Determining the Sublimation Pressure of Capsaicin Using High-Pressure Solubility Data of Capsaicin + CO_2 Mixtures

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Experimental solubility data (pressure−concentration) of capsaicin in high-pressure carbon dioxide at three temperatures has been tested for consistency and then used to determine the sublimation pressure of capsaicin. The experimental data have been modeled and thermodynamically tested using the Peng−Robinson equation of state with the mixing rules of Wong and Sandler using a method previously developed by one of the authors. The system capsaicin + carbon dioxide is highly asymmetric and presents inherent difficulties of analysis. Despite this, the model employed in this work allows for the correlation of the solubility of solid capsaicin in the high-pressure gas phase with deviations much lower than other models presented in the literature for asymmetric mixtures. Therefore, the sublimation pressure determined by the proposed method can be used with confidence in modeling and simulation processes where the sublimation pressure of capsaicin is required.

Introduction

The production of plant extracts is currently limited by safety and regulatory constraints to the concentration of toxic residues of organic solvents.[1−3] The use of carbon dioxide (CO_2) as a solvent is an attractive alternative due to its inertness, nontoxicity, nonflammability, and low cost.[4] Additionally, the use of CO_2 in supercritical fluid extraction processes, near-environmental temperatures, is advantageous to minimize heat requirements and avoid thermal damage to labile compounds.[5] In this respect, having experimental solute solubility data and applying good methods for the modeling of such data and for testing the goodness of the data are essential in the simulation, optimization, and design of supercritical fluid processes.

The pungency characteristic of hot peppers and paprika is due to the presence of compounds called capsaicinoids, among which capsaicin ($C_{18}H_{27}O_3N$) is the most pungent. Capsaicin is of interest in foods because of its hot flavor.[6] It is also of interest in pharmaceuticals, because of its direct action on pain receptors; when topically applied, capsaicin is useful in alleviating the pain associated with diabetic neuropathy, osteoarthritis, and psoriasis.[7,8]

The literature shows that de la Fuente et al.,[9] Hansen et al.,[10] Škerget and Knez,[11] and Knez and Steiner[12] measured the solubility of solid capsaicin in CO_2, with different experimental methodologies and comparable results, at several temperatures (between 298 and 333 K) and over a pressure range from 6 to 40 MPa. Within this experimental region, the mole fraction of capsaicin in the fluid phase was of the order of 10^{-4} and lower. This low value is explained due to the poor solvent power of CO_2 for polar solutes and the low volatility of capsaicin.

The modeling and simulation of supercritical fluid separation processes require that the phase equilibrium properties (temperature, pressure, and concentration) be well calculated by a defined thermodynamic model. The equilibrium concentration of the solute determines the highest concentration of the solute that can be extracted by the supercritical fluid solvent and therefore is one of the most important variables in supercritical fluid extraction.[13] Current methods for modeling the phase equilibrium in these systems consider the application of equations of state (EoS), a method in which the effect of concentration is specially considered through the so-called mixing rules.

There are four main problems with the modeling of mixtures such as solid capsaicin in supercritical CO_2: (i) the large difference in size between the solute capsaicin and the solvent CO_2, (ii) the chemical complexity of the solute, (iii) the very low concentration of the solute in the high-pressure gas phase, and (iv) the sublimation pressure of the solid capsaicin is not known with sufficient accuracy as needed for thermodynamic modeling and analysis.

