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Solubility of Methyl Salicylate in Supercritical Carbon Dioxide at Several Temperatures

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The solubility of methyl salicylate in supercritical carbon dioxide was measured in static mode at five different temperatures, (343.15, 363.15, 383.15, 403.15, and 423.15) K, at pressures up to 31 MPa. The experimental results were correlated by the Chrastil and Peng−Robinson equation of state with quadratic mixing rules. Critical constants of methyl salicylate were predicted with the Joback method and the Lee−Kesler method.

Introduction

Methyl salycilate is a colorless (pure form), yellowish, or reddish liquid, having the characteristic odor and taste of wintergreen, and is found naturally in many species of plants. This ester is also known as salycilic acid methyl ester and oil wintergreen and is sometimes called betula oil. Methyl salicylate has a long history of use in consumer products as a counterirritant and as an analgesic in the treatment and temporary management of aching and painful muscles and joints. Methyl salicylate is also used as an UV absorber and in perfumery as a modifier of blossom fragrances. Methyl salicylate can also be derived synthetically, and this synthetic variety of methyl salicylate is considered structurally and functionally equivalent to the naturally occurring oil of wintergreen.

Natural methyl salicylate is obtained by steam distillation or solvent extraction of macerated leaves from the low growing plant, *Gaultheria procumbens* Lime. (fam. Ericaceae), or from the bark of *Betula lenta* (Sweet Birch). However, the main problem using these methods for the extraction of natural compounds is in the purity of the product. The growing popularity of natural materials for flavors and foodstuffs and of green technologies for their extraction has increased the interest in environmentally friendly routes to obtain these products. One such technology that has received wide attention in recent decades and has been successfully employed in a variety of applications is that of supercritical fluid extraction (SCFE) using carbon dioxide.[1]

The solubilities of solids and liquids in supercritical fluids are a very important consideration in developing any supercritical extraction process.[2,3] In the literature, solubility measurements for esters in supercritical carbon dioxide have been reported.[4−7] Due to the strong dependence of solubility on density, temperature, and pressure of supercritical fluids, extensive amounts of data are still needed. In this paper, solubilities of methyl salicylate in supercritical carbon dioxide were measured at five different temperatures (343.15, 363.15, 383.15, 403.15, and 423.15) K in a range of pressures from (9 to 31) MPa. The experimental data were then correlated using the Peng−Robinson equation of state with quadratic mixing rules and the Chrastil equation. To the best of our knowledge, there is no literature available on the solubilities of methyl salicylate in supercritical carbon dioxide especially in the range of pressures and temperatures studied.

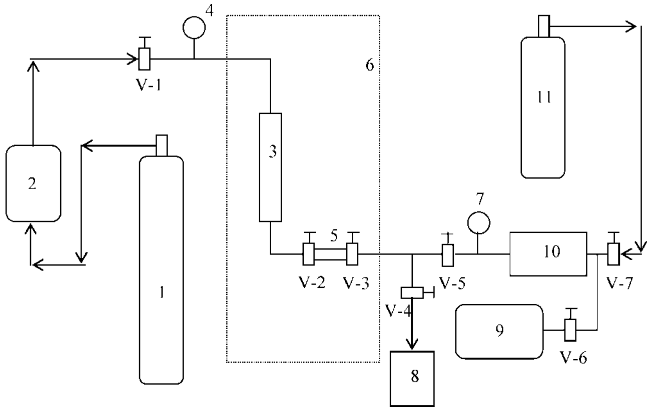

Figure 1. Schematic diagram of the supercritical equipment. 1, Liquid CO_2 cylinder; 2, Gilson high-pressure pump system; 3, equilibration cylinder; 4, high-pressure transducer; 5, sampling tube; 6, temperature controller; 7, low-pressure transducer; 8, collecting tank; 9, vacuum pump; 10, volume calibrator; 11, helium cylinder.

