Solubilities of Undecanolide and Pentadecanolactone in Supercritical Carbon Dioxide

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The solubilities of undecanolide (UDL) and pentadecanolactone (PDL) in supercritical carbon dioxide (SC-CO_2) were measured at 308.2 K and 318.2 K over the pressure range from 9.1 MPa to 25.3 MPa by a flow type apparatus. The solubilities were determined from the mass of solute trapped by decompression and the volume of CO_2. Solubility data were correlated by a solution model based on the regular solution concept.

Introduction

Enzymatic polymerization of lactones, such as undecanolide (UDL) and pentadecanolactone (PDL), has been attracting much attention as a new procedure for synthesizing biodegradable polymers (Noda et al., 1997). In our previous paper (Mishima et al., 1999a), structural ring-opening of lactones driven by enzymatic polymerization has been performed using low-concentration dosages of surfactant-coated lipase in supercritical carbon dioxide (SC-CO_2). SC-CO_2 is expected to be a promising means of reaction medium for enzymes (Jessop and Leitner, 1999), because enzyme activity and selectivity can be manipulated by varying either the pressure or temperature of the system. To aid design and optimization of enzymatic polymerization of lactones in SC-CO_2, solubilities of lactones are needed. Although studies have been performed on solubilities of many compounds in SC-CO_2 (Bartle et al., 1991; Uchiyama et al., 1997; Mishima et al., 1999b, 2000), little is known about lactones.

In this work, the solubilities of UDL and PDL in SC-CO_2 at 308.2 K and 318.2 K over the pressure range from 9.1 MPa to 25.3 MPa were measured by a flow type apparatus. The solubilities of these substances were correlated by a solution model based on the regular solution concept proposed by Ziger and Eckert.

Experimental Section

Apparatus and Procedures. A flow type apparatus was used to measure the solubilities of undecanolide (UDL) and pentadecanolactone (PDL) in supercritical carbon dioxide (SC-CO_2). A detailed description of the apparatus and operating procedures is given in our previous paper (Uchiyama et al., 1997). The liquefied carbon dioxide (CO_2) leaving a gas cylinder was passed through a cooling unit to prevent vaporization of CO_2 from warming up and directed to a compressor which was capable of delivery pressures up to about 60 MPa and delivery rates up to 5.2 mL·min^{-1} (liquefied CO_2 basis). A back-pressure regulator was used to maintain a constant pressure with the pressure control accuracy of ±0.1 MPa. The equilibrium pressure was measured by a Bourdon gauge calibrated against a strain pressure gauge (accuracy ±0.3%). CO_2 passed through

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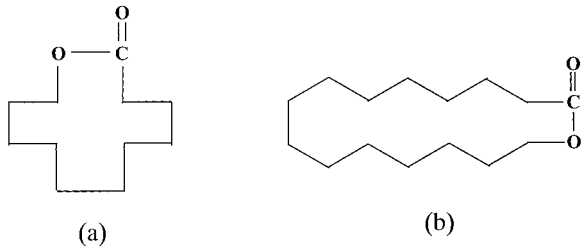

Figure 1. Chemical structures of undecanolide (a) and pentadecanolactone (b).

Table 1. Mole Fraction Solubilities *y* of Undecanolide and Pentadecanolatone in SC-CO_2

undecanolide				pentadecanolactone			
T = 308.2 K		T = 318.2 K		T = 308.2 K		T = 318.2 K	
p/MPa	10^3y_2	p/MPa	10^3y_2	p/MPa	10^3y_2	p/MPa	10^3y_2
9.1	1.66	9.1	2.71	9.1	0.567	9.1	0.825
10.1	2.31	10.1	3.19	10.1	0.753	10.1	1.16
15.2	3.41	15.1	4.80	15.1	1.18	15.1	2.20
20.3	3.94	20.3	5.90	20.3	1.33	20.3	2.44
25.3	4.36	25.3	6.63	25.3	1.62	25.3	3.13

Table 2. Coefficients of Eq 1

solute	T/K	A	10^3B/m^3 kg^{-1}
undecanolide	308.2	0.9669	6.30
	318.2	7.555	3.90
pentadecanolactone	308.2	0.5129	6.50
	318.2	3.127	4.60

