SOLUBILITY OF *TRANS*-CINNAMIC ACID IN SUPERCRITICAL CO$_2$ + ETHANOL MODIFIER: MEASUREMENTS AND CORRELATION

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Abstract. 2-propenoic acid (cinnamic acid; *trans*-cinnamic acid) is widely used in food (as flavouring), cosmetics (perfumes, decorative cosmetics, fine fragrances, shampoos, toilet soaps, etc) and pharmaceuticals (because of its functional properties). Recent studies related to the use of *trans*-cinnamic acid in cosmetics revealed also its importance as a non-photosynthetic pigment in photoprotection. Furthermore, there is a growing interest in the use of cinnamic acid as a food supplement because of its reported antimicrobial, antifungal and antioxidant properties. Supercritical Fluid Extraction (SFE) is a viable technique for extraction of a great variety of compounds from their natural vegetable matrixes. The design of SFE processes requires knowledge of the solute solubility in the supercritical phase and the ability to efficiently model and predict it. This paper is devoted to the experimental measurement and correlation of the solubility of *trans*-cinnamic acid in pure supercritical CO$_2$ and with ethanol as a modifier, which, to our knowledge, has not been reported in the literature till present. Measurements were carried out at temperatures in the range of 313.15 K to 343.15 K and at pressures ranging from 100 to 400 bar. Two thermodynamic models were used and compared in the correlation of the experimental solubility data for *trans*-cinnamic acid - a cubic type equation of state, the Soave-Redlich-Kwong SRK-EoS, and the Group Contribution Associating EoS (GCA-EoS). In addition, values for the thermophysical properties of trans-cinnamic acid are also advocated.

INTRODUCTION

Despite of trans-cinnamic acid is widely used in food (as flavouring) and cosmetics [1] (perfumes, decorative cosmetics, fine fragrances, shampoos, toilet soaps, etc) there is a growing interest in new uses of this product because of its functional properties.

Edreva [2] related the use of trans-cinnamic acid in cosmetics revealing also its importance as a non-photosynthetic pigment in photoprotection. Furthermore, there is a growing interest in the use of cinnamic acid as a food supplement because of its reported properties. In this sense Narasimhan et al. [3] have reported their antimicrobial and antifungal activity. On the other hand, natural antioxidants derived from plants are now of considerable interest as dietary supplements and food preservatives [4], as a result of the synthetic antioxidants are being restricted because of their toxic and carcinogenic effects [5, 6]. What makes a good antioxidant and how they work are questions that need to be addressed [7]. In this sense González Moa et al. [8] have studied the antioxidant activity of natural cinnamic acids and have concluded its important antioxidant activity.

This work reports for the first time the experimental measurements and thermodynamic correlation of *trans*-cinamic acid solubility in pure supercritical CO$_2$ (SC-CO$_2$) and in SC-CO$_2$ with ethanol as a co-solvent. 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) % wt.

Two different thermodynamic models were applied to calculate the solubility of *trans*-cinamic acid. The GCA-EoS [9], based on the group contribution approach for both dispersive and associative interactions, and the SRK-EoS [10]. In addition, values for the thermophysical properties, sublimation pressure and solid molar volume of *trans*-cinnamic acid are also given.

MATERIALS AND METHODS

Chemicals: *trans*-cinnamic acid (>99 mass %) was supplied by Aldrich. Co. Ethanol from Merck (>99.9 % HPLC gradient grade) was used 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 vol % purity, SFC grade) supplied by AIR LIQUIDE was used as received. Silica extra pure (more than 99.8 mass %) from Sigma Chemical Co. Inc. was utilized as support of the products.
Equipment and procedure: The solubilities were measured with an SFX 3560 extractor with two syringe pumps (Model 260D) manufactured by ISCO (Lincoln, NE, USA). A detailed description of the equipment was presented in a previous paper [11] and will not be given here. 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.
Ethanol was used as a modifier and to trap the *trans-c*innamic acid extracted. After that, the extract was transferred to 10 mL calibrated flasks and diluted with ethanol for determination by UV-spectrometry. A detailed explanation of the experimental sample preparation is given elsewhere [11,12]. A 8453 Hewlett-Packard diode array UV-Vis spectrophotometer was used to determine the amount of *trans-c*innamic acid in the extract, after calibration with gravimetrically prepared standard solutions.
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 (5 values at least). The uncertainty associated with *trans-c*innamic acid solubility measurements, expressed in absolute deviation of the mole fractions reported, varied within the following range $2.1 \cdot 10^{-7}$ for the highest to $1.3 \cdot 10^{-10}$ for the lowest measured solubility.

RESULTS

Experimental solubility data: 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-c*innamic acid solubility in pure SC-CO_2 considerably increases with pressure, while the influence of temperature is smaller and of changing sense. The use of small amounts (2 and 4 % wt) of a polar modifier like ethanol also considerably increases the solubility of *trans-c*innamic acid in the SC-CO_2.

