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Trans-Cinnamic Acid Solubility Enhancement in the Presence of Ethanol As a Supercritical CO_2 Cosolvent

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Trans-3-phenyl-2-propenoic acid (cinnamic acid; *trans*-cinnamic acid) is widely used in food, cosmetics, and pharmaceuticals because of its reported antimicrobial, antifungal, and antioxidant properties. This paper is devoted to the experimental measurement of the solubility of solid *trans*-cinnamic acid in pure supercritical CO_2 and in supercritical CO_2 with ethanol as a cosolvent. Measurements were carried out at $T = (313.15$ to $343.15)$ K and at $p = (10$ to $40)$ MPa. Two different thermodynamic models were applied to represent the solubility data obtained: a cubic type equation of state, the Soave−Redlich−Kwong (SRK-EoS) was employed to correlate the solubility data and the group contribution associating EoS (GCA-EoS) was also applied but in a completely predictive manner. In addition, values for the thermophysical properties of *trans*-cinnamic acid are also advocated.

Introduction

Trans-3-phenyl-2-propenoic acid (cinnamic acid; *trans*-cinnamic acid), because of its functional properties, is widely used in food (as flavoring and as an important food supplement), cosmetics (perfumes, decorative cosmetics, fine fragrances, shampoos, toilet soaps, etc.), and pharmaceuticals.[1] Recent studies, devoted to the use of *trans*-cinnamic acid in cosmetics, revealed its importance as a nonphotosynthetic pigment in photoprotection.[2,3] The chemical structure of *trans*-cinnamic acid is shown in Figure 1.

Additionally, as the current tendency is to further restrict synthetic antioxidants, because of their toxic and carcinogenic effects,[4,5] the application of natural antioxidants derived from plants as dietary supplements and food preservatives has drawn considerable research interest.[6] In particular, the research devoted to the examination and the validation of the importance of natural cinnamic acid's antioxidant activity should be mentioned.[7−9]

Supercritical fluid extraction (SFE) has proved to be a viable technology for antioxidants' extraction from natural matrices. However, efficient process design requires knowledge of the solubility of the compounds to be extracted.

This work reports experimental measurements and calculation of solid *trans*-cinnamic acid solubility in pure supercritical CO_2 (SC-CO_2) and in SC-CO_2 with ethanol as a cosolvent. The measurements were carried out in the temperature range (313.15 to 353.15) K and at pressures ranging from (10 to 40) MPa. The ethanol content in the SC-CO_2 solvent ranged between (0 and 4) % in mass fraction. To the best of our knowledge, the only similar data available in the literature were recently reported by Chen et al.[10] who measured the solubility of cinnamic, phenoxyacetic, and 4-methoxyphenylacetic acids in pure SC-CO_2 at three temperatures, (308.15, 318.15, and 328.15) K, and in the pressure range (11 to 24) MPa.

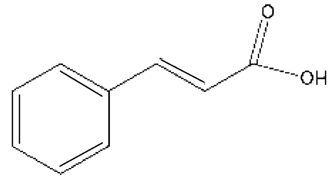

Figure 1. *trans*-Cinnamic acid chemical structure.

Two different thermodynamic models were applied to calculate the solubility of *trans*-cinnamic acid: the Group Contribution Associating Equation of State (GCA-EoS)[11] and the Soave−Redlich−Kwong cubic equation of state (SRK-EoS).[12] In addition, values for the thermophysical properties, sublimation pressure, and solid molar volume of *trans*-cinnamic acid are also given.

Experimental Section

Materials. *Trans*-cinnamic acid (> 99 % in mass fraction) was supplied by Aldrich Co. Ethanol from Merck (> 99.9 % HPLC gradient grade) was used as a cosolvent of supercritical CO_2 and also as a solvent to collect the extract and for UV−vis spectrometry analysis. The reagents were used without further purification. High-purity CO_2 (more than 99.9 % in volume purity, SFC grade) supplied by AIR LIQUIDE was used as received. Silica extra pure (more than 99.8 % in mass fraction) from Sigma Chemical Co. Inc. was utilized as support of the products.