To the best of our knowledge, the only known information on the sublimation pressure of capsaicin is that given by Škerget and Knez.[11] These authors provided the constants for the generalized Riedel's equation. Valderrama and Zavaleta[14] have indicated that a reasonably accurate value of the sublimation pressure of the pure solid must be available if accurate values of solubility are needed for the modeling and correlation of the data. These authors showed that variations of ±10 % in p_2^s may produce deviations between 5 and 19 % in solubility calculations. Therefore, it is proposed here to determine the sublimation pressure of capsaicine as a function of temperature using accurate solubilty data of capsaicine in high-pressure carbon dioxide. The accuracy of the data used is checked using a consistency test method developed by one of the authors.[15]

Sublimation Pressure and Solubility. The fundamental equation of phase equilibria establishes that, at a given temperature and pressure, the fugacity of a component *i*, for instance the solid solute, in the gas phase f_i^g must be equal to the fugacity of the same component in the solid phase f_i^s. If

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subscript 2 stands for the solid component, then the equation is[16]

$$f_2^{\mathrm{s}} = f_2^{\mathrm{g}} \tag{1}$$

If the solid phase is considered to be a pure substance, then

$$p_2^{\mathrm{s}}\phi_2^{\mathrm{s}} = y_2\phi_2^{\mathrm{g}}p \tag{2}$$

Here, y_2 is the mole fraction of the solid component in the gas phase, p_2^{s} is the sublimation pressure of the pure solid, ϕ_2^{g} is the fugacity coefficient of solid (2) in the gas phase, ϕ_2^{s} is the fugacity coefficient of solid (2) at saturation, and p is the system pressure.

Since the sublimation pressure is normally low, ideal gas behavior for the gas phase over the pure solid can be assumed and $\phi_2^{\mathrm{s}} \approx 1$. Also, the volume of the solid can be considered to be pressure independent, and the mole fraction of the solute in the gas phase, or solubility, at temperature T and pressure p for component 2 is

$$y_2 = \frac{p_2^{\mathrm{s}}\mathrm{e}^{V_2^{\mathrm{s}}(p-p_2^{\mathrm{s}})/RT}}{p\phi_2^{\mathrm{g}}} \tag{3}$$

Here, R is the ideal gas constant and V_2^{s} is the solid molar volume.

If solubility data (concentration of the solid solute in the compressed gas phase at different pressures) at a given constant temperature are available, it can be seen from eq 3 that the sublimation pressure p_2^{s} can be determined. The calculation reduces then to an optimization problem solved in this work using genetic algorithms.

The fugacity coefficient is calculated from standard thermodynamic equations that relate the fugacity coefficient with the pressure p, the temperature T, the volume V, and the critical compressibility factor $Z = pV/RT$[17]

$$RT\ln(\phi_i) = \int_V^{\infty}\left[\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]\mathrm{d}V - RT\ln Z \tag{4}$$

The Peng–Robinson EoS,[18] with the mixing rules proposed by Wong and Sandler,[19] are used as the thermodynamic model to evaluate the fugacity coefficient ϕ_2. The Peng–Robinson equation and the Wong–Sandler mixing rules for the PR EoS that are used in this work are summarized in Table 1.[20] In the equations presented in the table, a and b are the equation of state constants, T_{c} is the critical temperature, p_{c} is the critical pressure, T_{r} is the reduced temperature defined as $T_{\mathrm{r}} = T/T_{\mathrm{c}}$, and ω is the acentric factor. Also, a_{m} and b_{m} are the equation of state constants for mixtures with k_{ij} as the adjustable parameter, $A_{\infty}^{\mathrm{E}}(y)$ is calculated assuming that $A_{\infty}^{\mathrm{E}}(y) \approx A_{\mathrm{o}}^{\mathrm{E}}(y) \approx G_{\mathrm{o}}^{\mathrm{E}}(y)$. In this work, $G_{\mathrm{o}}^{\mathrm{E}}(y)$ has been calculated using the van Laar model that has been shown to perform well in high-pressure phase equilibrium calculations.[21]

