

PHASE EQUILIBRIA FOR THE CARBON DIOXIDE - ETHANOL - WATER SYSTEM WITH TRACE AMOUNTS OF ORGANIC COMPONENTS

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Fluid-liquid and liquid-liquid equilibria were measured for carbon dioxide-ethanol-water mixtures containing trace amounts of ethyl acetate, acetaldehyde, 2-pentanol, 1-propanol, diacetyl, acetic acid and methanol at temperatures near the critical temperature of carbon dioxide. Large separation factors were observed in the extraction of all the trace components except for acetic acid and methanol from ethanol aqueous solutions using supercritical or liquid carbon dioxide as solvent. The separation factor increased with increasing solvent density.

A simple empirical model was developed to correlate the experimental data assuming the infinite dilution state for the trace components. The model correlates the separation factors with fairly good agreement with the experimental data.

1. Introduction

Ethanol is a well-known feedstock for detergent, food additives, cosmetics and pharmaceuticals. At present a large quantity of ethanol is produced by fermentation from biomass feedstock due to its established safety for human consumption. But crude fermentation ethanol contains numerous trace components which are generated during fermentation. The concentration of each trace component is less than 0.1 wt% but may be enough to render the ethanol useless due to strong scent and/or reactivity. Product ethanol is required to be completely free from trace components, while rather large amounts of water are allowed to remain in the product.

For removal of the trace components, conventional ethanol refining processes often employ extractive distillation in which separation factors are enhanced by dilution with water⁶. But the conventional system requires the addition of a large quantity of water which leads to an increase of energy consumption.

A novel extraction process using the near-critical condition of solvent is a potential technology for reducing the energy consumption¹². Since all the trace components except for methanol are presumed to be more lipophilic than ethanol, a lipophilic solvent can be expected to extract the components separately from ethanol. Liquid or supercritical carbon dioxide is well-known for its lipophilic character^{1, 2} and is used as the solvent in the present work because of its non-toxicity, which is the decisive criterion for food services.

To optimize and evaluate the extraction process, the phase equilibria should be known. Experimental data

of phase equilibria are essential because no reliable a priori prediction method is yet available for mixtures of polar substances and near-critical fluids⁴. Although some experimental data were reported for the carbon dioxide-ethanol-water ternary system^{3, 7, 10, 11, 13, 17} and the carbon dioxide-higher alcohol binary systems^{8, 9, 14, 16}, few have been reported for the behavior of the trace components in mixtures of aqueous ethanol solution and carbon dioxide. In this paper we discuss the phase equilibria for the mixtures system of carbon dioxide-ethanol-water and trace amounts of ethyl acetate, acetaldehyde, 2-pentanol, 1-propanol, diacetyl, acetic acid, and methanol, which are impurities commonly contained in the fermentation ethanol from various feed stocks.

2. Experimental

2.1 Apparatus and procedures

A static-type apparatus was employed to measure the phase equilibrium in the present work. Each coexisting phase can be circulated through a sampling device in which a small amount of sample can be collected without significant change in system pressure. The apparatus consists of an equilibrium cell, a sampling system for each phase, an evaporation system, a feed system and a gas chromatograph.

The sampling system for each phase is equipped with a magnetic pump and a sampling device connected to the evaporation system. The evaporation system consists of a flash tank, a magnetic pump and an injection device connected to a gas chromatograph for the anal-

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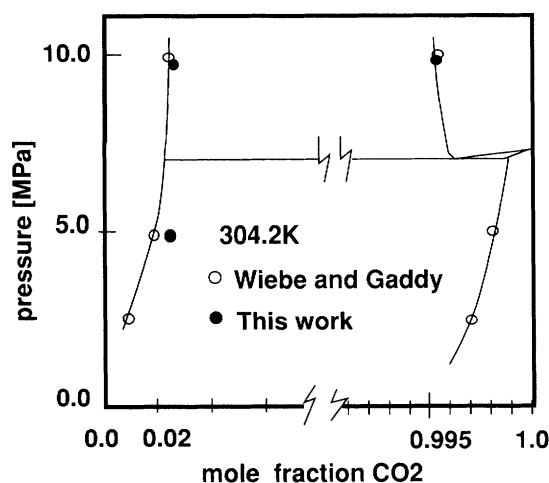


Fig. 1 Phase equilibria for the carbon dioxide-water system at 304.2K

ysis of composition. The gas chromatograph was supplied by Shimadzu Co. and was equipped with a thermal conductivity detector (TCD).

