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Measurement and Correlation of the Solid−Liquid−Gas Equilibria for Carbon Dioxide + Octadecanoic Acid (Stearic Acid) and Carbon Dioxide + 1-Octadecanol (Stearyl Alcohol) Systems

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The pressure p−temperature T projections of solid−liquid−gas (S−L−G) three-phase coexistence lines for the carbon dioxide + octadecanoic acid (stearic acid; $C_{18}H_{36}O_2$) system and the carbon dioxide + 1-octadecanol (stearyl alcohol; $C_{18}H_{38}O$) system were measured by the first melting point method in which the initial appearance of the liquid phase was observed. The experimental $p-T$ projections of the S−L−G lines were also correlated by the Peng−Robinson equation of state and the van der Waals type mixing rules with two binary interaction parameters introduced into attraction term and size terms, respectively. The present model gave good correlation results for all of the experimental S−L−G lines with maximum average absolute relative deviations of 0.32 % for the carbon dioxide + octadecanoic acid system and 0.32 % for the carbon dioxide + 1-octadecanol system.

Introduction

Supercritical fluids have been given much attention as a new type of solvent and have been applied in various industries. Their solvent power is moderate, and their transport properties are favorable for mass transfer rates. Supercritical fluids are therefore thought to be attractive solvents for several techniques such as separation, reaction, and material processing. In particular, carbon dioxide has been commonly used as a solvent for many industrial applications because it is environmentally benign, nonhazardous, and inexpensive and has a low critical temperature and a moderate critical pressure. Recently, supercritical carbon dioxide has been widely used as a crystallization solvent for the rapid expansion of supercritical solutions (RESS), supercritical antisolvent recrystallization (SAS), and particles from gas saturated solution (PGSS) processes and so forth.[1−3]

A knowledge of solid−liquid−gas (S−L−G) equilibria is very important to understand and design the processes with supercritical fluids. In particular, S−L−G equilibria can be used to predict the applicability of the micronization and crystallization processes using supercritical fluids mentioned above and to optimize the choice of operation variables in the processes. For example, in the RESS process, the properties of products such as particle size and morphology have often been reported to be strongly influenced by the phase behavior, the S−L−G equilibria of the pre-expansion region.[4−7]

Measurement of the S−L−G equilibria has been performed over the past several years by several techniques. For the determination of only the $p-T$ projection of S−L−G curves, the most popular and widely used method is the first melting point method, which consists of the observation of the initial appearance of a liquid phase.[5,8−31] As a similar approach, the observation of the initial appearance of a solid phase, the first freezing point method, has also been used for the determination of the $p-T$ projection of S−L−G lines.[16,17,21,32−36] Static solubility measurements using known quantities of solid and gas are employed to deduce the $p-T$ projection of the S−L−G line as well as the compositions of both the liquid and gas phases.[37−42] A precise measurement technique of S−L−G equilibria using a scanning transitiometer has also been reported by Fischer et al.[43,44]

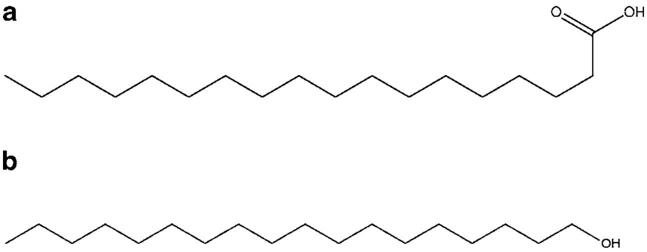

Figure 1. Chemical structures of (a) octadecanoic acid and (b) 1-octadecanol.

The present work focuses on the measurement and comparison of the S−L−G equilibria for two carbon dioxide + C_{18}-normal chain saturated aliphatic hydrocarbon (octadecanoic acid, $C_{18}H_{36}O_2$; and 1-octadecanol, $C_{18}H_{38}O$) systems. The $p-T$ projections of the S−L−G three-phase coexistence lines for the carbon dioxide + octadecanoic acid (stearic acid) and carbon dioxide + 1-octadecanol (stearyl alcohol) systems were determined by the first melting point method. This measurement approach was chosen because of its simplicity and quickness of operation.

Octadecanoic acid and 1-octadecanol are useful as ingredients in making cosmetics and oil products such as candles and lubricants. Figure 1 depicts the chemical structures of octadecanoic acid and 1-octadecanol.

