Solubility of 2-Ethyl-1-hexanol, 2-Ethylhexanoic Acid, and Their Mixtures in Supercritical Carbon Dioxide

Hassan S. Ghaziaskar,* Habibollah Eskandari, and Ali Daneshfar

Department of Chemistry, Isfahan University of Technology, Isfahan, 84154, I.R. Iran

---

Solubilities of 2-ethyl-1-hexanol (1), 2-ethyl hexanoic acid (2), and their mixtures in supercritical carbon dioxide (SC-CO_2) (3) were reported. Solubilities were measured at a constant temperature of 313 K and 323 K, at pressures varying from (68 to 180) bar for the binary systems and at a constant pressure of 138 bar at temperatures varying from (313 to 373) K for the ternary system. Temperature dependences of the solubilities for a $x_1 = 0.5$ mixture were determined. The effect of the mixture composition of the acid + alcohol mixture in SC-CO_2 was studied. The total solubility of the mixtures in SC-CO_2 is independent of the x_1 of the liquid mixture in the equilibrium cell. The Chrastil model for solubilities at 313 K and 323 K was evaluated.

Introduction

Supercritical carbon dioxide (SC-CO_2) has had a considerable impact on environmental, industrial, pharmaceutical, and fundamental studies. It has seen many applications in material and food processing, polymer modification, defatting of beans, and decaffeination of raw coffee beans.[1−5] Among the range of applications of SC-CO_2, reactions and extractions in SC-CO_2 are perhaps the most promising. These studies need solubility information for the chemicals in diverse matrixes (i.e. in the presence of other solutes or impurities).[6−8] The solubilities of ethyl esters of oleic acid (C18:1), eicosatrienoic acid (C20:3), arachidonic acid (C20:4), and *cis*-4,7,10,13,16,19-docosahexaenoic acid (C22:6) were measured.[9] In these investigations, the ethyl ester of C18:1 (ethyl oleate) has solubilities in the range 0.3−2.2 mol %, but longer chain esters have had lower solubilities, in the range 0.02−0.1 mol %. Studies of straight chain alcohols such as 1-octanol, 1-hexanol, and lower molecular weight alcohols[10] show a relationship between solubility and number of carbon atoms. In this study the logarithm of solubility was linearly proportional to the carbon number of *n*-alkanols. The solubility of some alcohols such as 1-nonanol, 1-undecanol, 1-tridecanol, 1-pentadecanol,[11] and 1-octadecanol[12] has also been studied in addition to those of certain carboxylic acids such as the hydroxy benzoic acid isomers[13] oleic acid[14] and stearic acid.[12] Because of the matrix effect on the solubility of compounds due to changes of interactions that can exist in mixtures, they can exhibit solubilities that differ from the solubilities of their pure components. The solubilities of oleyl glycerol mixtures in SC-CO_2 show a positive deviation from the solubility of the pure compound, possibly due to intermolecular hydrogen bonding. SC-CO_2 appears to be a good solvent for the removal of the mono- and diacylglycerol byproducts from synthetic triglyceride reaction mixtures.[14] The influence of the matrix composition on the solubility of hydroxybenzoic acid isomers has also been studied. These studies show that the solubility of pure *p*-hydroxybenzoic acid is lower than that of the pure ortho isomer. However, in a mixture of the ortho and para compounds, the para isomer is solubilized in SC-CO_2 better than the pure solid para isomer. The enhancement of the para isomer solubility was found to be independent of matrix composition.[13] The solubility of methyl oleate and oleic acid mixtures has also been studied. Their solubilities vary for the solutes in the liquid mixtures with different compositions. Interaction parameters between methyl oleate and oleic acid were obtained.[15]

Solubility measurement and esterification of oleyl alcohol and oleic acid in SC-CO_2 have also been studied. At the 1:1 acid to alcohol mole ratio in the equilibrium cell the solubility of the alcohol was found to be two times that of the acid at 147 bar and 333 K. Oleyl oleate has been continuously prepared using solid *p*-toluenesulfonic acid catalyst. The purity of the product was low because unreacted alcohol has also been found in the outcoming effluent.[16]

In this work, the binary and ternary solubilities of the C8 alcohol 2-ethyl-1-hexanol and the C8 acid 2-ethylhexanoic acid in SC-CO_2 have been studied. The effect of initial liquid composition of the alcohol and the acid on the solubility was also studied. The results can be used in the continuous esterification reactions in SC-CO_2 under conditions of isosolubility for preparation of pure products using appropriate catalysts.