For a binary mixture such as the case considered in this study, the general equations presented in Table 1 are reduced to

$$b_{\mathrm{m}} = \frac{{y_1}^2(b - a/RT)_1 + 2y_1y_2(b - a/RT)_{12} + {y_2}^2(b - a/RT)_2}{1 - \dfrac{y_1a_1}{b_1RT} - \dfrac{y_2a_2}{b_2RT} - \dfrac{G_{\infty}^{\mathrm{E}}(y)}{\Omega RT}} \tag{5}$$

$$\left(b - \frac{a}{RT}\right)_{12} = \frac{1}{2}\,[b_1 + b_2] - \frac{\sqrt{a_1a_2}}{RT}\,(1 - k_{12}) \tag{6}$$

$$a_{\mathrm{m}} = b_{\mathrm{m}}\left(\frac{y_1a_1}{b_1RT} + \frac{y_2a_2}{b_2RT} + \frac{G_{\infty}^{\mathrm{E}}(y)}{\Omega}\right) \tag{7}$$

$$\frac{G_{\mathrm{o}}^{\mathrm{E}}}{RT} = \frac{(L_{12}/RT)y_1y_2}{y_1(L_{12}/L_{21}) + y_2} \tag{8}$$

The expressions for the fugacity coefficient using the PR equation with the above-described WS mixing and combination rules can be found elsewhere.[20] The problem is then reduced here to determine the parameters L_{12} and L_{21} in the van Laar model, the k_{12} parameter included in the combining rule for $(b - a/RT)_{12}$, and the sublimation pressure p_2^{s} that appears in the solubility eq 3, using available high-pressure TPy data for gas–solid systems. The main goal in this problem is to find a minimum value of the objective function defined below that gives an acceptable sublimation pressure, that provides model parameters of acceptable physical meaning, that gives low deviations between experimental and calculated solubility values, and that is shown to be consistent according to the method developed by the authors[15] and summarized in the following section.

The optimization procedure in the genetic algorithm scheme requires an objective function. This objective function is arbitrarily but conveniently defined, and several criteria have been presented in the literature.[22] For modeling the solubility of a solid solute in a compressed gas, the deviation between calculated and experimental values of the solubility is defined as the objective function W. That is

$$W = |\%\ \Delta y_2| \tag{9}$$

The average absolute deviation Aver $|\%\ \Delta y_2|$ is calculated as

$$\text{Aver}\ |\%\ \Delta y_2| = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{|y_2^{\mathrm{cal}} - y_2^{\mathrm{exp}}|}{y_2^{\mathrm{exp}}}\right]_i \tag{10}$$

while the average relative deviation Aver % Δy is determined as

$$\text{Aver}\ \%\ \Delta y_2 = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{y_2^{\mathrm{cal}} - y_2^{\mathrm{exp}}}{y_2^{\mathrm{exp}}}\right]_i \tag{11}$$

Valderrama and Alvarez[13] have demonstrated that these two deviations, relative and absolute, give the global information needed to decide about the goodness of a model. Besides that, the consistency test developed by the authors considers the individual deviation for each point, as explained in what follows.

Consistency Criteria. The consistency criteria have been well described by the authors.[15,23,24] Thus, a brief summary only is given in what follows.

To define the criteria for thermodynamic consistency, it is first required that the model is able to correlate the data within acceptable deviations. The model is accepted and the consistency test is applied if the deviations defined by eq 9, for each point, are within −20 % to 20 % for the solute mole fraction in the gas phase (y_2). After the model is found appropriate, it is required that the Gibbs–Duhem equation conveniently written

Table 1. Peng−Robinson Equation of State and Wong−Sandler Mixing Rules

The Peng-Robinson Equation

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)}$$

$$a = 0.457235(R^2 T_c^2/P_c)\,\alpha(T_r)$$

$$b = 0.077796(RT_c/P_c)$$

$$\alpha(T_r)^{0.5} = [1 + F(1 - T_r^{0.5})]$$

$$F = 0.37646 + 1.54226\,\omega - 0.26992\,\omega^2$$

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + b_m(V - b_m)}$$

The Wong-Sandler mixing rules

$$b_m = \frac{\sum_i^N \sum_j^N y_i y_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i^N \frac{y_i a_i}{b_i RT} - \frac{G_o^E(y)}{\Omega\, RT}}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[b_i + b_j\right] - \frac{\sqrt{a_i a_j}}{RT}\left(1 - k_{ij}\right)$$

