Solubility of caffeine from green tea in supercritical CO₂: a theoretical and empirical approach

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Abstract Decaffeination of fresh green tea was carried out with supercritical CO₂ in the presence of ethanol as co-solvent. The solubility of caffeine in supercritical CO₂ varied from 44.19×10^{-6} to 149.55×10^{-6} (mole fraction) over a pressure and temperature range of 15 to 35 MPa and 313 to 333 K, respectively. The maximum solubility of caffeine was obtained at 25 MPa and 323 K. Experimental solubility data were correlated with the theoretical equation of state models Peng–Robinson (PR), Soave Redlich–Kwong (SRK), and Redlich–Kwong (RK). The RK model had regressed experimental data with 15.52 % average absolute relative deviation (AARD). In contrast, Gordillo empirical model regressed the best to experimental data with only 0.96 % AARD. Under supercritical conditions, solubility of caffeine in tea matrix was lower than the solubility of pure caffeine. Further, solubility of caffeine in supercritical CO₂ was compared with solubility of pure caffeine in conventional solvents and a maximum solubility 90×10^{-3} mol fraction was obtained with chloroform.

Keywords Supercritical CO₂ · Green tea · Solubility · Caffeine · Equation of state · Redlich–Kwong

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Abbreviations

AARD	Average absolute relative deviation
EOS	Equation of state
PR	Peng–Robinson
SRK	Soave–Redlich–Kwong
RK	Redlich–Kwong
SCF	Supercritical fluid
CO ₂	Carbon dioxide
PE	Phase equilibria

Nomenclature

a, b	EOS mixture parameter
k_{ij}	Binary interaction parameter
P	Pressure
R	Universal gas constant
T	Temperature
v, V	Molar volume
y, y_2	Mole fraction of solute in supercritical phase

Greek letters

φ	Fugacity coefficient
ω	Acentric factor
ρ	Density

Subscripts

2	component 2 refers to caffeine
c	Critical
i, j	Component indices
exp	Experimental value
pred	Predicted value
ideal	as per ideal gas law

Superscripts

sat	saturation
sub	sublimation

Introduction

Caffeine is a natural compound present in the leaves, seed or fruit of a number of plants including coffee, tea, cocoa, kola, guarana and yerba mate. It is mostly consumed through soft beverages such as tea, coffee, guarana, and cacao (Icen and Guru 2010). It possesses many health benefits and is known to play an important role in the prevention of Alzheimer's disease and cancer. Caffeine is added to pharmaceuticals to improve analgesic effects (Kumar and Ravishankar 2009). However, the excess intake has also been reported to cause health problem in humans. According to [American Beverage Association](#), a daily intake of caffeine of 300 mg is considered as safe. Green tea is the best source for producing commercial quantities of caffeine as it contains high levels of caffeine at 2 to 5 % of dry weight (Vuong and Roach 2014). Besides, the world production is estimated to grow at an annual rate of 4 %, and projected to reach 1.6 million tons by 2017.

There is an increasing demand for decaffeinated tea and coffee for those who would like to consume these beverages without caffeine (Gummadi et al. 2012). Caffeine can be extracted from the plants such as cacao, tea and coffee using solvents such as water, ethyl acetate, ethanol, carbon tetrachloride, methanol, chloroform, dichloromethane, acetone and supercritical CO₂ (Vuong and Roach 2014). Although decaffeination can be achieved efficiently using conventional solvents, use of organic solvents is discouraged owing to their carcinogenic effects. Hence, use of non-toxic solvents such as ethanol, water and supercritical CO₂ has been extensively explored for decaffeination of tea (Kim et al. 2008). Selective extraction of caffeine from black and green tea employing supercritical CO₂ has been reported (Icen and Guru 2010; Park et al. 2012). The loss of catechins such as epicatechin (EC), epicatechin gallate (ECG), epigallocatechin (EGC) and epigallocatechin gallate (EGCG) can be minimized by optimizing the extraction pressure and temperature of CO₂ during decaffeination (Chang et al. 2000; Gadkari and Manohar 2015).