Because the experimental determination of high-pressure phase equilibria is difficult and costly, it would be advantageous to extend and complement the experimental data by using thermodynamic models. In previous work,[5,16,23−25,30,33,41,45−49] a cubic equation of state, such as the Soave−Redlich−Kwong

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(SRK) equation of state[50] or the Peng−Robinson equation of state,[51] has been applied to the representation of S−L−G equilibria. In the present work, the $p-T$ projections of the S−L−G lines obtained were correlated by the Peng−Robinson equation of state and the van der Waals type mixing rules with two binary interaction parameters introduced into attraction and size terms, respectively.

Experimental Section

Materials. Octadecanoic acid (supplied by Wako Pure Chem. Ind., Ltd.; its purity is greater than 99 wt %) and 1-octadecanol (supplied by Wako Pure Chem. Ind., Ltd.; its purity is greater than 98 wt %) were used as solutes. High-purity carbon dioxide (supplied by Showa Tansan Co.; its purity is greater than 99.990 vol %) was used as received.

Apparatus and Procedures. A static equilibrium apparatus was used in this work. A detailed description of the apparatus and operating procedures is given in a previous work.[24] In the previous work,[24] the reliability of the present apparatus and experimental procedures was verified by measuring the $p-T$ projections of the S−L−G line for the carbon dioxide + benzoic acid system and then showing the fair agreement with reliable literature data.[43] The melting point was determined by finding the first melting temperature at a constant pressure or finding the first melting pressure at a constant temperature after approximately 2 h to ensure thermal equilibrium. In preliminary experiments, the verification of thermal equilibrium was carefully examined for 1 min to 48 h, and we confirmed that the result for (1 to 2) h was the same as those for more than 2 h. In the pressure region lower than about 10 MPa, pressure was slowly raised until the initial appearance of the liquid phase. In the higher-pressure region above 10 MPa where the $p-T$ line became almost parallel to the pressure axis, temperature was slowly raised until melting was first observed. Repeated measurements were made to reduce the uncertainty in the temperature measurement to less than 0.1 K or in the pressure measurement to less than 0.1 MPa. Afterward, the initial solidification of the solute that is the first freezing point was also checked by lowering temperature or pressure. No hysteresis was found within the experimental accuracy of ± 0.1 K and ± 0.1 MPa in each measurement. The reproducibility of the S−L−G equilibria of carbon dioxide + octadecanoic acid and carbon dioxide + 1-octadecanol systems was within 0.1 %.

Results and Discussion

The experimental pressure−temperature data for the three-phase S−L−G line for the carbon dioxide + octadecanoic acid and carbon dioxide + 1-octadecanol systems are listed in Tables 1 and 2, respectively. These data are also shown in Figure 2 along with the literature data for the carbon dioxide + octadecanoic acid system reported by Alessi et al.[23] and Bertakis et al.[30] and the vapor pressure line[52] and the critical point[53] of carbon dioxide. The present data are in agreement with the literature data in the pressure region lower than 10 MPa, while in the pressure region higher than 10 MPa, the present data show relatively higher temperature (about 5 K) at the same pressure than those reported by Bertakis et al.[30] This deviation may be caused by the different purity of the materials used. The purity of this work is 99 wt %, but that of previous work is 97 wt %.

Table 1. Experimental and Calculated Pressure−Temperature Data of the Solid−Liquid−Gas Line for the Carbon Dioxide + Octadecanoic Acid System

p/MPa	T_{exp}/K	T_{calc}/K
0.1	342.4	342.3
1.4	339.9	339.3
2.3	338.8	337.5
3.0	337.9	336.3
3.8	337.0	335.0
4.6	335.9	333.8
5.3	334.9	332.8
5.9	333.9	332.1
6.7	332.8	331.2
7.6	331.9	330.4
8.4	331.0	329.8
9.3	329.9	329.3
11.3	328.9	328.9
12.5	328.6	328.9
13.5	328.6	328.9
15.6	328.7	328.9
16.8	328.8	329.2
17.7	328.9	329.5
18.7	328.9	329.8
22.0	329.2	331.1