Apparatus and Procedure. The solubilities were measured with an SFX 3560 extractor with two syringe pumps (model 260D) manufactured by ISCO (Lincoln, NE, USA). With the proper plumbing, a two-pump system can deliver either a modified supercritical fluid or a continuous flow of supercritical fluid. The cylinder capacity of the pump is 266 mL, and a maximum pressure of 51 MPa can be attained. The temperature can range from (313.2 to 423.2) K and the supercritical fluid

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Table 1. Cinnamic Acid (1) Solubility in Pure Supercritical Carbon Dioxide (2) and with Ethanol (3) As Cosolvent at $T = 313.15$ K

	ethanol/%		
	0	2	4
p/MPa	$y_1 \cdot 10^4$		
10		2.3	2.9
15		3.2	3.9
20	1.6	4.0	4.8
25	2.5	4.6	5.6
30	3.6	5.6	6.7
35	4.7	6.2	7.3
40	5.7	6.8	8.1

Table 2. Cinnamic Acid (1) Solubility in Pure Supercritical Carbon Dioxide (2) and with Ethanol (3) As Cosolvent at $p = 20$ MPa

	ethanol/%		
	0	2	4
T/K	$y_1 \cdot 10^4$		
313.15	1.6	4.0	4.8
323.15	1.5	3.6	4.4
333.15	1.4	3.4	4.2
343.15	1.2	3.3	3.8
353.15	1.0	3.0	3.5

flow rate from (0.5 to 5) mL·min^{-1}. A detailed description of the equipment was presented elsewhere.[13]

The extractor measured the amount of supercritical CO_2 used during the extraction. The flow rate of the supercritical fluid used for all experiments was 0.5 mL·min^{-1}, which ensured that saturation of the supercritical phase was achieved in a reasonable time.

Ethanol was used as a cosolvent and also to trap the *trans*-cinnamic acid extracted. After that, the extract was transferred to 10 mL calibrated flasks and diluted with ethanol. In some cases, a higher dilution might be necessary to achieve a concentration level adequate for determination by UV spectrometry. A detailed explanation of the experimental sample preparation is given elsewhere.[13,14] The uncertainties of the temperature and pressure measurements were ± 0.1 K and ± 0.25 MPa, respectively. The uncertainty associated with volume measurements was ± 0.1 mL.

A 8453 Hewlett-Packard diode array UV−vis spectrophotometer was used to determine the amount of *trans*-cinnamic acid in the extract, after calibration with gravimetrically prepared standard solutions. The gravimetric measurements were performed on an analytical balance with 0.00001 g resolution, and the expanded uncertainty was ± 4.2·10^{-5} g with coverage factor 2.

Solubility is obtained as the value of the slope of the linear representation of the amount of *trans-c*innamic acid extracted vs the amount of solvent used, on a molar basis, at different extraction times (five values at least). The linear regression coefficients obtained in the solubility calculations were employed to estimate the uncertainty associated with *trans*-cinnamic acid solubility measurements. The mean absolute deviation of the mole fractions reported is 3·10^{-5}.

Results and Modeling

Experimental Solubility Results. The results of the solubility measurements obtained in this work are reported in Tables 1 and 2, respectively. In the pressure and temperature ranges explored, *trans*-cinnamic acid solubility in SC-CO_2 is increased with pressure, while the influence of temperature is almost negligible. The use of small amounts, (2 and 4) % in mass fraction, of ethanol as a polar cosolvent enhances the solubility of the acid. The data of the experimentally measured solubility of *trans*-cinnamic acid at $T = 313.15$ K, as a function of pressure, in SC-CO_2 with ethanol mass content (0, 2, and 4) % in mass fraction, respectively, is given in Figure 2.