The design of the supercritical CO₂ decaffeination process with minimum loss of catechins depends upon the ability to predict the solubility of caffeine in supercritical CO₂ (Coimbra et al. 2006). Solute solubilities in supercritical CO₂ is not easy to predict due lack of accurate models to predict equilibrium solubilities of complex compounds (Jha and Madras 2004). Solubility measurement in supercritical CO₂ is the first step to determine the viability of supercritical fluid extraction (SFE) process, and thermodynamic modeling can provide feasibility analysis and reduce the number of experimental measurements required (Burgos-Solorzano et al. 2004). The most common models used for correlating solid-supercritical phase equilibria are cubic equations of state (EOS), non-cubic EOS, activity coefficient models, semi-empirical and empirical correlations based on density, pressure, and temperature

(Coimbra et al. 2005). Peng-Robinson (PR), Redlich–Kwong (RK) and Soave-Redlich-Kwong (SRK) models are the most commonly used cubic EOS for solubility studies which are derived from the van der Waals family together with mixing and combining rules (Coimbra et al. 2005; Peng and Robinson 1976). The above referred EOS models require one or more temperature-dependent interaction parameters that must be correlated from the experimental solubility data (Coimbra et al. 2006). These EOS models require critical pressure (P_c), critical temperature (T_c), critical volume (V_c) and Pitzer's acentric factor (ω) of solute that are not always available in the literature and need to be experimentally found in many cases. To avoid such difficulties and complicated computational techniques, most researchers prefer to employ empirical correlations such as density based correlations like Chrastil, Jouyban and Mendez-Santiago-Teja models (Chrastil 1982; Mendez-Santiago and Teja 2000; Jouyban et al. 2002a, b).

Even though there are some reports on solubility of pure caffeine in supercritical CO₂, there has been no such study on caffeine solubility in a real natural system like fresh tea leaves. The major objective of the works is to develop the process of decaffeination for fresh tea leaves and to understand the behavior of caffeine solubility during extraction with application of theoretical and empirical models. Results were compared to the solubility of pure caffeine reported in the literature (Burgos-Solorzano et al. 2004; Ebeling and Franck 1984; Johannsen and Brunner 1994; Li et al. 1991; Saldana et al. 1999). Experimental solubility data were also correlated using well known density-based empirical correlations (Chrastil, Del Valle and Aguilera, Gordillo, Yu, Jouyban, and Modified Teja models) as well as by the theoretical models such as PR, SRK and RK EOS.

Materials and methods

Material

Fresh green tea leaves (*Camellia sinensis* L.) were procured from M/s Dollar Tea Estate, Ooty, India. The leaves were stored at 253 K in a deep freezer (150DL, Blue star, India) until further use. Pure caffeine (99 %) was obtained from Sigma-Aldrich Company Ltd., Bangalore, India. Carbon dioxide (99 %) was procured from M/s Kiran Corporation, Mysore, India. Absolute ethanol, methanol, chloroform, ethyl acetate and HPLC grade solvents were purchased from M/s Merck Chemicals, Mumbai, India.

Supercritical CO₂ extraction

Extraction was carried out in a pilot scale high pressure system (NOVA Swiss WERKE AG, Switzerland) designed for a working pressure up to 100 MPa and temperature up to

373 K. A detailed description about working of the system along with a schematic diagram is given elsewhere (Zarena et al. 2012). Supercritical CO₂ at pressures from 15 to 35 MPa and temperatures from 313 to 333 K was used as an extraction solvent. The frozen tea leaves were ground to a particle size in the range of 1 to 1.5 mm in an analytical mill (A10, IKA, Germany) prior to extraction. Dry ice was added to tea leaves while grinding. One hundred grams of crushed frozen tea leaves were loaded to the high pressure system with an injection of 1.2 % (w/w) of ethanol as cosolvent into the extractor vessel, where CO₂ is continuously circulated through a closed loop system. Fractions were collected at predefined time intervals up to 9 h extraction and weighed in an analytical balance (AT-201, Mettler, USA). The flow rates of CO₂ were measured by a flow meter and the amount of CO₂ used for extraction was indirectly calculated from the calibration chart provided by the manufacturer.

