Measurement of the Density of Carbon Dioxide/Methanol and Ethanol Homogeneous Mixtures and Correlation with Equation of State

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Abstract

Equations of state (EoS) can be used to estimate a wide variety of physical properties. However, there has been limited verification of the applicability of parameter sets derived from specific physical properties to correlate and estimate various other physical properties. Furthermore, the association of molecules was expected to affect the estimation using the EoS. The densities of homogeneous phase fluid mixtures of the carbon dioxide (CO_2)/methanol (MeOH) and CO_2/ethanol (EtOH) binary systems were measured. The density measurements were performed using a high-pressure vibration-type density meter equipped with a circulation pump and variable-volume viewing cell, which guaranteed the homogeneity of the mixtures. The densities were measured at temperatures ranging from 313 to 353 K, pressures up to 20 MPa, and CO_2 concentrations from 0 to 80 mol%. The experimental data obtained were correlated with two EoSs, namely Sanchez–Lacombe (SL) and Perturbed Chain statistical associating fluid theory (PC-SAFT) EoS. The reliability of the density correlations between SL and PC-SAFT EoS was almost the same. Association between CO_2 and alcohols in PC-SAFT EoS did not affect the reliability of the density correlations significantly. Using parameter sets

determined from the density measurements, the vapor liquid equilibrium (VLE) of the CO_2/MeOH and CO_2/EtOH mixtures was estimated. Both EoS showed similar estimation accuracy, with inferior estimation near the critical region of the mixtures. We also attempted to determine the densities from VLE correlations. Considering the association between CO_2 and alcohols in the PC-SAFT EoS, it was found that a good correlation of the VLE was obtained, including near the critical region of the mixture. From the results of the study, it is clear that the parameter sets must be determined under a wide range of conditions, not to mention considering the associations occurring in the system.

Keywords
Density; Carbon dioxide; Methanol; Ethanol; Peng-Robinson equation of state; Sanchez-Lacombe equation of state; PC-SAFT equation of state

1. Introduction

The phase equilibria of carbon dioxide (CO_2)/alcohol binary systems have been measured and modeled due to their use in many industrial applications. For example, Rudyk *et al*. [1] reported on the extraction of crude oil with supercritical (sc) CO_2 using methanol (MeOH) and ethanol (EtOH) as co-solvents. The total recovery yield increased significantly by an average of about 20% when compared to pure CO_2. Kim *et al*. [2] evaluated the use of methanol as an inhibitor during CO_2 clathrate hydrate formation. MeOH is also used as a physical absorbent for CO_2 capture in the Rectisol® process [3]. Taking advantage of its biocompatibility, EtOH is used as a co-solvent in the extraction of natural products such as caffeine [4] and α-pinene [5] by scCO_2. Furthermore, EtOH is also used to prepare micro particles of poly(vinylpyrrolidone) [6] and poly(vinyl alcohol) [7] by supercritical anti solvent method.

Phase equilibria of CO_2/alcohol binary systems, especially those of CO_2/MeOH binary system, have been reported repeatedly to verify the reliability of high-pressure phase equilibria measurement systems. However, phase equilibrium is not the only physical property required for chemical industrial process design. There is a wide variety of properties such as density, viscosity, and interfacial tension. Unfortunately, the number of reports on these properties is much smaller than the number of reports on phase equilibria. The measurement of physical properties under high pressure, including phase equilibria, requires specialized equipment and long acquisition periods. Therefore, the number of reports does not increase easily. Therefore, the estimation of physical properties through calculations is an important supplementary method to experimental measurements.

In systems that are under high pressure such as mixtures containing scCO_2, the

equation of state (EoS) is powerful for estimating physical properties. EoS is often used to calculate VLE and solubility because it not only describes the basic pressure-volume-temperature relationships of a system, but also allows the calculation of thermodynamic parameters such as Gibbs free energy and enthalpy. Further, EoS can also calculate various physical properties such as viscosity and interfacial tension. Since a wide variety of physical properties are required in chemical process design, it is not efficient to use only specialized equations to estimate specific properties. The properties of EoS, which allow to estimate various properties, are very attractive. However, in order to utilize the EoS to obtain various physical properties, it would be desirable to be able to correlate and estimate as many properties as possible from appropriate parameter sets, determined from a simple single set of experimental data. At present, many types of EoSs are available though, all EoSs can be classified into three main types, namely, EoS based on van der Waals model, lattice fluid model, and perturbation theory. There have been many discussions on the selection of an appropriate EoS for accurate estimation of phase equilibria. Focusing on CO_2/alcohol binary systems, Joung *et al*. [8] correlated vapor-liquid equilibrium (VLE) of CO_2/alcohol (MeOH, EtOH, 2-methoxyethanol and 2-ethoxyethanol) systems using the Peng-Robinson (PR) EoS [9] and the multi-fluid nonrandom lattice fluid hydrogen-bonding (MF-NLF-HB) EoS [10, 11]. The MF-NLF-HB EoS could correlate accurately the liquid phase composition except for in the critical region. They concluded that the PR EoS fit the data better. Khalifa *et al.* [12] correlated the phase behavior of CO_2/MeOH and CO_2/EtOH binary systems using different types of EoS: Perturbed Chain statistical associating fluid theory (PC-SAFT) EoS [13, 14], Perturbed Chain Polar (PCP) - SAFT EoS [15-17], Cubic-Plus-Association (CPA) EoS [18], and General cubic (G) EoS [19-23]. In terms of correlation, there was no difference in EoS in the low-pressure region though, similar to Joung *et al*., there was a difference in EoS in the critical region, and they reported that PC-SAFT EoS was slightly superiority.