The following procedures were used. Mixtures of ethanol-water-trace components of known composition and carbon dioxide were pumped into the equilibrium cell. Coexisting phases were agitated by a magnetic stirrer to promote mass transfer between the phases. The stirrer was halted for long enough to achieve complete separation and settling of the phases. Each phase was circulated with a magnetic pump. Agitation, settling and circulation were repeated until no further change was detected in the pressure. A small amount of each phase was enclosed in a sampling device. The sample was carried into the flash tank and completely vaporized in the evaporation system, which was kept at 463K. The vapor composition was homogenized by circulation with a magnetic pump throughout the evaporation system. The temperatures of the tubes and the sampling device were elevated to 373K to vaporize the liquid sample and to avoid condensation in tubes and sampling device. A small quantity of each sample was then injected into a carrier gas line to a chromatograph for composition analysis.

The pressure in the equilibrium cell was measured with a Bourdon-tube gauge calibrated with a dead-weight gauge. The temperature was controlled to a degree of error of 0.2K and was measured by a platinum resistance thermometer.

The ethyl acetate, acetaldehyde, 2-pentanol, 1-propanol, methanol, diacetyl and ethanol, supplied by Wako Pure Chemical Ind. Co., Ltd. were of 98 vol% purity and were used without further purification. The liquefied carbon dioxide supplied by Nippon Sanso K.K. was of 99.9 vol% purity and was used without further purification. The composition of each trace component in feed was set at 0.5-1.0 wt% for accuracy of composition analysis.

2.2 Results and discussion

1) Test of experimental apparatus To confirm the

Table 1. Phase equilibria for the carbon dioxide-ethanol-water system with trace components at 313.2K, 10MPa

T [K]	P [MPa]	Component	Mole fraction			K [-]
			Feed	Fluid	Liquid	
313.2	10.2	carbon dioxide		0.98248	0.04230	23.23
		ethanol	0.0544	0.00718	0.04791	0.15
		water	0.9330	0.00343	0.90152	0.00
		acetaldehyde	0.0031	0.00230	0.00160	1.44
		methanol	0.0042	0.00028	0.00420	0.07
		1-propanol	0.0022	0.00073	0.00176	0.42
		ethyl acetate	0.0015	0.00205	0.00023	8.74
		2-pentanol	0.0015	0.00155	0.00049	3.15
313.2	10.0	carbon dioxide		0.97257	0.04476	21.73
		ethanol	0.1196	0.01586	0.10383	0.15
		water	0.8666	0.00562	0.84283	0.01
		acetaldehyde	0.0034	0.00210	0.00147	1.43
		methanol	0.0046	0.00029	0.00432	0.07
		1-propanol	0.0025	0.00066	0.00182	0.36
		ethyl acetate	0.0017	0.00165	0.00025	6.51
		2-pentanol	0.0017	0.00125	0.00071	1.76
313.2	9.7	carbon dioxide		0.94709	0.09920	9.55
		ethanol	0.3171	0.03733	0.26634	0.14
		water	0.6655	0.01120	0.62335	0.02
		acetaldehyde	0.0042	0.00189	0.00200	0.95
		methanol	0.0058	0.00041	0.00479	0.09
		1-propanol	0.0031	0.00044	0.00222	0.20
		ethyl acetate	0.0021	0.00120	0.00068	1.76
		2-pentanol	0.0021	0.00045	0.00142	0.32

reliability of the experimental apparatus, vapor-liquid equilibria were measured for the carbon dioxide-water binary system, for which reliable experimental data were available. The results are shown in **Fig.1**. Good agreement was observed between the data obtained in the present work and those of Wiebe and Gaddy^{18, 19)}.

2) Measurement at extraction condition Fluid-liquid equilibria were measured for the mixture of carbon dioxide-ethanol-water and trace amounts of ethyl acetate, acetaldehyde, 2-pentanol, 1-propanol, methanol at 313.2K, 10 MPa. The results are shown in **Table 1**. The K-values and separation factors shown in **Fig.2** were calculated from the composition using the following equations.

$$K_i = y_i/x_i \quad (1)$$

$$\alpha_{i,j} = K_i/K_j \quad (2)$$

Significantly large separation factors α_{i,C_2H_5OH} were observed for all the trace components except methanol. The separation factors are markedly larger than the values obtained by Ikari *et al.*⁶⁾ at ambient pressure.

