Levulinic Acid Solubility in Supercritical Carbon Dioxide with and without Ethanol as Cosolvent at Different Temperatures

Jinlong Fan,[†] Yucui Hou,[‡] Weize Wu,*[,†] Jianwei Zhang,[†] Shuhang Ren,[†] and Xiaoting Chen[†]

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China, and Department of Chemistry, Taiyuan Normal University, Taiyuan 030012, China

---

The solubility of levulinic acid in supercritical carbon dioxide in the absence and presence of ethanol (mole fraction of ethanol $x_3 = 0.0$, 0.027, and 0.051) as a cosolvent was measured with a synthetic method at temperatures from (313.0 to 342.4) K and pressures from (8.0 to 19.0) MPa. It is demonstrated that, at a fixed temperature, the solubility of levulinic acid increases with increasing pressure; at a fixed pressure, it decreases with increasing temperature. When ethanol is added into supercritical carbon dioxide as a cosolvent, the solubility of levulinic acid increases greatly, and it increases with the concentration of the added ethanol. The experimental solubility data can be correlated using the Chrastil model and a modified Chrastil model with four adjustable parameters.

Introduction

Levulinic acid (LA) is a well-known product of hexose sugars by acid-catalyzed dehydration and is inexpensively obtained from cellulose feed stocks, a renewable biomass. Consequently, it is an attractive starting material in producing many useful five-carbon compounds such as γ-valerolactone, methyltetrahydrofuran, and derivatives. Among the derivatives, γ-valerolactone has been proposed as a precursor to a biomass-derived acrylic monomer and a sustainable liquid, due to its very attractive physical and chemical properties.[1] For example, levulinic acid can be easily converted into γ-valerolactone by hydrogenation and intramolecular cyclization. However, the traditional processes of conversion of levulinic acid are not environmentally benign, because many harmful or corrosive solvents, such as TPPT and dioxane, are used in the process.[2,3]

Supercritical carbon dioxide has been studied widely as a promising alternative solvent for chemical reaction, separation, and extraction processes because it is essentially nontoxic, inexpensive, and environmentally benign and has easily available critical constants ($T_C = 304.2$ K, $P_C = 7.38$ MPa).[4] Recently, supercritical carbon dioxide was employed as the reaction and separation media for the hydrogenation of levulinic acid to γ-valerolactone.[5] Manzer and Hutchenson[6] reported series reactions about levulinic acid in supercritical carbon dioxide in their patent. Poliakoff et al.[5] demonstrated that in supercritical carbon dioxide levulinic acid could be converted to γ-valerolactone with a high γ-valerolactone yield of more than 99 %. To perform these reactions effectively, the solubility of levulinic acid in supercritical carbon dioxide needs to be studied. A cosolvent is needed to improve the solubility of levulinic acid in supercritical carbon dioxide because the solubility of levulinic acid in supercritical carbon dioxide, as will be demonstrated in the present work, is very low. Considering that ethanol is capable of hydrogen bonding and dipole−dipole interactions with organic acid[7,8] and is conveniently available and stable for hydrogenation, it can be reasonably used as a cosolvent to improve the solubility of levulinic acid in supercritical carbon dioxide.

In this work, we have studied the solubility of levulinic acid in supercritical carbon dioxide with and without ethanol as a cosolvent. The experimental data of the solubility of levulinic acid in supercritical carbon dioxide were correlated with the Chrastil model and a modified Chrastil model.

Experimental Section

Materials. Carbon dioxide with a mass fraction of 0.99995 was from the Beijing Haipu Company. Levulinic acid with a mass fraction of > 0.99 was analytical grade from Aladdin, Shanghai Jingchun Chemical Reagent. Ethanol with a mass fraction of ≥ 0.998 was analytical grade from Beijing Chemical Reagent Plant. Naphthalene with a mass fraction of > 0.99 was analytical grade from Tianjin Fucheng Chemical Reagent Plant. All of the chemicals were used without further purification.