Table 2. Experimental and Calculated Pressure−Temperature Data of the Solid−Liquid−Gas Line for the Carbon Dioxide + 1-Octadecanol System

p/MPa	T_{exp}/K	T_{calc}/K
0.1	330.9	330.9
1.8	329.2	328.8
2.8	328.0	327.5
3.9	327.1	326.0
4.9	326.1	324.8
5.7	325.0	323.8
6.9	324.1	322.6
7.9	323.1	321.7
9.4	322.1	320.8
10.8	321.6	320.6
11.7	321.6	320.6
12.7	321.7	320.6
14.9	322.0	320.6
16.6	322.1	320.7
21.1	322.8	321.7
23.0	323.0	322.1

The $p-T$ projections of the S−L−G line for the carbon dioxide + octadecanoic acid and carbon dioxide + 1-octadecanol systems are quite similar, and they have an inflection point at around (10 to 12) MPa. That is, the melting temperature of the solutes in carbon dioxide gradually decreases from the normal melting point to the inflection point and increases from the point. The maximum temperature drop from the normal melting temperature of octadecanoic acid in carbon dioxide (13.4 K) is higher than that of 1-octadecanol in carbon dioxide (9.3 K). A melting temperature drop of a solid solute in carbon dioxide would be caused by the dissolution of carbon dioxide

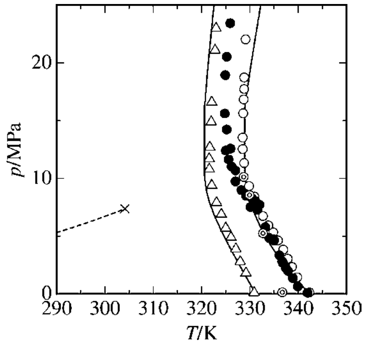

Figure 2. $p-T$ projections of the solid−liquid−gas lines for carbon dioxide + octadecanoic acid and carbon dioxide + 1-octadecanol systems: ○, octadecanoic acid; △, 1-octadecanol, experimental results; ◎, octadecanoic acid, Alessi et al.;[23] ●, octadecanoic acid, Bertakis et al.;[30] solid line, calculated results; ×, critical point of carbon dioxide;[53] broken line, vapor pressure line of carbon dioxide.[52]

in the solute in proportion to increasing the density of carbon dioxide. The greater temperature drop for the carbon dioxide + octadecanoic acid system will mean that the interaction between carbon dioxide and octadecanoic acid is larger than that between carbon dioxide and 1-octadecanol. This difference of the interaction would be caused by the difference of the number of carbon dioxide molecules around a functional group in a solute molecule; that is, the number of carbon dioxide molecules around a carboxyl group in octadecanoic acid is greater than that around a hydroxyl group in 1-octadecanol.[54]

Correlation

For components 1 and 2 in a mixture, the thermodynamic condition of phase equilibria at a constant temperature and pressure is that the fugacities of components 1 and 2 of each phase are equal

$$f_2^{\mathrm{S}} = f_2^{\mathrm{G}} \tag{1}$$

$$f_2^{\mathrm{G}} = f_2^{\mathrm{L}} \tag{2}$$

$$f_1^{\mathrm{G}} = f_1^{\mathrm{L}} \tag{3}$$

where f represents the fugacity; subscripts 1 and 2 denote solvent and solute, respectively; and superscripts S, L, and G show solid, liquid, and gas phases, respectively.

For the calculation of the fugacity of the solute in a solid phase, the approach proposed by Kikic et al.[47] and Mukhopadhyay[55] was used. Because the fugacity of the solute in a solid phase cannot be directly calculated by a conventional equation of state, the fugacity in the solid phase can be estimated by using that in the subcooled liquid phase, f_2^{SCL}, the heat of fusion, $\Delta h_2^{\mathrm{fus}}$, and the triple-point temperature, T_{tp}, of the solute, neglecting the difference in the heat capacities in the solid and liquid states as follows[56]

$$\ln \frac{f_2^{\mathrm{S}}}{f_2^{\mathrm{SCL}}} = \frac{\Delta h_2^{\mathrm{fus}}}{RT_{\mathrm{tp}}}\left(1 - \frac{T_{\mathrm{tp}}}{T}\right) \tag{4}$$