Solubility determination

The techniques available for estimation of solubility of components in supercritical fluid (SCF) are dynamic, static and recirculation methods. Most of the solubility measurements in SCF reported in the literature were based on the dynamic method (Ismadji and Bhatia 2003), and the same has been preferred in this study because of its simplicity. The density of supercritical CO₂ varied between 603 and 934.5 kg/m³ depending on pressure and temperature. Superficial velocity calculated from flow rate and superficial cross sectional area of extractor vessel was found to be between 2.9×10^{-5} and 4.6×10^{-5} m/s. An assumption was made that saturation of solute into the CO₂ was attained at these low velocities. The velocity employed in our study was comparable to the velocities reported in the literature dealing with dynamic method of solubility measurement (Danielski et al. 2007; Ozkal et al. 2005). Extraction curves are represented by the amount of CO₂ used for extraction and amount of caffeine extracted (Figs. 1 & 2). A second order polynomial equation was obtained fitting to the experimental data, and a straight line was drawn through the linear portion of the curve in order to find the initial slope (Danielski et al. 2007; Ozkal et al. 2005). Solubility values determined as weight fractions (kg caffeine/kg CO₂) were converted to mole fractions as required in the modeling equations.

Theoretical and empirical modeling

Theoretical models as well as empirical models were employed to predict and correlate the solubilities of solute in supercritical CO₂. Even though there are more than 40 different forms of equations of state and 15 various mixing rules available in the literature, well known theoretical models such as PR, SRK and RK EOS listed in Table 1 are only employed

for the solubility estimation. In the fluid–solid phase equilibria, the mole fraction of solute in the fluid phase can be obtained from the thermodynamic relationship shown in Eq. (1). There are many assumptions in the application of EOS to the experimental data for the estimation of solubility of a solute:

1. The system consists of CO₂ (component 1) and solute (component 2).
2. The component 2 is assumed to be insoluble in the component 1.
3. The fugacity of solute in solid phase is equal to the fugacity of solute in the fluid phase.
4. The molar volume of the solute is independent of pressure.
5. Solid phase is incompressible.
6. The fugacity coefficient of the solute at saturation is unity.

$$y_2 \varphi_2^F P = P_2^S \varphi_2^S \exp \left(\int_{P_2^S}^P \frac{v_2^S}{RT} dP \right) \quad (1)$$

The solid molar volume (v_2^S) is approximately constant with pressure and the fugacity coefficient (φ_2^S) is nearly equal to 1. Therefore, the mole fraction of solute in supercritical CO₂ (y_2) in Eq. (1) can be integrated and rewritten as below (Prausnitz et al. 1986):

$$y_2 = \frac{P_2^S \exp \left(\frac{P v_2^S}{RT} \right)}{\varphi_2^F P} \quad (2)$$

The steps involved in predicting the solubility using theoretical models are given below:

1. The experimental data such as CO₂ pressure, temperature, and experimental mole fractions of solute were the inputs for Phase Equilibria software (PE2000 ver 2.085, TUHH, Hamburg, Germany).
2. The critical values of T_c, P_c and acentric factor (ω) for solute was estimated by using group contribution methods such as Lydersen, Joback, Kincewicz-Reid and Fedors. Critical properties of CO₂ were taken from literature (Manohar and Kadimi 2011).
3. The pure component parameters “a” and “b” of PR-EOS (Table 1) were estimated.
4. Interaction parameter “k_{ij}” value was assumed in the beginning of iteration.
5. The parameters “a” and “b” for mixture (solute + CO₂) were calculated on the basis of van der Waals mixing rules.
6. The cubic equation of state was solved for finding compressibility factor. The fugacity coefficient of the solute was calculated and predicted solubility, y_{pred} was then determined.

Fig. 1 Effect of extraction temperatures on caffeine yield (% w/w) in supercritical CO₂ at pressures **a** 15 MPa; **b** 25 MPa; **c** 35 MPa

7. Steps 5 to 6 were repeated for each pressure and then deviation from experimental solubility was calculated.

The procedure (steps 5–6) was repeated by varying the k_{ij} parameter so that the average absolute relative

Fig. 2 Overall extraction curves of caffeine as a function CO₂ used at various temperatures and pressures **a** 15 MPa; **b** 25 MPa; **c** 35 MPa

Table 1 Theoretical models employed in this work

Model	Equation	Reference
General EOS	$y = \frac{P^{sat}}{P} - \frac{1}{\varphi_2^{sat}} \exp \left[\frac{v_2 (P - P_2^{sat})}{RT} \right]$	(McHugh and Krukonis 1994)
PR	$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$	(Peng and Robinson 1976)
SRK	$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$	(Mukhopadhyay 2010)
RK	$P = \frac{RT}{v-b} - \frac{a/\sqrt{T}}{v(v+b)}$	(Mukhopadhyay 2010)

deviation (AARD) reaches the minimum for the entire set of experiments.

$$\text{AARD, \%} = \frac{100}{N} \sum_{i=1}^N \frac{|y_{\text{exp}} - y_{\text{pred}}|}{y_{\text{exp}}} \quad (3)$$

Where, y_{exp} is the experimental solubility; y_{pred} is the predicted solubility and N is the total number of experiments.