Apparatus and Procedure. In this work, we employed a synthetic method to measure the solubility of levulinic acid in supercritical carbon dioxide with and without ethanol. The solubility measurement was carried out in a stainless steel variable-volume view cell with two sapphire windows, which permitted visual observation of the phase behavior as described previously.[9] The schematic diagram of the apparatus is shown in Figure 1. It is composed mainly of a carbon dioxide sampling bomb, a constant temperature water bath, a pressure gauge, a variable-volume view cell with a piston, and a magnetic stirrer. The volume of the view cell could be changed from (23 to 50) cm^3 by moving the piston on the view cell. The temperature of the water bath was controlled by a temperature controller (A2, Beijing Changliu Scientific Instrument Company), and the temperature was monitored by a Pt resistance with an uncertainty of better than ± 0.1 K. The pressure gauge was composed of a pressure transducer and an indicator (Beijing Tianchen Instrument Company). Its uncertainty was ± 0.025 MPa in the pressure range of (0 to 20) MPa. The maximum working pressure and temperature of the system are 19.00 MPa and 343.15 K, respectively.

---

* To whom correspondence should be addressed. E-mail: wzwu@mail.buct.edu.cn. Tel./Fax: +86 10 64427603.

[†] Beijing University of Chemical Technology.

[‡] Taiyuan Normal University.

10.1021/je900727r

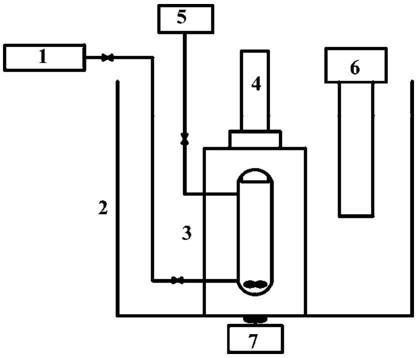

Figure 1. Schematic diagram of the apparatus for solubility measurements: 1, carbon dioxide sampling bomb; 2, constant temperature water bath; 3, high-pressure variable-volume view cell; 4, piston; 5, pressure gauge; 6, temperature controller; 7, magnetic stirrer.

The procedures were similar to those reported previously.[10] The following static mode experimental procedure was used to measure the solubility of levulinic acid in supercritical carbon dioxide. The cell was cleaned and purged with enough carbon dioxide to remove any entrapped air present in the cell. A stirring bar was loaded into the cell, and then desired amounts of the mixtures of the levulinic acid and ethanol were loaded into the cell by an injector. The amounts of the levulinic acid and ethanol were determined using an accurate balance (Sartorius BS224S) with an accuracy of 0.1 mg. About (0.1 to 5) g of a mixture of levulinic acid and ethanol was loaded into the cell, depending on the desired composition. After that, the cell was sealed quickly. Carbon dioxide was then added using a sampling bomb. The mass of carbon dioxide in the view cell was calculated from the mass difference of the sampling bomb before and after charging the system. The cell was placed into the water bath at a desired temperature, and the system was stirred. It was supposed that equilibrium was reached when the system pressure and temperature were constant for at least half an hour. After thermal equilibration, the piston in the optical cell was moved up and down to change the volume and the pressure of the

Table 1. Solubility of Levulinic Acid (2) in Supercritical Carbon Dioxide (1) with Different Concentrations of Ethanol (3) at Various Temperatures and Pressures

