Solubility of Ferulic Acid in Supercritical Carbon Dioxide with Ethanol as Cosolvent

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The solubility of ferulic acid in supercritical carbon dioxide (SC-CO_2), both pure and ethanol modified, was measured using a flow type apparatus. The mass of solute trapped after decompression was determined spectrophotometrically. The solubility was measured at (313.2, 323.2, and 333.2) K over the pressure range from (12 to 28) MPa. Solubility data in pure SC-CO_2 were correlated by the Chrastil equation. When ethanol cosolvent was added to SC-CO_2 in concentrations from (0.2 to 3.6) mass %, the solubility increase was proportional to the product $w_{et}^{1.08}S^{0.6}$, where w_{et} is the mass fraction of ethanol in CO_2 and S is the mass fraction solubility of ferulic acid in pure SC-CO_2.

Introduction

One of the modern mild methods used for obtaining natural products is the extraction with supercritical carbon dioxide (SC-CO_2). Though this solvent dissolves preferably nonpolar and low-polarity substances of small and medium molecular size, the polar and/or large-molecular antioxidants contained in materials of natural origin may be at least partially coextracted and thus their extracts may be preserved. The solubility of natural antioxidants in SC-CO_2 is therefore of interest. Recently, the solubilities of ascorbic acid, ascorbyl palmitate, dodecyl gallate, gallic acid, propyl gallate, and α-succinate acid[1] have been measured in SC-CO_2. Special attention has been focused on the solubility of β-carotene,[2−9] which can be increased by addition of ethanol to the supercritical carbon dioxide.[2,3]

Another strong antioxidant that could stabilize natural products is ferulic acid. This phenolic aromatic component is found widely in nature. It is used in traditional Chinese medicine[10] as well as in modern nutraceuticals and functional food ingredients. The present investigation was undertaken to determine the solubility of ferulic acid in SC-CO_2, both pure and with ethanol as cosolvent.

Experimental Section

Apparatus and Procedure. A schematic diagram of the apparatus is shown in Figure 1. CO_2 was supplied to the extractor from a cylinder by the compressor (Novaswiss 560.007) equipped at its outlet with a pressure regulator unit (Novaswiss 560.0009) that maintained the outlet pressure within ±0.05 MPa. The CO_2 then flowed through line A to the pressure gauge (uncertainty 0.01 MPa) measuring the operating pressure. Alternatively, in the experiments with the ethanol cosolvent, the pressurized CO_2 flowed to the pressure gauge through line B and the vessel of volume 0.17 L containing a homogeneous solution of ethanol in CO_2. The extractor was a stainless steel tube of length 25 cm and 8 mm i.d. with glass wool and a porous frit at either end. It was filled with glass beads covered with ferulic acid and immersed in the water bath whose temperature can be controlled to ±0.1 K. The switching valve behind the extractor allowed rinsing the downstream part of the equipment with ethanol. The CO_2 flow rate was regulated using the micrometer valve inside which the loaded solvent expanded to ambient pressure and ferulic acid was separated from the gas. Part of the extract settled inside the micrometer valve, and the rest was collected behind the valve in the trap, a U-tube equipped at its outlet with a glass-wool filter. The gas flowed through the U-tube further to the gas meter where its volume was monitored.

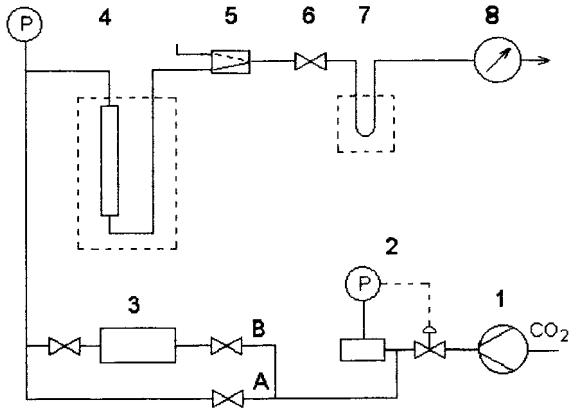

Figure 1. Schematic diagram of the apparatus: 1, compressor; 2, pressure regulator; 3, vessel with ethanol solution; 4, extractor; 5, switching valve; 6, micrometer valve; 7, trap; 8, gas meter.

The volume and flow rate of CO_2 were measured at ambient conditions. The sampling procedure started by adjusting the solvent flow rate to (40 to 50) $cm^3\ min^{-1}$. This flow rate was checked by preliminary experiments to be sufficiently low to obtain a fully saturated solvent at the extractor outlet. After 1 L of CO_2 had passed through the equipment, the flow was stopped. The metering valve was rinsed with ethanol, and the amount of ferulic acid in the solution collected in the trap was determined by UV spectrophotometry at 322 nm. The procedure was repeated until four samples were obtained at identical operating conditions, and the average value was used to calculate the solubility.