The solubility and separation factor $\alpha_{C_2H_5OH,H_2O}$ for the extraction of ethanol from aqueous ethanol aqueous solution are shown in **Figs.3** and **4** respectively and compared with the values obtained from the carbon dioxide-ethanol-water ternary system. Good agreement was observed between the data obtained by the present work and those of Gilbert *et al.*³⁾, Inomata *et al.*⁷⁾ and Martinez *et al.*¹¹⁾. The addition of the trace component did not affect the solubility or the separation factor of ethanol to water, as shown in Figs. 3 and 4 respectively.

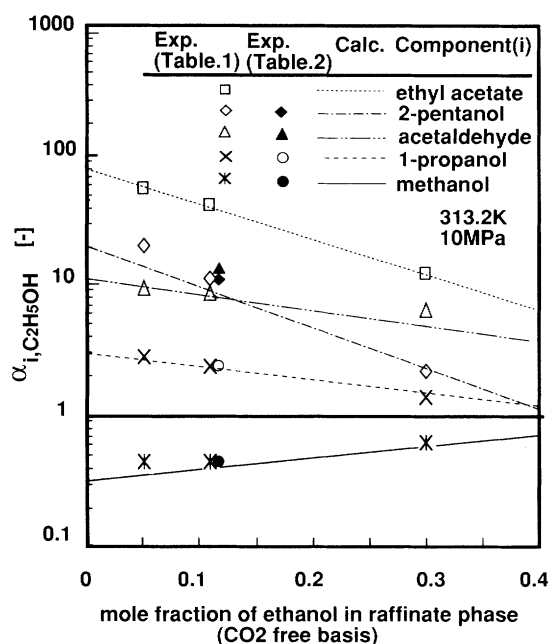


Fig. 2 Separation factors of trace components to ethanol at 313.2K, 10MPa

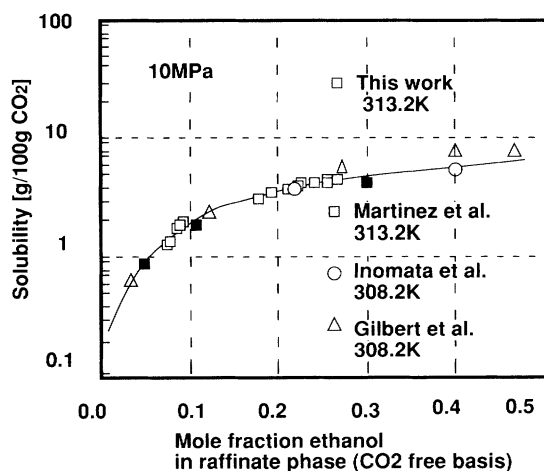


Fig. 3 Solubility of aqueous ethanol solution in carbon dioxide

Table 2 shows the phase equilibria for the mixture with trace amounts of acetic acid, diacetyl, acetaldehyde, 2-pentanol, 1-propanol and methanol at 313.2K, 10 MPa. Large separation factors are also observed for diacetyl. The separation factors for acetaldehyde, 2-pentanol, 1-propanol and methanol calculated from the data in Tables 1 and 2 are compared in Fig.2. Tables 1 and 2 give almost the same separation factor for each component, although the concentrations of the same and other trace components differ significantly. The result implies that the concentration of each trace component was small enough to regard the coexisting phases approximately as the infinite dilution state for the trace component.

The separation factors increased when the concentration of ethanol in raffinate phase decreased as shown in Fig.2 for all the trace components except methanol. This phenomenon is well-known for vapor-liquid equilibrium at ambient condition⁶⁾ and can be caused by the stronger affinity of ethanol for the trace component in raffinate phase than is that of water. The logarithm of the separation factor α_{i,C_2H_5OH} for each component was approximately expressed as a linear function of the mole fraction of ethanol on a carbon dioxide-free basis in raffinate phase.