	$x_3 = 0$			$x_3 = 0.027$			$x_3 = 0.051$		
T/K	P/MPa	ρ/kg·m^{-3}	$10^3 x_2$	P/MPa	ρ/kg·m^{-3}	$10^3 x_2$	P/MPa	ρ/kg·m^{-3}	$10^3 x_2$
313.0	8.41	346.9	0.491	8.76	434.0	0.972	8.18	306.8	2.62
	8.88	467.3	0.930	8.89	470.1	2.27	8.37	339.1	4.11
	9.04	507.9	1.34	9.22	545.0	3.79	8.57	383.1	5.94
	9.45	580.4	2.14	9.75	613.4	5.64	8.89	470.1	7.73
	9.96	631.0	3.05	10.88	683.1	8.07	9.18	537.6	8.83
	10.41	660.3	4.19	12.20	727.4	9.91	9.47	583.0	9.70
	11.23	697.0	5.52	12.82	742.7	10.9	9.67	605.7	10.4
	12.19	727.1	6.62	14.35	772.8	12.7	10.49	664.5	12.3
	14.61	777.1	7.76	16.13	799.5	14.7	11.01	688.5	13.8
	18.25	824.7	9.00	18.36	825.9	16.3	11.66	711.6	15.6
							12.52	735.5	17.7
							13.59	758.9	20.4
							14.61	777.1	21.5
							15.33	788.5	23.0
							16.08	798.8	24.0
							17.15	812.3	25.4
							18.38	826.1	26.8
322.6	9.41	330.0	0.491	10.68	483.1	0.972	10.05	405.1	2.62
	10.29	435.7	0.930	10.97	514.3	2.27	10.50	461.8	4.11
	10.83	499.7	1.34	11.54	564.4	3.79	11.05	522.3	5.94
	11.41	554.3	2.14	12.19	606.7	5.64	11.55	565.2	7.73
	12.49	622.2	3.05	13.66	669.0	8.07	11.96	593.1	8.83
	13.09	648.5	4.19	15.12	709.2	9.91	12.35	615.2	9.70
	14.18	685.0	5.52	16.22	732.3	10.9	12.61	628.0	10.4
	15.14	709.7	6.62	18.25	765.8	12.7	13.38	659.4	12.3
	18.27	766.1	7.76				14.13	683.6	13.8
							14.89	703.8	15.6
							15.56	719.3	17.7
							16.87	744.1	20.4
							18.70	772.1	21.5
332.4	10.01	296.5	0.491	12.55	489.3	0.972	11.90	440.8	2.62
	11.27	390.1	0.930	12.92	514.0	2.27	12.48	484.4	4.11
	12.10	456.3	1.34	13.61	553.9	3.79	13.11	525.7	5.94
	13.08	524.0	2.14	14.50	595.1	5.64	13.73	560.0	7.73
	14.55	597.1	3.05	16.20	652.1	8.07	14.49	594.7	8.83
	15.51	631.6	4.19	17.84	691.3	9.91	14.85	608.8	9.70
	16.78	667.4	5.52	18.99	713.2	10.9	15.26	623.4	10.4
	18.21	698.7	6.62				16.29	654.6	12.3
							17.56	685.4	13.8
							18.68	707.6	15.6
342.4	10.39	268.2	0.491	14.47	491.5	0.972	13.82	457.8	2.62
	12.02	354.2	0.930	14.72	503.5	2.27	14.24	479.9	4.11
	13.14	419.6	1.34	15.43	535.0	3.79	15.09	520.4	5.94
	14.49	492.4	2.14	16.35	570.1	5.64	15.71	546.3	7.73
	16.13	562.2	3.05	18.18	624.8	8.07	16.33	569.4	8.83
	17.53	607.3	4.19				16.68	581.3	9.70
	18.83	640.6	5.52				17.23	598.6	10.4
							18.76	639.0	12.3

system until a single phase transparent solution was observed. When the temperature and pressure became constant for a period of time greater than 0.5 h, the pressure was decreased slowly at about 0.5 MPa·min^{-1} by moving the piston until the system became cloudy, and the pressure was then slowly increased slightly to obtain a clear solution. The transition pressure was defined as the dew-point pressure or solubility pressure at the temperature and fixed composition. Every measurement was repeated at least three times for consistent measurements. Then the system temperature was raised, and the above procedure was repeated to measure the solubility of levulinic acid at other temperatures. The solubility (x_2) of levulinic acid in supercritical carbon dioxide with or without ethanol is calculated from the following eq 1.

$$x_2 = \frac{n_{\mathrm{LA}}}{n_{\mathrm{LA}} + n_{\mathrm{CO_2}} + n_{\mathrm{EtOH}}} \tag{1}$$

where x_2 is the solubility of levulinic acid in mole fraction; n_{LA} is the amount of levulinic acid charged in the view cell, mol; $n_{\mathrm{CO_2}}$ is the amount of carbon dioxide charged in the view cell, mol; and n_{EtOH} is the amount of ethanol charged in the view cell, mol, if present. In the Correlation Section, the solubility of levulinic acid, s, is expressed in a unit of g·L^{-1}. The conversion of solubility of levulinic acid s in g·L^{-1} into x_2 or x_2 into s can be done through the following eq 2.

$$x_2 = \frac{\dfrac{s}{M_2}}{\dfrac{s}{M_2} + \dfrac{\rho}{M_1} \cdot \dfrac{1}{1 - x_3}} \tag{2}$$

where s is the solubility of levulinic acid in the mixture of supercritical carbon dioxide and ethanol (g·L^{-1}); x_3 is the mole fraction of cosolvent ethanol; M_1 is the molecular weight of carbon dioxide (g·mol^{-1}); M_2 is the molecular weight of levulinic acid (g·mol^{-1}); and ρ is the density of pure carbon dioxide (g·L^{-1}). When there is no cosolvent in supercritical carbon dioxide, x_3 can be set to zero. The densities of supercritical carbon dioxide were obtained from the equation proposed by Huang et al.[11] which is shown in Table 1.