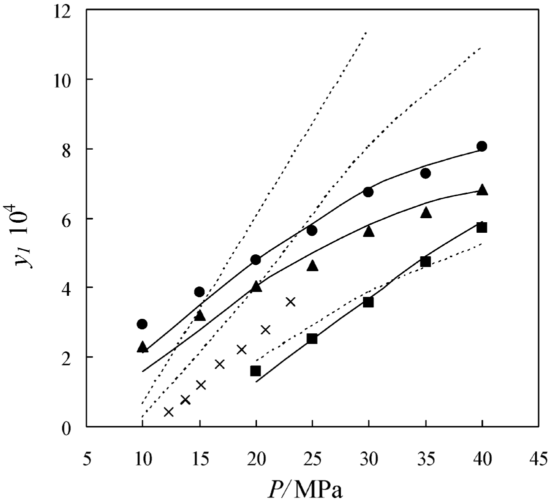

Figure 2. Cinnamic acid solubility measured in this work at $T = 313.15$ K. Symbols represent experimental solubility; lines represent the solubility correlated by the SRK EoS and predicted by the GCA-EoS. ■, 0 % ethanol; ▲, 2 % ethanol; ●, 4 % ethanol; ×, cinnamic acid solubility in pure SC-CO_2 at 318.15 K (Chen et al.[10]); —, SRK-EoS correlation; - - -, GCA-EoS prediction.

The solubility values of cinnamic acid in pure SC-CO_2, reported by Chen et al.,[10] are of the same order of magnitude as the values measured in the present work. Because of a difference in the experimental conditions, a direct comparison cannot be made; still, it must be pointed out that the solubility values measured by Chen et al.[10] at $p = 20$ MPa at the three temperatures of the experiment exhibit a different trend than the solubilities measured in our work at the same pressure. Namely, in the former case, the solubility increased with temperature, while in the latter case the solubility decreased, though in both cases small increments or decrements were observed. This discrepancy can be attributed to the difference in the location of the crossover point of the solubility isotherms. Chen et al.[10] experimentally observed this crossover point at a pressure around 17.5 MPa, while in our experiments the isotherms' crossover would have been observed at pressures higher than 20 MPa. Furthermore, this dissimilarity can be attributed to the different experimental techniques employed by the two groups of researchers to obtain the solubilities.

Solubility Data Modeling. For solid−gas phase equilibria, the following relation holds

$$f_s^{\text{solid}} = f_s^{G} \tag{1}$$

where the subscript s stands for the solid solute; f_s^G is the fugacity of the solid solute in the gas (supercritical fluid phase); and f_s^{solid} is that in the solid phase.

The fugacity of the solute in the supercritical phase is

$$f_s^{G} = y_s P \varphi_s^{G} \tag{2}$$

where P is the pressure; φ_s^G is the fugacity coefficient; and y_s is the solubility (mole fraction) of the solute in the supercritical fluid. For phase equilibrium between a solid compound and a supercritical fluid, the following three assumptions can be introduced: (1) the solid solute remains pure since the size and the shape of solute and solvent molecules are ordinarily sufficiently different and hence solid solutions do not form; (2) the molar volume of the solid solute can be treated as a constant with respect to pressure; and (3) the saturated vapor of the pure solid solute at sublimation behaves as an ideal gas.[15]

If the solid vapor pressure is used as the reference fugacity of the solid and since the solid phase is pure (assumption 1), the fugacity of the solute in the solid state is equal to the pure solid fugacity, and hence the following holds:

$$f_{\mathrm{s}}^{\mathrm{solid}} = P_{\mathrm{s}}^{\mathrm{sub}} \varphi_{\mathrm{s}}^{\mathrm{sub}} \exp \int_{P_{\mathrm{s}}^{\mathrm{sub}}}^{P} \frac{v_{\mathrm{s}}^{\mathrm{solid}} \mathrm{d}P}{RT} \tag{3}$$

where $P_{\mathrm{s}}^{\mathrm{sub}}$ is the sublimation (vapor) pressure of the pure solid; $\varphi_{\mathrm{s}}^{\mathrm{sub}}$ is the fugacity coefficient at sublimation pressure; and $v_{\mathrm{s}}^{\mathrm{solid}}$ is the molar volume of the solid, all at temperatures T.

Then, applying assumption 2 and the thermodynamic equilibrium condition (eq 1), the mole fraction of the solid component in the supercritical phase can be expressed as

$$y_{\mathrm{s}} = \frac{P_{\mathrm{s}}^{\mathrm{sub}}}{P} E \tag{4}$$

where

$$E \equiv \frac{\varphi_{\mathrm{s}}^{\mathrm{sub}} \exp \int_{P_{\mathrm{s}}^{\mathrm{sub}}}^{P} \frac{v_{\mathrm{s}}^{\mathrm{solid}} \mathrm{d}P}{RT}}{\varphi_{\mathrm{s}}^{\mathrm{G}}} = \frac{\varphi_{\mathrm{s}}^{\mathrm{sub}} \exp\left[\frac{v_{\mathrm{s}}^{\mathrm{solid}} P - P_{\mathrm{s}}^{\mathrm{sub}}}{RT}\right]}{\varphi_{\mathrm{s}}^{\mathrm{G}}} \tag{5}$$