Table 1. Experimental Solubility Data of Methyl Salycilate in Supercritical CO_2

	solubility, y_2				
p/MPa	343.15 K	363.15 K	383.15 K	403.15 K	423.15 K
9	0.00051	0.00082	0.00129	0.00272	0.00413
11	0.00346	0.00149	0.00198	0.00344	0.00503
13	0.00574	0.00293	0.00281	0.00446	0.00641
15	0.01003	0.00538	0.00475	0.00636	0.00806
17	0.03179	0.00972	0.00693	0.00854	0.01020
19		0.01875	0.01122	0.01117	0.01124
21		0.04093	0.01503	0.01526	0.01473
23			0.02122	0.02254	0.02341
25			0.04320	0.03318	0.02433
27				0.04226	0.03630
29				0.05689	0.04982
31					0.07533

Experimental Section

Materials. Methyl salicylate was purchased from Sigma Aldrich with a purity of 99 % and used without any further purification. Food grade carbon dioxide was used as the supercritical solvent as supplied as liquid CO_2 (in the deep tube liquid supply cylinder) with a minimum purity of 99.98 %.

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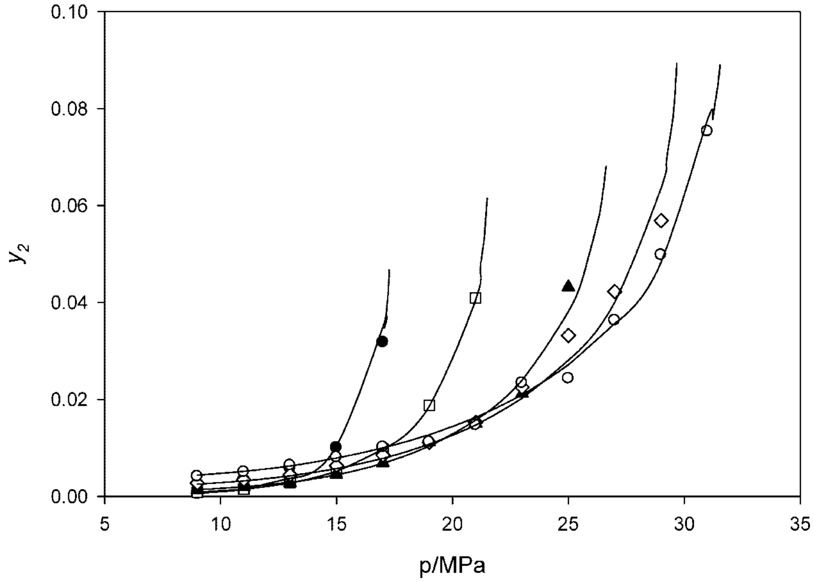

Figure 2. Solubility of methyl salicylate at various pressures and temperatures and those calculated using the PR−EoS with quadratic mixing rules. ●, Experimental data at 343.15 K; □, experimental data at 363.15 K; ▲, experimental data at 383.15 K; ◇, experimental data at 403.15 K; ○, experimental data at 423.15 K; and —, Peng−Robinson EoS.

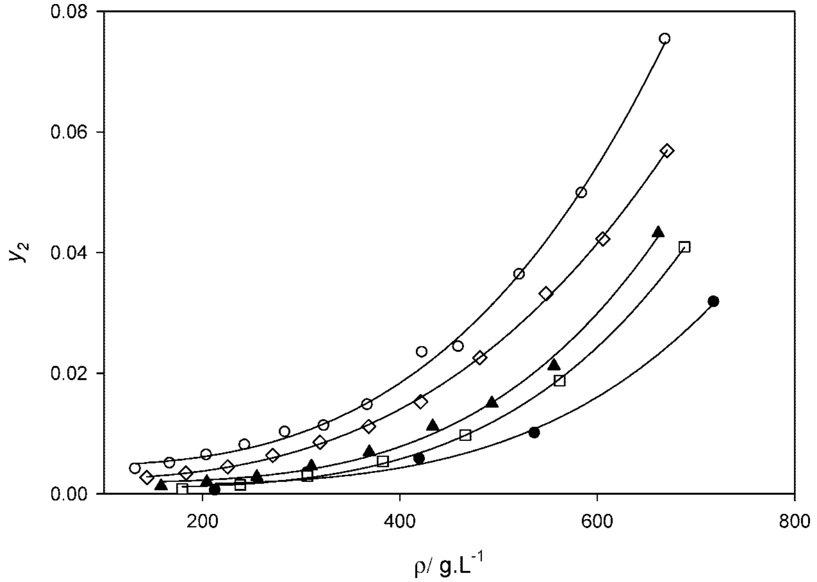

Figure 3. Solubility of methyl salicylate in supercritical carbon dioxide and those estimated from the Chrastil equation. ●, Experimental data at 343.15 K; □, experimental data at 363.15 K; ▲, experimental data at 383.15 K; ◇, experimental data at 403.15 K; ○, experimental data at 423.15 K; and —, Chrastil equation.