On the other hand, there has been limited verification of the validity of applying parameter sets obtained from specific physical properties to correlate and estimate various other physical properties. Although the only used EoS was the PR EoS, Cadoso *et al.* [24] discussed vapor-liquid equilibrium and volume expansion of organic solvents by carbon dioxide using several mixing rules. They concluded that none of the mixing rules used can predict the mixture density or volume expansion satisfactorily. Moine *et al*. [25] compared the Soave-Redlich-Kwong (SRK) EoS [26] and the PC-SAFT EoS for estimating the physical properties of pure components. They pointed out that due to the difference in the parameterization method for pure component parameters, the SRK EoS failed in accurately reproducing liquid density and the PC-SAFT EoS overestimated critical pressure. Further, they also suggested that the unification of the parameterization method for pure component parameters that involved the combined analysis of saturated vapor pressure and liquid density results in no significant

difference in the accuracy of the estimation of various physical properties between the two EoSs. Mallepally *et al*. [27] compared the SRK EoS, PC-SAFT EoS, and modified Sanchez-Lacombe (MSL) EoS [28] for estimating the phase behavior and densities of propylene/toluene and ethylene/toluene systems. MSL EoS is the modification of Neau's version of the SL EoS [29-31] in that it includes a Péneloux-type volume translation. It was reported that both SRK and PC-SAFT EoSs facilitate the accurate estimation of the phase behavior and densities of various systems; however, they slightly overpredicted the densities. In a previous work [32], we evaluated the accuracy of correlation and estimation of homogeneous mixed fluid density and phase equilibrium by three EoS, PR, SL, and PC-SAFT, for the CO_2/Toluene binary system. The results show that the pure component parameters of individual EoS have a significant effect on the calculation accuracy.

It is well known that alcohol molecules associate with each other by hydrogen bonds. It also well known that association occurs between CO_2 and alcohols under high pressure. Reilly *et al*. [33] investigated the solvent properties of liquid CO_2 and MeOH by means of FT-IR spectroscopy. The spectra for the combination bands for CO_2 show that there are interactions between CO_2 and MeOH. Then, they concluded that the interactions between CO_2 and MeOH are Lewis acid-base interactions rather than hydrogen bonding. The association of molecules affects the physical properties. Therefore, some EoS with modifications for association was reported [10, 11, 18]. In PC-SAFT EoS, which is one of a perturbation theory type EoS, a molecule is regarded as constituted by a chain of several rigid hard spheres. And the PC-SAFT EoS is organized into terms that account for different types of intermolecular interactions, including terms for the hard chain reference and dispersion. For systems in which association of molecules occurs, the contribution by association is added [14, 34-36]. In the case of previously reported CO_2/Toluene binary system [32], no association between components occurred. Perturbation theory is a methodology for obtaining solutions by adding perturbation terms to the main solution. Therefore, we can deepen our discussion by focusing on the systems in which the association of molecules occur.

The homogeneous phase fluid density is different from the saturated liquid density (the density at the VLE line in the phase diagram) and is the density at the homogeneous phase region. There are many reports on the saturated liquid density though, few researchers were reported on the homogeneous phase fluid density. Smith *et al*. [37] reported the densities of the CO_2/MeOH mixtures at temperature from 313.2 to 323.2 K and at pressures from 10 to 20 MPa. Kato *et al*. [38] and Cunico *et al*. [39] measured the densities of the CO_2/EtOH mixtures at temperature 313.15 K and (308 and 323) K, respectively. Unfortunately, the experimental data reported is very limited in terms of measurement conditions. In this work, the densities of homogeneous phase fluid mixtures of the CO_2/MeOH and CO_2/EtOH systems were measured at temperatures ranging from 313 to 353 K and pressures up to 20 MPa using a high-pressure

vibration-type density meter. The CO_2 composition was varied from 0 to 80 mol% at 20 mol% intervals. The experimental data obtained were correlated with the SL and the PC-SAFT EoS. Using the parameter sets obtained from each of the two EoSs, the VLE of the CO_2/MeOH and CO_2/EtOH systems was estimated. Further, the validity of the parameter sets obtained by correlating the density and VLE data and vice versa was discussed, and the difference in the estimation accuracy for the densities and phase behavior by the basic calculation method of each EoS was determined.

2. Experimental

2.1. Materials

Carbon dioxide (CO_2, CAS number [124-38-9], mass fraction purity >99.99%) was purchased from Fujii Bussan Co. Methanol (CH_3OH, CAS number [67-56-1], mass fraction purity 99.5%) and Ethanol (C_2H_5OH, CAS number [64-17-5], mass fraction purity 99.5%) were obtained from Kanto Kagaku Co. The specifications of pure CO_2, MeOH, and EtOH are listed in Table 1.

Table 1. Specifications of pure components.

Component	CAS number	Molecular weight M_w / g mol^{-1}	Supplier	Mass fraction purity (supplier)
Carbon dioxide, CO_2	124-38-9	44.01	Fujii Bussan Co.	0.9999
Methanol, MeOH	67-56-1	32.04	Kanto Kagaku Co.	0.995
Ethanol, EtOH	64-17-5	46.07	Kanto Kagaku Co.	0.995

2.2. Apparatus and Procedure

In this study, the density of the homogeneous phase of the CO_2/MeOH and CO_2/EtOH binary mixtures was measured with an experimental apparatus containing a variable-volume viewing cell (Tamaseiki Ind. Co., H-050151-1), high-pressure vibration-type density meter (Anton Paar Co., DMP 512), and circulation pump (Nihon Seimitsu Kagaku Co., NP-AP-20(J)). In addition, it was equipped with a piston head temperature controller and constant temperature air bath (Yamato Scientific Co., Ltd., DKN602). The high-pressure vibration type density meter measures the oscillation period of the U-tube, which contains the sample. The following equation [40] was used to determine the densities from the measured period of oscillation.

$$\rho = A\tau^2 - B$$

$$with \begin{cases} A = a + bP + cP^2 \\ B = d + eP + fP^2 \end{cases} \quad (1)$$

where ρ, P, and τ are the density, pressure, and oscillation periods, respectively, and a, b, c, d, e, and f are the apparatus constants. In order to determine the values of these constants, two samples of known density which have higher and lower densities than the unknown sample are need to be measured at the experimental pressure and temperature. It should be noted that the temperature dependence was not considered due to the lack of measurement data. Therefore, the apparatus constants were determined at each temperature. The details of the experimental apparatus and procedures employed have been described elsewhere. [41] The homogeneity of the phase was confirmed from the VLE phase diagram as well as visual observation through the viewing window of the variable-volume cell.

