

VAPOR-LIQUID EQUILIBRIUM PROPERTIES OF CARBON DIOXIDE + ETHANOL MIXTURE AT HIGH PRESSURES

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An experimental apparatus equipped with three density meters was newly developed for measuring vapor-liquid-liquid phase separation properties at high pressures. Coexisting phase composition and saturated density of each phase can be measured by means of the present apparatus with a maximum temperature of 400 K and pressure of 20 MPa. The phase compositions of carbon dioxide + ethanol mixture and their densities at high pressures were measured at 308.15 K with the apparatus. The sensitivity and absolute reliability of the equilibrium compositions appear to be 0.0001 and 0.001 mole fractions, respectively. The accuracy of saturated densities is 0.1 kg/m³. The equilibrium compositions obtained in the present study were correlated with the pseudocubic equation of state previously proposed by the authors and the Soave-Redlich-Kwong equation of state. Saturated densities obtained in the present study were further evaluated by the equations of state with the interaction parameters determined from vapor-liquid equilibrium data.

Introduction

Phase equilibrium properties of mixtures at high pressures are required for practical use such as in the design and operation of separation equipment in the petroleum, natural gas, and related industries. Supercritical fluid extraction is attractive as a new separation technology. Multiphase separation behaviors at high pressures are sometimes in mixtures containing supercritical fluids.

Parrish⁸⁻¹⁰⁾ and Takac *et al.*¹⁴⁾ have introduced the Mettler Paar vibrating-tube density meter for PVT measurement of liquids. Nagarajan *et al.*^{5, 6)}, Panagiotopoulos *et al.*⁷⁾, and Sandler *et al.*^{11, 12)} have recently used vibrating-tube density meters in their circulation-type vapor-liquid equilibrium apparatus.

The equilibrium compositions of vapor and liquid were determined by gas chromatography. The saturated densities of vapor and of liquid were further measured with the density meters.

The authors³⁾ have recently proposed an apparatus for determination of binary vapor-liquid equilibria at high pressures which uses effectively the density meters. The equilibrium vapor and liquid compositions can be evaluated by combining a couple of data at the same temperature and pressure without any analysis of phase compositions, based on mass balance and the phase rule.

Vapor-liquid equilibria and saturated densities at high pressures were determined for the carbon dioxide+acetone system. Applying the experimental apparatus, a new experimental method for determination of gas solubilities in nonvolatile liquid mixtures has been proposed by the

authors⁴⁾. The solubility of gas in liquid can be evaluated, based on mass balance. The solubilities of carbon dioxide in heavy hydrocarbons and their mixtures have been recently determined without any analysis of phase compositions.

In the present study, a new experimental apparatus equipped with three density meters for measuring vapor-liquid-liquid phase separation properties at high pressures has been developed. The phase compositions and their saturated densities at high pressures can be measured with the present apparatus. The composition of each phase is determined by gas chromatography. With the new apparatus, the coexisting phase compositions and their saturated densities for carbon dioxide+ethanol mixture at high pressures were measured at 308.15 K, including the vicinity of critical regions. Jennings *et al.*²⁾ (at 314.5 K) and Takishima *et al.*¹⁵⁾ (at 308.15 K) previously measured the VLE relations of carbon dioxide+ethanol system. The equilibrium data reported by Jennings *et al.*²⁾ and Takishima *et al.*¹⁵⁾, however, have no density data.

The vapor-liquid equilibrium compositions obtained in the present study were correlated with the equations of state.

1. Experimental

An experimental apparatus equipped with three density meters was developed for measuring vapor-liquid-liquid phase separation properties at high pressures as schematically shown in **Fig. 1**. Coexisting phase composition and saturated density of each phase can be measured by means of the present apparatus with a maximum

