Solubility of 5-Hydroxymethylfurfural in Supercritical Carbon Dioxide with and without Ethanol as Cosolvent at (314.1 to 343.2) K

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The solubility of 5-hydroxymethylfurfural (HMF) in supercritical carbon dioxide (scCO$_2$) with and without ethanol (mole fraction of ethanol $x_3 = 0$, 0.025, and 0.050) as a cosolvent was measured by the cloud point at temperatures from (314.1 to 343.2) K and pressures from (8.54 to 19.71) MPa. It is demonstrated that the solubility of HMF increases with the increase of pressure at a fixed temperature but decreases with the increase of temperature at a fixed pressure. When ethanol is added into scCO$_2$ as a cosolvent, the solubility of HMF increases greatly with the increase of the mole fraction of ethanol. The experimental data can be correlated by the Chrastil model and a modified Chrastil model with four adjustable parameters. The correlation results indicate that the association of HMF and CO$_2$ is an endothermic process, and ethanol can reduce the energy of the process.

Introduction

As a versatile intermediate, 5-hydroxymethylfurfural (HMF) obtained from renewable biomass resources can be converted into 2,5-furandicarboxyl acid, 2,5-dihydroxymethylfuran, 2,5-bis(hydroxymethyl)tetrahydrofuran, dimethylfuran, and other liquid alkanes by oxidation, hydrogenation, hydrogenolysis, or aldol condensation.[1,2] Imidazolium-based ionic liquids (ILs) have been used as the environmental benign solvents and catalysts for carbohydrates. Recently, several research groups reported that carbohydrates can be converted into HMF in ILs[3,4] and both the yield and selectivity of HMF could be higher than 90 %. However, the industrialization is restricted because the separation of the products is inefficient, most involving environmentally unfriendly solvents, such as tetrahydrofuran,[5] toluene,[4] and ether.[6]

As an alternative separation technique, supercritical fluid extraction (SFE) has drawn much attention in the past 30 years. Among the solvents used as supercritical fluids (SCFs), supercritical carbon dioxide (scCO$_2$) is particularly suited to practical applications because it is essentially nontoxic, inexpensive, and environmentally friendly and has easily available critical constants ($T_c = 304.2$ K, $P_c = 7.38$ MPa).[7] Palma and Taylor[8] reported that HMF can be separated from raisins via scCO$_2$ extraction. However, the solubilities of HMF in scCO$_2$, which are important data in developing the SFE process, cannot be found in the literature, to the best of our knowledge.

Unfortunately, because CO$_2$ is nonpolar and has weak van der Waals forces, it is not suitable for dissolving polar substances. Thus, the application of pure CO$_2$ in the separation processes of polar substances is limited. Up to now, the most efficient and easily available method to improve the solvation ability of the extraction fluid is to add organic modifier as cosolvent. Considering that ethanol is capable of hydrogen bonding and dipole−dipole interactions with hydroxyl and carbonyl groups,[9] it can be reasonably used as a cosolvent to improve the solubility of HMF in scCO$_2$.

In this work, we studied the solubility of HMF in scCO$_2$ with and without ethanol as a cosolvent. The experimental data of the solubility of HMF in scCO$_2$ were correlated with the Chrastil model and a modified Chrastil model.

Experimental Section

Materials. CO$_2$ with a mass fraction purity of ≥ 0.99995 was supplied by the Beijing Haipu Company. HMF with a mass fraction purity of ≥ 0.98 was analytical grade, purchased from J&K Chemical Co., Ltd., and the mass fraction of water in the HMF is 0.0084. Ethanol with a mass fraction purity of ≥ 0.998 was analytical grade, purchased from Beijing Chemical Reagent Plant. All of the chemicals were used without further purification.

Apparatus and Procedure. A synthetic method was used to measure the solubility of HMF in scCO$_2$ with and without ethanol. The experimental apparatus and procedure have been described in detail in our previous work and elsewhere.[10,11] Briefly, 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. The solubilities of HMF in scCO$_2$ with and without ethanol were determined by measuring the cloud points (the point at which a new liquid phase formed and dropped out of solution) of the solutions with different compositions.[12] The volume of the system was known from the position of the piston on the view cell, which was calibrated accurately using water as a medium. The density of the mixture could be calculated easily from the mass of the samples charged into the view cell and the volume of the system. The mole fraction (x_2) of HMF in scCO$_2$ with or without ethanol is calculated on the basis of their amounts charged into the view cell.