The uncertainty of the mole fraction of levulinic acid was estimated to be ± 0.5 %. The equilibrium temperature and dew-point pressure were measured with uncertainties of ± 0.1 K and ± 0.025 MPa, respectively.

To test the performance of the apparatus, the solubility of naphthalene in supercritical carbon dioxide was measured with a synthetic method at temperatures from (308.15 to 328.15) K and pressures from (8.0 to 19.0) MPa. The results are compared with those obtained by McHugh and Paulaitis[12] at the same temperatures in Table 2 and graphically in Figure 2. The figure indicates that our results are in good agreement with the literature's data, which suggests that the apparatuses we employed are reliable.

Correlation

There are several models suggested for correlating the solubility of solids or liquids in supercritical fluid.[13] In this work, the experimental data of solubility in supercritical fluid were correlated with a density-based model. The model was developed based on the common observation that the logarithm of the solubility is linearly dependent on the density of supercritical fluid.[14] Chrastil[15] was the first to develop a semiempirical solubility correlation based on this approach. He assumed that the solute molecule combination with the supercritical solvent molecules produced solvate complexes in terms of the following equilibrium: A + kB ↔ AB$_k$, where A stands for solute and B for solvent. Therefore, the equilibrium concentration can be calculated from the mass action law. The semi empirical Chrastil equation has the form shown as follows.

Table 2. Comparison of the Measured Solubility of Naphthalene (2) in Supercritical Carbon Dioxide (1) by This Work with That of Reference 12

	ref 12		this work	
	P/MPa	10^3x_2	P/MPa	10^3x_2
T = 308.15 K	8.57	7.50	8.48	7.57
	9.69	9.75	10.57	10.7
	10.51	10.66	16.72	17.4
	13.13	14.10		
	16.68	16.05		
	19.69	17.09		
	21.95	18.30		
	23.93	19.08		
	25.20	19.22		
T = 328.15 K	8.11	1.313	11.38	7.57
	9.11	1.672	11.96	10.7
	10.10	2.920	12.86	17.4
	10.83	5.464		
	12.01	12.29		
	13.15	21.14		
	14.18	25.44		
	15.85	30.53		
	16.94	33.87		
	17.26	34.73		
	18.71	39.28		
	20.76	42.24		
	22.06	43.66		
	23.47	45.86		
	24.83	49.69		
	28.40	53.82		

$$s = \rho^k \exp(\alpha/T + \beta) \tag{3}$$

where s is the solubility of the solute in the supercritical carbon dioxide (g·L^{-1}); ρ is the density of pure carbon dioxide (g·L^{-1}); T is the temperature in K; k is the association numbers of carbon dioxide; and α and β are parameters of the Chrastil equation. α depends on the total reaction enthalpy, $\Delta H_{\mathrm{Total}}$, by the following eq 4.[15]

$$\alpha = \frac{-\Delta H_{\mathrm{Total}}}{R} \tag{4}$$

$\Delta H_{\mathrm{Total}}$ is the total reaction enthalpy of the solution process. β depends on the molecular weight and melting point of the three compounds (solute, solvent, and cosolvent).

The Chrastil model has widely been used to correlate the experimental solubility data without cosolvent.[16–18] Taking into

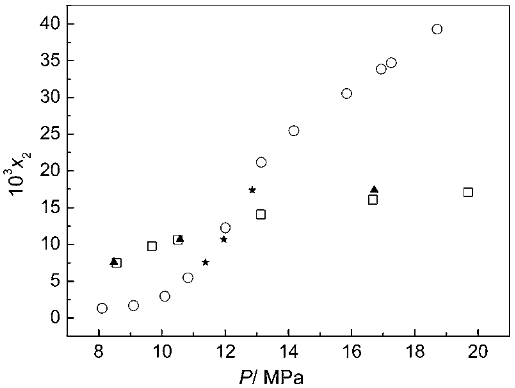

Figure 2. Comparison of the measured solubility of naphthalene (2) in supercritical carbon dioxide (1) in this work with those of ref 12. □, ref 12 at 308.15 K; ○, ref 12, at 328.15 K; ▲, this work at 308.15 K; ★, this work at 328.15 K.