Experimental Section

Materials. Carbon dioxide with purity of 99.99 mass % was purchased from Zamzam Co. Ltd. (Isfahan, Iran). Merck Chemical Co. supplied 2-ethyl-1-hexanol and cyclohexanol (99% pure). 2-Ethylhexanoic acid (bp = 498 K and $n_D{}^{20} = 1.4250$) was provided by Tata Chemical Co. (Isfahan, Iran) with minimum purity of 99%, verified by GC.

Apparatus and Procedures. A detailed schematic diagram of the continuous flow apparatus is shown in Figure 1. The liquid CO_2 was transferred from a cylinder equipped with a dip-tube inserted through a cleanup trap to the cooling coil and the conventional HPLC pump (Shimadzu Co. model LC-6A). An air oven was used to control the equilibrium cell temperature to within ±0.1 K. The temperature was monitored using a thermocouple−temperature controller device (Alton Ray model TC14, Tehran, Iran). The equilibrium cell of about 10 mL volume was filled with glass beads (o.d. = 4 mm) to lower its dead

---

* E-mail: ghazi@cc.iut.ac.ir. Fax: 098-311-3912350.

10.1021/je020074l CCC: $25.00

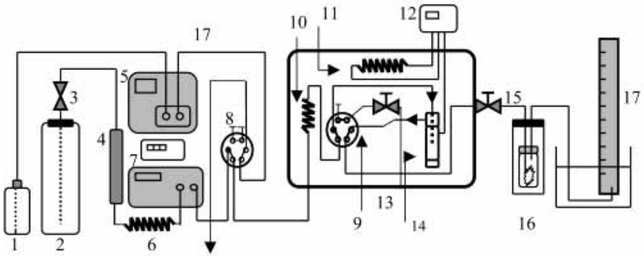

Figure 1. Schematic diagram of the solubility measurement apparatus: 1, washing liquid bottle; 2, carbon dioxide cylinder; 3, valve; 4, carbon dioxide purifier; 5, HPLC pump; 6, liquid carbon dioxide pump with cooled head; 7, pressure transducer; 8 and 9, six-port two-position valve; 10, prewarming coil; 11, heating coil; 12, thermocouple and temperature controller; 13, oven; 14, equilibrium cell; 15, backpressure regulator; 16, collection vial; and, 17, wet gas meter.

volume and to increase the contact surface. An automatic back-pressure regulator (model BP-1580-81, JASCO, Japan) was used to maintain a constant pressure. The accuracy in the pressure was achieved by using an Indumart 5000 Series test gauge with Bourdon tube with the accuracy of 0.1% to calibrate system pressure. In practice, all reported pressure measurements have a precision better than ±1 bar. A JASCO PU-980 HPLC pump was used for pumping the washing solvent to clean the connection lines at the end of each experiment. Two 6-port, 2-position Rheodyne model 7000 switching valves were used in the system. The first 6-port valve was used to switch the lines between the CO_2 pump and the washing solvent pump. The second was used to bypass the equilibrium cell at the end of each experiment. A two-way on−off valve was connected to the second 6-port, 2-position valve to depressurize the cell at the end of each experiment. A wet gas meter measured the expanded-gas volume.