The relative uncertainty of the mole fraction of HMF was estimated to be ± 0.5 %. The equilibrium temperature and cloud point pressure were measured with uncertainties of ± 0.1 K and ± 0.05 MPa, respectively. The uncertainty of the density data is ± 5 g·L^{-1}.

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The reliability of the apparatus used in this work has been tested in our previous work,[10] which indicates that the apparatus employed in this work is reliable.

Correlation

The Chrastil equation[13] and the modified Chrastil equation[14] are simple models to correlate the solubility in SCF, and they have been widely used to correlate the experimental solubility data with and without cosolvent.[15−17] In this work, we used the two simple models to correlate HMF solubility in $scCO_2$ with and without ethanol cosolvent.

The Chrastil equation is based on the hypothesis that each molecule of a solute, A, associates with k molecules of supercritical solvent, B, to form a solvate complex, AB_k, which is in equilibrium with the system.

$$\mathrm{A} + k\mathrm{B} \leftrightarrow \mathrm{AB}_k \tag{1}$$

Taking in consideration several thermodynamic equations, we can easily obtain the following expression for the solid solubility in a SCF:

$$\ln(S/\mathrm{g}\cdot\mathrm{L}^{-1}) = k\ln(\rho/\mathrm{g}\cdot\mathrm{L}^{-1}) + \frac{\alpha}{T/\mathrm{K}} + \beta \tag{2}$$

where S is the solubility of the solid substance in the SCF; ρ is the density of the system; k is the association number; T is the temperature; α is a constant, which is defined as $-\Delta H/R$ (where ΔH is the total reaction enthalpy of the solution process and R is the ideal gas constant); and β is another constant, which is related to the molecular weight of the solute and solvent.

González et al.[14] modified the Chrastil equation. They assumed that each molecule of a solute, A, associates with k molecules of supercritical solvent, B, and γ molecules of a cosolvent, C, to form a solvate complex, AB_kC_γ.

$$\mathrm{A} + k\mathrm{B} + \gamma\mathrm{C} \leftrightarrow \mathrm{AB}_k\mathrm{C}_\gamma \tag{3}$$

Then an equation to correlate the solubility of involatile substance in SCF with the cosolvent can be obtained, shown as follows:

$$\ln(S/\mathrm{g}\cdot\mathrm{L}^{-1}) = k\ln(\rho/\mathrm{g}\cdot\mathrm{L}^{-1}) + \gamma\ln(C/\mathrm{g}\cdot\mathrm{L}^{-1}) + \frac{\alpha}{T/\mathrm{K}} + \beta \tag{4}$$

where S, ρ, T, k, α, and β have the same meaning with eq 2; γ is the association number of the cosolvent; C is the concentration of the cosolvent.

The average relative deviation (ARD) of the solubility is expressed as follows:

$$\mathrm{ARD}/\% = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{S_i^{\mathrm{cal}}/\mathrm{g}\cdot\mathrm{L}^{-1} - S_i^{\mathrm{exp}}/\mathrm{g}\cdot\mathrm{L}^{-1}}{S_i^{\mathrm{exp}}/\mathrm{g}\cdot\mathrm{L}^{-1}}\right|\cdot 100 \tag{5}$$

where n is the number of experimental points; S_i^{exp} and S_i^{cal} are the experimental and calculated solubilities of HMF in $scCO_2$, respectively. The experimental solubility of HMF, S_i^{exp}, can be calculated by the following eq 6.

$$S/\mathrm{g}\cdot\mathrm{L}^{-1} = \frac{m_{\mathrm{HMF}}/\mathrm{g}}{m_{\mathrm{CO_2}}/\mathrm{g} + m_{\mathrm{HMF}}/\mathrm{g} + m_{\mathrm{EtOH}}/\mathrm{g}}\cdot(\rho/\mathrm{g}\cdot\mathrm{L}^{-1}) \tag{6}$$

where m_{EtOH}, $m_{\mathrm{CO_2}}$, and m_{HMF} are the masses of ethanol, CO_2, and HMF, respectively; ρ is the density of the mixture. When there is no cosolvent in $scCO_2$, m_{EtOH} can be set to zero.