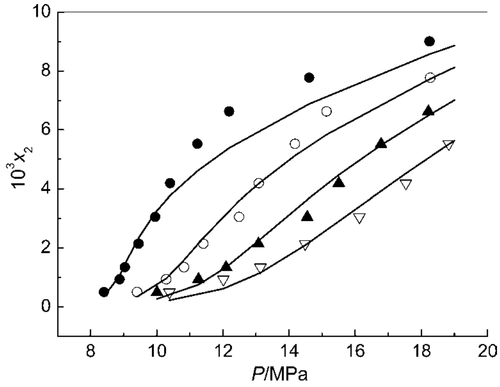

Figure 3. Dependence of the solubility of levulinic acid (2) in supercritical carbon dioxide (1) on pressure at different temperatures: ●, 313.0 K; ○, 322.6 K; ▲, 332.4 K; ▽, 342.4 K. Experimental data (symbols) and calculated results by the Chrastil equation (in lines).

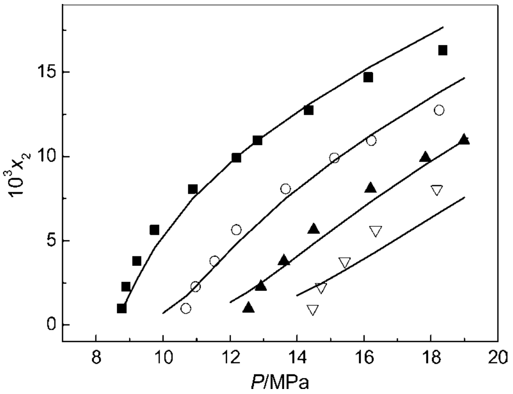

Figure 4. Solubility of levulinic acid (2) in carbon dioxide (1) + ethanol (3) at $x_3 = 0.027$ and different temperatures: ■, 313.0 K; ○, 322.6 K; ▲, 332.4 K; ▽, 342.4 K. Experimental data (symbols) and calculated results by the modified Chrastil equation (in lines).

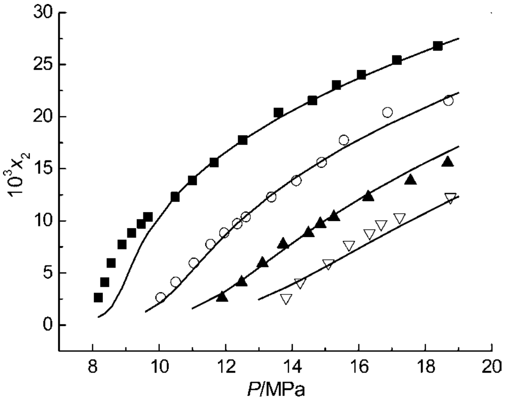

Figure 5. Solubility of levulinic acid (2) in carbon dioxide (1) + ethanol (3) at $x_3 = 0.051$ and different temperatures: ■, 313.0 K; ○, 322.6 K; ▲, 332.4 K; ▽, 342.4 K. Experimental data (symbols) and calculated results by the modified Chrastil equation (in lines).

account the cosolvent contribution to the solubility, González et al.[19] modified the Chrastil equation. First they considered the formation of the solute−cosolvent−solvent complexes: A + kB + γC $\leftrightarrow$ AB$_k$C$_\gamma$, where A stands for solute, B for solvent, and C for cosolvent, and then obtained an equation to correlate the solubility of solids or liquids in supercritical carbon dioxide with cosolvent as follows.

$$s = \rho^k m^\gamma \exp(\alpha/T + \beta) \qquad (5)$$

where s, ρ, T, k, α, and β have the same meaning with eqs 3 and 4; m is the concentration of cosolvent (g·L^{-1}); and γ is the association number of the cosolvent.

