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11**Fluid Phase Equilibria** 358 **(2013)** 220–225 **Contents lists available at ScienceDirect Fluid Phase Equilibria journal homepage: www.elsevier.com/locate/fluid**

22**Catechin sublimation pressure and solubility in supercritical carbon dioxide Felycia Edi** Soetaredjoa, **Suryadi** Ismadjib,∗∗, **Maria Yuliana** Liauwa, **Artik Elisa**

Angkawijayaa,

7**Yi-Hsu Jua,∗ a Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Sec 4, Keelung** Road, **Taipei, Taiwan b Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia**

13**article info Article history: Received** 7 **February 2013 Received in revised form 6 August 2013 Accepted 8 August 2013 Available online 29** August **2013 Keywords:**

(+)-Catechin Solubility Sublimation pressure Density based correlation abstract Solubility of (+)-catechin in SC-CO2

2**was measured at several temperatures (313.15, 323.15, 333.15 and 343.15 K) and pressure in the range of 12–26 MPa** using ethanol as **the**

co-solvent (5 mol.%). The experimental data were used for the correlation of density dependent solute solubility parameters. The equations

3**of Chrastil, del Valle and Aguilera, Adachi and Lu,** González, and **Méndez-Santiago and**

Tejawere fitted very well for the solubility of (+)-catechin. The rate of mass loss of (+)-catechin showed that its sub- limation pressure is very low, an indication of the stability of the compound. Thermogravimetric analysis was used to determine the sublimation pressure. © 2013 Elsevier B.V. All rights reserved. 1. Introduction Supercritical fluid extraction is superior to conventional extrac- tion techniques because the absence of organic solvents and operates at lower temperature which reduces the incidence of degradation of the product and does not require subsequent purifi- cation steps. Supercritical fluids are attractive solvents because they have diffusivities between those of gases and liquids, densi- ties much greater than those of typical gases and slightly less than those of organic liquids, and viscosities comparable to gasses [1]. Supercritical carbon dioxide (SC-CO2) is commonly used for most of the applications because it has a relatively low critical pressure (7.374 MPa) and critical temperature (304.12 K). The other reasons are

17**it is non-toxic, non-flammable,** and **non-explosive; and**

it is spontaneously separated from the extracted compounds by reduc- ing the pressure and/or the temperature. The knowledge of solubility of a compound in SC-CO2 is cru- cial for evaluating the feasibility of supercritical separation of the compound and for establishing optimum operation condition. The solubility of a solid in SC-CO2 depends on its polarity. SC-CO2 is not a good solvent for polar organic compounds due to its low of polar- ity and its lack of specific solvent-solute interactions. The addition ∗ Corresponding author. Tel.: +886 2 2737 6611; fax: +886 2 2737 6644. ∗∗ Corresponding author.

24**Tel.: +62 31 3891264; fax: +62 31 3891267. E-mail** addresses: **suryadiismadji@yahoo.com (S. Ismadji),**

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012 of a small amount of proper co-solvent to SC-CO2 can increase its solvent power dramatically. The concentration of added co-solvent should be less than 15 mol.% [2,3]. Co-solvent

4**is usually one of the common liquid solvents**

such as

4**benzene, methylene chloride, carbon tetrachloride, hexane, acetone, methanol, ethanol, toluene and water**

[1,3–8]. The role of co-solvent has been limited in the area of food and pharmaceutical

4**because of the toxic nature of most organic solvents and the associated problem of removing** co- solvent **residue completely from the processed material.**

Among organic solvents, ethanol is appropriate because it is polar and per- mitted in food industries.

21**Catechin ((2R,3S)-2-(3,4-Dihydroxyphenyl)-3,4-dihydro- 1(2H)-benzopyran-3,5,7-triol)**

is a phytochemicals in the group of flavonoids. It is abundantly in various plants such as tea [9–11], grape [12–15] and cocoa [16]. Catechin is also found in the sago (Metroxylon sago) pith. During sago starch extraction, catechin is oxidized by latent polyphenol oxidase and the color of the wastewater become dark brown with strong odor [17]. Since catechin has many benefits on health especially as an antioxidant, the separation of catechin will not only reduce water pollution but also obtain valuable compound. Catechin solubility in SC-CO2 was studied by Berna et al. using ethanol (5–30 mol.%) as the co-solvent operated at 313 K and 8–12 MPa [4]. TheSC-CO2 extraction of catechin without using co- solvent was not feasible since only trace amount was extracted. However, the presence of a high amount of ethanol in SC-CO2 (≥15 mol.%) will change the supercritical condition to subcrit- ical since ethanol has a high critical temperature of 513.9 K F.E. Soetaredjo et al. / Fluid Phase Equilibria 358 (2013) 220–225 221