Two grams (±0.01 g) of either 2-ethyl-1-hexanol or 2-ethylhexanoic acid or their appropriate mixtures was placed into the equilibrium cell before it was placed into the oven to start the solubility measurements. The amount was chosen to be high enough to saturate SC-CO_2 from the solutes in the equilibrium cell. Some glass wool was placed at the outlet of the cell to prevent physical entrapment of nondissolved liquid sample in the SC-CO_2. The cell was placed into the oven, and the lines were connected to the inlet and outlet of the cell. After 20 min, the cell was pressurized by SC-CO_2 over about 3 min. Under a constant flow rate of liquid CO_2 and a constant pressure applied by a backpressure regulator, the solubilized compounds were collected in a 10 mL vial filled with glass wool as a trap. The trap was inserted in a mixture of ice and water. The collected pure solutes in the binary systems were weighed (±0.1 mg), and the collected mixtures in the ternary system were separated and analyzed by GC-TCD for calculating the solubility of the solutes. The solubility was defined as the mole fraction of the solutes in the expanded CO_2 gas. The total relative standard deviation (RSD) of at least three solubility measurements, including a 3% uncertainty of the GC analysis, was less than 10%. In each experiment the weight loss of the equilibrium cell and the weight of trapped solute, after passing by the backpressure regulator, were meticulously compared to ensure 97% trapping efficiency and avoid a precipitous fall of the solubility or possible air contamination resulting from melting the solutes in air followed by CO_2 flooding. In cases for which trapping efficiencies were lower than 97%, the transfer lines were washed with *n*-hexane and the solution was added to the collected solutes. The temperature of the backpressure regulator was also kept at the oven's temperature.

The collected mixtures of solutes in vials were dissolved in *n*-hexane and transferred to a 5.0 mL volumetric flask. After addition to the flask of 0.60 mL of a solution of cyclohexanol in *n*-hexane (16.2 g per 100 mL) as an internal standard to the flask, *n*-hexane was added to bring the final volume up to 5.0 mL. A packed-column gas chromatograph (model GC-14A, Shimadzu Co.) with an OV-17 column (2.0 m length and i.d. of 4 mm) with helium as a carrier gas was used to analyze the samples with triplicate injections of 2 μL of the solution. The calculated RSD of the GC analysis of a standard solution of the acid and the alcohol was less than 3%.

The temperatures of the injection port and TCD detector were set at 503 K. Column temperature was programmed as 323 K for 1 min, increasing the temperature to 398 K with the rate 25 K·min^{-1}, and then setting of the final temperature at 398 K for 2 min.

Results and Discussion

To verify the accuracy of the solubility measurements and the method employed in the study, the solubility of oleic acid in SC-CO_2 was determined at 323 K and 136 bar. The average solubility of oleic acid for six measurements was 0.61 ± 0.04 mass %, which was comparable with data reported as 0.58 mass % in the literature.[14] There is an acceptable agreement between the two sets of data. The reliability of the solubility measurements by our system at low pressures of (65 to 80) bar for 1-hexanol was also checked and reported.[17]

To ensure saturation and equilibrium conditions, the solubilities of 2-ethyl-1-hexanol and 2-ethylhexanoic acid were determined in a series of experiments (at 313 K and 99 bar) at different flow rates of SC-CO_2. With a flow rate from (65 to 600) mL·min^{-1} of expanded CO_2 gas, equilibration was achieved and constant solubilities were observed.[17]

The effect of pressure on the binary solubilities of the acid and the alcohol in the SC-CO_2 at temperatures of (313 and 323) K is shown in Table 1 and Figure 2. The solubilities increase with increasing pressure for the temperatures studied and are higher for the alcohol compared to the acid. As the pressure is increased, that is, the SC-CO_2 density, the intermolecular interaction between the solutes and the SC-CO_2 molecules increases. Therefore, the solvating power and the solubility are increased. The extent of the increase in the solubility depends on the CO_2 and/or solute parameters such as polarity, molecular weight, volatility, and so on. The solubilities of the alcohol at (313 and 323) K in the pressure range (80 to 180) bar were higher than those of the acid due to higher volatility and lower polarity and intermolecular interactions of the alcohol. At pressures ranging from (124 to 180) bar, the binary-solubility variation stays within experimental uncertainty for both the alcohol and the acid. In this pressure range the sensitivity of the method is insufficient to detect their solubility differences.