The Chrastil eq 3 is employed to correlate the solubility of levulinic acid in supercritical carbon dioxide without cosolvent and the modified Chrastil eq 5 for the data with cosolvent ethanol. By fitting the experimental data presented in this work, we obtained the values of k, γ, α, and β. The average absolute relative deviation (AARD) is expressed as follows:

$$\text{AARD} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{x_i^{\text{exptl}} - x_i^{\text{calcd}}}{x_i^{\text{exptl}}}\right| \cdot 100\ \% \qquad (6)$$

where n is the number of experimental points and x_i^{exptl} and x_i^{calcd} are the experimental and calculated mole fractions of the solute in the supercritical phase, respectively.

Results and Discussion

The solubility of levulinic acid in the mixture of supercritical carbon dioxide and ethanol is listed in Table 1.

Figure 3 graphically shows the influence of pressure and temperature on the solubility of levulinic acid in supercritical carbon dioxide. As we expected, the solubility of levulinic acid increases with the elevation of pressure at a fixed temperature due to the increase of the density of carbon dioxide. The increase of the density of the fluid can decrease the mean distance of the molecules and hence increase specific interaction between the solute and the solvent molecules, which results in improving the solubility of the solute levulinic acid. However, it decreased with the increase of temperature at fixed pressure. This phenomenon has also been observed for the solubility of other organic compounds in supercritical carbon dioxide.[20,21] The increase of temperature results in two aspects, (1) an increase of the volatility of levulinic acid, which is benefit for its solubility, and (2) a decrease of the density of the fluid, which is unfavorable to its solubility. Our results indicate that the latter is the dominant factor in this system. It was reported that there was a crossover pressure for the solubility of a nonvolatile substance in supercritical carbon dioxide.[16,18,22] When the pressure is greater than the crossover pressure, an increase of temperature will increase the solubility; while the pressure is less than the crossover pressure, an increase of temperature will decrease the solubility. Therefore, the crossover pressure for the solubility of levulinic acid in supercritical carbon dioxide is supposed to be above the pressures we studied.

The solubility of levulinic acid in carbon dioxide + ethanol mixtures shows completely similar behavior to the solubility in pure carbon dioxide from Table 1 and Figures 4 and 5.

To examine the effect of the cosolvent, the solubility of levulinic acid in supercritical carbon dioxide with different concentrations of ethanol at 313.0 K was plotted in Figure 6. The effects of the cosolvent on the solubility at other temperatures of (322.6, 332.4, and 342.4) K are similar to that at 313.0 K and have not been shown. When 0.027 mol fraction of ethanol is present, the solubility is increased to about 0.9 times; when 0.051 mol fraction of ethanol is added into carbon dioxide, the solubility is increased from (2.9 to 8.8) times. From Figure 6, we can conclude that the solubility of levulinic acid in supercritical carbon dioxide increases with the increase of the mole fraction of ethanol in the mixture at fixed temperatures and pressures. This result is due to the strong molecular interactions between the solute and the cosolvent.[23−25]

Experimental data obtained in this work were correlated with the semiempirical equation of the Chrastil model and the modified Chrastil model with four parameters. The comparison

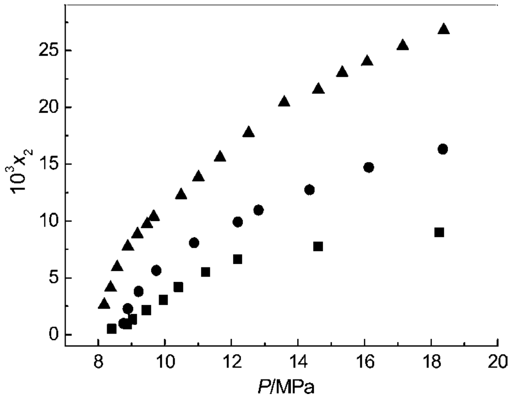

Figure 6. Solubility of levulinic acid (2) in supercritical carbon dioxide (1) without and with different concentrations of ethanol (3) at 313.0 K. ■, pure carbon dioxide; ●, carbon dioxide + ethanol ($x_3 = 0.027$); ▲, carbon dioxide + ethanol ($x_3 = 0.051$).