6**Table 1 Specification of chemicals used in** this **study. Chemical name Source Initial mass fraction purity Purification method Final fraction purity**

Caffeine (+)-Catechin hydrate Sigma–Aldrich Sigma–Aldrich ≥98 wt.% ≥99.9 wt.% Ethanol Liquid CO2 Aneka Gas Pty. Ltd., Indonesia Food grade ≥99.99 wt.% Merck, Germany ≥99.9 wt.% None Recrystallized twice and tempered at 110 ◦C to obtain the ?-anhydrous phase (form II) as described by Pinto and Diogo[26]. None None ≥98 wt.% ?-Anhydrous caffeine ≥99.9 wt.% ≥99.9 wt.% ≥99.99 wt.% [2,3,18,19]. In this work, catechin solubility in SC-CO2 was investi- gated in a wider range of pressure and temperature (12–26 MPa and 313.15–343.15 K, respectively) than the published data.

11**In order to** maintain **the** supercritical condition **of carbon dioxide,** the **co-**

solvent ethanol concentration was kept at 5 mol.% [20]. The solubility profile of a compound in SC-CO2 is influenced by its density as well as pressure and temperature. Density based correlation was developed based on the observation that the loga- rithm of the solubility is linearly dependent on the density [21,22]. Chrastil [23] was the first in developing a semi-empirical solu- bility correlation based on this approach, taking into account the dependence of solubility upon temperature. Although the Chrastil model is limited to low solubility and temperature, it has the advantage of avoiding the difficulty of determination of equation of states parameters, especially for high molecular mass solutes [24]. Another density based correlation was proposed by Méndez- Santiago and Teja (MST) [25] for ternary co-solvent systems by taking account of sublimation pressure of the solute. The objec- tive of this study was to measure the sublimation pressure and

5**the solubility of** catechin **in SC-CO2** with ethanol **as**

the co-solvent and then correlated the data using density based model. 2. Experimental 2.1. Materials (+)-Catechin and caffeine were obtained from Sigma Aldrich (Singapore). (+)-catechin was used without any further treat- ment. Analytical grade ethanol was supplied by Merck (Darmstadt, Germany) and used as a co-solvent in SC-CO2 and a solvent to collect extract for further analysis. Food grade carbon dioxide was supplied as liquid CO2 by Aneka Gas Pty. Ltd., Indonesia. Table 1 shows the specification of chemicals used in this study. 2.2. Sublimation pressure Thermogravimetric analysis (TGA) is usually used to study the thermal stability of a material. In addition, it can be used to study its phase transitions such as sublimation and the related prop- erties such as vaporpressure [27–29]. TGA provides a fast and reliable method to study a number of compounds that are ther- mally stable up to their melting point at ambient pressure [27,29]. Using this method, the evaporation rate of a compound determined under isothermal conditions is directly related to its vapor pressure [27–31]. In this study, the rate of sublimation was measured using a highly sensitive microbalance in TGA (Perkin Elmer Diamond

23**TG/DTA).** The **measurements were carried out**

in dynamic

23**nitrogen atmosphere with a flow rate of 40 ml/min.**

The amount of the sam- ple was kept low (approximately 3 mg) and it should fully covered the bottom of the platinum pan (ø5 mm) in order to minimize ther- mal gradients. The experiments were conducted at a temperature range from 423 to 443 K (±0.01 K) under isothermal conditions. The heating temperature was rising linearly at 40 K/min from ambient to the targeted temperature and then maintained at that tempera- ture. Mass loss rates (dm/dt) were determined from a region where the temperature was constant.

10**Analysis of the** gravimetric **data is based on the**

mass loss rate of a substance that is related to its vapor pressure and can be expressed by the Langmuir equation √ P = 2?R dm ¸ × dt × T M (1) √ where P is the vapor pressure, R is the universal gas constant, ¸ is the vaporizations coefficient (usually assumed to be 1 in vacuum condition),

10**dm/dt is the rate of mass loss**

with respect to time, T is the absolute temperature and M is the molecular weight of the substance in the vapor phase.