Table 1. Cinnamic acid (1) solubility in pure supercritical carbon dioxide (2) and with ethanol (3) as co-solvent at T = 313.15 K.

	% Ethanol		
	0	2	4
p/MPa	$y_1 \cdot 10^7$		
10	---	7.21	10.8
20	0.14	19.60	36.05
30	20.48	45.50	69.75
40	57.86	85.38	121.50

Solubility data correlation: For solid-gas phase equilibria the general equilibrium relation is:

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

where the subscript s stands for the solid solute, f_s^{G} is the fugacity of component s 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 - 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 [13]: (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.

Table 2. Cinnamic acid (1) solubility in pure supercritical carbon dioxide (2) and with 2% ethanol (3) as co-solvent at p = 200 MPa.

T / K	% Ethanol	
	0	2
	$y_1 \cdot 10^8$	
313.15	1.38	196.03
323.15	1.69	177.70
333.15	1.92	171.20
343.15	2.20	164.30
353.15	2.48	147.10

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:

$$f_s^{\text{solid}} = P_s^{\text{sub}} \varphi_s^{\text{sub}} \exp \int_{P_s^{\text{sub}}}^{P} \frac{v_s^{\text{solid}} dP}{RT} \tag{3}$$

where P_s^{sub} is the sublimation (vapor) pressure of the pure solid, φ_s^{sub} is the fugacity coefficient at sublimation pressure and v_s^{solid} is the molar volume of the solid, all at temperature 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:

$$y_s = \frac{P_s^{\text{sub}}}{P} E \tag{4}$$

where:

$$E \equiv \frac{\varphi_s^{\text{sub}} \exp \int_{P_s^{\text{sub}}}^{P} \frac{v_s^{\text{solid}} dP}{RT}}{\varphi_s^G} = \frac{\varphi_s^{\text{sub}} \exp \left[\frac{v_s^{\text{solid}} \left(P - P_s^{\text{sub}} \right)}{RT} \right]}{\varphi_s^G} \tag{5}$$

In most practical cases, the P_s^{sub} value is quite small and thus φ_s^{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 (φ_s^G) is significantly different from unity and can produce very large enhancement factors.

According to Eq (4) and (5), information about cinnamic acid sublimation pressure and solid molar volume is required in order to calculate its solubility in SC-CO$_2$. Furthermore, a reliable thermodynamic model is necessary to evaluate φ_s^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_m = 406.15 K), the normal boiling temperature (T_b = 573.15 K), and the enthalpy of fusion (ΔH_{fus} = 22 626 J·mol^{-1}) of

the acid were obtained from http://webbook.nist.gov/chemistry/. There are also some limited data on the vapor pressures of *trans*-cinnamic acid measured at several temperatures using the Knudsen effusion method [14].

Thus, the rest of the properties required had to be estimated. To do this, the algorithm discussed in detail in Fornari et al. [15] was followed and hence herewith only a concise summary of the relevant steps is given: (1) 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, estimated in the present study (see Table 3). The values obtained are in excellent agreement with the values measured by Monte and Hillesheim [14] at some of the temperatures of our experiment. (2) The solid volume was estimated applying the method proposed by Goodman et al. [15]. (3) The critical parameters and acentric factor were estimated applying the method of Cholakov et al. [16] and Wakeham et al. [17].

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	
triple point pressure/MPa	2.388×10^{-3}
sublimation enthalpy/J·mol^{-1}	109600
critical temperature, T_c/K	803.94
critical pressure, P_c/Mpa	3.86
acentric factor	0.712
solid volume /m^3·mol^{-1}	$167 \cdot 10^{-6}$
sublimation pressure /MPa	$6.15 \cdot 10^{-6}$ at $T = 343.15$ K
	$1.94 \cdot 10^{-6}$ at $T = 333.15$ K
	$5.72 \cdot 10^{-7}$ at $T = 323.15$ K
	$1.55 \cdot 10^{-7}$ at $T = 313.15$ K

The calculation of cinnamic acid fugacity coefficients (φ_s^G) was carried out by applying two different thermodynamic models: the Soave-Redlich-Kong (SRK) [10] equation and the Group Contribution Associating Equation of State (GCA-EoS) [9].

The SRK-EoS with the one-fluid van der Waals mixing rules and the following combining rules for the cross-energy and cross-co-volume parameters are used:

$$a_{ij} = \left(a_{ii}a_{jj}\right)^{0.5}\left(1 - k_{ij}\right) \tag{6}$$

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2}\right)\left(1 - l_{ij}\right) \tag{7}$$

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

Optimum values for the interaction parameters between cinnamic acid and CO_2 were determined at each temperature and ethanol concentration, and are given in Table 4. The following standard objective function was minimized:

$$F = \sum_{i=1}^{N_{\exp}} \left| \frac{y_s^{\exp} - y_s^{cal}}{y_s^{\exp}} \right|_i \tag{8}$$

where $N_{\exp}$ is the number of data points and the superscripts "calc" and "exp" mean the calculated and experimental results, respectively.