For all measurements, the temperature and pressure uncertainties were ±0.153 K and ±0.033 MPa, respectively. The combined standard uncertainties in the composition and experimental density values were calculated for each data point. Details of the calculation methods have been described previously [41].

2.3. Experimental Data Correlation and Estimation of Density
2.3.1. SL EoS

SL EoS [29, 30], which is a lattice fluid-type EoS, is mainly used to study polymeric solutions and is applicable to large-molecule systems such as macromolecules because it does not require a critical value as a pure parameter. In this study, the experimental data were correlated to SL EoS and is shown below:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left\{\ln\left(1-\tilde{\rho}\right) + \left(1-1/r\right)\tilde{\rho}\right\} = 0$$

$$\tilde{T} = T/T^*, \quad \tilde{P} = P/P^*, \quad \tilde{\rho} = \rho/\rho^* = V^*/V \qquad (2)$$

$$r = P^*V^*/RT^*$$

where T, P, and ρ are the temperature, pressure, and density, respectively. $\tilde{T}$, $\tilde{P}$, and $\tilde{\rho}$ represent the reduced parameters; T^*, P^*, and ρ^* are characteristic parameters of the pure component; R is the gas constant; and r is the number of segments. In order to calculate the mixture using the EoS, it is necessary to apply mixing rule. The mixing rule for SL EoS used in this study is described by the following set of equations [42].

$$\frac{1}{V^*} = \sum_i \frac{\phi_i}{V_i^*} \qquad (3)$$

$$\phi_i = \frac{w_i / \rho_i^*}{\sum_j w_j / \rho_j^*} \tag{4}$$

$$P^* = \sum_i \phi_i P_i^* - RT \sum_j \sum_{i<j} \phi_i \phi_j \chi_{ij} \tag{5}$$

$$\chi_{ij} = \frac{P_i^* + P_j^* - 2\left(1 - \delta_{ij}\right)\left(P_i^* P_j^*\right)^{1/2}}{RT} \tag{6}$$

$$T^* = \frac{P^* v_0}{R} \tag{7}$$

$$\frac{1}{v_0} = \sum_i \phi_i \left(\frac{P_i^*}{RT_i^*}\right) \tag{8}$$

where v_0 is the volume of a lattice site. ϕ_i and w_i are the close-packed volume fraction and mass fraction of the ith component, respectively. χ_{ij} is the i-j interaction term, and δ_{ij} is the i-j interaction parameter. The interaction parameters were used as fitting parameters in the correlation. Methods underlying the calculations involved have been detailed in a previous work [32]. The pure component parameters used in this study are summarized in Table 2 [30].

2.3.2. PC-SAFT EoS

PC-SAFT EoS [13, 14], which is representative of the SAFT-type EoS, is derived from the perturbation theory. Perturbation theory is a methodology for obtaining solutions by adding perturbation terms to the main solution. In this study, the experimental data were correlated with the PC-SAFT EoS and is shown below:

$$\frac{A^{res}}{NkT} = \tilde{a}^{res} = \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} \tag{9}$$

where A^{res} is the residual Helmholtz free energy, and $\tilde{a}^{hc}$, $\tilde{a}^{disp}$, and $\tilde{a}^{assoc}$ are contributions to the Helmholtz free energy by a chain of hard spheres, by diffusion, and association, respectively. The compression factor Z is expressed in terms of the Helmholtz free energy as shown in equation (10):

$$Z = 1 + \eta \left(\frac{\partial \tilde{a}^{res}}{\partial \eta}\right)_{T, x_i} \tag{10}$$

where η is the packing fraction. Details of the calculation methods for $\tilde{a}^{hc}$ and $\tilde{a}^{disp}$ have been described previously [32]. Association was not expected to occur between the components in previous study, and thus, the contribution by association $\tilde{a}^{assoc}$ was ignored. In this study, it

was expected that association occur between alcohols and between CO_2 and alcohols. The contribution to the Helmholtz free energy by association is shown follows [34-36]:

$$\tilde{a}^{assoc} = \sum_i X_i \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \tag{11}$$

where X^{A_i} is the mole fraction of ith component not bonded at site A, and M_i is the number of association sites on i^{th} component. X^{A_i} is given by

$$X^{A_i} = \left[1 + N_{Av} \sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j} \right]^{-1} \tag{12}$$

($\sum_{B_j}$ over all sites on j^{th} component, A_j, B_j, C_j, ...; $\sum_j$ over all components)

where N_{Av} and ρ_j are the Avogadro's number and molar density of jth component, respectively, and $\Delta^{A_i B_j}$ is the strength of interaction between site A on i^{th} component and site B on j^{th} component. $\Delta^{A_i B_j}$ is shown below:

$$\Delta^{A_i B_j} = d_{ij}{}^3 g_{ij} \left(d_{ij} \right)^{seg} \kappa^{A_i B_j} \left[\exp\left(\varepsilon^{A_i B_j} / kT \right) - 1 \right] \tag{13}$$

$$d_{ij} = \left(d_i + d_j \right) / 2 \tag{14}$$

where k is the Boltzmann constant. d_i is the temperature-dependent segment diameter of ith component and is given by