Table 2. Parameters of the Peng−Robinson Equation of State Using Quadratic Mixing Rules for CO_2 (1) + Methyl Salicylate (2)

T/K	k_{ij}	l_{ij}	deviation, %
343.15	−0.062638	−0.068847	5.13
363.15	−0.013400	−0.030971	1.99
383.15	−0.002907	−0.002150	3.91
403.15	−0.000827	−0.001482	5.92
423.15	−0.005762	0.007216	4.89

Table 3. Fitted Charstil Equation Parameters for CO_2 (1) + Methyl Salycilate (2)

	parameter			
T/K	k	d	f	deviation %
343.15	4.0439	−10027.18	0.00150	0.14
363.15	3.8914	−9544.55	0.00094	0.20
383.15	3.8199	−9331.14	0.00190	0.10
403.15	2.9771	−7423.49	0.00230	0.10
423.15	3.1714	−7758.41	0.00460	0.11

Experimental Procedure. The schematic diagram of the equipment used to obtain the solubility data in supercritical condition is given in Figure 1. The main components, tubing, and fittings of the supercritical desorption equipment are made of stainless steel 316. The equipment consists of two high-pressure piston pumps (Gilson 305 and 306 piston pumps), a manometric module (Gilson model 805), a dynamic mixer (Gilson 811), and a stainless steel equilibration column. The maximum working pressure and temperature of the system are 35 MPa and 473.15 K, respectively. The uncertainties in the temperature and pressure measurements were ± 1 K and ± 0.01 MPa, respectively. The pressure of the system was monitored using a Druck pressure transducer PDCR 910 coupled with DPI 280 pressure reading. The temperature of the system was controlled by a thermostat oven (BTC-9090).

The following static mode experimental procedure was used to measure the solubility of flavor ester in supercritical carbon dioxide. First, equilibration columns were loaded with about 4 mL of the methyl salicylate. The system was evacuated to remove air using a vacuum pump, and after evacuation was complete, the system was then heated until the desired temperature was reached. Subsequently, the liquid CO_2 was pumped to the system using a high-pressure piston pump. For the static supercritical experiment, valves V-3, V-4, and V-5 were closed, while valves V-1 and V-2 were opened. After equilibrium at the desire temperature and pressure was achieved (1 h), the sampling tube (1.6 mL) was disconnected from the system by closing valve V-2. The sample in the sampling tube was released (by opening valves V-3 and V-4) to the collector containing a known amount of absolute ethanol to separate the ester and carbon dioxide. At least three replicated samples were taken at an experimental condition, and equilibrium composition was determined by averaging the replications. The uncertainty of each measurement was within ± 3 %. The concentration of the ester in the ethanol was determined by means of a Shimadzu gas chromatograph (GC-17A) provided with a flame ionization detector. Gas chromatography was calibrated externally using methyl salicylate solutions with different concentrations. The uncertainty of the GC measurement was ± 0.1 $\text{mg}\cdot\text{L}^{-1}$.

Results and Discussion

Table 1 summarizes the solubility of methyl salicylate in supercritical carbon dioxide at temperatures (343.15, 363.15, 383.15, 403.15, and 423.15) K and pressures up to 31 MPa. In general, the solubility of methyl salicylate in supercritical carbon dioxide at constant temperature increased as pressure increased. At pressures (15 to 17) MPa, the effect of density is more dominant than vapor pressure, indicated by decrease of the solubility as the temperature increases. Similar solubility behavior in supercritical CO_2 for other organic compounds has also been observed.[1,3,6−9]