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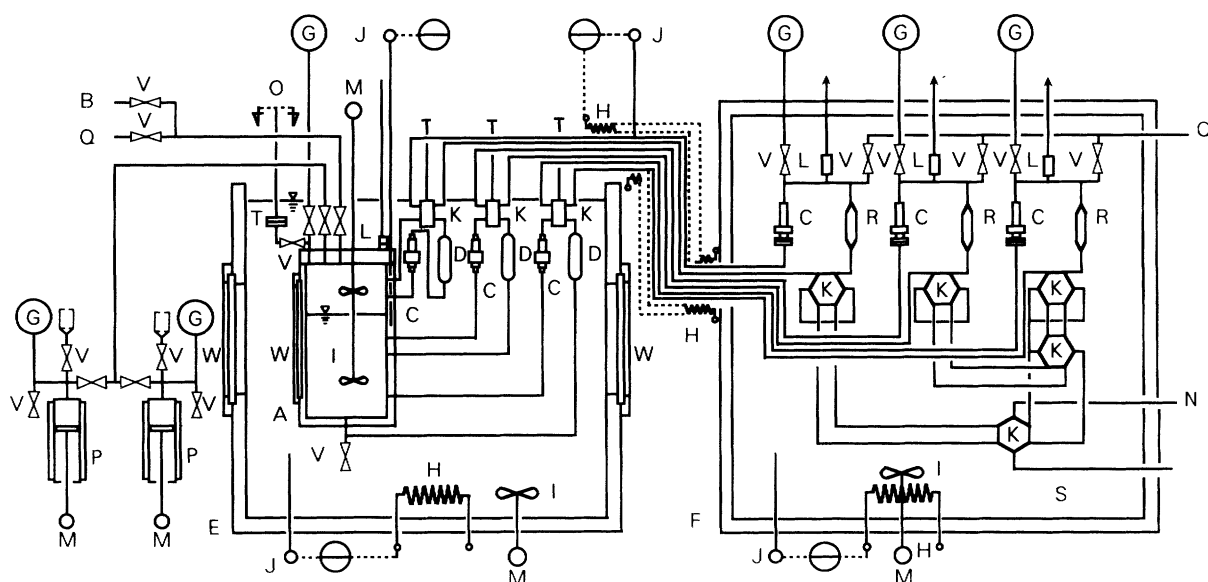


Fig. 1 Schematic diagram of experimental apparatus A, Equilibrium Cell; B, to Sample Cylinder; C, Recirculation Pump; D, Density Meter E, Constant Temperature Liquid Bath; F, Constant Temperature Air Bath; G, Pressure Gage H, Heater; I, Fan; J, Thermometer; K, Sampling Valve; M, Motor; N, to GC; O, to Dead Weight Gage; P, Sample Charging Pump; Q, to Vacuum Pump; R, Surge Tank S, Sampling System; T, Pressure Transducer; V, Valve; W, Viewing Window

temperature and pressure of 400 K and 20 MPa, respectively. The main parts of the apparatus are an equilibrium cell A, circulation pumps C, Anton Paar DMA 512S density meters D, sampling system S, and gas chromatograph N.

The density meters were calibrated with degassed pure water and dry air at atmospheric pressure and 308.15 K.

The densities obtained from the present density meters were checked with the literature value of ethanol at atmospheric pressure and at 308.15 K. The density values indicated by the present density meters have to be corrected with a pressure coefficient characteristic of each density meter. All densities obtained in the present study were corrected with the following equation of pressure effect.

$$\rho = \rho^* + K_\rho (P - P_0), K_\rho = -1.8 \times 10^{-1} [\text{kg/m}^3 \text{MPa}] \quad (1)$$

where, ρ , ρ^* , K_ρ , P , and P_0 , respectively, represent the corrected density, density value indicated in the density meter, pressure correction factor, system pressure, and atmospheric pressure.

The apparatus is in a constant-temperature liquid bath controlled within ± 0.01 K. The cell volume is approximately 320 cm³. The coexisting phases are continuously recirculated through the sampling valves and density meters with the three magnetic circulation pumps C. Temperatures are measured with the Hewlett Packard 2804A quartz thermometer J. Pressures are measured with the Ruska 2480-700 oil dead weight gage O and the Ruska 2439-702 pressure transducer T. The analysis of the composition was carried out with a Shimadzu GC-14A gas chromatograph equipped with a 3 m Porapak Q column.

Table 1. Meters used in the present apparatus

Meters	Type	Pressure range	Accuracy
Density meter	Anton Paar DMA 512S	0-40MPa	0.1 kg/m ³
Thermometer	Hewlett Packard 2804A	Resolution 0.0001 K	
Pressure gage	Ruska 2480-700 (Oil DWG)	0.22-103.4MPa	0.01%
Pressure transducer	Ruska 2413-705	-103.4MPa	5ppm

Helium was used as a carrier gas at a flow rate of 52 cm³/min. The column temperature was about 373.15 K, and the current as measured by a thermal conductivity detector (TCD) was 100 mA. The meters used in the present apparatus and their accuracies are given in **Table 1**.

At the start of the experiment, carbon dioxide and ethanol are charged into the cell after the evacuation of cell A. The fluid in the cell is mixed with the magnetic-driven fan I. Each phase is circulated through the circulation pump D.

After the 2 hours necessary to attain equilibrium state, the fan I and circulation pumps C are stopped. After 30 minutes, the densities and the pressure are measured with the density meters D and the dead weight gage O, respectively. Each phase is sampled by the valve K. After circulation of 2 hours, each sample is analyzed by gas chromatography.