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-3 \frac{\varepsilon_i}{kT} \right) \right] \tag{15}$$

where σ_i and ε_i are the segment diameter and depth of the pair potential of ith component, respectively. $g_{ij}(d_{ij})^{seg}$ is the temperature-dependent segment diameter of ith component and the segment radial distribution function. $g_{ij}(d_{ij})^{seg}$ can be approximated to the radial distribution function of the hard-sphere fluid $g_{ij}(d_{ij})^{hs}$ as follows:

$$g_{ij} \left(d_{ij} \right)^{seg} \approx g_{ij} \left(d_{ij} \right)^{hs} = \frac{1}{1 - \zeta_3} + \left(\frac{d_i d_j}{d_i + d_j} \right) \frac{3 \zeta_2}{\left(1 - \zeta_3 \right)^2} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2 \zeta_2^2}{\left(1 - \zeta_3 \right)^3} \tag{16}$$

where ζ_n is defined as

$$\zeta_n = \frac{\pi}{6} \rho_m \sum_i x_i m_i d_i^n \quad n \in \{0,1,2,3\} \tag{17}$$

where x_i and m_i are the molar fraction and number of segments per chain of ith component, respectively. ρ_m is the total number density of molecules. Finally, $\kappa^{A_i B_j}$ and $\varepsilon^{A_i B_j}$ are the

volume of interaction and association energy of interaction between site A on i^{th} component and site B on j^{th} component, respectively. In the PC-SAFT EoS, m_i, σ_i, and ε_i are pure component parameters independent on the contribution by association. When the contribution by association is introduced, the association parameters $\kappa^{A_i B_i}$ and $\varepsilon^{A_i B_i}$ are added as pure component parameters. In this study, it was assumed that alcohols have two association sites, one for the oxygen atom (O) of the hydroxy group and the other for the hydrogen atom (H), and that association occurs between the O and H atoms. This is classified as type 2B [36]. All pure component parameters of the PC-SAFT EoS including the association parameters were obtained by fitting the experimentally from saturated liquid density and saturated vapor pressure of pure component. The PC-SAFT EoS parameters, which are the pure component parameters used in this study, are summarized in Table 2 [13, 14].

The following mixing rule for the PC-SAFT EoS was used in this study:

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right) \qquad (18)$$

$$\varepsilon_{ij} = \left(1 - \theta_{ij}\right)\sqrt{\varepsilon_i \varepsilon_j} \qquad (19)$$

where θ_{ij} is the interaction parameter and is a fitting parameter in the correlation. For association, instead of applying the mixing rule to obtain the mixing parameters, it needed to consider the way of association between different components and association site. In this study, the 1st component, CO_2, was not expected to cause intermolecular association, while the 2nd component, alcohol, was expected to cause intermolecular association (O_2 and H_2). Reilly et $al.$ [33] reported that the association occurs between CO_2 and alcohol, where the association occurs between the oxygen atom (O_1) of CO_2 and the hydrogen atom (H_2) of the hydroxy group of the alcohol. We introduced the contribution by the association between CO_2 and alcohol into the PC-SAFT EoS in a similar way to Fu et $al.$ [43] The mole fraction not bonded at each site is given by:

$$X^{O_1} = \left[1 + N_{Av}\rho_2 X^{H_2}\Delta^{O_1 H_2}\right]^{-1} \qquad (20)$$

$$X^{O_2} = \left[1 + N_{Av}\rho_2 X^{H_2}\Delta^{O_2 H_2}\right]^{-1} \qquad (21)$$

$$X^{H_2} = \left[1 + N_{Av}\left(\rho_1 X^{O_1}\Delta^{O_1 H_2} + \rho_2 X^{O_2}\Delta^{O_2 H_2}\right)\right]^{-1} \qquad (22)$$

where $\Delta^{O_1 H_2}$ is shown as:

$$\Delta^{O_1 H_2} = d_{12}^{\ 3} g_{12}\left(d_{12}\right)^{seg} \kappa^{O_1 H_2}\left[\exp\left(\varepsilon^{O_1 H_2}/kT\right) - 1\right] \qquad (23)$$

In this study, the experimental data were correlated in two different ways, with and without introducing the association between CO_2 and alcohol. When not introduced, the interaction

parameter θ_{ij} is the fitting parameter, and when introduced, the three parameters with the addition of $\kappa^{O_1H_2}$ and $\varepsilon^{O_1H_2}$ are the fitting parameters.

Table 2. Pure component parameters for the SL EoS and PC-SAFT EoS.

Sanchez-Lacombe equation of state

	P^* (MPa)	T^* (K)	ρ^* (kg m^{-3})		Ref.
CO$_2$	574.5	305	1510		[30]
MeOH	1202	468	922		[30]
EtOH	1069	413	963		[30]

PC-SAFT equation of state

	m	σ (Å)	ε/k (K)	κ^{AiBi} / -	ε^{AiBi}/k / K	Ref.
CO$_2$	2.0729	2.7852	169.21			[13]
MeOH	1.5255	3.23	188.9	0.035176	2899.5	[14]
EtOH	2.383	3.177	198.24	0.0323	2653.4	[14]