$$a_m = b_m\left(\sum_i^N \frac{y_i a_i}{b_i} + \frac{G_o^E(y)}{0.34657}\right)$$

van Laar model for $G_O^E(y)$

$$\frac{G_o^E}{RT} = \sum_i^N y_i \frac{\sum_j^N y_j L_{ij}}{1 - y_i} \cdot \left[1 - \frac{y_i \sum_j^N y_j L_{ij}}{y_i \sum_j^N y_j L_{ij} + (1 - y_i) y_i \sum_j^N y_j L_{ji}}\right]^2$$

in terms of the fugacity coefficients is fulfilled.[25] This equation as discussed in previous works is[15,23]

$$\int \frac{1}{py_2}\,\mathrm{d}p = \int \frac{1}{(Z - 1)\phi_2}\,\mathrm{d}\phi_2 + \int \frac{(1 - y_2)}{y_2(Z - 1)\phi_1}\,\mathrm{d}\phi_1 \quad (12)$$

In this equation, p is the system pressure, y_2 is the gas-phase solute mole fraction, φ_1 and φ_2 are the fugacity coefficients of components 1 and 2 in the gas phase mixture, and Z is the compressibility factor of the gas mixture. The properties φ_1, φ_2, and Z can be calculated using an equation of state and suitable mixing rules.

The consistency method requires that the difference between the integral on the left-hand side of eq 12, denoted as A_P, and the sum of the integrals on the right-hand side, denoted as A_φ, be between defined margins (−20 % to +20 %), to declare the data as being thermodynamically consistent. The percentages defined for the consistency criterion (solubility and areas) are based on information presented in the literature related to the accuracy of experimental data in this type of mixture. Valderrama and Zavaleta[15] have clearly explained how these limits of acceptance were determined.

The data are considered to be thermodynamically consistent (TC) if the deviations in all the individual deviations in the areas are within the defined limits (−20 % to 20 %). The data are considered to be thermodynamically inconsistent (TI) if the deviations in correlating the solute solubility are within the established limits but the individual deviations in the areas are outside the established limits, for more than 25 % of the data points in the data set. If the data points giving area deviations outside the established limits are less than 25 % of the data points in the data set (say two out of 10 original points), then these points showing high area deviations can be eliminated and the remaining data checked again for consistency. Once the data with high area deviations are removed, the calculated sublimation pressure is taken as the true value. Therefore, the values for the sublimation pressure presented in this work are calculated with data that not only can be accurately correlated using a thermodynamic model but also was shown to be thermodynamically consistent.

Table 2. Properties of Capsaicin Used in This Work

property	carbon dioxide	capsaicin	
molecular weight	44.0	305.4	Škerget and Knez[11]
normal boiling point T_b/K		853.7	
critical temperature T_c/K	304.2	1062.1	
critical pressure p_c/MPa	7.38	1.71	
acentric factor	0.224	1.185	
density ρ(298 K)/g·cm^{-3}		1.06	Vafai et al.[27]
molar volume V_m(298 K) m^3·kmol^{-1}		0.289 8	

[a] The data for CO_2 were taken from Daubert et al.[26]

Data Used. Table 2 shows the properties used in this work for both carbon dioxide and capsaicin. The data for pure carbon dioxide have been taken from Daubert et al.[26] The data for pure capsaicin were obtained from Škerget and Knez[11] and Vafai et al.,[27] except the sublimation pressure of capsaicin that has been estimated from the experimental solubility data. The method used for estimating the sublimation pressure has shown to be highly reliable and provides better flexibility to the modeling.[14]

The experimental solubility data of solid capsaicin in high-pressure CO_2 used in this work were presented previously by de la Fuente et al.[9] in graphical format and consisted of 101

Table 3. Details on the Phase Equilibrium Data for the System Considered in This Study[a]