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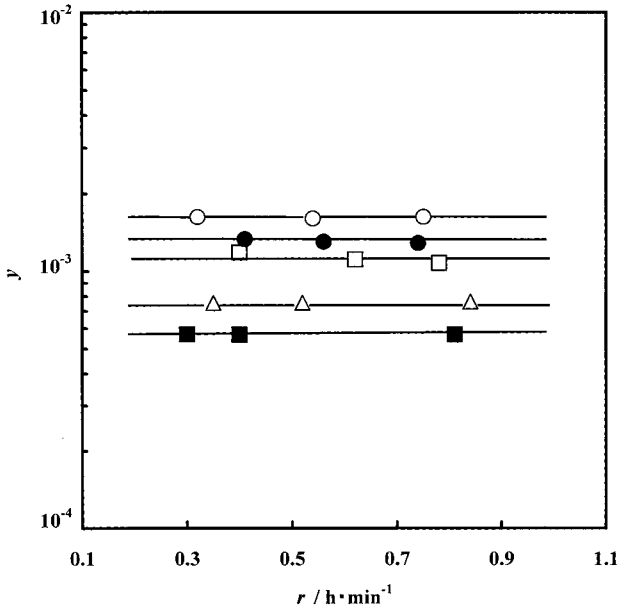

Figure 2. Relationship between the mole fraction solubility of pentadecanolactone in SC-CO_2 at 308.2 K over the pressure range from 9.1 MPa to 25.3 MPa and the flow rate of expanded CO_2: (■) 9.1 MPa; (△) 10.2 MPa; (□) 15.2 MPa; (●) 20.3 MPa; (○) 25.3 MPa.

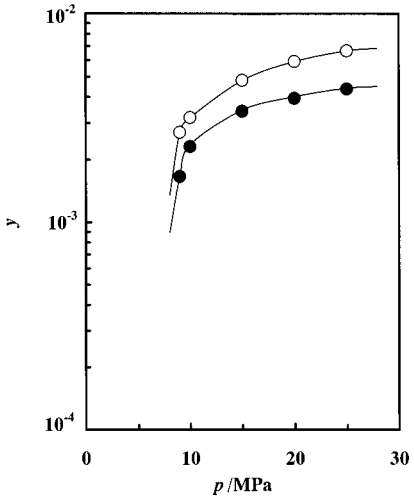

Figure 3. Mole fraction solubilities of undecanolide in SC-CO_2: (●) experimental data at 308.2 K; (○) experimental data at 318.2 K; (—) calculated results.

a preheating coil and then entered in two equilibrium cells containing UDL or PDL. The cells were constructed from 316 Stainless Steel, and the inner diameter, height, and volume were 30 mm, 30 cm, and 210 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 with a temperature control accuracy of ±0.1 K. The supercritical fluid (SCF) saturated with the solid component was decompressed through an expansion valve and introduced into a U-shaped glass tube cooled in an ice bath. Gaseous CO_2 and the solid component were separated in the tube. The amount of the trapped solid component was determined by mass. The solute collected in the tubes was weighed by a direct reading balance (Exact A-V; accuracy 0.1 mg). The volume of CO_2 was measured by a wet-gas meter that was calibrated to an accuracy of ±0.4%. Usually 0.1−0.3 g of solute was trapped, and the flow rate of expanded CO_2 was adjusted to be 0.30−0.85 L·min^{-1} (gaseous CO_2 basis). A small amount of the solid remaining in the tube and the expansion valve was removed and trapped by using SC-CO_2 through a bypass line.

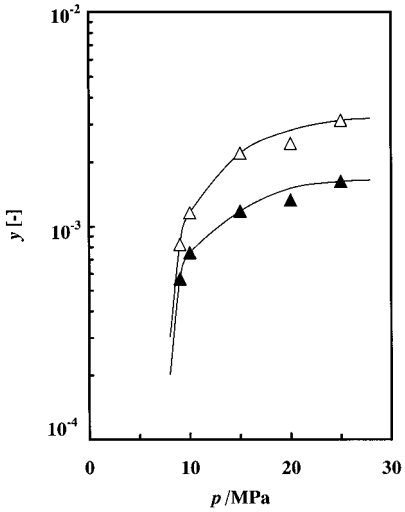

Figure 4. Mole fraction solubilities of pentadecanolactone in SC-CO_2: (▲) experimental data at 308.2 K; (△) experimental data at 318.2 K; (—) calculated results.

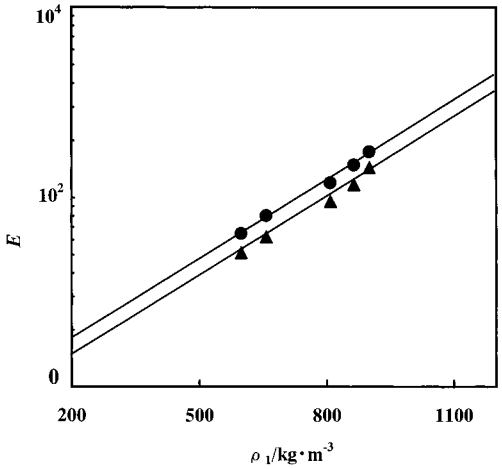

Figure 5. Relationship between the enhancement factor E and the density of pure CO_2 ρ_1: (●) undecanolide at 308.2 K; (▲) pentadecanolactone at 308.2 K; (—) results calculated by eq 1.