3. *Results and Discussion*

3.1. *Experimental data*

Experimental measurements of the density of two systems (CO$_2$/MeOH, CO$_2$/EtOH) are shown in Figures 1. Figures 1(a) and (b) show the density–composition relationships for the CO$_2$/MeOH and CO$_2$/EtOH systems, respectively. From figures 1(a) and (b), at low CO$_2$ concentrations, the density of the CO$_2$/MeOH and CO$_2$/EtOH system increases with the increase in CO$_2$ mole fraction to a certain maximum to decrease (approaching the density of pure CO$_2$) at higher CO$_2$ concentrations. This tendency can be explained by the fact that at low CO$_2$ concentrations, the penetration of CO$_2$ into between the organic molecules to makes the mixture dense. In contrast, at high CO$_2$ compositions, the organic molecules are surrounded by CO$_2$ to result in the properties of CO$_2$ become dominant.
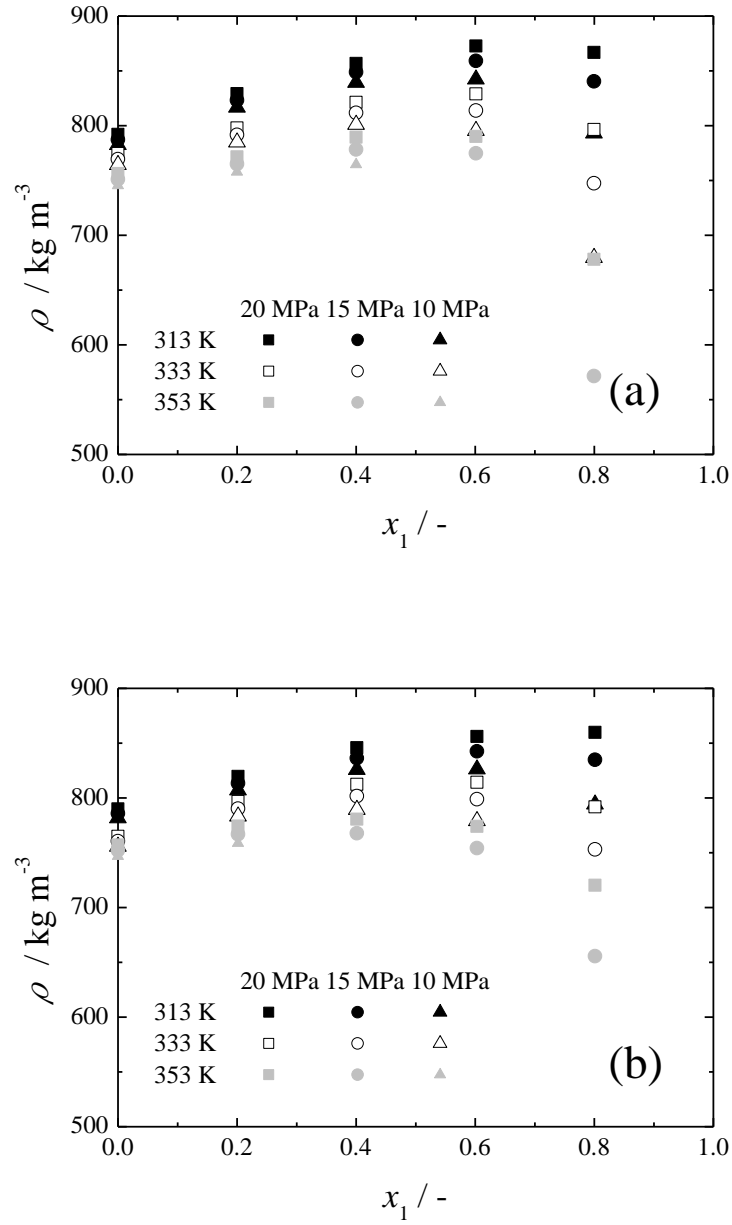
Figure 1 Density behavior of (a) the $CO_2(1)$/MeOH(2) and (b) the $CO_2(1)$/EtOH(2) system.

