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# Solubilities of Stearic Acid, Stearyl Alcohol, and Arachidyl Alcohol in Supercritical Carbon Dioxide at 35 °C

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The solubilities of stearic acid (octadecanoic acid), stearyl alcohol (1-octadecanol), and arachidyl alcohol (1-eicosanol) in supercritical carbon dioxide were measured by using a flow-type apparatus at 35 °C up to 23.7 MPa. The solubilities of those substances and other fatty acids and higher alcohols in supercritical carbon dioxide at 35 °C were correlated by a solution model based on the regular solution model coupled with the Flory–Huggins theory.

## Introduction

Supercritical fluid extraction has been given much attention recently as one of the new separation technologies in the chemical industry. Solubility data of natural products in supercritical fluids are critical; consequently the solubilities of stearic acid, stearyl alcohol, and arachidyl alcohol in supercritical $CO_2$ at 35 °C were measured by a flow-type apparatus. The solubilities of stearic acid and stearyl alcohol had been measured previously (*1*, *2*); however, all of the data were measured at temperatures higher than 40 °C. A small pressure change in the region of 5–7 MPa at 35 °C causes a large change of solubility of the solid component. On the other hand, this change in solubility is not dramatic at higher temperatures. Therefore, solubility data are needed slightly above the critical temperature of $CO_2$.

Also, correlative methods for the solubilities of fatty acids and higher alcohols are necessary in the design of a supercritical fluid extraction process. Correlations using equations of states (EOS) have been found to be promising. However, critical constants are required to obtain the constants of EOS, and for fatty acids and higher alcohols these are not available. Nonetheless, a solution model requires no critical constants.

In this work, the solubilities of myristic acid ($C_{13}H_{27}COOH$) (*3*), palmitic acid ($C_{15}H_{31}COOH$) (*3*), stearic acid ($C_{17}H_{35}COOH$), cetyl alcohol ($C_{16}H_{33}OH$) (*3*), stearyl alcohol ($C_{18}H_{37}OH$), and arachidyl alcohol ($C_{20}H_{41}OH$) in supercritical $CO_2$ at 35 °C were correlated by using a solution model based on the regular solution model coupled with the Flory–Huggins theory (*4*).

## Experimental Section

***Equipment and Procedures.*** A flow-type apparatus was used to measure the solubilities of solid components (stearic acid, stearyl alcohol, and arachidyl alcohol) in supercritical $CO_2$. A detailed description of the equipment and operating procedures is given in a previous work (*3*). Carbon dioxide supplied from a gas cylinder was liquefied through a cooling unit and directed to a compressor. A back-pressure regulator was used to maintain a constant pressure within the system. The equilibrium pressure was measured by a Bourdon gauge. Two equilibrium cells were used. The inner diameter, height, and volume of each cell are 30 mm, 45 cm, and 315 cm$^3$, respectively. The solid component was packed in the second cell with glass beads to prevent channeling, while the first cell was used as a buffer tank. These cells were attached to a preheating coil and submerged in a water bath controlled within ±0.1 °C. Supercritical fluid saturated with the solid component was depressurized through an expansion valve and introduced into a U-shaped glass tube cooled in an ice bath. In the tube, gaseous $CO_2$ and the solid component were separated. The amount of solid component trapped was determined by mass. The volume of $CO_2$ was measured by a wet-gas meter. Usually, 0.1–0.3 g of solute was trapped, and the flow rate of $CO_2$ was adjusted to be 5.3–9.1 cm$^3$·s$^{-1}$. A small amount of solid remaining in the tubing and the expansion valve was removed and trapped by using supercritical $CO_2$ through a bypass line.