The pressure crossover of the alcohol and the acid, that is, in agreement with their vapor pressures and molecular weights, appears at 118 bar and 124 bar, respectively. In the retrograde region before the crossover point of both the alcohol and the acid, the solubility is controlled by the solvating power (i.e. density) of the SC-CO_2 (at lower temperature, the density is higher and vice versa). However, after the crossover points the solubilities are controlled by the vapor pressure of the solutes.

Table 1. Mole Fraction Solubility (S) of 2-Ethyl-1-hexanol (1) and 2-Ethylhexanoic Acid (2) in the SC-CO$_2$ (3) at 313 K and 323 K

			10^2S			
T/K	P/bar	$\rho_3{}^a$/(g·L^{-1})	10^2S_2	AARD$_2{}^b$ (%)	10^2S_1	AARD$_1{}^b$ (%)
313	68	186.75	0.07	12.22	0.06	12.76
	72	210.37	0.08		0.08	
	81	289.82			0.16	
	90	485.50	0.40		1.50	
	99	620.73	1.81		3.79	
	110	683.52	2.22		4.45	
	120	717.76	3.36		4.34	
	126	733.68	3.57		4.47	
	135	753.64	3.59		4.49	
	144	770.38	4.15		4.45	
	153	784.84	4.38		4.84	
	180	819.51	4.13		4.58	
323	68	163.99	0.09	13.93	0.08	13.71
	72	180.44	0.11		0.10	
	81	224.73			0.14	
	90	285.00	0.24			
	99	372.63	0.67			
	110	502.64	1.47		1.48	
	120	584.71	2.54		4.46	
	126	618.01	3.92		6.92	
	135	655.50	4.83		6.66	
	144	683.99	4.73		6.91	
	153	706.91	5.31		6.64	
	180	757.12	6.21		6.87	

[a] Reference 19. [b] Average absolute relative deviation.[13]

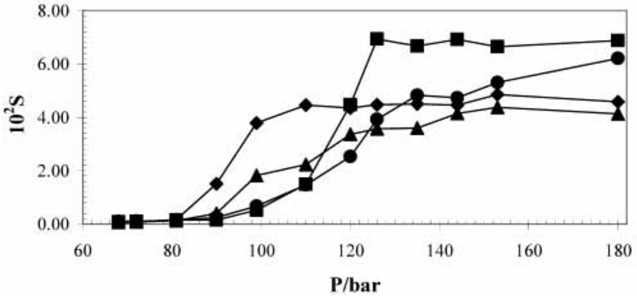

Figure 2. Solubility of 2-ethyl-1-hexanol [(◆) 313 K; (■) 323 K] and solubility of 2-ethylhexanoic acid [(▲) 313 K; (●) 323 K] at different pressures.

On the basis of the Chrastil model,[18] the molecules of solute associate with the molecules of the SC-CO$_2$ forming a solvation complex, AB$_k$, which is in equilibrium with the fluid. A, B, and k are respectively solute molecule, solvent molecule, and number of associated solvent molecules, that is, an association number. Isotherms at 313 K and 323 K for 2-ethyl-1-hexanol and 2-ethylhexanoic acid have been fitted with the model $\ln S = k \ln \rho + a/T + b$, in which S is the solubility in g·L^{-1}, $a = \Delta H/R$, and $b = \ln(M_A + kM_B) + q - k \ln M_B$ (Figures 3 and 4). a depends on $\Delta_{\mathrm{solv}}H + \Delta_{\mathrm{vap}}H$; b is a function of k, the molecular weight of the solute (M_A), and the molecular weight of the fluid (M_B); and q is a constant. k, a, b, and the correlation coefficient ($=R^2$) of the data used in the Chrastil model are given in Table 2.

Cosolubility of 2-ethyl-1-hexanol and 2-ethylhexanoic acid in SC-CO$_2$ (i.e. ternary solubility) was also studied using an equal mole ratio ($x = 0.5$) of the two compounds. The temperature effect on the solubility is shown in Table 3 and Figure 5. The solubility of each compound decreased in comparison with the solubilities of the pure alcohol and the acid. The data in Figure 5 show an isosolubility range from (313 to 343) K for the two compounds. The changes in the solubilities are within the experimental uncertainties.