Table 3. Fitted Modified Chrastil Equation Parameters for Different Ethanol Concentrations

system	k	α/K	β	γ	AARD/%
$x_3 = 0$	4.71	−1798.1	−22.95		13.11
$x_3 = 0.027$	3.54	−990.3	−23.28	2.02	15.82
$x_3 = 0.051$	2.51	−395.1	−19.44	2.11	11.68

between the experimental solubility data and the predicted values using the Chrastil equation and the modified Chrastil equation are shown in Figures 3 to 5, and the corresponding AARDs are given in Table 3. The correlation results indicate that the models can reasonably fit the experimental data, but the AARDs are relatively high up to 15.82 %. The high deviation may result from two reasons: (1) the cosolvent ethanol can form hydrogen bonding with levulinic acid, and the strong interaction cannot be reflected by the modified Chrastil equation; or (2) as suggested by González et al.,[19] the density of pure supercritical carbon dioxide is employed for the correlation process, instead of the density of the (supercritical carbon dioxide + ethanol) mixture. However, there is a difference between the density of (supercritical carbon dioxide + ethanol) mixture and that of pure supercritical carbon dioxide.

Table 3 shows the fitted modified Chrastil equation parameters which are essentially independent of temperature. It can be seen that the parameter α is a negative value. According to eq 4, $\Delta H_{\mathrm{Total}}$ is positive, which indicates that the association is an endothermic process.[15,19] Particularly, the value of α increases with the concentration of ethanol, which suggests that ethanol can reduce the energy of absorption in the association process of solute and solvent, and this is why the solubility of levulinic acid in supercritical carbon dioxide increases with the increasing concentration of ethanol at fixed temperatures and pressures. It also can be seen from Figure 6. The value of k is larger than that of γ, which hints that there are more supercritical carbon dioxide molecules in combination with solute than cosolvent. This may be caused by the fact that the concentration of carbon dioxide is much larger than that of the cosolvent.

Conclusion

The solubility of levulinic acid (1) in the mixture of supercritical carbon dioxide (2) and ethanol (3) with mole fractions of ethanol $x_3 = 0.0$, 0.027, and 0.051 at temperatures ranging from $T = (313.0 \text{ to } 342.4)$ K and pressures ranging from $P = (8.0 \text{ to } 19.0)$ MPa has been measured. From this work, we can conclude that the solubility of levulinic acid in supercritical carbon dioxide increases with the increase of pressure at the fixed temperature but decreases with the increase of temperature at the fixed pressure. Besides, the solubility of levulinic acid in the mixtures of supercritical carbon dioxide and ethanol increases with the ethanol concentrations at fixed temperatures and pressures. Furthermore, the experimental data could be correlated using the Chrastil model and the modified Chrastil model with AARDs from (11.68 to 15.82) %.

Acknowledgment

The authors thank Prof. Chengyue Li, Prof. Zhenyu Liu, and Dr. Qingya Liu for their help.