**Table I. Solubilities ($y_2$) of Stearic Acid, Stearyl Alcohol, and Arachidyl Alcohol in Supercritical $CO_2$ at 35 °C**

| stearic acid | | stearyl alcohol | | arachidyl alcohol | |
|---|---|---|---|---|---|
| $p$/MPa | $10^4y_2$ | $p$/MPa | $10^4y_2$ | $p$/MPa | $10^4y_2$ |
| 9.0 | 0.25 | 9.0 | 2.24 | 8.9 | 0.705 |
| 9.9 | 0.41 | 10.4 | 4.07 | 9.8 | 0.979 |
| 11.9 | 0.638 | 12.0 | 5.25 | 11.8 | 1.52 |
| 13.9 | 0.828 | 13.9 | 7.00 | 14.8 | 1.98 |
| 15.9 | 0.942 | 15.9 | 7.21 | 17.8 | 2.21 |
| 17.8 | 1.04 | 17.8 | 7.82 | 20.7 | 2.46 |
| 20.8 | 1.21 | 19.8 | 8.12 | 23.7 | 2.57 |
| 23.7 | 1.32 | 21.8 | 8.28 | | |
| | | 23.7 | 9.00 | | |

***Materials.*** Stearic acid, stearyl alcohol, and arachidyl alcohol supplied by Sigma Chemical Co. were used. Their purities were approximately 99%. After impurity components were extracted with supercritical $CO_2$ by the apparatus, the remaining component was used for measurement of solubilities. High-purity $CO_2$ (more than 99.9%, Sumitomo Seika Co.) was used as received.

## Results and Discussion

The measurements were carried out for several flow rates of $CO_2$ at known pressures. The solubilities obtained were independent of the flow rate of $CO_2$. The reproducibility of the solubilities was within ±4%, when the pressure was higher than 9.0 MPa. The reproducibility was within 10% when the pressure was lower than 9.0 MPa. The experimental values listed in Table I were obtained from an arithmetic average of several measurements at each pressure.

The enhancement factor, $E = py_2/p_2°$, was plotted against the density of pure $CO_2$, $\rho_1/(\mathrm{kg{\cdot}m^{-3}})$. Usually, the saturated vapor pressure of the solute is used as $p_2°$ to calculate $E$. However, the saturated vapor pressures of stearic acid, stearyl alcohol, and arachidyl alcohol at 35 °C are not available. So, the value $p_2°$ is fixed to be 1 Pa. The density of $CO_2$ was calculated by a five-parameter van der Waals type cubic equation of state proposed by Adachi et al. (*5*) with the optimized parameters. Figure 1 shows a good linear rela-

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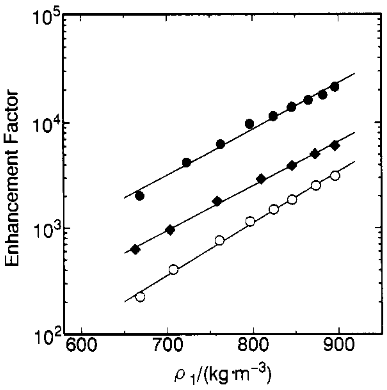

**Figure 1.** Relationship between the enhancement factor $E$ and density of pure $CO_2$ $\rho_1$: (○) stearic acid; (●) stearyl alcohol; (◆) arachidyl alcohol; (—) results calculated by eq 1.

tionship between ln $E$ and $\rho_1$ for each component. The relationship can be represented by using the following equation:

$$\ln E = A + B\rho_1 \quad (1)$$

where coefficients $A$ and $B$ are given in Table II.

## Correlation

Iwai et al. (4) have assumed that the solubility of a solid component in a supercritical fluid is expressed by a solution model based on the regular solution model coupled with the Flory–Huggins theory:

$$\ln y_2 = \frac{\Delta h_2^{\mathrm{m}}}{RT}\left(\frac{T}{T_2^{\mathrm{m}}}-1\right)-\frac{v_2}{RT}\left[\delta_1-\left(\frac{\Delta U_2}{v_2}\right)^{1/2}\right]^2+1-\frac{v_2}{v_1}+\ln\frac{v_2}{v_1} \quad (2)$$

where $y_2$ is the solubility of solid component 2 in the supercritical fluid, $T$ is the absolute temperature, $R$ is the gas constant, $\Delta h_2^{\mathrm{m}}$ and $T_2^{\mathrm{m}}$ are the heat of fusion and melting point for pure solid component 2, respectively, and $v_i$ is the molar volume of component $i$ in the supercritical fluid phase. The molar volume $v_2$ in eq 2 is treated as an adjustable parameter for optimizing the solubility. The solubility parameter of supercritical $CO_2$, $\delta_1$, was calculated by the method proposed by Giddings et al. (6). The value of $\Delta U_2$ can be calculated by the following equation:

$$\Delta U_2 = \Delta U_2^{*}\{1 + 1.13\alpha_{v,2}(T^{*} - T)\}^2\{1 - \alpha_{v,2}(T^{*} - T)\} \quad (3)$$

where $\Delta U_2^{*}$ is the internal energy change of vaporization at $T^{*}$ and $\alpha_{v,2}$ is the isobaric thermal expansivity. The value of $\Delta U_2^{*}$ at 298.15 K can be calculated by the group contribution method proposed by Fedors (7). The value of $\alpha_{v,2}$ was fixed to be $1.0 \times 10^{-3}\ \mathrm{K^{-1}}$ for all solid components for simplification.

The relationship between the parameter $v_2$ and the density of supercritical $CO_2$, $\rho_1$, can be approximated by the following equation (4):

$$\ln [v_2/(\mathrm{m^3\cdot mol^{-1}})] = \alpha \ln [\rho_1/(\mathrm{kg\cdot m^{-3}})] + \beta \quad (4)$$

where the density of supercritical $CO_2$ can be calculated by the equation of state proposed by Adachi et al. (5).

In this work, the solubilities of fatty acids and higher alcohols in supercritical $CO_2$ were correlated. The properties of fatty acids and higher alcohols used for the solubility correlation are listed in Table III. The coefficients $\alpha$ and $\beta$ of eq 4 were determined to give the best fit of the solubilities. They are listed in Table IV. The solubilities of fatty acids and higher alcohols in supercritical $CO_2$ can be well represented with the parameters $\alpha$ and $\beta$ in Table IV as shown in Figure 2.

**Table II. Coefficients of Equation 1**

| solute | $A$ | $B/(\mathrm{m^3\cdot kg^{-1}})$ |
|---|---|---|
| stearic acid | −2.051 | 0.011 33 |
| stearyl alcohol | 1.085 | 0.009 972 |
| arachidyl alcohol | 0.011 54 | 0.009 768 |

**Table III. Properties of Fatty Acids and Higher Alcohols**

| solute | $t_2^{\mathrm{m}}/°\mathrm{C}$ | $\Delta h_2^{\mathrm{m}}/(\mathrm{J\cdot mol^{-1}})$ | $\Delta U_2^{*\,a}/(\mathrm{J\cdot mol^{-1}})$ |
|---|---|---|---|
| myristic acid | 54.4[b] | 45 100[c] | 91 630 |
| palmitic acid | 62.9[b] | 53 711[c] | 101 500 |
| stearic acid | 69.6[b] | 61 209[c] | 111 400 |
| cetyl alcohol | 49.3[b] | 57 800[d] | 100 700 |
| stearyl alcohol | 57.9[e] | 66 900[f] | 110 600 |
| arachidyl alcohol | 66.5[b] | 75 700[f] | 120 400 |

[a] Calculated by the group contribution proposed by Fedors (7) at 298.15 K. [b] Reference 8. [c] Reference 9. [d] Reference 10. [e] Reference 11. [f] Extrapolated by using the values of $\Delta h_2^{\mathrm{m}}$ of $C_{13}H_{27}OH$ to $C_{16}H_{31}OH$.

**Table IV. Optimized Values of α and β in Equation 4**

| solute | $\alpha$ | $\beta$ | $100\sigma$ |
|---|---|---|---|
| myristic acid[a] | −1.134 | −1.139 | 13.0 |
| palmitic acid[a] | −1.447 | 0.9691 | 8.8 |
| stearic acid | −1.420 | 0.8581 | 7.5 |
| cetyl alcohol[a] | −1.511 | 1.484 | 5.2 |
| stearyl alcohol | −1.498 | 1.487 | 8.8 |
| arachidyl alcohol | −1.478 | 1.442 | 5.9 |

[a] Reference 3. $\sigma = (1/N)\sum^{N} |y_2^{\mathrm{calc}} - y_2^{\mathrm{exp}}|/y_2^{\mathrm{exp}}$.