2. Results and Discussion

With the present apparatus, coexisting phase compositions and saturated densities were measured for a carbon dioxide+ethanol system at 308.15 K, including the vicinity of critical regions. Carbon dioxide was supplied by Nihon Sanso Co. Ltd. with the guarantee of 99.99 percent

Table 2. Vapor-liquid equilibrium properties for carbon dioxide + ethanol mixture at 308.15 K

Pressure [MPa]	Mole fraction of carbon dioxide		Density[kg/m ³]	
	Liquid	Vapor	Liquid	Vapor
1.552	0.1098	0.9833	790.0	30.4
2.616	0.1904	0.9892	799.2	52.6
3.591	0.2469	0.9937	807.8	76.6
4.004	0.2813	0.9937	811.4	88.2
4.941	0.3755	0.9942	819.5	118.2
5.732	0.4587	0.9915	825.8	150.1
5.992	0.5160	0.9952	827.5	163.8
6.595	0.6152	0.9953	827.4	200.7
6.615	0.6415	0.9954	827.1	202.0
6.865	0.7206	0.9924	818.1	223.0
6.918	0.7511	0.9898	813.3	228.1
7.012	0.8010	0.9956	798.9	237.8
7.063	0.8376	0.9978	786.8	243.4
7.246	0.9289	0.9971	727.0	269.5
7.428	0.9687	0.9978	664.0	305.0
7.473	0.9752	0.9951	647.2	316.7
7.604	0.9926	0.9963	575.6	373.9
7.712	0.9944	0.9964	547.4	423.5
7.748	0.9945	0.9960	545.4	443.0
7.794	0.9940	0.9940	509.3	489.5

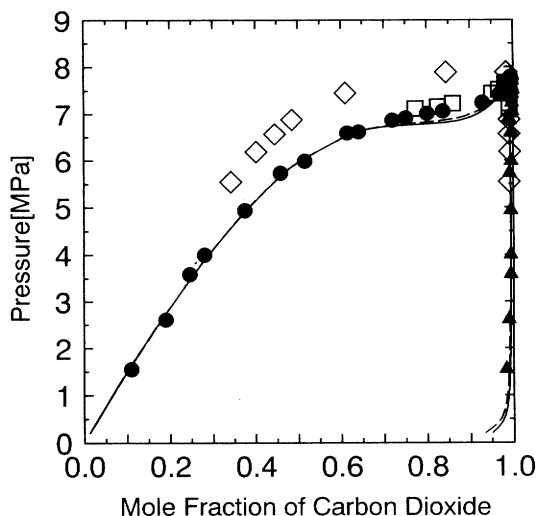


Fig. 2 Phase equilibria for carbon dioxide + ethanol system at 308.15 K

●, Liquid Phase; ▲, Vapor Phase; □, Takishima *et al.*¹⁵⁾ ◇, Jennings *et al.*²⁾ at 314.5 K
—, Pseudo cubic equation of state; ---, SRK equation of state

purity. Ethanol was a special-grade reagent of Wako Pure Chemicals Co. Ltd. The moisture contents of ethanol used in the present study were negligible, as shown by gas chromatography. **Table 2** gives the experimental results of coexisting phase compositions and their densities. The sensitivity and absolute reliability of the equilibrium compositions appear to be 0.0001 and 0.001 mole fractions, respectively. The accuracy of saturated densities is 0.1 kg/m³. The temperature was controlled within 0.003 K.

The reliability of the temperature is 0.01 K. The accuracy of the pressures is 0.01 percent. **Figure 2** gives the pressure-composition diagram, showing the differences between the present experimental results and the ones reported by Jennings *et al.*²⁾ at 314.5K and Takishima *et*

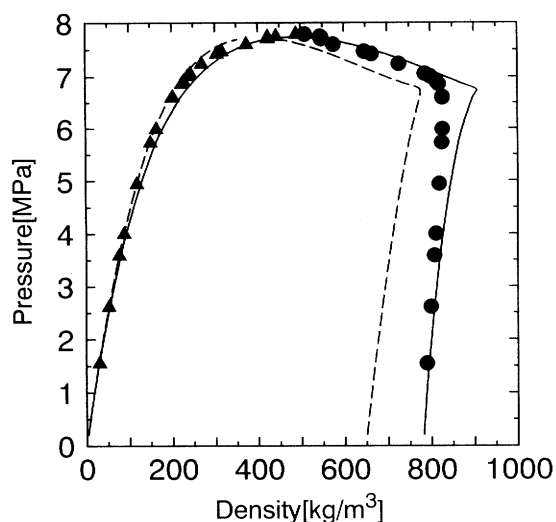


Fig. 3 Densities for carbon dioxide + ethanol system at 308.15 K
●, Liquid Phase; ▲, Vapor Phase; —, Pseudo cubic equation of state; ---, SRK equation of state