Results and Discussion

The solubility of HMF in $scCO_2$ and densities of the mixtures were measured at temperatures of (314.10, 323.98, 333.76, and

Table 1. Solubility x_2 of HMF (2) in $scCO_2$ (1) with Different Mole Fractions of Ethanol (3) and Densities ρ of the Mixtures at Various Temperatures and Pressures

	$x_3 = 0$			$x_3 = 0.025$			$x_3 = 0.050$		
T/K	P/MPa	ρ/$\mathrm{g}\cdot\mathrm{L}^{-1}$	$10^3\,x_2$	P/MPa	ρ/$\mathrm{g}\cdot\mathrm{L}^{-1}$	$10^3\,x_2$	P/MPa	ρ/$\mathrm{g}\cdot\mathrm{L}^{-1}$	$10^3\,x_2$
314.10	9.74	582.9	0.506	8.76	584.5	1.056	8.54	646.3	2.063
	11.58	695.4	0.983	9.60	688.2	1.466	9.34	727.0	3.026
	13.31	743.3	1.238	11.03	759.4	2.016	11.00	786.4	4.036
	14.78	771.4	1.531	12.60	808.6	2.542	12.74	834.1	4.996
	16.60	798.3	1.990	14.42	840.2	3.015	14.86	870.6	5.891
	18.74	823.4	2.384	17.05	886.2	3.976	17.79	910.2	7.060
323.98	10.99	489.2	0.506	10.64	555.6	1.056	10.63	616.2	2.063
	12.82	619.7	0.983	11.49	633.0	1.466	11.69	693.8	3.026
	14.43	678.7	1.238	12.99	709.4	2.016	13.32	747.8	4.036
	15.83	713.6	1.531	14.57	762.7	2.542	14.94	818.6	4.996
	17.65	747.4	1.990	16.50	801.3	3.015	17.44	841.4	5.891
	19.58	775.4	2.384	19.03	848.8	3.976	19.71	876.0	7.060
333.76	11.85	419.8	0.506	11.97	521.9	1.056	12.49	585.0	2.063
	14.00	557.2	0.983	13.04	578.6	1.466	13.02	661.2	3.026
	15.29	610.9	1.238	14.60	657.1	2.016	15.50	719.4	4.036
	16.59	650.8	1.531	16.26	717.5	2.542	17.27	767.8	4.996
	18.37	691.8	1.990	17.83	751.3	3.015	19.65	810.2	5.891
343.20	12.74	389.6	0.506	12.87	462.6	1.056	14.09	554.2	2.063
	14.94	505.9	0.983	14.20	521.0	1.466	15.45	625.5	3.026
	15.72	540.5	1.238	15.87	605.8	2.016	17.41	688.2	4.036
	17.20	590.9	1.531	17.63	671.4	2.542	18.81	728.4	4.996
	19.07	640.2	1.990	18.83	701.0	3.015			

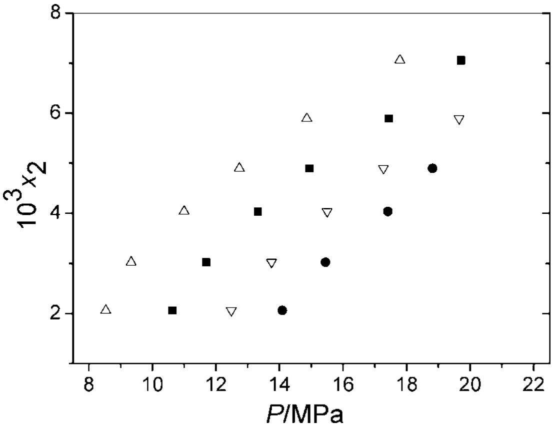

Figure 1. Solubility of HMF (2) in $scCO_2$ (1) + ethanol (3) at $x_3 = 0.050$ and different temperatures: △, 314.10 K; ■, 323.98 K; ▽, 333.76 K; ●, 343.20 K.

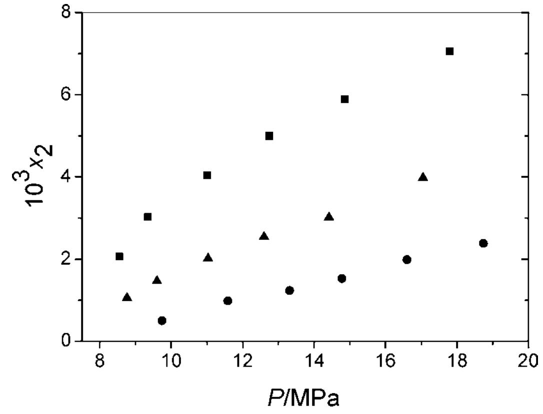

Figure 2. Solubility of HMF (2) in $scCO_2$ (1) without and with different mole fractions of ethanol (3) at 314.10 K. ●, pure CO_2; ▲, $scCO_2$ + ethanol ($x_3 = 0.025$); ■, $scCO_2$ + ethanol ($x_3 = 0.050$).