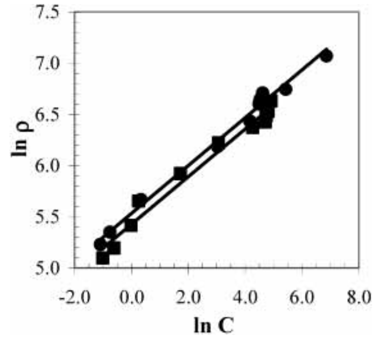

Figure 3. Chrastil model evaluation for 2-ethyl-1-hexanol: (●) 313 K; (■) 323 K.

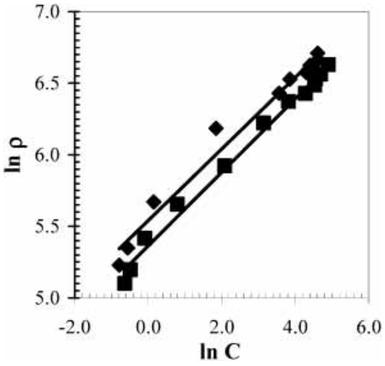

Figure 4. Chrastil model evaluation for 2-ethylhexanoic acid: (◆) 313 K; (■) 323 K.

Table 2. Chrastil Parameters for 2-Ethyl-1-hexanol and 2-Ethylhexanoic Acid at 313 K

solute	k^a	a^a	b^a	$R^{2\,b}$
2-ethyl-1-hexanol	4.29	−14 246.48	21.80	0.9899
2-ethylhexanoic acid	3.91	−11 535.71	15.30	0.9812

[a] k is the association number, $b = \ln(M_A + kM_B) + q - k \ln M_B$, and $a = \Delta H/R$. [b] R^2 is the correlation coefficient of data used in the Chrastil model at 313 K.

Table 3. Mole Fraction Solubility (S) of 2-Ethyl-1-hexanol (1) and 2-Ethylhexanoic Acid (2) in the SC-CO$_2$ (3) in an Equimolar Mixture at 138 bar

		10^2S		
T/K	$\rho_3{}^a$/(g·L^{-1})	10^2S_2	10^2S_1	total
313	759.52	3.16	3.02	6.18
323	665.78	2.51	2.58	5.09
333	551.36	2.30	2.34	4.64
343	445.98	1.26	1.50	2.76

[a] Reference 19.

The mole fraction solubilities of 2-ethylhexanoic acid and 2-ethyl-1-hexanol in SC-CO$_2$ at 333 K versus the acid to alcohol mole ratio of a series of mixtures ranging from 1:3 to 3:1 were measured and shown in Table 4 and Figure 6. A composition effect of the liquid mixture on the solubilities of the solutes in the SC-CO$_2$ was observed. The solubility of each solute in the ternary system was lower than the solubility of the solute in the binary system. This is possibly due to changes of the intermolecular interactions such as hydrogen bonding in the liquid mixture and/or in SC-CO$_2$. The acid molecules as a pure compound in a nonpolar solvent probably exist as dimers due to hydrogen bonding. It is shown that the total amount of the solutes does not depend on the mole ratio of the mixture of the components.

The selectivity (α) of SC-CO$_2$ for the acid may be defined in terms of the ratio of the solubility of the acid to that of

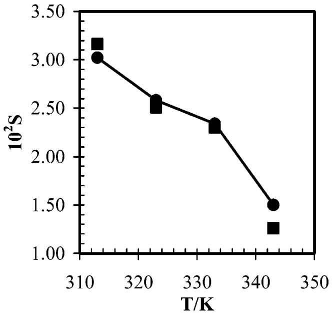

Figure 5. Solubility of 2-ethyl-1-hexanol (●) and 2-ethylhexanoic acid (■) in an $x = 0.5$ mixture at 138 bar and different temperatures.