In most practical cases, the $P_{\mathrm{s}}^{\mathrm{sub}}$ value is quite small, and thus $\varphi_{\mathrm{s}}^{\mathrm{sub}}$ is nearly equal to unity. The Poynting correction (exponential term in eq 5) is not negligible, but it generally accounts for an enhancement factor less than 2 or 3. However, the solute fugacity coefficient in the supercritical phase ($\varphi_{\mathrm{s}}^{\mathrm{G}}$) is significantly different from unity and can produce very large enhancement factors.

According to eqs 4 and 5, information about cinnamic acid sublimation pressure and solid molar volume is required to calculate its solubility in SC-$\mathrm{CO_2}$. Furthermore, a reliable thermodynamic model is necessary to evaluate $\varphi_{\mathrm{s}}^{\mathrm{G}}$ which, in turn, requires information about pure solute physical properties such as critical temperature and pressure, acentric factor, etc.

For cinnamic acid, as for a great majority of solid solutes extracted from vegetable material, there is a limited amount of thermophysical properties data. The melting temperature ($T_{\mathrm{m}} = 406.15$ K), the normal boiling temperature ($T_{\mathrm{b}} = 573.15$ K), and the enthalpy of fusion ($\Delta H_{\mathrm{fus}} = 22626\ \mathrm{J \cdot mol^{-1}}$) of the acid were obtained from http://webbook.nist.gov/chemistry.[16] There are also some limited data on the vapor pressures of *trans*-cinnamic acid measured at several temperatures using the Knudsen-effusion method.[17]

Thus, the rest of the properties required had to be estimated. To do this, the algorithm discussed in detail in Fornari et al.[18] was followed, and hence here we mark only the relevant main steps: The sublimation pressures at the temperatures of interest to the experiment were calculated from the Clapeyron equation, applying the data for the melting properties of cinnamic acid available and estimated in the present study (see Table 3). The value for the solid volume $v_{\mathrm{s}}^{\mathrm{sol}}/(\mathrm{m^3 \cdot mol^{-1}}) = 118 \cdot 10^{-6}$ was taken from the literature.[19] The critical parameters were estimated applying the methods proposed in ref 20. The values obtained for cinnamic acid physical properties, and employed in the thermodynamic modeling, are shown in Table 3.

Table 3. Cinnamic Acid Physical Properties Estimated in This Work

physical property	
T_{c}/K	797.34
P_{c}/MPa	3.848
acentric factor	0.712
$P_{\mathrm{s}}^{\mathrm{sub}}$/MPa at T = 353.15 K	$1.87 \cdot 10^{-06}$
$P_{\mathrm{s}}^{\mathrm{sub}}$/MPa at T = 343.15 K	$6.15 \cdot 10^{-07}$
$P_{\mathrm{s}}^{\mathrm{sub}}$/MPa at T = 333.15 K	$1.94 \cdot 10^{-07}$
$P_{\mathrm{s}}^{\mathrm{sub}}$/MPa at T = 323.15 K	$5.72 \cdot 10^{-08}$
$P_{\mathrm{s}}^{\mathrm{sub}}$/MPa at T = 313.15 K	$1.55 \cdot 10^{-08}$

The critical parameters estimated in this study differ from the values estimated by Mota et al.,[21] who report $T_{\mathrm{c}} = 782.8$ K and $P_{\mathrm{c}} = 3.63$ MPa, respectively. However, the $T_{\mathrm{c}}/P_{\mathrm{c}}$ ratios of both predictions agree well with the value, calculated according to the generalized semitheoretical expression advocated by Zbogar et al.,[22] and which can be used to check the reliability of critical properties' estimation; namely:

$$T_{\mathrm{c}}/P_{\mathrm{c}} = 9.0673 + 0.43309({Q_{\mathrm{w}}}^{1.3} + {Q_{\mathrm{w}}}^{1.95}) \tag{6}$$

where T_{c} is in Kelvin and P_{c} is in bar. The dimensionless parameter Q_{w} is a measure of the van der Waals molecular surface area and is calculated as the sum of the group area parameters, Q_k:

$$Q_{\mathrm{w}} = \sum_k \nu_k Q_k \tag{7}$$

where ν_k is the number of times group k appears in the molecule. The group area parameters Q_k are available in the UNIFAC tables and were used herewith in eq 7.