- The calculations from step 3 were repeated applying SRK-EOS and RK-EOS (Table 1)

The enhancement factor (E), the ratio of the solubility of a solute in a supercritical fluid to the solubility in an ideal gas, was obtained by using following equation:

$$E = \frac{y_{\text{pred}}}{y_{\text{ideal}}} \quad (4)$$

where y_{pred} , predicted solubility at supercritical conditions, $y_{\text{ideal}} = \frac{P_s}{P}$, P_s = vapor pressure of solute, and P = extraction pressure.

The theoretical models are complicated in nature for computation requiring the solute properties such as critical properties, acentric factor, molar volumes and vapor pressure which often cannot be easily determined experimentally. The empirical models (Table 2) avoid the calculation of critical properties of the solute and supercritical fluid. One of the best known and commonly used empirical equations is proposed by Chrastil (1982) which is based on the hypothesis that solute molecule will associate with k molecules of solvent and form solvato complex molecule. The main difference between these empirical models is the number of parameters employed in the equation. The number of parameters in these models (Table 2) vary between 3 and 6. Determination of coefficients (parameters) of the empirical models was carried out using Microsoft Excel software. The solubility values obtained using theoretical models and empirical models were compared using AARD and coefficient of

determination (R^2) as criteria in order to arrive at the best model suitable for predicting solubility of caffeine in supercritical CO_2 .

Solubility in conventional solvents

Apart from the determination of caffeine solubility in supercritical CO_2 , it is also desirable to know the solubility behavior of caffeine in conventional solvents. Solubility of pure caffeine (99 %) was measured in ethanol, methanol, ethyl acetate, chloroform and water. The experiments were carried out at three different temperatures (298, 308 and 313 K) under atmospheric pressure (0.1013 MPa). Glass vials with stopper, and magnetic stirrer (Cole-Parmer, USA) were used to prepare a saturated solution (about 10 ml) of caffeine. The vials were stoppered and sealed with parafilm to prevent evaporation of solvents, and then these vials were brought to a constant temperature (298, 308 and 313 K) in thermostatic water bath. The solutions in vials were continuously stirred at least for 4 h to ensure solid–liquid phase equilibrium. Then, undissolved solids were allowed to settle down without disturbing the system for 4 h, and approximately 2 g of the clear saturated solution was sampled out into pre-weighed petri plates. The petri plates were then kept in an oven (378 K; 5 h) for removing the solvent and then followed by weighing till constant reading was obtained on a precision weighing balance (Model AT201, METTLER, Switzerland) having an accuracy of ± 0.01 mg. All the solubility experiments were conducted in duplicates and solubility was reported on mole fraction basis.

Determination of caffeine

The caffeine content of fresh tea leaves was determined by extracting with 50 % (v/v) ethanol at 353 K for 80 min, and the aliquots were filtered through 0.22 μm filter before injecting to HPLC system. The HPLC analysis was performed on Shimadzu LC-10A (Japan) with PDA detector. The elution was carried out in RP C-18 (Waters, 4.6×250 mm) column. Mobile phases included an aqueous solution of 0.2 % acetonitrile (A) and methanol (B), and it was degassed prior to pumping into the system. Gradients of 0–50 % B for 0–12 min and 50–100 % B for 13–20 min were used (He et al. 2009). The flow rate of the solvent system was kept constant at 1.2 ml min. The PDA acquisition wavelength was set in the range of 200–600 nm, but the display wavelength was kept as 280 nm. Instrumentation control, data collection and analysis were done using the LC solution software. Identification and quantification were made by peak integration using the external standard method.