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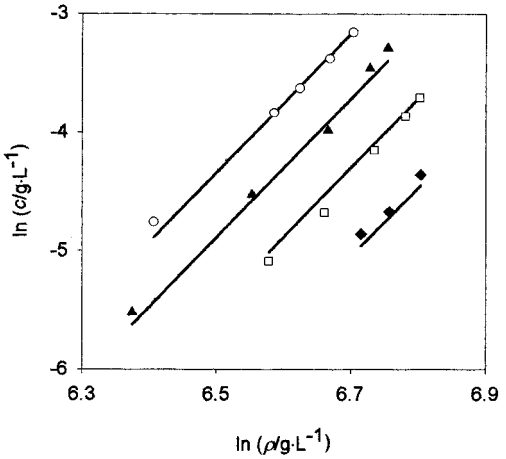

Figure 2. Solubility of ferulic acid in SC-CO_2 as a function of CO_2 density: ◆, 28 °C; □, 40 °C; ▲, 50 °C; ○, 60 °C; lines, calculated using eq 3.

Table 1. Ferulic Acid Mass Fraction Solubility, *S*, and Mole Fraction Solubility, *y*, in Supercritical CO_2, and Pure CO_2 Density, ρ, at 28, 40, 50, and 60 °C

t/°C	*P*/MPa	ρ/g·L^{-1}	10^5S	10^6y
28	12	824.7	0.94	2.13
	15	859.7	1.09	2.47
	20	900.8	1.42	3.22
40	12	718.9	0.86	1.95
	15	781.2	1.19	2.70
	20	840.6	1.88	4.25
	25	880.2	2.38	5.40
	28	899.3	2.74	6.21
50	12	586.4	0.68	1.55
	15	701.0	1.54	3.49
	20	785.1	2.37	5.38
	25	835.0	3.77	8.53
	28	857.8	4.35	9.85
60	15	605.6	1.42	3.22
	20	724.5	2.99	6.77
	22	753.1	3.52	7.98
	25	787.2	4.33	9.81
	28	814.7	5.22	11.8

In one of four measurements with ethanol as cosolvent, the trap was cooled in a dry ice + ethanol bath in order to prevent loss of volatile ethanol. Before the valve was rinsed, the amount of ethanol collected in the trap was determined gravimetrically using an analytical balance (readability 0.1 mg). In the whole set of experiments the collected amounts ranged from (5 to 60) mg. Ethanol concentration in CO_2 was monotonically decreasing, as the solution flowing from the mixing vessel (3) to the extractor was substituted by pure CO_2 from the compressor. It was checked by comparing a series of ethanol amounts collected successively in the trap with mathematical simulation that the mixing vessel could be described as an ideal mixer. During each measurement with 1 L of CO_2 (at ambient conditions) the outlet ethanol concentration in CO_2 decreased to 99% of its initial value.

The reproducibility of the solubility determination was within ±8% for the experiments with pure CO_2 and within ±20% for the experiments with ethanol cosolvent. The main source of the variation of measured values was most probably an early precipitation of a small part of extracted ferulic acid in front of the switching valve and irregular discharge of this precipitate into the trap. Therefore, we can assume that the measured values fluctuate around the correct solubility value, which should be within the above given reproducibility limits.

Table 2. Effect of Ethanol Mass Fraction in Supercritical CO_2, w_{et}, on the Ferulic Acid Mass Fraction Solubility, S_c, at 40, 50, and 60 °C

40 °C			50 °C			60 °C		
P/MPa	10^2w_{et}	10^5S_c	*P*/MPa	10^2w_{et}	10^5S_c	*P*/MPa	10^2w_{et}	10^5S_c
12	0	(0.93)	12	0	(0.62)	12	0	(0.25)
	0.29	2.58		0.28	1.51		0.27	1.01
	0.64	4.01		0.61	2.95		0.58	1.70
	1.00	6.32		3.35	26.0		3.15	16.6
	3.57	26.6						
15	0	(1.39)	15	0	(1.47)	15	0	(1.25)
	0.34	3.65		0.33	3.08		0.31	3.14
	0.74	6.07		0.71	6.62		0.67	5.39
	3.00	24.9		2.78	20.2		2.61	15.7
20	0	(1.98)	20	0	(2.55)	20	0	(2.98)
	0.45	6.41		0.48	8.46		0.78	14.9
	0.86	8.32		0.82	9.50		1.74	26.1
	1.85	31.3		1.97	36.2		2.16	25.0
	2.45	2.26		2.30	24.6			
25	0	(2.47)	25	0	(3.43)	25	0	(4.46)
	0.40	8.82		0.38	8.08		0.36	9.41
	0.42	7.17		0.40	8.34		0.37	10.5
	1.00	15.1		0.96	15.7		0.91	18.3
	2.03	26.1		1.54	25.3		1.80	26.5
				1.91	27.5			
28	0	(2.75)	28	0	(3.91)	28	0	(5.27)
	0.46	12.0		0.44	10.8		0.42	13.8
	1.20	18.1		1.12	20.2		1.06	20.8
	1.69	24.5		1.58	28.6		1.49	33.7