3.2. Correlation of Density with EoS

The correlated results are shown in Figures 2. From the figure, it is clear that SL and PC-SAFT EoS show identical results. Furthermore, in the PC-SAFT EoS, considering the association between CO_2 and alcohols did not have a significant effect on the density correlation results.
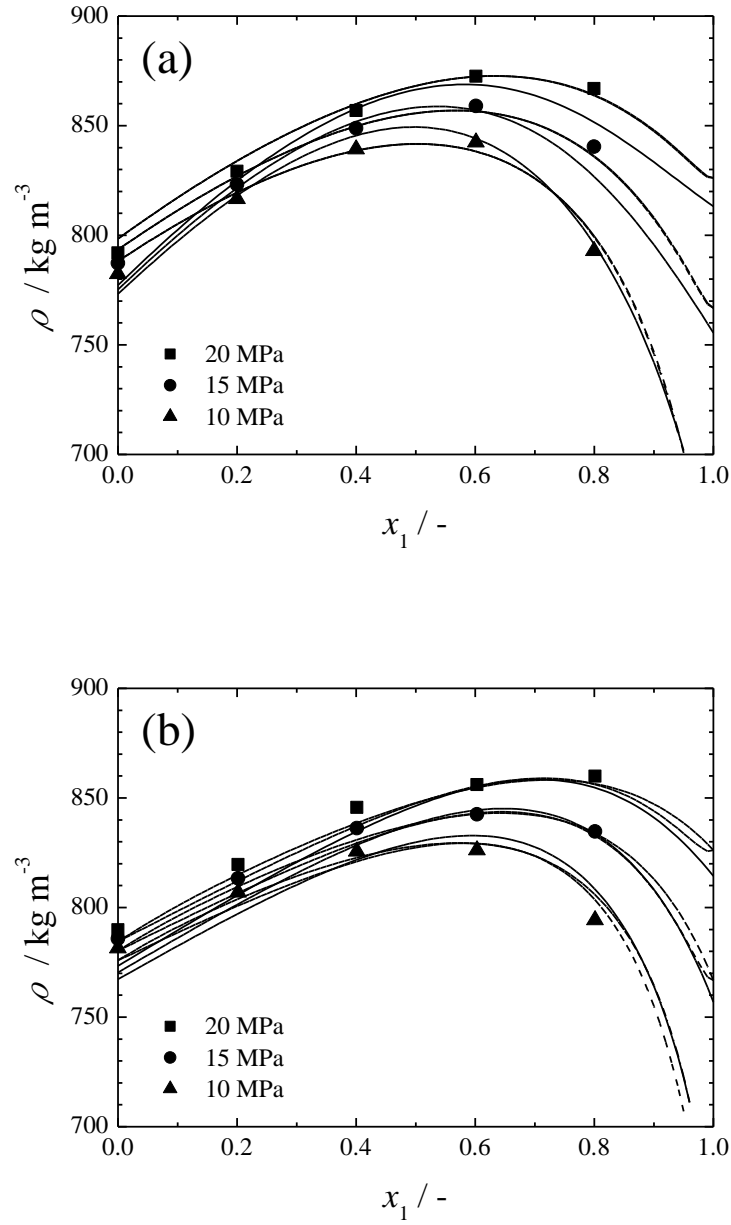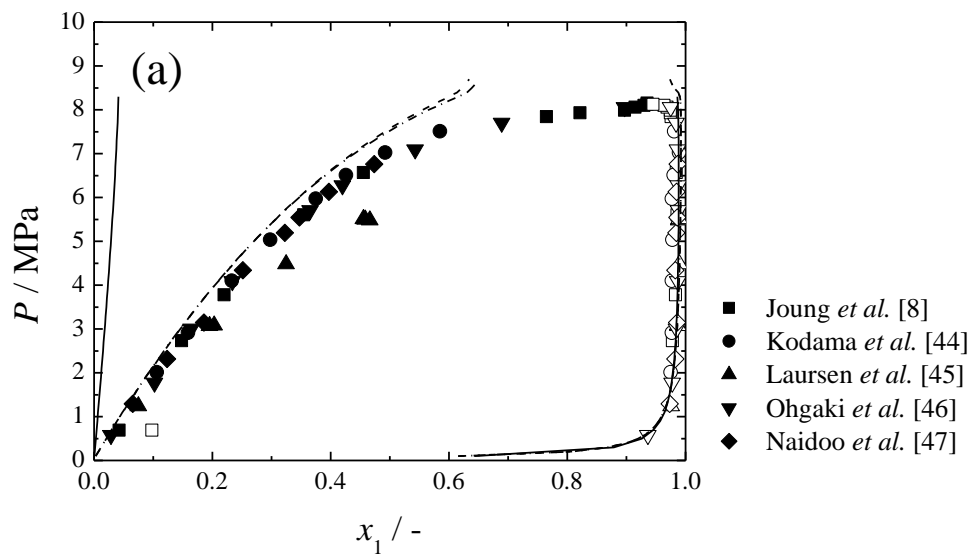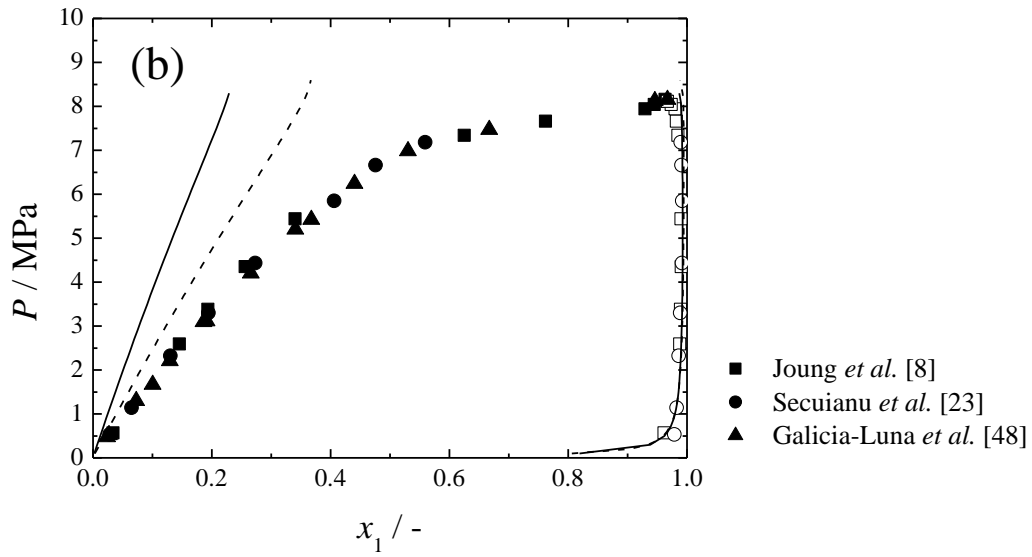
Figure 2 Correlation results of the densities at 313 K with the SL (solid line), PC-SAFT (dashed line), and PC-SAFT considering the association between CO_2 and Alcohols (dashed-and-dotted line) EoS: (a) $CO_2(1)/MeOH(2)$ system and (b) $CO_2(1)/EtOH(2)$ system.

3.3. Estimation of VLE with EoS

The VLE line of the $CO_2/MeOH$ and $CO_2/EtOH$ system was estimated using the various EoS with the interaction parameters obtained using the density correlations. The estimated results are shown in Figure 3. The interaction parameters in each EoS represent the

differences in structure and energy between the component molecules, and not the physical properties. Ideally, the VLE line can be estimated using the parameters obtained from the density correlations. It could be seen that PC-SAFT EoS was able to estimate the VLE better than SL EoS. In addition, PC-SAFT EoS could further improve the estimation accuracy by considering the association between CO_2 and alcohol. The SL EoS does not consider the association between molecules because the molecules are arranged completely randomly on the lattice. It is clear that the consideration of association affects the results of VLE estimation. The figure shows that all results by each EoS are inferior near the critical region of the mixture. It is known that both SL EoS and PC-SAFT EoS are poor at estimating in the critical region.