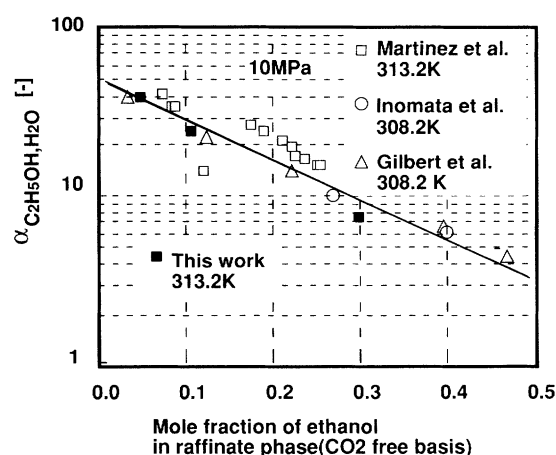


Fig. 4 Separation factor of ethanol to water

Table 2. Phase equilibria for the carbon dioxide-ethanol-water system with altered trace components and concentrations

T [K]	P [MPa]	Component	Mole fraction			K [-]
			Feed	Fluid	Liquid	
314.2	9.9	carbon dioxide		0.96780	0.03406	28.41
		ethanol	0.1373	0.01887	0.11499	0.16
		water	0.8507	0.00933	0.84408	0.01
		acetaldehyde	0.0025	0.00150	0.00074	2.03
		methanol	0.0035	0.00028	0.00309	0.09
		1-propanol	0.0019	0.00041	0.00113	0.36
		diacetyl	0.0018	0.00104	0.00047	2.20
		acetic acid	0.0011	0.00007	0.00102	0.07
		2-pentanol	0.0013	0.00071	0.00040	1.75

librium at ambient condition⁶⁾ and can be caused by the stronger affinity of ethanol for the trace component in raffinate phase than is that of water. The logarithm of the separation factor α_{i,C_2H_5OH} for each component was approximately expressed as a linear function of the mole fraction of ethanol on a carbon dioxide-free basis in raffinate phase.

Table 3 shows the liquid-liquid equilibria for the mixture with trace amounts of ethyl acetate, acetaldehyde, 2-pentanol, 1-propanol and methanol at 293.2K, 6.7MPa. An empirical linear relationship was also observed for the case of 293.2K, 6.7MPa as is shown in Fig.5. A similar gradient in the linear relationship was observed for each trace component, both at 293.2K, 6.7MPa and at 313.2K, 10MPa. Separation factors were larger at 293.2K, 6.7MPa than at 313.2K, 10MPa.

The fluid-liquid equilibria shown in Table 4 were measured for the mixture with trace amounts of ethyl acetate, acetaldehyde, 2-pentanol and 1-propanol at 333.2K, 10MPa. The K-values plunged as temperature increased from 313K to 333K at constant pressure, even though the saturated vapor pressure for each component increased. The separation factors shown in Fig.6 are significantly smaller than those at 313.2K, 10MPa. An empirical linear relationship was also observed at 333K, 10MPa although the gradients were largely different from those at 313.2K, 10MPa. The result implies that the

Table 3. Phase equilibria for the carbon dioxide-ethanol-water system with trace components at 293.8, 6.7MPa

T [K]	P [MPa]	Component	Mole fraction			K [-]
			Feed	Liquid (Light)	Liquid (Heavy)	
293.2	6.7	carbon dioxide		0.98641	0.03428	28.77
		ethanol	0.0587	0.00583	0.05292	0.11
		water	0.9322	0.00318	0.90672	0.00
		acetaldehyde	0.0022	0.00150	0.00117	1.29
		methanol	0.0030	0.00014	0.00308	0.04
		1-propanol	0.0016	0.00044	0.00137	0.32
		ethyl acetate	0.0011	0.00145	0.00007	20.72
		2-pentanol	0.0011	0.00105	0.00040	2.65
293.2	6.6	carbon dioxide		0.96337	0.04373	22.03
		ethanol	0.2012	0.02625	0.17341	0.15
		water	0.7879	0.00659	0.77483	0.01
		acetaldehyde	0.0027	0.00110	0.00132	0.83
		methanol	0.0037	0.00027	0.00446	0.06
		1-propanol	0.0019	0.00037	0.00121	0.30
		ethyl acetate	0.0013	0.00110	0.00014	7.98
		2-pentanol	0.0013	0.00095	0.00091	1.04
293.2	6.7	carbon dioxide		0.94902	0.09472	10.02
		ethanol	0.3557	0.03863	0.28774	0.13
		water	0.6314	0.00902	0.60803	0.01
		acetaldehyde	0.0031	0.00100	0.00210	0.48
		methanol	0.0043	0.00027	0.00405	0.07
		1-propanol	0.0023	0.00037	0.00182	0.20
		ethyl acetate	0.0016	0.00125	0.00043	2.93
		2-pentanol	0.0016	0.00045	0.00111	0.40