343.20) K and pressures from (8.54 to 19.71) MPa. Ethanol (at mole fractions of 0, 0.025, and 0.050) was used as cosolvent. The experimental results are listed in Table 1.

The solubility of HMF in $scCO_2$ with 0.050 mole fraction of ethanol was plotted in Figure 1. The plots of the solubility in other mole fractions (0 and 0.025) are similar to that of 0.050, so they have not been shown. As expected, the solubility of HMF increases with the increase of pressure at a fixed temperature. However, it decreases with the increase of temperature at a fixed pressure. The increase of temperature results in two effects on the solubility of HMF: (1) an increase of the volatility of HMF, which is favorable to its solubility; (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.

The effects of the cosolvent ethanol on the solubility of HMF in $scCO_2$ at 314.10 K are shown in Figure 2. When 0.025 mole fraction of ethanol is present, the solubility is about (0.97 to 1.90) times larger than that in pure $scCO_2$, and when 0.050 mole fraction of ethanol is added into CO_2, the solubility is increased from (2.85 to 4.98) times. The effects of the cosolvent on the solubility of HMF in $scCO_2$ at (323.98, 333.76, and 343.20) K show similar results to that at 314.10 K, and their figures are not shown. It can be concluded that the solubility of HMF in $scCO_2$ increases with the increase of the mole fraction of ethanol in the $scCO_2$ mixture at fixed temperatures and pressures. This is due to the strong molecular interactions between the solute and the cosolvent.[18]

Table 2. Fitted Chrastil Equation Parameters and Corresponding Values of ARDs at Different Ethanol Mole Fractions

system	k	α	β	γ	ARD/%
$x_3 = 0$	4.11	−3306.2	−15.60		7.9
$x_3 = 0.025$	3.71	−2102.1	−16.66	0.08	5.3
$x_3 = 0.050$	3.99	−1493.6	−20.37	0.19	3.7

In this work, the solubility of HMF in $scCO_2$ and that in $scCO_2$ with ethanol as cosolvent are correlated by eqs 2 and 4, respectively, on the basis of the densities in Table 1. The parameters k, α, β, and γ are obtained by performing a multiple linear regression on the experimental solubility data, and their values are listed in Table 2. The parameter α, defined as $-\Delta H/R$, is a negative value, indicating that ΔH is positive, (27.49, 17.48, and 12.42) $kJ \cdot mol^{-1}$ at mole fractions of ethanol of 0, 0.025, and 0.050, respectively, which indicates that the association is an endothermic process. In addition, the values of γ and α increase with the mole fraction of ethanol, which suggests that ethanol molecules participate in the association process of solute and solvent and reduces the energy of the solvation process. Therefore, the solubility of HMF in $scCO_2$ increases with the increase of the mole fraction of ethanol. It also can be seen that the value of k is larger than that of γ from Table 2, which hints that there are more CO_2 molecules in combination with solute than cosolvent. This may be caused by the fact that the concentration of CO_2 is much higher than that of the cosolvent.

As expected, the correlation result is consistent with Chrastil's initial hypothesis.[13] It is apparent that the logarithm of the solubility is linearly dependent on the logarithm of density of the mixture (Figure 3). The average relative deviation (ARD) is 7.9 %. When ethanol is present, the solubility shows the same behavior with that in pure CO_2, which are illustrated in Figures 4 and 5.

When ethanol is charged into the cell as cosolvent, the concentration of ethanol can be calculated by the following eq 7:

$$C/g \cdot L^{-1} = \frac{m_{EtOH}/g}{m_{CO_2}/g + m_{HMF}/g + m_{EtOH}/g} \cdot (\rho/g \cdot L^{-1}) \tag{7}$$

Substitution of eq 7 in eq 4 yields:

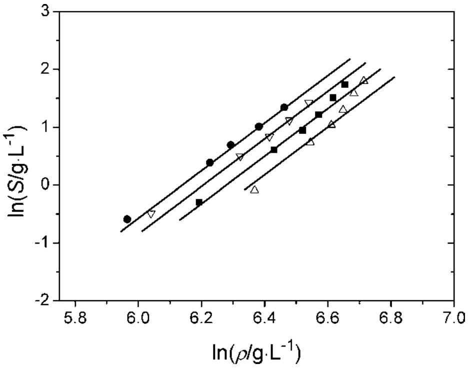

Figure 3. Dependence of solubility of HMF (2) in $scCO_2$ (1) on pressure at different temperatures: △, 314.10 K; ■, 323.98 K; ▽, 333.76 K; ●, 343.20 K. Experimental data (symbols) and calculated results by the Chrastil equation (lines, $R^2 = 0.969$).