Materials. Ferulic acid (3-(4-hydroxy-3-methoxyphenyl)-2-propenoic acid, $M_w = 194.19$ g mol^{-1}) of purity better than 98% was purchased from Fluka. Ethanol for UV spectroscopy was supplied by Lachema Neratovice. Carbon dioxide of purity better than 99% was obtained from Linde Technoplyn. All chemicals were used without further purification.

Results and Discussion

Pure CO_2. Experimental solubilities of ferulic acid in SC-CO_2 are listed in Table 1. The table contains also the density values of carbon dioxide, ρ, calculated according to the Altunin−Gadetskii equation of state.[11] The density was used to convert the solubility values expressed originally in mass fraction, *S*, to equilibrium concentration, *c*,

$$c/\mathrm{g{\cdot}L^{-1}} = S\rho/\mathrm{g{\cdot}L^{-1}} \quad (1)$$

and further to correlate the solubilities according to the Chrastil equation[12]

$$\ln c = k \ln \rho + a/T + b \quad (2)$$

with the result

$$\ln(c/\mathrm{g{\cdot}L^{-1}}) = 5.85 \ln(\rho/\mathrm{g{\cdot}L^{-1}}) - 5900\ \mathrm{K}/T - 24.65 \quad (3)$$

The agreement of the Chrastil equation with experimental data is illustrated in Figure 2. The average deviation of the equation from experimental data was calculated according to the following formula:

$$\mathrm{AARD}(\%) = \frac{100}{m}\sum_{i=1}^{m}\frac{|S_{\mathrm{calc}} - S_{\mathrm{exp}}|}{S_{\mathrm{exp}}} \quad (4)$$

and its value was 6.5%.

The ferulic acid solubility in SC-CO_2 is comparable with the solubilities reported for the antioxidants ascorbyl palmitate, dodecyl gallate, and propyl gallate.[1]

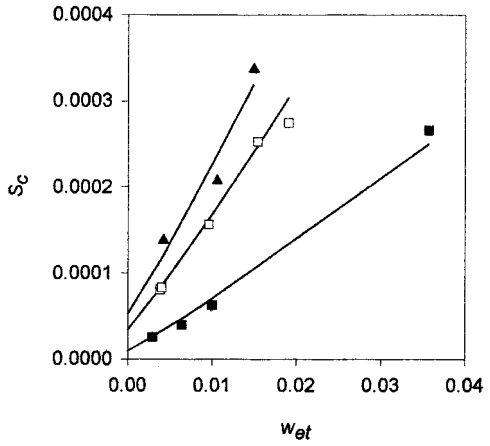

Figure 3. Ferulic acid solubility as a function of ethanol concentration in CO_2: ■, 12 MPa and 40 °C; □, 25 MPa and 50 °C; ▲, 28 MPa and 60 °C; lines, calculated using eq 6.

CO_2 with Ethanol Cosolvent. The experimental solubilities obtained with ethanol cosolvent, S_c, are listed in Table 2. The values given in the parentheses are the solubilities of ferulic acid in pure CO_2 calculated according to eq 3. When the gravimetrically determined ethanol mass fraction in CO_2, w_{et}, varied between 0.003 and 0.036, the ferulic acid solubility increased by 100% to 6500%. The increase in solubility was fitted to a power function:

$$S_c - S = (\text{constant}) w_{et}^{\ m} S^n \tag{5}$$

The following empirical equation for the ferulic acid solubility in SC-CO_2 with ethanol was obtained:

$$S_c = S + 9.23 w_{et}^{\ 1.08} S^{0.6} \tag{6}$$

where S_c is the mass fraction solubility in CO_2 with cosolvent, S is the mass fraction solubility in pure CO_2, and w_{et} is the mass fraction of ethanol in CO_2. The average deviation of eq 6 from experiment was 14%. Three examples of the solubility dependence on ethanol concentration are shown in Figure 3. The maximum ferulic acid solubility attained in this study was 0.03 mass %.

Acknowledgment

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