To take into account the effect of pressure, these fugacities can be written

$$f_2^{\mathrm{S}}(T,p) = f_2^{\mathrm{S}}(T,p_{\mathrm{tp}})\exp\left[\frac{v_2^{\mathrm{S}}(p - p_{\mathrm{tp}})}{RT}\right] \tag{5}$$

$$f_2^{\mathrm{SCL}}(T,p) = f_2^{\mathrm{SCL}}(T,p_{\mathrm{tp}})\exp\left[\frac{v_2^{\mathrm{SCL}}(p - p_{\mathrm{tp}})}{RT}\right] \tag{6}$$

where v_2^{S} and v_2^{SCL} are, respectively, the molar volumes of component 2 in the solid and subcooled liquid phases. Combining these eqs 4 to 6, the following equation can be obtained

$$f_2^{\mathrm{S}}(T,p) = f_2^{\mathrm{SCL}}(T,p)\exp\left[\frac{(v_2^{\mathrm{S}} - v_2^{\mathrm{SCL}})(p - p_{\mathrm{tp}})}{RT} + \frac{\Delta h_2^{\mathrm{fus}}}{RT_{\mathrm{tp}}}\left(1 - \frac{T_{\mathrm{tp}}}{T}\right)\right] \tag{7}$$

Equation 7 can be written as

$$p\varphi_2^{\mathrm{G}}y_2 = f_2^{\mathrm{SCL}}(T,p)\exp\left[\frac{(v_2^{\mathrm{S}} - v_2^{\mathrm{SCL}})(p - p_{\mathrm{tp}})}{RT} + \frac{\Delta h_2^{\mathrm{fus}}}{RT_{\mathrm{tp}}}\left(1 - \frac{T_{\mathrm{tp}}}{T}\right)\right] \tag{8}$$

where φ_2^{G} is the fugacity coefficient of solid component 2 in the gas phase, and y is a gas-phase mole fraction. The values of v_2^{S} can be obtained from the literature, and the values of v_2^{SCL} can be evaluated by an equation of state assuming that the volume was independent of pressure and temperature and equal to the value at the normal melting point. The fugacity of a pure solute in the subcooled liquid phase can be calculated by an equation of state. In practice, it is common to substitute the normal melting temperature, T_{m} for T_{tp}, atmospheric pressure for p_{tp}, and to use for $\Delta h_2^{\mathrm{fus}}$ the heat of fusion at the normal melting temperature.

Equations 2 and 3 can be written as

$$\varphi_2^{\mathrm{G}}y_2 = \varphi_2^{\mathrm{L}}x_2 \tag{9}$$

$$\varphi_1^{\mathrm{G}}y_1 = \varphi_1^{\mathrm{L}}x_1 \tag{10}$$

where x represents a liquid-phase mole fraction.

The fugacity coefficients of the solvent and solute in gas and liquid phases, φ_i^{G} and φ_i^{L}, are usually evaluated by adopting an appropriate equation of state. The Peng−Robinson equation of state[51] was adopted to evaluate the fugacity coefficients of components 1 and 2 in the liquid and gas phases, the fugacities of component 2 in the subcooled liquid phase, and the molar volumes of component 2 in the subcooled liquid phase because the equation is improved to give a good representation of liquid properties

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{11}$$

where a and b are the pure component parameters that can be calculated with the critical properties and the Pitzer acentric factor.

To apply eq 11 to a binary system, we use the conventional mixing rules for parameters a and b as follows

$$a = \sum_i \sum_j y_i y_j a_{ij},\ a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{12}$$

$$b = \sum_i \sum_j y_i y_j b_{ij},\ b_{ij} = (1 - l_{ij})\frac{b_i + b_j}{2} \tag{13}$$

where k_{ij} and l_{ij} denote the binary interaction parameters between components i and j. When eqs 11 to 13 are used, fugacity coefficients φ_i^{G} and φ_i^{L} will be thermodynamically derived.

S−L−G lines can be calculated by solving eqs 8 to 10 simultaneously. The S−L−G lines were obtained in the manner proposed by Bertakis et al.[30] and McHugh et al.[41] The calculation procedure used was explained in a previous work.[24] The physical properties of octadecanoic acid and 1-octadecanol were available in the literature. The physical properties are listed in Table 3.