Table 4. Mole Fraction Solubility (*S*) of 2-Ethyl-1-hexanol (1) and 2-Ethyl Hexanoic Acid (2) Mixtures in the SC-CO$_2$ at 333 K and 138 bar

acid to alcohol mole ratio in the cell	10^2S		acid to alcohol mole ratio in the SC-CO$_2$	10^2S total
	10^2S_2	10^2S_1		
0.33	1.17	3.18	0.37	4.35
0.50	1.35	2.59	0.52	3.94
1.00	2.17	2.24	0.99	4.41
2.00	2.80	1.65	1.70	4.45
3.00	2.93	1.36	2.15	4.29

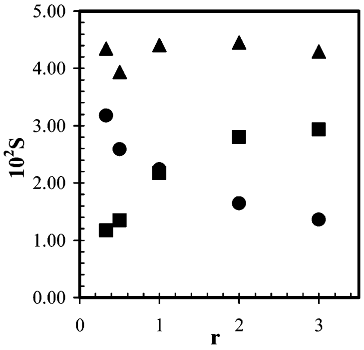

Figure 6. Mole fraction solubility of 2-ethylhexanoic acid (■) and 2-ethyl-1-hexanol (●) in SC-CO$_2$ (*S*) versus the acid to alcohol mole ratio (*r*) in the equilibrium cell and their total solubility (▲) for different *r* values at 138 bar and 333 K.

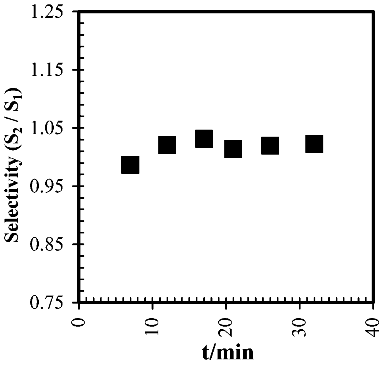

Figure 7. Selectivity of 2-ethylhexanoic acid versus time.

the alcohol.[20] The selectivity with an equimolar mixture of the acid and the alcohol in the equilibrium cell, at 313 K and 138 bar, was studied at different times, as shown in Figure 7. The data show that the selectivity of the acid through the entire period of the study is constant due to strong intermolecular interactions.

Spectroscopic studies of 2-ethyl-1-hexanol and 2-ethylhexanoic acid and their mixtures under SC-CO$_2$ conditions may be undertaken to verify the interactions responsible for the observed behavior. A study of the continuous esterification reaction at isosolubility conditions of the alcohol (2-ethyl-1-hexanol) and the acid (2-ethylhexanoic acid) by using a variety of catalysts[16,21,22] to produce a pure product is currently in progress in our laboratory.

Conclusion

The binary solubilities of 2-ethyl-1-hexanol and 2-ethylhexanoic acid were measured at pressures from (68 to 180) bar and temperatures from (313 to 323) K. Their ternary solubilities in SC-CO$_2$ were measured at the pressure 138 bar and temperatures from (313 to 343) K. An isosolubility range was observed for the two pure compounds at the temperature 323 K and pressures from (68 to 110) bar, and for their mixture of $x = 0.5$ in the equilibrium cell at temperatures from (313 to 343) K and the pressure 138 bar. At various acid to alcohol mole ratios, different solubilities were found. Aggregation or clustering may be responsible for these observations.

Acknowledgment

Professor M. Yalpani is acknowledged for his comments and critical review of the work.