For cinnamic acid, the $T_{\mathrm{c}}/P_{\mathrm{c}}$ ratio should be 19.027 according to eq 6. Our estimations of the critical parameters give 20.721, and with the values cited in Mota et al.,[21] this ratio is 21.565.

The values of cinnamic acid sublimation pressure calculated by us (Table 3) are in excellent agreement with the values measured by Monte and Hillesheim[17] at some of the temperatures of our experiment. However, for consistency, in our calculations we used the values reported in Table 3, rather than the experimentally measured ones at T/K = 333.193 and T/K = 343.124, namely, $P_{\mathrm{s}}^{\mathrm{sub}}/\mathrm{MPa} = 1.886 \cdot 10^{-7}$ and $P_{\mathrm{s}}^{\mathrm{sub}}/\mathrm{MPa} = 5.635 \cdot 10^{-7}$, respectively.[17]

As mentioned previously, the calculation of cinnamic acid fugacity coefficients ($\varphi_{\mathrm{s}}^{\mathrm{G}}$) was carried out by applying two different thermodynamic models: the GCA-EoS and the SRK-EoS. The group contribution character of the GCA-EoS model makes it particularly attractive to be applied as a predictive tool, while the SRK-EoS offers high correlative capability due to its molecular interaction parameters.

The GCA-EoS model has three contributions to the residual Helmholtz energy of the system: a repulsive free volume term, a contribution which accounts for dispersive attractive interactions, and a contribution from association effects. The repulsive term is modeled assuming hard sphere behavior for the molecules, each substance characterized by its critical hard sphere diameter d_{c}. The dispersive and associative interactions are based on the group contribution approach. The attractive term has five pure-group parameters (T^*, q, g^*, g', and g'') and

Table 4. SRK Binary Interaction Parameters for the Cinnamic Acid (1) + CO_2 (2) + Ethanol (3) System

i	j	k_{ij}
1	2	0.0785
1	3	0.0
2	3	0.0890

four binary interaction parameters ($k_{ij}*$, k_{ij}', α_{ij}, and α_{ji}). The association term has two pure-group parameters (association energy ε and volume κ). For a detailed description of the model, the reader is referred to the work of Gros et al.[11]

The SRK-EoS was applied employing the van der Waals one fluid mixing rule and the following combining rules for the cross energy:

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - k_{ij}) \tag{8}$$

and cross-co-volume parameters

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2}\right) \tag{9}$$

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2}\right)(1 - l_{ij}) \tag{10}$$

where k_{ij} and l_{ij} are, respectively, the energy and size binary interaction parameters.

Solubility Correlation Using the SRK-EoS. In principle, the binary interaction parameters are determined minimizing the average absolute relative deviation (AARD) between experimental (y_{exp}) and calculated (y_{cal}) solubility data. In this work, two types of data have been measured: isothermal (at T/K = 313.15) and isobaric (at p/MPa = 20). With the view to obtain a single set of parameters for correlating both types of experimental data measured, the binary interaction parameters were taken as temperature independent. Thus, the isothermal solid−fluid equilibrium P−y data and the isobaric T−y data were regressed simultaneously, and the parameters given in Table 4 were obtained. It should be pointed out that the VDW1 mixing rule (one-binary-interaction-parameter-per-pair version of the mixing rule, namely, eqs 8 and 9) proved to be sufficient for achieving an acceptable accuracy of the correlation, while the VDW2 mixing rule (two-binary-interaction-parameters-per-pair version of the mixing rule, namely, eqs 8 and 10) did not lead to any noticeable improvement. However, these values of the binary interaction parameters represent just one of the possible sets as local methods were employed in the optimization.