$T = 298$ K		$T = 308$ K		$T = 313$ K	
p	y_2	p	y_2	p	y_2
MPa	10^{-4}	MPa	10^{-4}	MPa	10^{-4}
7.60	0.643	8.56	0.435	7.75	0.051
9.21	0.723	11.79	0.887	9.43	0.300
10.72	0.740	15.43	1.110	12.65	0.850
15.69	0.979	17.37	1.190	13.15	1.090
17.28	1.020	20.76	1.390	14.63	1.190
20.03	1.110	23.05	1.430	18.48	1.550
24.64	1.230	26.83	1.530	19.25	1.640
28.11	1.260	28.25	1.640	22.47	1.860
36.67	1.290	32.15	1.740	27.40	2.100
		34.40	1.950	30.70	2.310
				35.71	2.37

[a] The estimated uncertainties of the experimental values are 0.15 % for the temperature T, 1 % for the pressure p, and 3.5 % for the solubility y_2.

data points, at pressures from 7.5 to 37.0 MPa, and at three temperatures (298, 308, and 313) K. Nevertheless, in the present contribution, a selection of solubility data are informed in a more useful tabular format (Table 3).

According to the methodology described in detail by de la Fuente et al.,[9] the mole fraction of capsaicin in the CO_2-rich phase was measured and calculated with a static-analytical setup. Capsaicin (>95.0 % pure, mass basis) from Sigma-Aldrich (St. Louis, MO) and carbon dioxide (99.99 % pure, mole basis) from AGA-Chile S. A. were used for these measurements. For each solubility isotherm, solid capsaicin (0.3 g) was loaded into a high-pressure 50 mL capacity equilibrium cell and then filled with CO_2. The temperature and pressure were adjusted to desired set values. Following a 12 h equilibration period, the concentration of capsaicin in the saturated CO_2-rich phase was determined on-line by withdrawing fluid phase samples (20 μL) from the cell by means of a six-port high-pressure valve that coupled the cell with a high-performance liquid chromatography device (HPLC). The estimated uncertainties in temperature and pressure were 0.5 K and 0.2 MPa, respectively. The HPLC analyses were performed according to the method proposed by Hansen and Bruno,[28] and the estimated uncertainties were of the order of 3.5 %. This value gives on the average approximately $\pm 0.3 \times 10^{-5}$ in mole fraction.

When the whole set of numerical information of the capsaicin solubility in high-pressure CO_2 was considered for analysis, several problems were detected: (i) the numerical method used diverges, (ii) parameters with no physical meaning are obtained, or (iii) very high deviations in the correlated solubility are obtained. Therefore, the data were analyzed and the repeated points were eliminated ending with a set of 30 points: 9 at $T = 298$ K, 10 at $T = 308$ K, and 11 at $T = 313$ K, as shown in Table 3. After that, the data was smoothed and 10 data points were used for analysis. Figure 1 shows the three data sets used to determine the sublimation pressure.

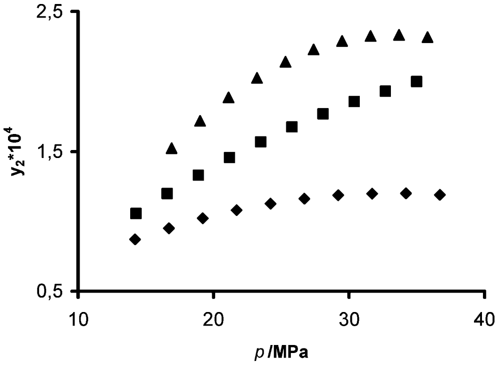

Figure 1. Smoothed data for the mixture CO_2 + capsaicin. In the figure, the symbols are: ◆, $T = 298$ K; ■, $T = 308$ K; ▲, $T = 313$ K.