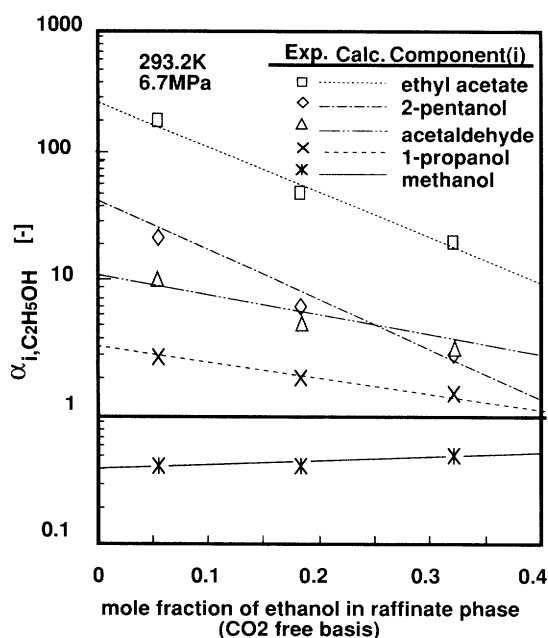


Fig. 5 Separation factors of trace components to ethanol at 293.2K, 6.7MPa

separation factors and solubilities are highly dependent on the density of solvent as well as temperature.

3) Effect of solvent density The fluid-liquid equilibria for the carbon dioxide-ethanol-water system with trace amounts of 2-pentanol, 1-propanol and methanol were measured at 313.2K and various pressures while the temperature and the concentration of ethanol were

Table 4. Phase equilibria for the carbon dioxide-ethanol-water system with trace components at 333.2K, 10MPa

T [K]	P [MPa]	Component	Mole fraction			K [-]
			Feed	Fluid	Liquid	
334.2	10.0	carbon dioxide		0.97711	0.11922	8.20
		ethanol	0.2810	0.01549	0.24557	0.06
		water	0.7073	0.00522	0.62552	0.01
		acetaldehyde	0.0029	0.00107	0.00236	0.45
		1-propanol	0.0043	0.00024	0.00375	0.06
		ethyl acetate	0.0015	0.00072	0.00118	0.61
		2-pentanol	0.0029	0.00015	0.00240	0.06
334.3	10.2	carbon dioxide		0.97399	0.30093	3.24
		ethanol	0.5253	0.01981	0.36445	0.05
		water	0.4601	0.00500	0.32446	0.02
		acetaldehyde	0.0037	0.00063	0.00259	0.24
		1-propanol	0.0054	0.00015	0.00388	0.04
		ethyl acetate	0.0018	0.00036	0.00133	0.27
		2-pentanol	0.0037	0.00006	0.00237	0.03
334.5	10.3	carbon dioxide		0.97700	0.20150	4.85
		ethanol	0.412869	0.01656	0.32880	0.05
		water	0.573884	0.00492	0.45904	0.01
		acetaldehyde	0.00334	0.00079	0.00275	0.29
		1-propanol	0.004898	0.00018	0.00404	0.04
		ethyl acetate	0.00167	0.00047	0.00140	0.34
		2-pentanol	0.00334	0.00008	0.00247	0.03
332.6	10.0	carbon dioxide		0.97340	0.05272	18.46
		ethanol	0.1763	0.01623	0.16208	0.10
		water	0.7998	0.00428	0.76492	0.01
		acetaldehyde	0.0053	0.00231	0.00359	0.64
		methanol	0.0073	0.00030	0.00625	0.05
		1-propanol	0.0059	0.00073	0.00624	0.12
		ethyl acetate	0.0027	0.00239	0.00185	1.29
		2-pentanol	0.0027	0.00036	0.00234	0.15