Table 2 Empirical models used in the present study

Model	Equation	Parameters	Variables	Reference
Chrastil	$\ln S = k \ln \rho + \frac{a}{T} + b$	k, a, b	S, T, ρ	(Chrastil 1982)
Del Valle and Aguilera	$\ln S = B_0 + \frac{B_1}{T} + B_2 \ln \rho + \frac{B_3}{T^2}$	B ₀ - B ₃	S, T, ρ	(Del Valle and Aguilera 1988)
Yu	$y_2 = C_0 + C_1P + C_2P^2 + C_3PT(1 - y_2) + C_4T + C_5T^2$	C ₀ - C ₅	y ₂ , P, T	(Yu et al. 1994)
Gordillo	$\ln y_2 = D_0 + D_1P + D_2P^2 + D_3PT + D_4T + D_5T^2$	D ₀ - D ₅	y ₂ , P, T	(Gordillo et al. 2003)
Jouyban-A	$\ln y_2 = M_0 + M_1P + M_2P^2 + M_3PT + \frac{M_4T}{P} + M_5 \ln \rho$	M ₀ - M ₅	y ₂ , P, T, ρ	(Jouyban et al. 2002a, b)
Jouyban-B	$\ln y_2 = K_0 + K_1\rho + K_2P^2 + K_3PT + \frac{K_4T}{P} + K_5 \ln \rho$	K ₀ - K ₅	y ₂ , P, T, ρ	(Jouyban et al. 2002a, b)
Modified Teja model	$T \ln y_2 P = A + B\rho + CT$	A, B, C	y ₂ , P, T, ρ	(Mendez-Santiago and Teja 2000)

Results and discussions

Extraction of caffeine in supercritical CO₂

The initial caffeine content of fresh leaves was 3.67 ± 0.05 (% w/w). Figure 1 shows the effect of supercritical CO₂ extraction pressures (15, 25, 35 MPa) and temperatures (313, 323, 333 K) on caffeine yield (% w/w). The increasing trend of caffeine yield (% w/w) with an increase in temperature at extraction pressures 15 to 25 MPa was observed. The highest caffeine yield of 3.11 % was obtained at 25 MPa and 333 K. At pressure 35 MPa and 333 K, there was 18 % reduction in yield compared to yield at 25 MPa and 333 K. This phenomenon may be attributed to reduced solubility of caffeine at higher pressures and discussed further in a subsequent section.

Solubility of caffeine in supercritical CO₂

Critical properties of caffeine estimated using group contribution methods such as Joback, Lydersen and Kincewicz-Reid method are presented in Table S1. There is no consistency in the reported values of critical properties as estimated by different methods. Caffeine content as a function of CO₂ consumed for all pressures and temperatures are presented in Fig. 2. Solubility of caffeine calculated from the initial slopes of these plots for all the pressures and temperatures are listed in Table 3. The highest solubility of 149.55×10^{-6} (mole fraction) was obtained at 25 MPa and 323 K. At 35 MPa, the solubility of caffeine decreased when compared to solubility at 15 MPa and 25 MPa for all the temperatures of the study (Fig. 3). The solubility of caffeine in supercritical CO₂ increased in response to the increasing temperature due to the dominant effect

Table 3 Comparison of solubilities of caffeine from this study with literature

P, MPa	T, K	Solubility (mole fraction, $\times 10^6$)							
		Present study ^a	Stahl and Schilz 1979 ^b	Ebeling and Franck 1984 ^b	Li et al. 1991 ^b	Johannsen and Brunner 1994 ^b	Saldana et al. 1999 ^b	Tzvetkova 2001 ^b	Burgos-Solorzano et al. 2004 ^b
15	313	60.96 ± 0.20	134	—	131	295	201	—	150
	323	83.62 ± 0.38	—	78	—	—	171	24.3	—
	333	106.28 ± 1.23	65	49.3	50	304	—	35.6	—
25	313	64.81 ± 0.49	—	—	197	401	389	—	—
	323	149.55 ± 1.14	—	—	—	—	410	—	—
	333	125.31 ± 0.78	—	—	306	512	—	—	—
35	313	44.19 ± 1.03	—	—	360	544	—	—	—
	323	87.01 ± 0.56	—	—	—	—	—	—	—
	333	66.62 ± 0.45	—	—	414	722	—	—	—

^a Solubilities of caffeine (mean $\pm$ SD) in presence of tea leaf matrix with moisture in CO₂

^b Solubilities with respect to pure caffeine in CO₂

Fig. 3 Experimental solubility isotherm with respect to different pressures

of the increased vapor pressure of the solute at higher temperature although it leads to decreased solvent density and reduced dissolving power of the solvent (Kim et al. 2008; Park et al. 2012). Such a phenomenon is visible for caffeine solubility as seen in Fig. 3 where isotherm solubility with respect to pressure is shown.