One additional comment concerning the robustness of the solubility calculations should be made. The usual approach is to compute the solid solubility by locating a mole fraction that satisfies the iso-fugacity criterion (eq 1), which might lead to numerical pitfalls, as multiple solutions to the equi-fugacity condition could exist. (For example, at T/K = 313.15, at lower values of the pressure, the EoS has two real roots.) The nonuniqueness is a particular problem, and special care should be taken to verify that the correct root of the EoS at each iteration step is selected. Thus, a stability analysis routine, based on a modified tangent-plane function, was employed, which guaranteed a steady convergence of the algorithm to the solution ("fixed point") corresponding with the minimum Gibbs energy.[23]

Using the SRK-EoS, a satisfactory correlation of the experimental isothermal and an excellent one of the experimental isobaric solubility of cinnamic acid in pure SC-CO_2 and in SC-CO_2 with ethanol as a cosolvent was obtained (see Figures 2 and 3). The absolute average percent deviation (AAPE) and the maximum absolute percent deviation (MAPE) for all cases is given in Table 5, respectively.

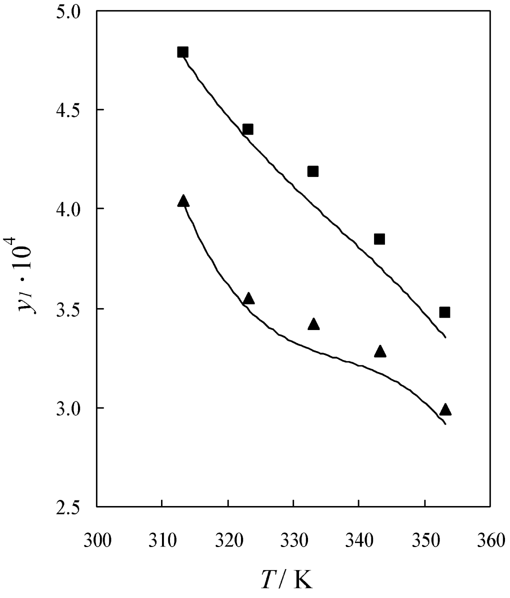

Figure 3. Cinnamic acid solubility at P = 20 MPa. ▲, 2 % ethanol; ■, 4 % ethanol; —, SRK-EoS correlation.

Table 5. Average (AAPE) and Maximum (MAPE) Deviations between the Experimental Data Measured in This Work and the Solubility Values Correlated with the SRK-EoS and Predicted by the GCA-EoS

	AAPE/%		MAPE/%	
	SRK-EoS	GCA-EoS	SRK-EoS	GCA-EoS
isothermal data (313.15 K)	7.20	39.97	31.65	88.27
isobaric data (20 MPa)	2.48	44.25	4.09	87.26

$$\mathrm{AAPE} = \frac{1}{N}\sum_{j=1}^{N}\frac{|y_i^{\mathrm{exp}} - y_i^{\mathrm{calc}}|}{y_i^{\mathrm{exp}}} \tag{11}$$

$$\mathrm{MAPE} = \left|\frac{y_i^{\mathrm{exp}} - y_i^{\mathrm{calc}}}{y_i^{\mathrm{exp}}}\right|_{\mathrm{max}} \tag{12}$$

The considerable improvement of the correlation for the isobaric case can be attributed to the fact that the influence of temperature on the solubility is very well represented via the solid solute sublimation pressure which is a function of T.

Solubility Correlation Using the GCA-EoS. The GCA-EoS was also applied to calculate the cinnamic acid fugacity coefficients ($\varphi_{\mathrm{s}}^{\mathrm{G}}$) and solubility. The associative parameters (ε and κ) were taken from Gros et al.[11] for the alcohol CH_2OH group and from Ferreira et al.[24] for the acid COOH group. Pure group and binary dispersive parameters for the constituent groups of the cinnamic acid + CO_2 + ethanol mixture were obtained from the literature,[11,24,25] except for the COOH-AC/ACH interaction which was accepted to be equal to the ACOOH-AC/ACH interaction (reported by Fornari et al.[18]) due to the lack of these parameters from previous works.