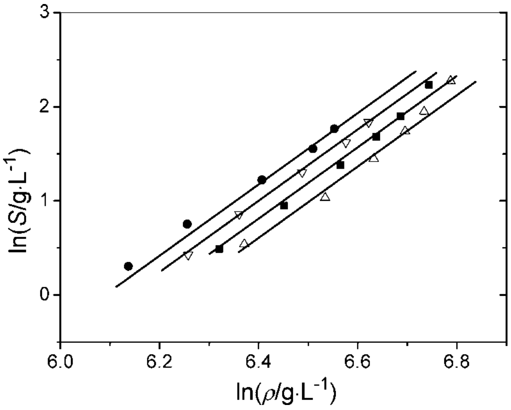

Figure 4. Solubility of HMF (2) in $scCO_2$ (1) + ethanol (3) at $x_3 = 0.025$ and different temperatures: △, 314.10 K; ■, 323.98 K; ▽, 333.76 K; ●, 343.20 K. Experimental data (symbols) and calculated results by the modified Chrastil equation (lines, $R^2 = 0.985$).

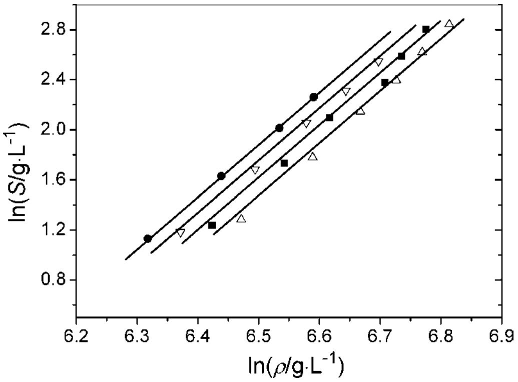

Figure 5. Solubility of HMF (2) in $scCO_2$ (1) + ethanol (3) at $x_3 = 0.050$ and different temperatures: △, 314.10 K; ■, 323.98 K; ▽, 333.76 K; ●, 343.20 K. Experimental data (symbols) and calculated results by the modified Chrastil equation (lines, $R^2 = 0.996$).

$$\ln(S/\mathrm{g \cdot L^{-1}}) = (k + \gamma)\ln(\rho/\mathrm{g \cdot L^{-1}}) + \gamma \ln\left(\frac{m_{\mathrm{EtOH}}/\mathrm{g}}{m_{\mathrm{CO_2}}/\mathrm{g} + m_{\mathrm{HMF}}/\mathrm{g} + m_{\mathrm{EtOH}}/\mathrm{g}}\right) + \frac{\alpha}{T/\mathrm{K}} + \beta \quad (8)$$

Compared with m_{EtOH} and $m_{\mathrm{CO_2}}$, the mass of HMF (m_{HMF}) can be neglected:

$$\ln(S/\mathrm{g \cdot L^{-1}}) = (k + \gamma)\ln(\rho/\mathrm{g \cdot L^{-1}}) + \gamma \ln\left(\frac{m_{\mathrm{EtOH}}/\mathrm{g}}{m_{\mathrm{CO_2}}/\mathrm{g} + m_{\mathrm{EtOH}}/\mathrm{g}}\right) + \frac{\alpha}{T/\mathrm{K}} + \beta \quad (9)$$

When the mole fraction of ethanol is fixed at 0.025 or 0.050, the second term on the right side of eq 9, $\gamma \ln((m_{\mathrm{EtOH}}/\mathrm{g})/(m_{\mathrm{CO_2}}/\mathrm{g} + m_{\mathrm{EtOH}}/\mathrm{g}))$, is a constant. Thus, at a fixed temperature, the logarithm of the solubility is linearly dependent on the logarithm of the mixture density. The ARDs at mole fractions of ethanol, 0.025 and 0.050, are 5.3 % and 3.7 %, respectively.

From Figures 3, 4, and 5, it can be seen that the deviations between the model and the experimental data at high pressures and low temperatures increase to a small extent. One reason is that the cosolvent ethanol can form hydrogen bonding with HMF, and the strong interaction cannot be reflected by the models. Another reason is that, at high pressures and low temperatures, the density of the fluid is high, which means the distance between solute molecules and solvent molecules is reduced, and hence their interaction increases because molecules have volume in space instead of no volume particles assumed in the modeling. However, the interaction resulted from high density is not considered in the correlation models.