Literature Cited

(1) Horváth, I. T.; Mehdi, H.; Fábos, V.; Boda, L.; Mika, L. T. γ-Valerolactone - A Sustainable Liquid for Energy and Carbon-Based Chemicals. *Green Chem.* **2008**, *20*, 238–242.
(2) Manzer, L. E. Production of 5-Methylbutyrolactone from Levulinic acid. U.S. Patent 6,617,414, 2003.
(3) Mehdi, H.; Fábos, V.; Tuba, R.; Bodor, A.; Mika, L. T.; Horváth, I. T. Integration of Homogeneous and Heterogeneous Catalytic Processes for a Multi-step Conversion of Biomass: From Sucrose to Levulinic Acid, γ-Valerolactone, 1,4-Pentanediol, 2-Methyl-tetrahydrofuran, and Alkanes. *Top. Catal.* **2008**, *48*, 49–54.
(4) Clifford, T. *Fundamentals of Supercritical Fluids*; Oxford University Press: New York, 1999; pp 1−5.
(5) Bourne, R. A.; Stevens, J. G.; Ke, J.; Poliakoff, M. Maximising Opportunities in Supercritical Chemistry: the Continuous Conversion of Levulinic Acid to γ-Valerolactone in Carbon Dioxide. *Chem. Commun.* **2007**, 4632–4634.
(6) Manzer, L. E.; Hutchenson, K. W. Production of 5-methyl-dihydrofuran-2-one from Levulinic Acid in Supercritical Media. U.S. Patent 6,946,543, 2004.
(7) Jin, J. S.; Zhong, C. L.; Zhang, Z. T.; Li, Y. Solubilities of Benzoic Acid in Supercritical Carbon Dioxide with Mixed Cosolvent. *Fluid Phase Equilib.* **2004**, *226*, 9–13.
(8) Yoshio, K.; Yoshio, I.; Yoshiaki, H.; Morio, Y.; Yasuhiko, A. Influence of Cosolvent on Solubilities of Fatty Acids and Higher Alcohols in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1996**, *125*, 115–128.
(9) Chen, X. T.; Hou, Y. C.; Wu, W. Z.; Ren, S. H.; Zhang, J. W.; Fan, J. L. High Pressure Phase Behavior and Density of the Carbon Dioxide + 1-Methylimidazole Binary System. *J. Supercrit. Fluids* **2009**, *49*, 310–314.
(10) Su, B. G.; Lv, X. B.; Yang, Y. W.; Ren, Q. L. Solubilities of Dodecylpoly-oxyethylene Polyoxypropylene Ether in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2006**, *51*, 542–544.
(11) Huang, F. H.; Li, M. H.; Lee, L. L.; Starling, K. E.; Chung, F. T. H. An Accurate Equation of State for Carbon Dioxide. *J. Chem. Eng. Japan* **1985**, *18*, 490–496.
(12) McHugh, M.; Paulaitis, M. E. Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1980**, *25*, 326–329.
(13) Duarte, A. R. C.; Coimbra, P.; Sousa, H. C.; Duarte, C. M. M. Solubility of Flurbiprofen in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2004**, *49*, 449–452.
(14) Guigard, S. E.; Stiver, W. H. A Density-Dependent Solute Solubility Parameter for Correlating Solubilities in Supercritical Fluids. *Ind. Eng. Chem. Res.* **1998**, *37*, 3786–3792.
(15) Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016–3021.
(16) Zhou, R.; Li, S. F.; Liu, T. J. Measurement and Correlation of Solubility of Uracil in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2008**, *53*, 2679–2682.
(17) Duarte, A. R. C.; Santiago, S.; Sousa, H. C.; Duarte, C. M. M. Solubility of Acetazolamide in Supercritical Carbon Dioxide in the Presence of Ethanol as a Cosolvent. *J. Chem. Eng. Data* **2005**, *50*, 216–220.
(18) Lee, L. S.; Huang, J. F.; Zhu, O. X. Solubilities of Solid Benzoic Acid, Phenanthrene, and 2,3-Dimethylhexane in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2006**, *46*, 1156–1159.
(19) González, J. C.; Vieytes, M. R.; Botana, A. M.; Vieites, J. M.; Botana, L. M. Modified Mass Action Law-Based Model to Correlate the Solubility of Solids and Liquids in Entrained Supercritical Carbon Dioxide. *J. Chromatogr., A* **2001**, *910*, 119–125.
(20) Ismadji, S. Solubility of Methyl Salicylate in Supercritical Carbon Dioxide at Several Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 2207–2210.

(21) Sparks, D. L.; Estévez, L. A.; Hernandez, R.; Barlow, K.; French, T. Solubility of Nonanoic (Pelargonic) Acid in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2008**, *53*, 407–410.
(22) Jia, L. Q.; Jiang, H. F.; Li, J. H. Selective Carbonylation of Norbornene in Supercritical Carbon Dioxide. *Green Chem.* **1999**, *2*, 91–93.
(23) Walsh, J. M.; Donohue, M. D. Hydrogen Bonding in Entrainer Cosolvent Mixtures: A Parametric Analysis. *Fluid Phase Equilib.* **1989**, *52*, 397–404.
(24) Sovová, H.; Stateva, R. P.; Galushko, A. A. Solubility of β-Carotene in Supercritical Carbon Dioxide and the Effect of Entrainers. *J. Supercrit. Fluids* **2001**, *21*, 195–203.
(25) Ke, J.; Mao, C.; Zhong, M. H.; Han, B. X.; Yan, H. K. Solubility of Salicylic Acid in Supercritical Carbon Dioxide with Ethanol Cosolvent. *J. Supercrit. Fluids* **1996**, *9*, 82–87.

Received for review September 05, 2009. Accepted March 11, 2010. This work was supported by the Beijing Natural Science Foundation (2082017), the Program for New Century Excellent Talents in University (NSET-08-0710), and SRF for ROCS, SEM.

JE900727R