The S−L−G lines of the carbon dioxide + octadecanoic acid and carbon dioxide + 1-octadecanol systems were calculated using two binary interaction parameters that were determined to give a good representation of both the experimental S−L−G lines and the solubility of the solutes in supercritical carbon dioxide at 308.2 K.[60] The solubilities of the solutes in supercritical carbon dioxide were calculated by using eq 8 with eqs 11 to 13, and the calculated results are shown in Figure 3. The binary interaction parameters were thus determined as $k_{12} = 0.146$ and $l_{12} = 0.054$ for the carbon dioxide + octadecanoic acid system and $k_{12} = 0.130$ and $l_{12} = 0$ for the carbon dioxide + 1-octadecanol system. The calculated S−L−G lines for the two systems are listed in Tables 1 and 2, respectively. These data are also shown in Figure 2, and the calculated compositions of the solute in liquid and vapor phases at S−L−G equilibrium for the two systems are shown in Figure 4. The present model

Table 3. Physical Properties of Carbon Dioxide, Octadecanoic Acid, and 1-Octadecanol

	T_m/K	T_c/K	p_c/MPa	ω	Δh^{fus} (kJ·mol^{-1})	$v^S \cdot 10^4$ (m^3·mol^{-1})	$v^{SCL} \cdot 10^4$ (m^3·mol^{-1})
carbon dioxide		304.12^a	7.374^a	0.225^a			
octadecanoic acid	342.85^b	803.0^c	1.33^c	1.040^d	61.2^b	3.024^b	4.161^e
1-octadecanol	331.05^b	790.0^a	1.440^a	0.892^a	45.0^b	3.330^b	3.791^e

[a] Poling et al.[53] [b] Lide.[57] [c] Nikitin et al.[58] [d] Calculated by the Pitzer's definition using the vapor pressure.[59] [e] Calculated by the Peng−Robinson equation of state assuming that the value is independent of pressure and temperature and equal to the that at the normal melting point.

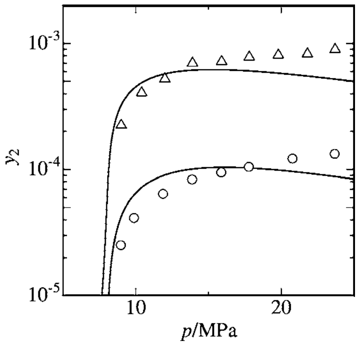

Figure 3. Calculated results of the solubility of octadecanoic acid and 1-octadecanol in supercritical carbon dioxide at 308.2 K: ○, octadecanoic acid; △, 1-octadecanol, Iwai et al.;[60] solid lines, calculated results.

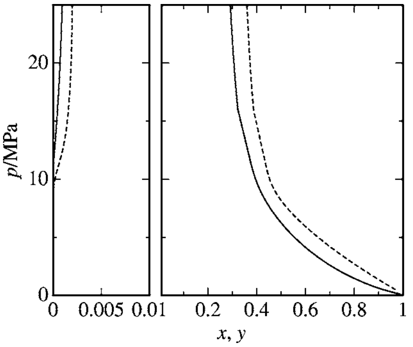

Figure 4. Calculated compositions of the solute (2) in vapor and liquid phases at S−L−G equilibrium for carbon dioxide (1) + octadecanoic acid (2) and carbon dioxide (1) + 1-octadecanol (2) systems: solid lines, carbon dioxide + octadecanoic acid system; broken lines, carbon dioxide + 1-octadecanol system.

gave fairly good correlation results for all of the experimental S−L−G lines with maximum average absolute relative deviations of 0.32 % for the carbon dioxide + octadecanoic acid system and 0.32 % for the carbon dioxide + 1-octadecanol system. As shown in Figure 4, the calculated $p-x-y$ diagrams for the two systems belong to typical asymmetric systems because the solutes have negligibly small composition in the gas phase. These results show that the present correlation method would be appropriate.

Conclusions

We measured the $p-T$ projections of the S−L−G three-phase coexistence lines for the carbon dioxide + octadecanoic acid system and the carbon dioxide + 1-octadecanol system by using the first melting point method. The profiles of the experimental $p-T$ projections of the S−L−G lines for the two systems were similar to each other; however, the maximum melting temperature drop of octadecanoic acid in carbon dioxide was higher than that of 1-octadecanol in carbon dioxide. This would be due to the difference of interaction between carbon dioxide and the solutes, the functional groups in the solutes.

The experimental $p-T$ projections of the S−L−G lines were correlated by the Peng−Robinson equation of state and the van der Waals type mixing rules with two binary interaction parameters introduced into attraction and size terms, respectively. The present model gave good correlation results for the experimental S−L−G lines of the carbon dioxide + octadecanoic acid and carbon dioxide + 1-octadecanol systems.

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