The value of the energy parameter for ethanol + CO_2 was accepted to be 0.09, while the interaction parameter for ethanol + cinnamic acid was set equal to zero in all cases. This last assumption can be justified by the fact that both ethanol and cinnamic acid are present in very low concentrations in the supercritical phase.

Table 4. Optimal SRK binary interaction parameters between CO_2 and cinnamic acid at 313.15 K and different ethanol concentration.

%Ethanol	k_{ij}	l_{ij}
0	0.1135	0.000
2	0.2037	-0.052
4	0.2916	-0.052

The SRK-EoS demonstrated good capability to correlate the experimental solubility data of cinnamic acid in pure SC-CO$_2$ and SC-CO$_2$ with ethanol as a co-solvent at T = 313.15 K (see Figure 1). The usual approach is to compute the solid solubility by locating a mole fraction that satisfies the equi-fugacity criterion, which might lead to numerical pitfalls, as multiple solutions to the equi-fugacity condition could exist. The non-uniqueness is a particular problem and special care should be taken to determine the correct solubility root. Thus, a stability analysis routine, based on a modified tangent-plane function and a phase identification procedure [18], was employed to determine all roots to the equi-fugacity condition.
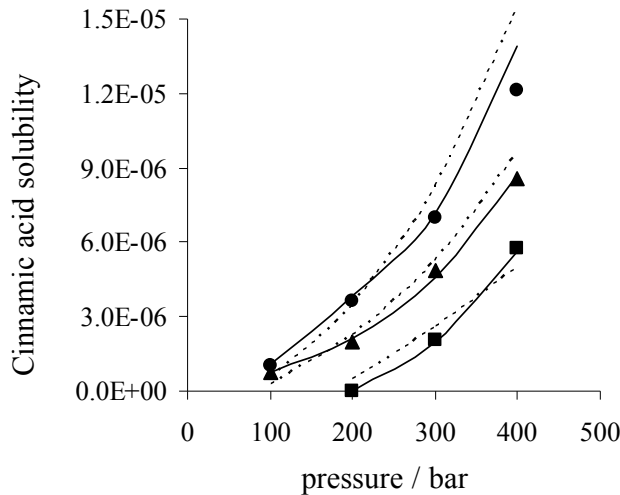
Figure 1. Cinnamic acid solubility measured in this work at 313 K: (■) 0% ethanol; (▲) 2% ethanol; (●) 4% ethanol; (—) SRK-EoS correlation; (---) GCA-EoS correlation.

The GCA-EoS was also applied in this work to calculate the cinnamic acid fugacity coefficients (φ_s^G) and solubility. Pure group and binary interaction parameters for the constituent groups of the cinnamic acid + CO$_2$ + ethanol mixture were obtained from the literature [9, 19, 20]. The associative parameters (energy and volume) were taken from Gros et al. [9] for the alcohol CH$_2$OH group and from Ferreira et al. [20] for the acid COOH group.

The hard sphere diameter of cinnamic acid (d$_c$) was estimated taking into account its solid molar volume [15] and a value of 5.2 cm^3/mol was obtained.

Using the cinnamic acid sublimation pressure calculated in this work (P_s^{sub} = 1.55·10^{-7} bar at 313.15 K) the GCA-EoS predictions resulted in solubilities rather higher than those reported in Table 1. An optimized value for the cinnamic acid sublimation pressure (1.6·10^{-9} bar, almost two order of magnitude lower than the value estimated in this work) resulted in a satisfactory correlation of the solubility variations with pressure and with ethanol content (see Figure 1).

CONCLUSION

The solubility of solid cinnamic acid in pure SC-CO_2 and with 2 and 4 %wt ethanol as co-solvent is reported in this study, in the typical temperature and pressure ranges of supercritical extraction processes.

In order to model the measured cinnamic acid solubilities, values for its pure component parameters, such as sublimation pressure, solid volume, critical parameters and acentric factor, are estimated. Then, two different thermodynamic models were applied to correlate the experimental solubility data: the group contribution model GCA-EoS and the cubic-type SRK-EoS. Both models were able to correlate the experimental data. The SRK-EoS was capable to provide a high correlation of the solubility data using binary interaction parameter in both the cross-energy and cross-co-volume expressions. About the GCA-EoS, fixing all its parameters (for the three repulsive, dispersive and associative terms) as reported in the literature, an optimized value of the cinnamic acid sublimation pressure provided a satisfactory representation of the solubility data. Nevertheless, this optimized value resulted to be too low, in comparison with the value estimated in this work. This discrepancy should be attributed to a deficiency in the model repulsive term but not to the dispersive or associative parameters, since appropriate variation of solubility with both pressure and ethanol content was achieved.

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