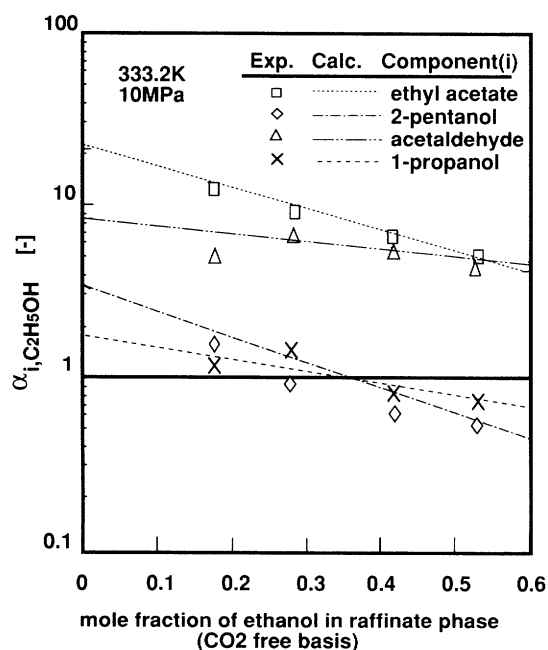


Fig. 6 Separation factors of trace components to ethanol at 333.2K, 10MPa

kept constant. The results are shown in **Table 5** and **Fig. 7**. The *K*-values and separation factors of the trace components except for methanol increased exponentially

Table 5. Phase equilibria for the carbon dioxide-ethanol-water system with trace components at 313.2K and various pressures

T [K]	P [MPa]	Component	Mole fraction			K [-]
			Feed	Fluid	Liquid	
313.2	11.7	carbon dioxide		0.96546	0.02983	32.37
		ethanol	0.0378	0.01131	0.03573	0.32
		water	0.9490	0.01027	0.92085	0.01
		methanol	0.0061	0.00086	0.00743	0.12
		1-propanol	0.0049	0.00387	0.00467	0.83
		2-pentanol	0.0022	0.00822	0.00149	5.52
313.2	8.0	carbon dioxide		0.99176	0.03118	31.80
		ethanol	0.0624	0.00405	0.06012	0.07
		water	0.9330	0.00364	0.90407	0.00
		methanol	0.0019	0.00004	0.00207	0.02
		1-propanol	0.0017	0.00015	0.00130	0.12
		2-pentanol	0.0011	0.00035	0.00126	0.28

as solvent density increased.

The experimental data indicate that all the trace components except for methanol and acetic acid can be separated from the ethanol aqueous solution by extraction with high-density carbon dioxide as solvent.

3. Correlation model

3.1 The model

A simple empirical model was developed to provide a correlation method that can estimate the separation factors with a practical accuracy in a narrow range of temperature, pressure and composition. The model assumes that the raffinate phase is an infinitely dilute solution for the trace components. Since the solubility of ethanol and water into carbon dioxide are less than 5 mol%, the extract phase is assumed to be an infinitely dilute solution not only for the trace components but also for ethanol and water.

The fluid-liquid and liquid-liquid equilibria can be predicted by the following equation.

$$P\phi_i^E y_i = P_i^{o, sat} \phi_i^{o, sat} \gamma_i^R x_i \exp\left(\frac{1}{RT} \int_{P_i^{o, sat}}^P v_i^{o, L} dp\right) \quad (3)$$

The saturated vapor pressures of trace components, water and ethanol are low enough to employ the approximation of $\phi_i^{o, sat} = 1$ at temperatures studied in this work. The K -values are expressed by the following equation by regarding the liquid molar volume as independent of pressure.

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{o, sat} \gamma_i^R}{P \phi_i^E} \exp\left\{\frac{v_i^{o, L} (P - P_i^{o, sat})}{RT}\right\} \quad (4)$$

Since the operating pressure is much higher than the saturated vapor pressure of trace components, the following approximation can be applied.

$$(P - P_i^{o, sat}) \approx P \quad (5)$$

By substituting Eqs.(4) and (5) for Eq.(2) the separation factor is expressed as:

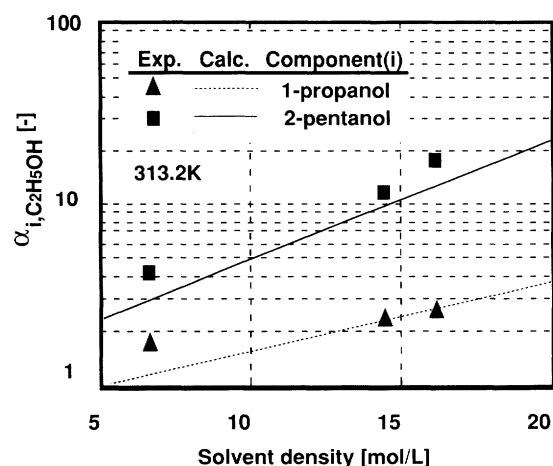


Fig. 7 Effect of solvent density on separation factors

$$\ln(\alpha_{i, C2H5OH}) = \ln\left(\frac{P_i^{o, sat}}{P_{C2H5OH}^{o, sat}}\right) + \frac{P(v_i^{o, L} - v_{C2H5OH}^{o, L})}{RT} + \ln\left(\frac{\gamma_i^R}{\gamma_{C2H5OH}^R}\right) - \ln\left(\frac{\phi_i^E}{\phi_{C2H5OH}^E}\right) \quad (6)$$