Conclusion

The solubility of HMF (2) in $scCO_2$ (1) with cosolvent ethanol (3), where $x_3 = 0$, 0.025, and 0.050, at temperatures $T = (314.10, 323.98, 333.76, \text{and } 343.20)$ K and pressures ranging from $P = (8.54 \text{ to } 19.71)$ MPa has been measured. The solubility of HMF in $scCO_2$ with cosolvent ethanol increases with the ethanol mole fraction at fixed temperatures and pressures. Besides, the solubility of HMF in $scCO_2$ increases with the increase of pressure but decreases with the increase of temperature. Furthermore, the experimental data could be correlated using the Chrastil model and the modified Chrastil model with ARDs less than 7.9 %. The association of HMF and CO_2 is an endothermic process, and ethanol can reduce the energy of the process.

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Literature Cited

(1) Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates. *Science* **2005**, *308*, 1446–1450.
(2) Leshkov, Y. R.; Chheda, J. N.; Dumesic, J. A. Phase Modifiers Promote Efficient Production of Hydroxymethylfurfural from Fructose. *Science* **2006**, *312*, 1933–1937.
(3) Zhao, H. B.; Holladay, J. E.; Brown, H.; Zhang, Z. C. Metal Chlorides in Ionic Liquid Solvents Convert Sugars to 5-Hydroxymethylfurfural. *Science* **2007**, *316*, 1597–1600.
(4) Lima, S.; Neves, P.; Antunes, M. M.; Pillinger, M.; Ignatyev, N.; Valente, A. A. Conversion of Mono/di/polysaccharides into Furan Compounds Using 1-Alkyl-3-methylimidazolium Ionic Liquids. *Appl. Catal., A* **2009**, *363*, 93–99.
(5) Young, J.; Chan, G.; Zhang, Y. G. Selective Conversion of Fructose to 5-Hydroxymethylfurfural Catalyzed by Tungsten Salts at Low Temperatures. *Chem. Sustainable Dev.* **2009**, *2*, 731–734.
(6) Moreau, C.; Finiels, A.; Vanoye, L. Dehydration of Fructose and Sucrose into 5-Hydroxymethylfurfural in the Presence of 1-H-3-methyl imidazolium Chloride Acting both as Solvent and Catalyst. *J. Mol. Catal. A: Chem.* **2006**, *253*, 165–169.
(7) Clifford, T. *Fundamentals of Supercritical Fluids*; Oxford University Press: New York, 1999.
(8) Palma, M.; Taylor, L. T. Supercritical Fluid Extraction of 5-Hydroxymethyl-2-furaldehyde from Raisins. *J. Agric. Food Chem.* **2001**, *49*, 628–632.
(9) 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.
(10) Fan, J. L.; Hou, Y. C.; Wu, W. Z.; Zhang, J. W.; Ren, S. H.; Chen, X. T. Levulinic Acid Solubility in Supercritical Carbon Dioxide with and without Ethanol as Cosolvent at Different Temperatures. *J. Chem. Eng. Data* **2010**, *55*, 2316–2321.
(11) Zhang, H. F.; Han, B. X.; Li, H. P.; Hou, Z. S. Measurement of Critical Points and Phase Behavior of $CH_3OH + CO + CO_2$ Ternary Mixture. *J. Chem. Eng. Data* **2001**, *46*, 130–133.
(12) Weinstein, R. D.; Hanlon, W. H.; Donohue, J. P.; Simeone, M.; Rozich, A.; Muske, K. R. Solubility of Felodipine and Nitrendipine in Liquid and Supercritical Carbon Dioxide by Cloud Point and UV Spectroscopy. *J. Chem. Eng. Data* **2007**, *52*, 256–260.
(13) Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016–3021.
(14) 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.

(15) 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.

(16) Tian, G. H.; Jin, J. S.; Guo, J. J.; Zhang, Z. T. Mixed Solubilities of 5-Sulfosalicylic Acid and *p*-Aminobenzoic Acid in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2007**, *52*, 1800–1802.

(17) Ismadji, S. Solubility of Methyl Salicylate in Supercritical Carbon Dioxide at Several Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 2207–2210.

(18) Walsh, J. M.; Donohue, M. D. Hydrogen Bonding in Entrainer Cosolvent Mixtures: A Parametric Analysis. *Fluid Phase Equilib.* **1989**, *52*, 397–404.

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