10**In the case of a material** volatiliz- ing **into a flowing gas stream at 1 atm,**

¸ cannot be assumed as unity. The value of ¸

12**is sample independent and can be evaluated by calibration with substances of known** vapor **pressures.** In this study **the**

calibration was conducted using ?-anhydrous caffeine. The vaporization rate of caffeine was determined between 423 and 433 K (the same temperature range used for catechin) [29]. The lin- ear logarithmic relationship between vapor pressure and mass loss rate [29] is determined as: ln P = a × ln dt + b dm (2) a and b are constants specific for the instrument and for the exper- ( ) imental procedures as described above. Estimating from the plot with R2 = 0.99, the value of a and b are 1.135 and 0.255, respectively. These values are independent of material and temperature range but depend on the equipment and the sample crucible [29,30]. 2.3. Solubility of catechin in SC-CO2 The solubility of catechin in SC-CO2 was performed in a static system. The system includes a 50 ml equilibration column (Swagelok, USA), a

1**high pressure pump** (Eldex **AA-100-S-2-CE, USA)** and pressure transducer **(Druck PTX 611, USA)** with **a** digital process indicator **(Druck DPI 280, USA)** which gives **pressure**

mea- surement uncertainties of ±0.01 MPa. A heating chamber (Oven Memmert, Germany) was used to control temperature to within ±1 K. The maximum working pressure and temperature of the sys- tem are 40 MPa and 373.15 K, respectively. All fitting

1**and tubing used in the system were made of stainless steel** 316 **(Swagelok, USA).**

A known mass of (+)-catechin (100 mg) and ethanol (5 mol.%) were added in a sample holder in the equilibration column. The heating chamber was heated to a desired temperature (313.15, 323.15, 333.15, or 343.15 K).

1**Liquid CO2 was** subsequently **pumped** into **the** system **using a high pressure pump**

until a targeted pres- sure was achieved (12–26 MPa). After equilibrium condition was achieved in 4 h, the sampling tube (1 ml) was disconnected from the system. The sample in the sampling tube was released, and the CO2 containing catechin flowed into a collector containing a known amount of ethanol while the CO2 was released into the air. At least 222 F.E. Soetaredjo et al. / Fluid Phase Equilibria 358 (2013) 220–225 Table 2 100 Mass loss rate and vapor pressure of (+)-catechin from TGA measurements. 0 Temperature (K) dm ?g dt min P (Pa) 80 423 0.3 ( ) 0.3 -2 428 0.8 0.9 433 1.4 1.8 438 2.5 3.6 3.8 5.8 Weight % (%) 60 -4 443 40 -6 three replications of trails were carried out for every set of temper- 20 -8 ature and pressure. The equilibrium composition was represented Decomposi?on temperature by average of the three replications. The determination of catechin Derivative weight % (%/min) was based on the method of Zuo et al. [32] by using a HPLC (JASCO 0 -10 300 400 500 600 700 800 900 1000 1100 HPLC PU-2089 plus) with a UV-vis detector (UV-2077 plus). T (K) 3. Results and discussion Fig. 2. Thermogravimetric curves of (+)-catechin. Weight loss (−). Derivative of weight loss (–). 3.1. Sublimation pressure of catechin 2.5 The mass loss rates and vapor pressure of (+)-catechin at dif- 2.0 ferent temperatures are shown in Table 2. The vapor pressure of (+)-catechin was calculated using Eq. (2). The sublimation kinetics 1.5 of (+)-catechin was calculated using the Arrhenius equation [29]: 1.0 ln dt = ln A − RT dm E a (3) ln P (Pa) 0.5 where dm/dt is the mass loss rate of catechin, A is the pre- 0.0

14**exponential factor, Ea is the activation energy, R is the universal gas constant and T is the absolute temperature.** From **the plot of** 1 **/T**

-0.5 versus ln(dm/dt) as shown in Fig. 1 (R2 = 0.98), the activation energy -1.0 and the pre-exponential factor was determined as 194.43 kJ/mol and 54.238, respectively. -1.5 Clausius–Clapeyron equation describes the temperature depen- 0.00224 0.00226 0.00228 0.00230 0.00232 0.00234 0.00236 0.00238 dence of the vapor pressure: 1/T (1/K) ln P = − ?H 1 T + ?S Fig. 3. The plot of 1/T versus ln P for determining the Clausius–Clapeyron parame- R R (4) ters.

12**where ?H is the** standard **enthalpy** change **of sublimation** and ?S ( ) is **the** standard entropy **of**

sublimation. (+)-Catechin sublimes with- 3.2.

5**Solubility of** catechin **in SC-CO2** out decomposition in **the** temperature range used in this study since (+)-catechin decomposes above 1108 K (Fig. 2). The enthalpy Pressure and temperature of SC-CO2 determine its effectiveness of sublimation and entropy were determined from the plot of ln P as a solvent through affecting its density. The density of SC-CO2 at versus 1/T (R2 = 0.98) in Fig. 3 and their values are 220.74 kJ/mol various pressures and temperatures were calculated using the Stry- and 514.05 J/mol K, respectively. jek