Materials. Undecanolide (UDL) and pentadecanolactone (PDL) were purchased from Lancaster Co. Ltd. and from Tokyo Kasei Kogyo Co. Ltd., respectively. The chemical structures of UDL and PDL are shown in Figure 1. Their purities were believed to be more than 98%. High-purity CO_2 (more than 99%, Fukuoka Sanso Co. Ltd.) was used as received.

Results and Discussion

The measurements were carried out for several flow rates of CO_2 at known pressures, as shown in Figure 2. The solubilities of UDL and PDL were independent of the flow rate of expanded CO_2, where the condition of CO_2 is standard state temperature and pressure. Similar results were obtained for flavone and 3-hydroxyflavone (Uchiyama et al., 1997). This shows that the solubilities of UDL and PDL were measured under equilibrium conditions in the flow type apparatus. The reproducibility of these solubilities was within ±4.0% when the pressure was varied from 9.1 MPa to 25.3 MPa. The experimental values listed in Table 1 were obtained from an arithmetic average of several measurements at each pressure. Experimental data

Table 3. Physical Properties of Undecanolide and Pentadecanolactone

substance	T_c/K	P_c/MPa	$10^3 v_2^s$/m^3 mol^{-1}	δ_2/MPa$^{1/2}$	$10^4 p_2^{sat}$/Pa	
					$T = 308.2$ K	$T = 318.2$ K
undecanolide	610.6	2.987[a]	0.1177[b]	19.61[c]	3.610[d]	6.917[d]
pentadecanolactone	594.6	2.325[a]	0.1590[b]	19.10[c]	1.960[d]	3.958[d]

[a] Estimated by the Lydersen method. [b] Estimated by the relation $v_2^s = 1.5V_w$, where V_w is given by the Bondi method. [c] Estimated by the Fedors method. [d] Estimated by the Lee−Kesler equation.

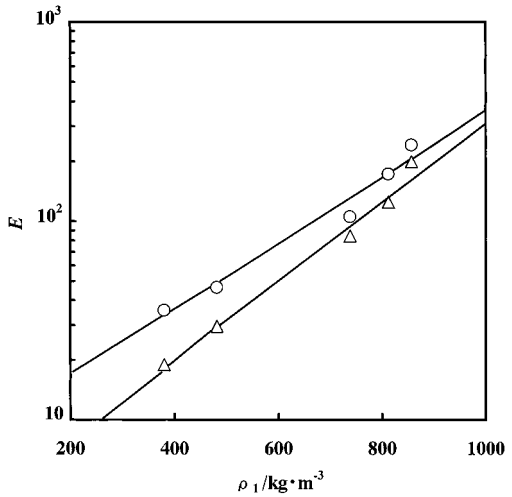

Figure 6. Relationship between the enhancement factor E and the density of pure CO_2 ρ_1: (○) undecanolide at 318.2 K; (△) pentadecanolactone at 318.2 K; (—) results calculated by eq 1.

of UDL and PDL at 308.2 K and 318.2 K are given in Figures 3 and 4. Just above the critical pressure of CO_2, the solubilities of UDL and PDL drastically increase because of a rapid increase in density with pressure. For pressures above 10 MPa, the solubility increases with increasing temperature because the decrease in CO_2 density cannot overcome the increase in vapor pressure.

To confirm the reliability of the experimental data, the enhancement factor, $E = py_2/p_2^{sat}$ (Brennecke and Eckert, 1989), was plotted against the density of pure CO_2, ρ_1, where y_2 is the solubility of the solid component in the SCF and p is the equilibrium pressure. The saturated vapor pressure, p_2^{sat}, was calculated by the Lee−Kesler equation, where the critical temperature, T_c, and critical pressure, P_c, were obtained by the Lydersen's method (Reid et al., 1987). The density of CO_2 was calculated by the equation of state of Angus et al. (1976). As shown in Figures 5 and 6, it was observed that the logarithm of the enhancement factor, ln E, was a linear function of the solvent density, ρ_1, for each component. The relationship can be represented by the following equation:

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

where coefficients A and B are given in Table 2.