Table 3. Calculation results of phase equilibrium compositions and saturated densities with equations of state for carbon dioxide + ethanol system at 308.15 K

Equation of state	k_{ij}	l_{ij}	Liquid phase		Vapor phase	
			$ \Delta x _{lav}$	$ \Delta \rho_L _{lav}$	$ \Delta y _{lav}$	$ \Delta \rho_V _{lav}$
Ours	0.1278	-0.0544	0.0085	32.3	0.0027	8.7
SRK	0.0795	---	0.0082	85.9	0.0022	3.1

SRK: Soave-Redlich-Kwong equation of state.

$|\Delta x|_{lav}$, $|\Delta y|_{lav}$: Mole fraction. $|\Delta \rho_L|_{lav}$, $|\Delta \rho_V|_{lav}$: kg/m³.

*al.*¹⁵⁾ at 308.15K. **Figure 3** shows the pressure-saturated density diagram. The equilibrium data reported by Jennings *et al.*²⁾ and Takishima *et al.*¹⁵⁾, however, have no density data.

The authors are planning to measure the vapor-liquid-liquid equilibrium properties of other systems in the near future using the present apparatus.

3. Correlations

Phase equilibrium compositions obtained in the present study were correlated with the Soave-Redlich-Kwong equation of state¹³⁾ and the pseudo cubic equation of state previously proposed by the authors¹⁶⁾ as follows.

$$P = \frac{RT}{V^* - b} - \frac{a}{V^{*2}}, V^* = \frac{(V - \varepsilon b)(V + \sigma b)}{V} \quad (2)$$

$$\varepsilon = (1 - \theta)(\xi - 2), \sigma = (1 - \theta)(\xi + 2) \quad (3)$$

$$\xi = \sqrt{\frac{4 - \theta}{1 - \theta}}, \theta = \frac{8Z_c}{3}, Z_c = \frac{P_c V_c}{RT_c} \quad (4)$$

$$a = K_a \cdot a_c, a_c = \frac{27(RT_c)^2}{64P_c}, b_c = \frac{RT_c}{8P_c} \quad (5)$$

$$\ln K_a = S(1 - \sqrt{T_r}), S = 1.1746 + 3.4539 \cdot \omega \quad (6)$$

The following mixing rules were used in the present calculations with the pseudo cubic equation of state.

$$a = \sum_i \sum_j x_i x_j a_{ij}, a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (7)$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, b_{ij} = (1 - l_{ij}) \frac{b_i + b_j}{2} \quad (8)$$

$$\theta = \sum_i x_i \theta_i \quad (9)$$

Data with an equilibrium ratio larger than 1.5 were used in the present correlations. Saturated densities were further evaluated from equations of state with the binary interaction parameters determined in the correlations of phase equilibrium compositions. Calculation results are shown in the Figs. 2 and 3, and Table 3.

Conclusion

A new experimental apparatus equipped with three density meters for measuring phase separation properties at high pressures was developed. Phase compositions and saturated densities for carbon dioxide+ethanol system at high pressures were measured at 308.15 K. The vapor-liquid equilibrium compositions were correlated with the equations of state. Saturated densities were further evaluated from equations of state with the binary interaction parameters determined from vapor-liquid equilibrium data, though the calculation performances were not satisfied.

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Nomenclature

$a, b, \varepsilon, \theta, \sigma, \xi$	= parameters in EOS	[-]
k, l	= binary interaction parameters	[-]
K_a	= correction factor given by Eq.(5)	[-]
K_p	= pressure correction factor by Eq.(1)	[kg/m ³ MPa]

P	= pressure	[MPa]
P_0	= atmospheric pressure	[MPa]
R	= gas constant	[MPa m ³ /kmol K]
S	= parameter given by Eq.(6)	[-]
T	= temperature	[K]
V	= molar volume	[m ³ /kmol]
V^*	= apparent molar volume	[m ³ /kmol]
x, y	= mole fraction	[-]
Z	= compressibility factor	[-]
ρ	= density	[kg/m ³]
ρ^*	= density value indicated in the density meter	[kg/m ³]
ω	= acentric factor	[-]

<Subscripts>

c	= critical property
i, j	= components
L	= liquid phase
V	= vapor phase

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