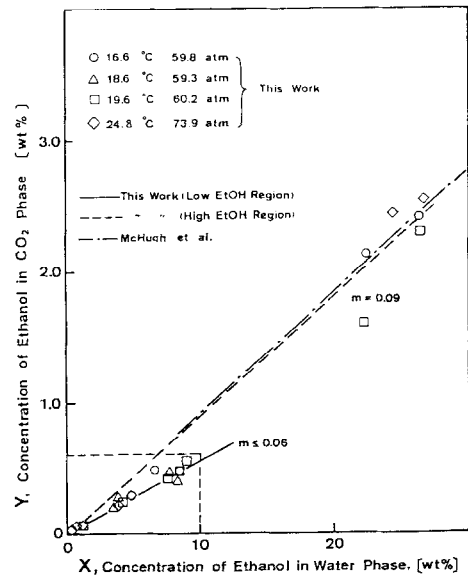

Fig.4 Separation factor of ethanol

Fig.5   Distribution plot of ethanol

CALCULATION RESULTS

Vapor-liquid equilibria for the CO_2-ethanol-water system were predicted using equations of state. We used Patel-Teja equation (Teja et al. 1982) and GC-EOS (Jorgensen et al. 1984). For the Patel-Teja equation, the following mixing rules proposed by Takishima et al. (1986) were used.

Mixing rules
$$a_m = \sum_i x_i \sum_j x_{ji}(a_j a_i)^{0.5}$$

$$x_{ji} = x_j \eta_{ji}/(\sum_k x_k \eta_{ki})$$

$$b_m = \sum_i x_i b_i$$

$$\eta_{ji} = \exp[-(\lambda_{ji} - \lambda_{ii})/RT]$$

$$c_m = \sum_i x_i c_i$$

where x_{ji} is the local mole fraction of molecule j around molecule i, and η_{ji} is the interaction energy between molecules j and i. For η_{ji}, we used the values determined in the previous paper from the binary data.

Figure 6 shows the predicted results for the ternary system. Agreement between the experimental and predicted binodal points with GC-EOS equation is fairly good, while that with Patel-Teja equation is poor. However as shown in Fig. 7, both GC-EOS and Patel-Teja equations fared poorly in predicting the behavior of the separation factor.
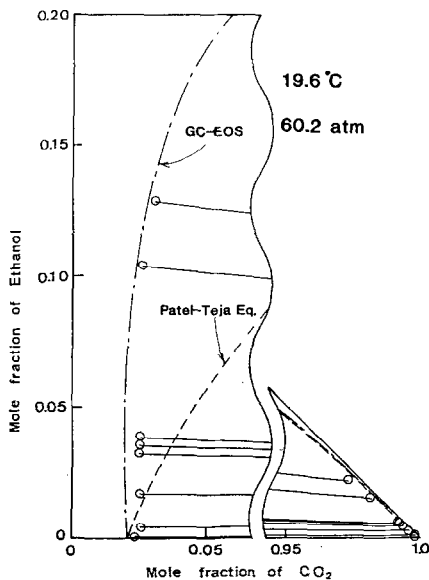

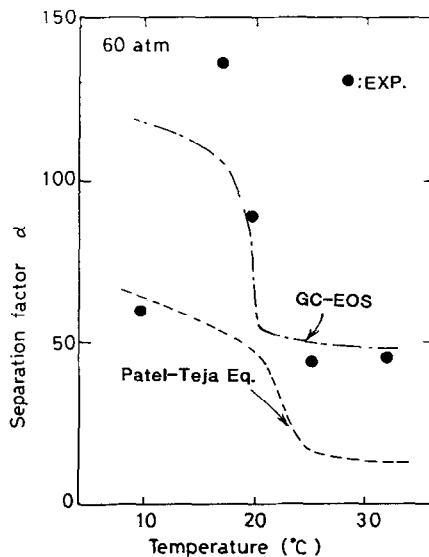**Fig.6** Vapor-liquid equilibria for the CO_2-ethanol-water system

Fig.7 Comparisom between the predicted and experimental separation factor of ethanol

CONCLUSIONS

Vapor-liquid equilibrium data were measured for the CO_2-ethanol-water system for wide ethanol feed concentrations using a flow type apparatus.

Experimental results revealed the followings;

1) The separation factor of ethanol becomes maximum at the operation condition of around 17°C and 60 atm.

2) In the very dilute region of ethanol, the distribution coefficient of ethanol decreases to 2/3 of the reported value by McHugh et al.

Both Patel-Teja equation and GC-EOS could accurately not represent the behavior of the separation factor, although GC-EOS did represent the binodal curve well.

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