Literature Cited

(1) Palmer, M. V.; Ting, S. S. T. Applications for Supercritical Fluid Technology in Food Processing. *Food Chem.* **1995**, *52*, 343−352.
(2) Muth, O.; Hirth, T.; Vogel, H. Polymer Modification by Supercritical Impregnation. *J. Supercrit. Fluids* **2000**, *17*, 65−72.
(3) Saus, W.; Knittel, D.; Schollmeyer, E. Dyeing with Supercritical Carbon Dioxide-An Alternative to High-Temperature Dyeing of Polyester. *Text.-Prax.* **1992**, *47*, 1052−1054.
(4) Zosel, K. Separation with Supercritical Gases: Practical Applications. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 702−709.
(5) Ghaziaskar, H. S.; Daneshvar, F. Extraction of Safflower Seed Oil by Supercritical Carbon Dioxide. *J. Jpn. Oil Chem. Soc.* **1998**, *47*, 1265−1271.
(6) Kurnik, R. T.; Reid, R. C. Solubility of Solid Mixtures in Supercritical Fluids. *Fluid Phase Equilib.* **1982**, *8*, 93−105.
(7) Chimowitz, E. H.; Pennisi, K. J. Process Synthesis Concepts for Supercritical Gas Extraction in the Crossover Region. *AIChE J.* **1986**, *32*, 1665−1676.
(8) Dobbs, J. M.; Johnston, K. P. Selectivities in Pure and Mixed Supercritical Fluid Solvents. *Ind. Eng. Chem. Res.* **1987**, *26*, 1476−1482.
(9) Liong, K. K.; Foster, N. R.; Ting, S. S. T. Solubility of Fatty Acid Esters in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1992**, *31*, 400−404.
(10) Gregorowicz, J.; Chylinski, K. On the Solubility of Chain Alcohols in Supercritical Carbon Dioxide. *Pol. J. Chem.* **1998**, *72*, 877−885.
(11) Manuela, A.; Veronique, P.; Munoz, E. J.; Jacques, J. Solubilities of 1-Nonanol, 1-Undecanol, 1-Tridecanol, and 1-Pentadecanol in Supercritical Carbon Dioxide at T = 323.15 K. *J. Chem. Eng. Data* **1998**, *43*, 983−985.
(12) Kramer, A.; Thodos, G. Solubility of 1-Octadecanol and Stearic Acid in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1989**, *34*, 184−187.
(13) Lucien, F. P.; Foster, N. R. Influence of Matrix Composition on the Solubility of Hydroxybenzoic Acid Isomers in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1996**, *35*, 4686−4699.
(14) Nilsson, W. B.; Gauglitz, E. J.; Hudson, J. K. Solubilities of Methyl Oleate, Oleic Acid, Oleyl Glycerols, and Oleyl Glycerol Mixtures in Supercritical Carbon Dioxide. *J. Am. Oil Chem. Soc.* **1991**, *68*, 87−91.
(15) Yu, Z. R.; Zou, M.; Bhaskar, A. R.; Rizvi, S. S. H.; Zollweg, J. A. Fluid-Liquid Equilibria of Supercritical Carbon Dioxide + Methyl Oleate + Oleic Acid. *J. Supercrit. Fluids* **1993**, *6*, 63−68.
(16) Ghaziaskar, H. S.; Ikushima, Y. Continuous Synthesis of Oleyl Oleate in Supercritical Carbon Dioxide Using Solid *p*-Toluenesulfonic Acid as Catalyst. *Iran. J. Chem. Chem. Eng.* **2000**, *19*, 79−83.
(17) Ghaziaskar, H. S.; Daneshfar, A. Role of Hydrogen Bonding on the Solubility Diminution of Carboxylic Acids and Alcohols in Supercritical Carbon Dioxide. *J. Supercrit. Fluids*, submitted for publication.
(18) Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016−3021.
(19) Taken from http://webbook.nist.gov/chemistry/fluid/.

(20) Lucien, F. P.; Foster, N. R. Solubilities of Solid Mixtures in Supercritical Carbon Dioxide: a review. *J. Supercrit. Fluids* **2000**, *17*, 111−134.
(21) Marty, A.; Chulalaksananukul, W.; Condoret, J. S.; Willemot, R. M.; Durand, G. Comparison of Lipase Catalysed Esterification in Supercritical Carbon Dioxide and in *n*-Hexane. *Biotechnol. Lett.* **1990**, *12*, 11−16.
(22) Ikushima, Y.; Saito, N.; Hatakeda, K.; Sato, O. Promotion of a Lipase-Catalyzed Esterification in Supercritical Carbon Dioxide in the Near-Critical Region. *Chem. Eng. Sci.* **1996**, *51*, 2817−2822.

Received for review April 22, 2002. Accepted December 2, 2002. The authors thank the research councils of Iran, IUT, and the ministry of mines and industry of Iran for their financial support.

JE020074L