Table 4. Calculated Deviations and Optimum Interaction Parameters for the Binary Mixtures CO_2 + Capsaicin and Sublimation Pressures at All Temperatures Studied with the PR/WS/VL Model and Using the Data Described in Table 2

T/K	298	308	313
N	10	8	7
Δp/MPa	14.2−36.7	18.9−35.0	23.2−35.8
k_{ij}	0.006 381	0.000 679	0.000 358
L_{ij}	5.875 3	4.699 8	4.231 9
L_{ji}	7.909 7	8.972 0	6.960 9
Aver % Δy_2	−3.56	−8.98	−12.61
Aver |% Δy_2|	7.12	12.12	15.19
Max % Δy_2	−19.41	−15.04	−15.09
Max % ΔA_2	14.19	10.47	13.65
Aver %ΔA_2	2.64	−0.06	2.05
Aver |% ΔA_2|	6.21	4.03	5.17
p^S/MPa calc.	8.09×10^{-19}	8.02×10^{-18}	2.59×10^{-17}
p^S/MPa Riedel	8.11×10^{-19}	7.92×10^{-18}	2.33×10^{-17}

Results and Discussion

The data presented in Table 3 was analyzed using the model presented in the preceding sections, the Peng−Robinson equation of state with the Wong−Sandler mixing rule including the van Laar model for the Gibbs free energy needed in the mixing rules (PR/WS/VL). Table 4 presents the optimum parameters and the deviations in the solute mole fraction in the compressed gas phase Aver |% Δy_2|. As observed in Table 4, deviations in the solid solubility increase with temperature, behavior that could be explained due to larger uncertainties in the experimental measurements at higher temperatures. The deviations in the concentration of the solvent carbon dioxide in the gas phase are always lower than 0.1 % and therefore are not shown in the table. In the same table, the values of the calculated sublimation pressures at the three temperatures with the PR−WS−VL model are presented. Also shown are the calculated sublimation pressures with the Riedel equation with the constants proposed by Škerget and Knez.[11] The difference between the values calculated using the solubility data and those determined using the generalized Riedel equation are between 1 % and 15 %. The calculated sublimation pressures were correlated using an equation of the form log(p_s) vs the inverse of the absolute temperature. The resulting equation is $-\log(p^s/\text{MPa}) = -11.517 + 8763.2(\text{K}/T)$, with p^s being the sublimation pressure in MPa and T the absolute temperature in Kelvin. As shown by Valderrama and Zavaleta,[14] the calculation of sublimation pressures using the procedure employed in this paper gives accurate results. Not only that, but the solubility data used in determining the sublimation pressure are those that are shown to be thermodynamically consistent. Error propagation calculations, as explained by the authors in previous works,[24] applied to the calculated sublimation pressure give errors of the order of 3.5 %.

The maximum deviations in the solubility and in the areas are presented in the 9th and 10th rows of Table 4, respectively. Only the 10 data point set at $T = 298$ K was shown to be thermodynamically consistent (TC), that is, area deviations are within the established range of −20 % to +20 %. For the other two isotherms at temperatures of (308 and 313) K, the 10 points data set resulted as not fully consistent (NFC), meaning that some few points gave area deviations outside the established range of ±20 %. The maximum area deviations observed for the data used are higher than 70 % for some points at temperatures of (308 and 313) K, although average area deviations are within the accepted range. Once the points with high solubility deviations are eliminated, the consistency analysis is applied to the remaining data, as explained above. The final result is that the original set of 10 data points are declared to be NFC while the remaining set (8 points at 308 K and 7 points at 313 K) are declared to be TC. As explained above, the values of the sublimation pressure calculated with the data set that was shown to be consistent are taken as the true values and correspond to those shown in Table 4.

Conclusions

According to the results, the following conclusions can be drawn: (i) raw experimental data must be first analyzed for physical consistency (repeated data, tendency of the data, doubtful points), before using them for correlating and consistency purposes, and (ii) the Peng−Robinson equation with the Wong−Sandler mixing rules can be used to correlate experimental solubility data of capsaicin in compressed supercritical carbon dioxide if appropriate interaction parameters are used.

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