The experimental solubility data of caffeine in supercritical CO_2 (present study) was also compared with the solubility data of pure caffeine in supercritical CO_2 available in the literature (Table 3). It should be noted that some of the reported literature data as presented in Table 3 have been sourced from graphs, and the data have been appropriately converted to the mole fraction. Surprisingly, literature data on pure caffeine solubility is not consistent, and there is a wide variation in the reported values of solubility which range from a low of 24.3×10^{-6} to a high of 722×10^{-6} . Generally, there is an increase in solubility reported in the literature as both pressure and temperature increased. But, a few reports indicated a decrease of solubility with increase in temperature at 15 MPa (Stahl and Schilz 1979; Ebeling and Franck 1984; Saldana et al. 1999). In contrast, the solubility reported in our study are lower than the literature values particularly at higher pressures. The lower values of caffeine solubility in the present study as compared to the literature values may be attributed to the interaction of other components of the tea matrix on solubility of caffeine (Park et al. 2007; Kim et al. 2008; Vuong and Roach 2014). Figure 3 showed that when pressure increased from 15 to 25 MPa, the solubility of caffeine also increased. But, further increasing the pressure from 25 to 35 MPa, the solubility is decreased by 1.6 times than that of the solubility found at 15 MPa. This trend is intriguing and may only be attributable to the complex nature of tea matrix (Ghoreishi and Heidari 2012).

Table 4 Enhancement factor and interaction parameters as predicted by various EOS

P (MPa)	Temperature (K)			AARD, %
	313	323	333	
PR	15 3.5767×10^5	15 1.1783×10^5	15 1.8621×10^4	35 4.2701×10^5
SRK	25 3.1684×10^5	25 1.5817×10^6	25 1.9441×10^6	25 1.6129×10^5
RK	35 2.7020×10^6	35 3.5820×10^6	35 1.9442×10^6	35 4.2701×10^5
	Interaction parameter (k_{ij})			
PR	0.1783			4.2701 $\times 10^5$
SRK	0.1488			4.1098 $\times 10^5$
RK	0.4072			15.52

Fig. 4 Caffeine solubility in supercritical CO₂: experimental solubility and predicted values as per RK model and Gordillo model

Prediction of caffeine solubility using theoretical models and empirical models

Solubility data of caffeine in supercritical CO₂ is important for designing the process of decaffeination. The prediction of such data becomes complicated because of the presence of i) a large number of components in the matrix and ii) the cellulose matrix which considerably influences the solubility characteristics in supercritical CO₂.

Theoretical models

The solubility of caffeine (component 2) in supercritical CO₂ (component 1) was obtained from fluid–solid phase equilibria as mentioned in experimental section. Acentric factor (ω) was

estimated based on the Lee-Kesler correlation. The enhancement factors and interaction parameter k_{ij} values as predicted by all theoretical models and % AARD values obtained are presented in Table 4. It was observed that PR and SRK models gave larger AARD (51.40 % and 52.40 %), therefore these models are not suitable to predict the solubility behavior of caffeine in supercritical CO₂ during the decaffeination process. On the other hand, RK model was well in agreement to our experimental solubility values with only 15.52 % AARD. Figure 4 shows the fitness of RK-EOS model to our experimental solubility values with coefficient of determination 0.62. Interaction parameter k_{ij} reported in our study was between 0.1488 and 0.4072 whereas k_{ij} reported in the literature was from -0.4355 to -0.3895 (Bozorgmehr and Housaindokht 2009). Kurnik and Reid (1982) have cautioned about the limitations of equation of state models when applied to polar solutes. Since caffeine is a polar molecule, fitting of EOS models to such a system with many polar molecules in green tea is to be carried out with a lot of cautions. The enhancement factor which reflects the deviation of the real gas from ideal gas pressure was in the order of 10^5 to 10^6 in our studies (Table 4). High enhancement factors between 10^3 and 10^6 are quite common at supercritical fluid conditions and enhancement factors as high as 10^{10} have been reported in the literature (Jessor and Leitner 2008; McHugh and Krukoniš 1994). Very large enhancement factors in the order of 10^{18} order have been reported for bakuchiol (Manohar and Kadimi 2011) which indicate high non-ideal behavior of the system.