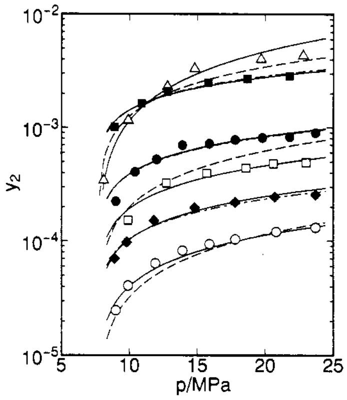

**Figure 2.** Solubilities of fatty acids and higher alcohols in supercritical $CO_2$ against pressure: (△) myristic acid; (□) palmitic acid; (○) stearic acid; (■) cetyl alcohol; (●) stearyl alcohol; (◆) arachidyl alcohol; (—) results calculated by the optimized parameters in Table IV; (- - -) results calculated by the generalized parameters in Table V for fatty acids; (– – –) results calculated by the generalized parameters in Table V for higher alcohols.

The values of $\alpha$ are close to −1.33 for fatty acids (an averaged value for $\alpha$ of fatty acids shown in Table IV) and −1.50 for higher alcohols (that of higher alcohols shown in Table IV). After the values of $\alpha$ were fixed, the values of $\beta$ were recalculated to give a good representation of the solubilities. They are listed in Table V.

Table V shows that the recalculated values of $\beta$ are dependent on the carbon numbers of the solutes in each component group (fatty acid or higher alcohol). Therefore, the values of $\beta$ are plotted against the carbon numbers of the solutes as shown in Figure 3. The figure shows that the values of $\beta$ increase linearly with the increase of the carbon numbers of the solutes in each component group (fatty acid or higher

**Table V. Carbon Numbers of the Solutes, Averaged Values of $\alpha$ for Fatty Acid and Higher Alcohol Groups, and Recalculated Values of $\beta$**

| solute | carbon number | $\alpha$ | $\beta$ |
|---|---|---|---|
| myristic acid[a] | 14 | -1.33 | 0.1665 |
| palmitic acid[a] | 16 | -1.33 | 0.1835 |
| stearic acid | 18 | -1.33 | 0.2604 |
| cetyl alcohol[a] | 16 | -1.50 | 1.413 |
| stearyl alcohol | 18 | -1.50 | 1.498 |
| arachidyl alcohol | 20 | -1.50 | 1.588 |

[a] Reference 3.

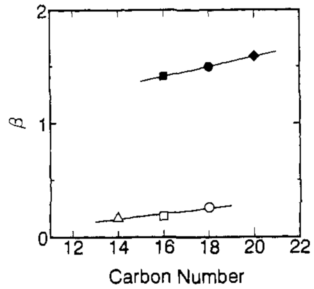

**Figure 3.** Relationship between $\beta$ in Table V and the carbon numbers of fatty acids and higher alcohols: (△) myristic acid; (□) palmitic acid; (○) stearic acid; (■) cetyl alcohol; (●) stearyl alcohol; (◆) arachidyl alcohol; (—) results calculated by eq 5 using $\beta^{(0)} = -0.1721$ and $\beta^{(1)} = 0.023\,48$ for fatty acids and $\beta^{(0)} = 0.7122$ and $\beta^{(1)} = 0.043\,75$ for higher alcohols.

alcohol). That can be expressed as

$$\beta = \beta^{(0)} + \beta^{(1)}N_c \tag{5}$$

where $N_c$ is the carbon number of the fatty acid or higher alcohol. The values of $\beta^{(0)}$ and $\beta^{(1)}$ are -0.1721 and 0.02348 for fatty acids, and 0.7122 and 0.04375 for higher alcohols, respectively. Figure 3 shows that the coefficients $\alpha$ and $\beta$ of eq 4 are influenced by the functional group such as -OH or -COOH and the carbon number. The calculated results of $y_2$ obtained by using the parameters of eq 5 were shown in Figure 2. The calculated results indicate good agreement with the experimental data.

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