The first term on the right-hand side of Eq.(6) represents the effect of saturated vapor pressure, which can be readily predicted by the well-known Antoine equation. Table 6 shows the parameters for the Antoine equation and liquid molar volume by Reid *et al.*^{15),} which are used in present work. The liquid molar volume was regarded as independent of temperature and pressure since its change was small enough at the temperatures studied in this work.

The third term on the right-hand side of Eq.(6) represents the effect of activity coefficients in the raffinate phase. The linear relationship empirically obtained between $\ln(\alpha)$ and $x_{C2H5OH}^{CO2 free}$ is attributed to the third term. The following equation for the third term was empirically obtained.

$$\ln\left(\frac{\gamma_i^R}{\gamma_{C2H5OH}^R}\right) = (A_i + B_i/T) \{ (1 + C_i \rho) D_i x_{C2H5OH}^{CO2 free} + 1 \} \quad (7)$$

In Eq.(7) the activity coefficient is regarded as a function of temperature and solvent density. The introduction of the density dependency term $(1 + C_i \rho)$ increased significantly the correlating capability of the linear relationship. The effect of solvent density on the activity coefficient might be caused by the change in solubility of carbon dioxide into the raffinate phase.

The fourth term on the right-hand side of Eq.(6) represents the effect of molecular interactions in the extract phase. The strong effect of solvent density on the separation factor observed in the experiment is mainly attributable to the fourth term. The fugacity coefficients for trace components and ethanol are derived as follows from the well-known van der Waals equation of state.

Table 6. Parameters for Eq. (12)

Component		acetaldehyde	1-propanol	ethyl acetate	2-pentanol	methanol
Parameters for Antoine eq. $\ln P [\text{mmHg}] = \text{Ant. A} - \text{Ant. B}/(\text{Ant. C} + T [\text{K}])$						
	Ant. A	[-]	16.25	17.54	16.15	18.59
	Ant. B	[-]	2465.15	3166.38	2790.50	3626.55
	Ant. C	[-]	-37.15	-80.15	-57.15	-34.29
Liquid molar volume	[L/mol]	0.05662	0.07475	0.09779	0.10816	0.04051
Parameters determined in present work	Ai	[-]	-0.329	1.073	1.700	0.970
	Bi	[K]	120.147	0.156	0.064	-1120.397
	Ci	[L/mol]	21.463	0.052	23.197	-0.048
	Di	[-]	-0.153	-1.317	-0.010	-2.284
	Ei	[-]	-0.00688	0.00818	0.01543	0.08369
	Fi	[K]	16.341	2126.744	2854.648	-55.865

$$RT \ln (\phi_i^E) = RT \ln \left(\frac{v}{v - \sum_j y_j b_j} \right) + \frac{RT b_i}{v - \sum_j y_j b_j} \dots$$

$$\dots - \frac{2 \sum_j a_{i,j} y_j}{v} - RT \ln Z \quad (8)$$

The fourth term of Eq.(6) becomes the following by substituting the limiting value of Eq.(8) at $y_{\text{CO}_2} \rightarrow 1$.

$$\ln \left(\frac{\phi_i^E}{\phi_{\text{C}_2\text{H}_5\text{OH}}^E} \right) = \frac{b_i - b_{\text{C}_2\text{H}_5\text{OH}}}{v - b_{\text{CO}_2}} - \frac{2(a_{i,\text{CO}_2} - a_{\text{C}_2\text{H}_5\text{OH}})}{RTv} \quad (9)$$

When $(b_{\text{CO}_2}/v) < 1$, Taylor's expansion related to (b_{CO_2}/v) can be applied to the first term on the right-hand side of Eq.(9). The following approximation can be obtained by neglecting the third and the higher terms of the Taylor's series.

$$\frac{1}{v - b_{\text{CO}_2}} = \frac{1}{v} \left(1 + \frac{b_{\text{CO}_2}}{v} \right) \quad (10)$$