Empirical models

Computation of the solubility estimation is simpler using empirical correlations based on density models such as Chrastil, Gordillo, Yu, Jouyban and Mendez-Santiago-Teja as listed in

Table 5 Coefficients and AARD values for empirical models

Model	Coefficients and their values						AARD, %
Chrastil model	k	a	b				
	2.91	−0.46	-2.50×10^3				2.69
Del Valle and Aguilera	B_0	B_1	B_2	B_3			
	-3.47×10^2	2.24×10^5	−0.51	-3.65×10^7			2.50
Gordillo	D_0	D_1	D_2	D_3	D_4	D_5	
	-3.76×10^2	0.30	-3.94×10^{-3}	-3.63×10^{-4}	2.23	-3.39×10^{-3}	0.96
Yu	C_0	C_1	C_2	C_3	C_4	C_5	
	-3.12×10^{-2}	3.69×10^{-5}	-3.84×10^{-7}	-5.75×10^{-8}	1.89×10^{-4}	-2.87×10^{-7}	11.93
Jouyban-A	M_0	M_1	M_2	M_3	M_4	M_5	
	-1.48×10^2	3.60	-4.90×10^{-2}	-1.16×10^{-4}	2.01	8.14	1.69
Jouyban-B	K_0	K_1	K_2	K_3	K_4	K_5	
	-1.51×10^2	-4.92×10^{-2}	3.16×10^{-3}	-8.57×10^{-4}	−0.37	2.87×10^1	1.70
Modified teja model	A	B	C				
	6.77×10^5	-2.81×10^2	-1.63×10^3				10.77

Table 2 (Chrastil 1982; Gordillo et al. 2003; Jouyban et al. 2002a; Mendez-Santiago and Teja 2000; Yu et al. 1994). Coefficients for the empirical models along with respective AARD values are presented in Table 5. All empirical models produced very good agreement between experimental and the predicted data with AARD ranging from 0.96 to 11.93 %. Gordillo model with 6 parameters regressed the best to the experimental data with the least AARD of 0.96 %. One can choose semi-empirical Chrastil model with only 3 coefficients which fitted experimental data with AARD of 2.69 %. Chrastil model has been the favorite of the researchers since it is applicable to various types of compounds. Figure 4 compares the prediction of caffeine solubility by Gordillo model with the solubility predicted by RK-EOS model. It can be observed that empirical models were the most suitable to correlate the solubility of caffeine in supercritical CO₂ in the range of pressure and temperature studied, because it avoids the complex process of calculating the critical parameters of the desired compound such as a critical pressure, temperature and acentric factor which are required to predict the solubility using theoretical models.

Solubility of caffeine in conventional solvents

Within the temperature range of the measurement, solubility of pure caffeine in the various solvents increased with increase in temperature (Table S2). The experimental solubility of caffeine in ethanol, methanol, ethyl acetate, chloroform and water were also compared with the literature data (Table S2). There is an agreement between solubilities reported in the present study and those reported in the literature (Shalmashi and Golmohammad 2010). The solubility of caffeine decreased from chloroform, ethyl acetate, water, methanol to ethanol (Table S2). Thus, chloroform was found to be the best solvent to separate and purify caffeine from the matrix of raw material (Guru and Icen 2004). Caffeine solubility in chloroform is about 13 times more than the solubility in water. The use of conventional solvent for decaffeination of green tea is not advised because along with caffeine some important catechins were leached out in the extract compared to supercritical CO₂ based decaffeination process (Icen and Guru 2010; Kim et al. 2008; Vuong and Roach 2014). Decaffeination using supercritical CO₂ is preferred over conventional solvents since about 85 % (w/w) of caffeine can be removed selectively using supercritical CO₂ with less loss of catechins, known much for their antioxidant properties.

Conclusions

The solubility of caffeine in supercritical CO₂ at pressures 15 to 35 MPa and temperatures 313 to 333 K varied from 44.19×10^{-6} to 149.55×10^{-6} mol fraction with the highest

solubility found at 25 MPa and 323 K. It was observed that solubilities of pure caffeine in conventional solvents were 61 times higher than that in supercritical CO₂. In comparison with solubility values of pure caffeine in supercritical CO₂ found in the literature, experimental solubility values reported in this work were about 2 times lesser owing to caffeine present in the matrix of fresh tea leaf. While theoretical equation of state models such as SRK and PR were not suitable for prediction of solubility. RK model led to better agreement with experimental values with 15.5 % AARD. The experimental solubilities correlated to empirical models well within 12 % AARD, but Gordillo model was found to be the most efficient to estimate solubility with only 0.96 % AARD.

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