Several correlations have been developed to correlate and extrapolate solubility data at various pressures and temperatures. Some of these correlations are highly empirical, while some have a strong fundamental basis. However, in most cases, these correlations still need one or more adjustable fitting parameters, so that experimental data are still needed. The most commonly used method to correlate solubility in supercritical fluids is the equation of state approach. In the equation of state method, a single equation of state is used to represent all fluid phases. In the vapor phase, fugacity of component i is

$$\ln \varphi_i = \frac{1}{RT}\int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]\mathrm{d}V - \ln\frac{PV}{n_T RT} \qquad (1)$$

where φ_i is fugacity of component i; P is pressure; R is the universal gas constant; and T and V are temperature and molar volume, respectively. The term $(\partial P/\partial n_i)_{T,V,n_j}$ is given by the equation of state. Details about eq 1 and its uses for supercritical equilibria can be found elsewhere.[10]

A number of equations of state (EOS) models are available, and the most widely used are the Peng and Robinson,[1,4−7,11−14] which has the form

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V^2 + 2bV - b^2} \qquad (2)$$

The pure component parameter a, which is a function of temperature and constant b, is given by

$$a(T) = a\cdot\alpha(T_r, \omega) \qquad (3)$$

$$a = 0.45724\frac{R^2T_c^2}{P_c} \qquad (4)$$

$$b = 0.07780\frac{RT_c}{P_c} \qquad (5)$$

$$\alpha(T_r, \omega) = (1 + \kappa(1 - \sqrt{T_r}))^2 \qquad (6)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26692\omega^2 \qquad (7)$$

Critical constants (P_c, T_c, and ω) were predicted with the Joback method and the Lee−Kesler method.

To use the Peng−Robinson EOS for the correlation and prediction of the solubility data in supercritical fluids, mixing and combining rules must be introduced for the EOS parameters. For a multicomponent mixture, the parameters a and b in Peng−Robinson are written in the forms of van der Waals combining rules

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_1 x_j a_{ij} \qquad (8)$$

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \qquad (9)$$

All mixing rules offer three adjustable binary interaction parameters, except the simple quadratic mixing rule, which only offers two adjustable parameters per binary system. Here we used the quadratic mixing rule to correlate our experimental solubility data.

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \text{ with } k_{ji} = k_{ij} \qquad (10)$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \text{ with } l_{ji} = l_{ij} \qquad (11)$$

The fitting of experimental data was performed at each temperature by minimizing the following objective function

$$E^2 = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{y_i^{\text{exptl}} - y_i^{\text{calcd}}}{y_i^{\text{exptl}}}\right)^2} \qquad (12)$$

Here y_i^{exptl} and y_i^{calcd} are the experimental and predicted mole fraction of the solute in the supercritical phase, respectively. The fitted parameters of the Peng−Robinson EoS with the quadratic mixing rule are given in Table 2. The parameters k_{ij} and l_{ij} are found to increase with increasing temperature. Figure 2 depicts the predicted solubility of methyl salicylate in supercritical carbon dioxide using the quadratic mixing rule. From this figure, it can be seen that the Peng−Robinson EoS with the quadratic mixing rule can correlate the experimental data fairly well.

Experimental solubility data of methyl salicylate in supercritical carbon dioxide obtained in this study were also correlated with the semiempirical equation of Chrastil. It may be applied to all cases because it does not require any physical−chemical property data for the solute.[6] This equation has the following form

$$y_2 = \rho_1^k \exp\left(\frac{d}{T} + f\right) \qquad (13)$$

where y_2 is the solute's solubility (mol/mol); ρ_1 is the supercritical fluid density ($\text{g}\cdot\text{cm}^{-3}$); T is the temperature (K); and d, f, and k are empirical fitting parameters.

The comparison between the experimental solubility data and the predicted values using the Chrastil equation is shown in Figure 3. The experimental values are represented as symbols and predicted values as solid lines. This figure clearly shown that the Chrastil equation can predict the experimental data very well. The charstil parameters obtained from fitting experimental data are given in Table 3. From this table, it is obvious that the parameters of Chrastil are temperature dependent.

Conclusion

New data on the solubility of methyl salicylate in supercritical carbon dioxide were obtained in this study. The solubility data were correlated by the Peng−Robinson equation of state and the Chrastil equation. Both of these models can represent the experimental data well.

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