Correlation. Ziger and Eckert (1983) have assumed that the solubility of the solid component in SCF is expressed by a solution model based on the regular solution model:

$$\ln E = \eta\left[\frac{v_2^s(2\delta_1\delta_2 - \delta_1^2)}{RT} - \ln\left(1 + \frac{\delta_1^2}{p}\right)\right] + \nu \qquad (2)$$

where T is the absolute temperature, R is the universal gas constant, δ_1 is the solubility parameter of SC-CO_2 calculated by the method proposed by Giddings et al. (1968), p is the experimental pressure, δ_2 is the solubility parameter of the solid component calculated by the Fedors' method (Fedors, 1974), v_2^s is the molar volume of the solid component, and η and ν are the parameters defined by eq 2, respectively. v_2^s is nearly proportional to the hard-core van der Waals volume, V_w, which was obtained by the method of Bondi (1968). As shown by Yamamoto et al. (1987), we assumed that the proportionality constant, $K = v_2^s/V_w$, was about 1.5. So the v_2^s for UDL and PDL was calculated with their values of V_w and $K = 1.5$. The physical properties of UDL and PDL are shown in Table 3. The values of η and ν can be calculated by using a generalized linear least-squares approach. They are listed in Table 4. The logarithm of the enhancement factor has been correlated well by the regular solution model. The solubilities of UDL and PDL in SC-CO_2 can also be well represented, as shown in Figures 3 and 4.

Table 4. Optimized Values of η and ν in Eq 2 and Deviations

substance	T/K	η	ν	100σ[a]
undecanolide	308.2	1.424	0.1923	0.122
	318.2	0.9527	1.953	13.2
pentadecanolactone	308.2	1.131	−0.565	1.96
	318.2	0.8613	1.047	7.91

[a] $\sigma = (1/N)\Sigma|y_{exp} - y_{calc}|/y_{exp}$, where N is the number of data.

Conclusion

The solubilities of UDL and PDL in SC-CO_2 were measured by using a flow type apparatus at 308.2 K and 318.2 K over the pressure range from 9.1 to 25.3 MPa. Furthermore, the solubilities of these substances in SC-CO_2 have been correlated by using a solution model based on the regular solution model. It was shown that the solubilities of these substances can be correlated with fairly good accuracy.

Literature Cited

Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of Fluid State—3 Carbon Dioxide*; IUPAC Project Center, Pergamon Press: London, 1976.

Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilstone, G. F. Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713−756.

Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; John Willey & Sons Inc.: New York, 1968.

Brennecke, J. F.; Eckert, C. A. Phase Equilibria for Supercritical Fluid Process Design. *AIChE J.* **1989**, *35*, 1409−1427.

Fedors, R. F. A Method for Estimating Both the Solubility Parameters and Molar Volumes of Liquids. *Polym. Eng. Sci.* **1974**, *14*, 147−154.

Giddings, J. C.; Myers, M. N.; McLaren, L.; Keller, R. A. High-Pressure Gas Chromatography of Nonvolatile Species. *Science* **1968**, *162*, 67−73.

Jessop, P. G.; Leitner, W. *Chemical Synthesis Using Supercritical Fluids*; Wiley−VCH: New York, 1999.

Mishima, K.; Matsuyama, K.; Yamauchi, S. *Proc. AIChE Annual Meeting;* 1999*a;* p 114.

Mishima, K.; Matsuyama, K.; Nagatani, M. Solubilities of Poly(ethylene glycol)s in the Mixtures of Supercritical Carbon Dioxide and Cosolvent. *Fluid Phase Equilib.* **1999b**, *161*, 315−324.

Mishima, K.; Matsuyama, K.; Tanabe, D.; Yamauchi, S.; Young, T. J.; Johnston, K. P. Microencapsulation of Proteins by Rapid Expansion of Supercritical Solution with a Nonsolvent. *AIChE J.* **2000**, *46*, 857−865.

Noda, S.; Kamiya, N.; Goto, M.; Nakashio, F. Enzymatic Polymerization Catalyzed by Surfactant-Coated Lipases in Organic Media. *Biotechnol. Lett.* **1997**, *19*, 307−309.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill Book Co.: New York, 1987.

Uchiyama, H.; Mishima, K.; Oka, S.; Ezawa, M.; Ide, M.; Takai, T.; Park, P. W. Solubilities of Flavone and 3-Hydroxyflavone in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1997**, *42*, 570−573.

Yamamoto, H.; Kanegae, F.; Mishima, K.; Iwai, Y.; Arai, Y. Correlation of Solubilities of Coal Liquefaction Products in Supercritical Gases by Equation of State. *Mem. Fac. Eng., Kyusyu Univ.* **1987**, *47*, 95−113.

Ziger, D. H.; Eckert, C. A. Correlation and Prediction of Solid Supercritical Fluid Phase Equilibria. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 582−588.

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