By substituting Eq.(10) for Eq.(9) and neglecting the quadratic term, the fourth term of Eq.(6) becomes:

$$\ln \left(\frac{\phi_i^E}{\phi_{\text{C}_2\text{H}_5\text{OH}}^E} \right) \approx \{ (b_i - b_{\text{C}_2\text{H}_5\text{OH}}) \dots$$

$$\dots - 2 \left(\frac{a_{i,\text{CO}_2} - a_{\text{C}_2\text{H}_5\text{OH}}}{RT} \right) \} \rho$$

$$= -E_i (1 + F_i/T) \rho \quad (11)$$

By substituting Eqs.(7) and (11) for Eq.(6), the following equation is obtained.

$$\ln (\alpha_{i,\text{C}_2\text{H}_5\text{OH}}) = \ln (P_i^{\text{O},\text{sat}}/P_{\text{C}_2\text{H}_5\text{OH}}^{\text{O},\text{sat}}) \dots$$

$$\dots + P (v_i^{\text{O},\text{L}} - v_{\text{C}_2\text{H}_5\text{OH}}^{\text{O},\text{L}}) / RT \dots$$

$$\dots + (A_i + \frac{B_i}{T}) \{ (1 + C_i r) D_i x_{\text{C}_2\text{H}_5\text{OH}}^{\text{CO}_2\text{free}} - 1 \} \dots$$

$$\dots + E_i (1 + \frac{F_i}{T}) \rho \quad (12)$$

3.2 The correlating capability of the model

Parameters A_i , B_i , C_i , D_i , E_i and F_i shown in Table. 6 were determined by the data shown in Tables 1, 3, 4

and 5 using the non-linear least squares method. The solvent density was estimated by the 21-constant modified BWR equation of state developed by Feng-hsin Huang *et al.*⁵⁾, which gives sufficient accuracy even in the vicinity of the critical point of carbon dioxide.

The model can predict the separation factors with fairly good agreement with experimental data, as is shown in Figs. 3, 6, 7 and 8. The effect of temperature and solvent density on separation factors was successfully predicted in the range of temperature 293K-333K, solvent density 6 - 12 mol/L and ethanol concentration 0 mol% - 40 mol% on a carbon dioxide-free basis in the raffinate phase. Since the model dose not require any iteration procedure, the computation time is so short that the model is expected to be useful in the design of extractors.

4. Conclusions

Phase equilibria were measured for the carbon dioxide-ethanol-water mixtures with trace organic components generated during fermentation. The fluid-liquid equilibria at 313.2K, 10MPa exhibited significantly large separation factors in the extraction of all the trace components except for methanol from ethanol aqueous solution.

Larger separation factors were observed in the liquid-liquid equilibria at 293.2K, 6.7MPa, where higher solvent density is available. But the separation factors plunged at 333K, 10MPa with the decrease in solvent density.

The strong effect of solvent density was demonstrated by experiments at 313.2K and various solvent densities. The separation factors and solubilities soared as solvent density increased.

A simple empirical model was developed to correlate the experimental data assuming infinite dilution state for the trace components. The model correlated separation factors with fairly good agreement with the experimental data.

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Nomenclature

A_i	= parameter of equation (7)	[-]
a_i, a_{ij}	= energy parameter of van der Waals equation of state	[kJL/mol ²]
B_i	= parameter of equation (7)	[K]
b_i	= parameter of van der Waals equation of state	[L/mol]
C_i	= parameter of equation (7)	[L/mol]
D_i	= parameter of equation (7)	[-]
E_i	= parameter of equation (11)	[-]
F_i	= parameter of equation (11)	[K]
K_i	= ($=y_i/x_i$) K-value for component i	[-]
n	= number of components	[-]
P	= pressure	[MPa]
R	= gas constant	[kJ/molK]
T	= temperature	[K]
v	= molar volume	[L/mol]
x_i	= mole fraction in raffinate phase	[-]
y_i	= mole fraction in extract phase	[-]
z	= compressibility factor	[-]
α_{ij}	= separation factor($=K_i/K_j$)	[-]
γ	= activity coefficient	[-]
ρ	= solvent density	[mol/L]
ϕ	= fugacity coefficient	[-]

<Subscripts>

i	= component identification number
j	= component identification number
m	= mixture

<Superscripts>

CO ₂ free	= carbon dioxide-free basis
E	= extract phase
L	= liquid phase
R	= raffinate phase
sat	= saturated state
o	= pure substance

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