The hard sphere diameter of cinnamic acid (d_{c}) was estimated taking into account its solid molar volume, as proposed by

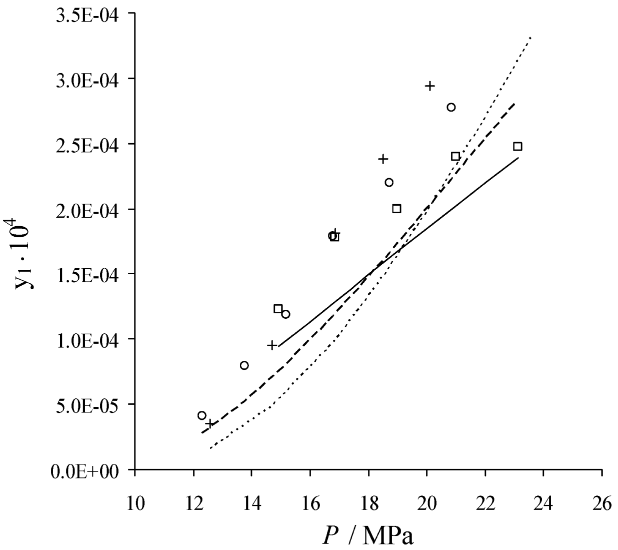

Figure 4. Solubility data of cinnamic acid in pure SC-CO_2. Symbols represent the experimental data of Chen et al.[10] □, 308.15 K; ○, 318.15 K; +, 328.15 K. GCA-EoS predictions: —, 308.15 K; — —, 318.15 K; and - - -, 328.15 K.

Fornari et al.,[18] and a value of 5.2 $cm^3 \cdot mol^{-1}$ was obtained. The values for the sublimation pressure were taken as those estimated in this work (Table 3).

Thus, the GCA-EoS model was applied in a completely predictive manner to calculate the solubility of cinnamic acid in pure SC-CO_2 and with ethanol as a cosolvent. Figure 2 shows a comparison between the experimental data measured in this work at 313.15 K and the values predicted using the GCA-EoS model. Additionally, Figure 4 shows a comparison between the cinnamic acid solubility reported by Chen el al.[10] and the GCA-EoS predictions. Despite that the COOH-AC/ACH binary interaction parameters were accepted to be equal to the ACOOH-AC/ACH interaction, good agreement could be observed in the prediction of cinnamic acid solubility in pure SC-CO_2. The AAPE obtained with respect to the data reported by Chen el al.[10] is 29.0 %. If no ethanol was used as a cosolvent, similar deviations were obtained between the GCA-EoS solubility predictions and the isothermal and isobaric data measured in this work (AAPE/% = 23). Nevertheless, higher AAPE values were obtained when ethanol was employed as a cosolvent, namely, (45.9 and 55.2) % for, respectively, (2 and 4) % ethanol in SC-CO_2. The higher deviations observed in the prediction of cinnamic acid solubility when there is an alcohol-type cosolvent could be attributed to the dispersive parameters employed to the CH_2OH-AC/ACH interaction; in the regression of this interaction, only the k_{ij}* parameter was considered[25] (i.e., no temperature dependence or nonrandomness parameters were estimated, i.e., $k_{ij}' = 0$ and $\alpha_{ij} = \alpha_{ji} = 0$).

Conclusions

Solubility data of solid cinnamic acid in pure SC-CO_2, and with (2 and 4) % in mass fraction ethanol as a cosolvent, in the typical temperature and pressure ranges of supercritical extraction processes, are reported for the first time in this study.

The solubilities measured at T/K = 313.15 were correlated applying two different thermodynamic models—the cubic-type SRK-EoS and the group contribution model GCA-EoS. The SRK-EoS provided a satisfactory correlation of the experimental isothermal and an excellent one of the experimental isobaric solubility data using binary interaction parameters for the cross-energy expression. The GCA-EoS, on the other hand, was applied in a completely predictive manner; all repulsive, dispersive, and associative model parameters were taken from the literature, and all pure component cinnamic acid parameters were either from the literature or estimated in this work. The average deviations between experimental and predicted values were acceptable (< 30 %) in the calculation of cinnamic acid solubility in pure SC-CO_2. The higher deviations obtained when ethanol was added as a cosolvent could be attributed to the lack of temperature dependence or nonrandomness parameters in the available set of CH_2OH-AC/ACH interaction parameters.

Supporting Information Available:

Experimental data summary. This material is available free of charge via the Internet at http://pubs.acs.org.

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