(a)

P / MPa

x_1 / -

- ■ Joung *et al.* [8]
- ● Kodama *et al.* [44]
- ▲ Laursen *et al.* [45]
- ▼ Ohgaki *et al.* [46]
- ◆ Naidoo *et al.* [47]

Figure 3 Estimation of the vapor-liquid phase diagram at 313 K with the SL (solid line), PC-SAFT (dashed line), and PC-SAFT considering the association between CO₂ and Alcohols (dashed-and-dotted line) EoS: (a) CO₂(1)/MeOH(2) system [8, 44-47] and (b) CO₂(1)/EtOH(2) system [8, 23, 48] (closed symbol: liquid phase, open symbol: vapor phase).

3.4. Estimation of Density with EoS
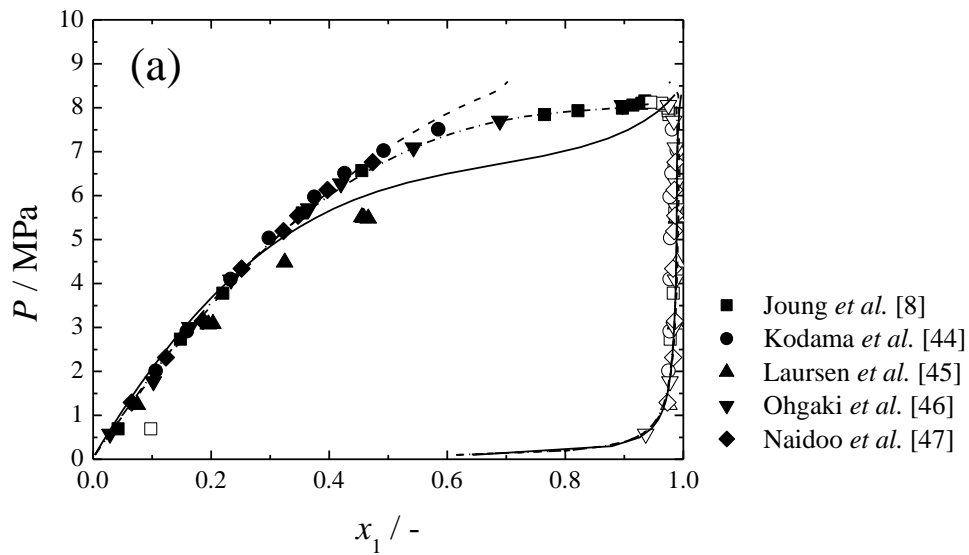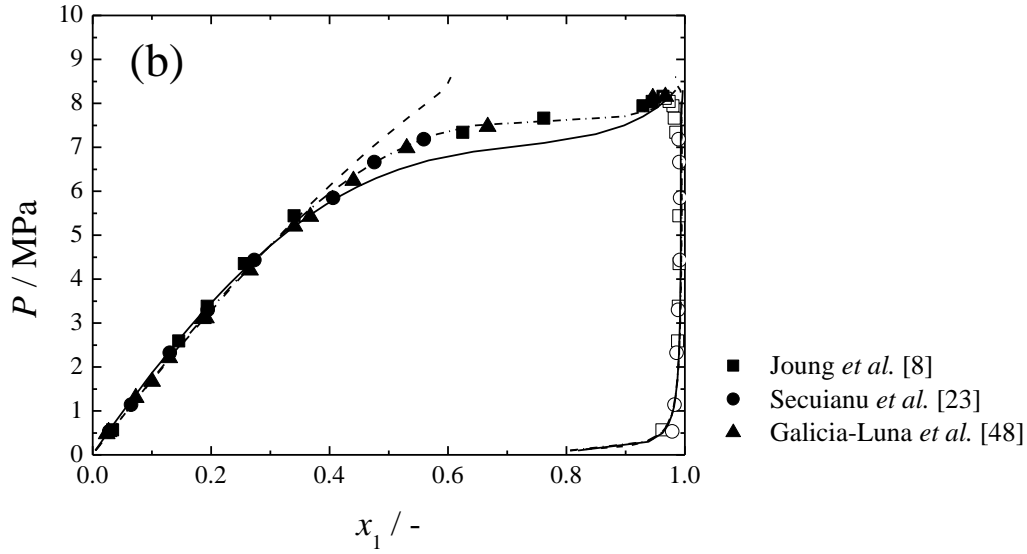
Figure 4 Correlation results of the vapor-liquid phase diagram at 313 K with the SL (solid line), PC-SAFT (dashed line), and PC-SAFT considering the association between CO_2 and Alcohols (dashed-and-dotted line) EoS: (a) $CO_2(1)$/MeOH(2) system [8, 44-47] and (b) $CO_2(1)$/EtOH(2) system [8, 23, 48] (closed symbol: liquid phase, open symbol: vapor phase).

Unlike the results reported in Sections 3.2., the densities of the CO_2/MeOH and CO_2/EtOH systems were estimated using each of the EoS with interaction parameters obtained from the VLE correlations. The correlation results for VLEs are showed in Figure 4. The figure shows that, unlike the other two methods, the estimating the VLE near the critical region of mixture were well by considering the association between CO_2 and alcohols. The effect of association between CO_2 and alcohols was not observed in the correlation of the density of homogeneous mixed fluids, whereas it was confirmed in the correlation of VLE, especially near the critical region. The work of Reilly *et al.* [33] described in Introduction was based on FT-IR measurements under CO_2-rich conditions. In other words, the measurements were made near the critical region of the mixture, and it was thought that the association between CO_2 and alcohol could be well confirmed near the critical region. Therefore, the association between CO_2 and alcohols had a significant effect on the accuracy of the VLE correlation. In contrast, the density of the homogeneous mixed fluid was under alcohol-rich conditions, and the effect of the association between CO_2 and alcohols was not confirmed to be significant. The estimated density results using the various EoS with the interaction parameters obtained using the VLE correlations are shown in Figure 5. From the figure, it can be seen that the density of the homogeneous mixed fluid is estimated with good accuracy by the PC-SAFT EoS, while the

change with respect to the CO_2 mole fraction is overestimated by the SL EoS. In summary, in systems where molecular associations occur, the estimation of various properties by EoS can be achieved by considering all the associations occurring and using a set of parameters determined under a wide range of experimental conditions.
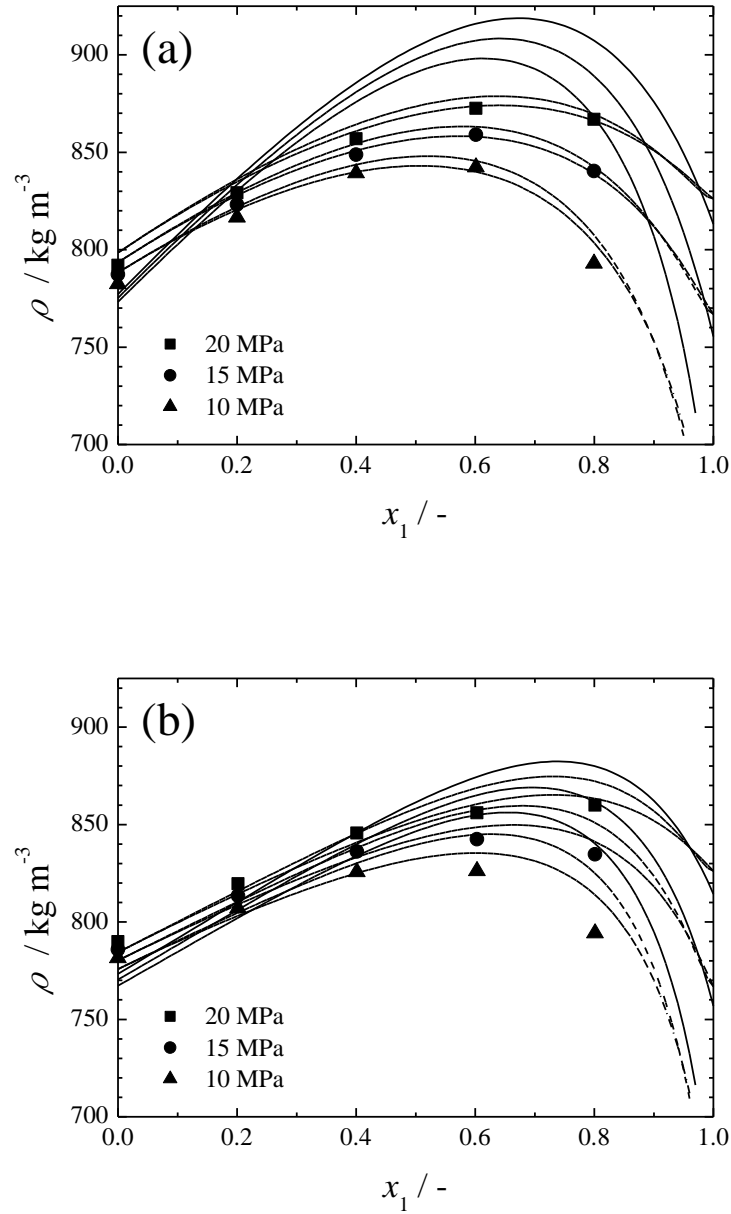
Figure 5 Estimation of the densities at 313 K with the SL (solid line), PC-SAFT (dashed line), and PC-SAFT considering the association between CO_2 and Alcohols (dashed-and-dotted line) EoS: (a) $CO_2(1)$/MeOH(2) system and (b) $CO_2(1)$/EtOH(2) system.

4. Conclusions

      The densities of homogeneous fluid mixtures of the CO_2/MeOH and CO_2/EtOH systems were measured over a wide range of temperature, pressure, and compositions using a high-pressure vibration-type density meter. The experimental results were also fit to two different EoS, namely SL and PC-SAFT EoS, and the individual parameter sets were determined for each EoS. The reliability of the density correlations between SL and PC-SAFT EoS was almost the same, and considering the association between CO_2 and alcohols in PC-SAFT EoS did not affect the reliability of the density correlations significantly. As a result of estimating the VLE using the interaction parameters obtained by correlating the density, the PC-SAFT EoS showed better estimation accuracy than the SL EoS. This was a result of considering the association of molecules. However, the accuracy of the estimation near the critical region of the mixture was poor for both EoS. As a result of correlating the VLE using each EoS, the PC-SAFT EoS, which considered the association between CO_2 and alcohols, showed a good correlation including the critical region of the mixture. The density of the homogeneous fluid mixture was well estimated using the interaction parameters obtained by correlating the VLE. The critical region of the mixture was the region where the association between CO_2 and alcohols was confirmed, and the correlation accuracy was affected by whether the association was considered. In contrast, since the conditions near the critical region of the mixture were not included in the measurement conditions of the density of the homogeneous fluid mixture, the correlation accuracy was not affected by the difference in EoS. In studying the efficient estimation of a wide variety of physical properties, it was found that the parameter sets must be determined under a wide range of conditions, not to mention considering the associations occurring in the system.

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