1**and Vera modification of the Peng–Robinson equation of state** [33]. In **the**

measuring of solubility of catechin in SC-CO2, insignif- icant increase of catechin concentration in CO2 was observed after 2.0 3 h as shown in Fig. 4. The calculated density of SC-CO2 and the 1.5 ln(dm/dt) (µg/min) 1.0 0.5 0.0 -0.5 -1.0 -1.5 0.00224 0.00226 0.00228 0.00230 0.00232 0.00234 0.00236 0.00238 1/T (1/K) Fig. 1. The plot of 1/T versus ln(dm/dt) for determining the Arrhenius parameters. Fig. 4. Solubility of (+)-catechin in SC-CO2versus time at various pressures. According to Adachi and Lu, if Chrastil equation fitting is not as density and

16**shows the dependence of the solubility on** the **density.** (referred to as **in the**

Chrastil equation) is the exponent of the Adachi and Lu [35,36] proposed that the association number ture is ?H(T) = R(a′ + 2d/T). equation the variation of enthalpy of vaporization with tempera- sented in the parameter of a (a = ?H/R). In del Valle and Aguilera the

20**sum of heat of solvation and heat of vaporization**

of solute pre- with temperature. In Chrastil equation, the total reaction heat was to compensate for the variation of heat of vaporization of solute y1 = k′ exp b′ + a′ Chrastil equation in the form of Valle and Aguilera [34] proposed an empirical modification on the There are a number of modified Chrastil equations available. Del characteristic constant for a given pair of gas and solute. expresses an average equilibrium association number, which is a complex was not stoichiometric, so that the association constant k a and b are parameters. It was found that in most cases the solvato

1**is the density of gas, k is** an **association number, T is temperature,**

where y1 is the concentration of the solute in gas (mole fraction), y1 = k exp T + b Chrastil equation has the form tion can be calculated from the law mass action. The semi-empirical solvato complex, A + kB ↔ ABk, so that the equilibrium concentra- solute associate with the molecules of the gas in equilibrium with in developing such a correlation by assuming that molecules of the in correlating existing solubility data [22]. Chrastil [23] was the first knowledge of solute properties and was found to be very successful is linearly dependent on the density. This approach does not require oped based on the observation that the logarithm of the solubility are still needed. Semi-empirical solubility correlation was devel- or more adjustable fitting parameters, therefore, experimental data have fundamental basis. However, these correlations still need one atures. Some of these correlations are empirical, while the others and extrapolate solubility data to various pressures and temper- Several correlations have already been developed to correlate even though the density of SC-CO2 decreases. which cause

5**the solubility of** (+)-catechin **in SC-CO2**

to increase constant pressure, the viscosity and diffusivity of SC-CO2 increase

5**solubility of** (+)-catechin **in SC-CO2.** As **the**

temperature increases at increases with increasing pressure which result in an increase in the ically in Fig. 5. At constant temperature,

17**the density of SC-** CO2 Table **3** and **the solubility of** (+)-catechin **in SC-**

CO2 is shown graph- measured

5**solubility of (+)-catechin in** SC **-CO2** are presented **in**

Fig. 5. Solubility of (+)-catechin versus density of SC-CO2 at various temperature. y1.106 300 0 2 4 6 8 10 12 ((a 400 T) + T 2 d 500) ρ (g.L-1) 600 700 800

9**T= 313.15 K T= 323.15 K T= 333.15 K T= 343.15 K**

900 (6) (5) Table 3 Solubility of (+)-catechin in SC-CO2 with 5 mol.% of co-solvent and the SC-CO2 density. F.E. Soetaredjo et al. / Fluid Phase Equilibria 358 (2013) 220–225 Pa (MPa) Ta =

9**313.15 K T = 323.15 K T = 333.15 K T = 343.15 K**

19**(g l−3) 104** c1 **(g l−3)** 107 yb **(g l−**

3) 104 c1 (g l−3) 107 ya

19**(g l−3) 104** c1 **(g l−3)** 107 yb **(g l−**

3) 104 c1 (g l−3) 107 yb 12 669 1.30 ± 0.026 0.67 ± 0.013 537 1.55 ± 0.031 0.80 ± 0.016 417 1.59 ± 0.032 13 701 1.74 ± 0.035 0.89 ± 0.018 588 3.09 ± 0.062 1.60 ± 0.032 474 3.51 ± 0.070 14 727 2.43 ± 0.049 1.26

± 0.025 627 4.12 ± 0.082 2.12 ± 0.042 523 5.76 ± 0.115 15 750 2.66 ± 0.053 1.37 ± 0.027 659 5.69 ± 0.114 2.94 ± 0.059 563 10.14 ± 0.203 16 769 3.41 ± 0.068 1.76 ± 0.035 685 7.32 ± 0.146 3.78 ± 0.075 598 13.33 ± 0.267 17 787 3.62 ± 0.072 1.87 ± 0.037 709 9.02 ± 0.180 4.66 ± 0.093 627 18.40 ± 0.368 18 803 4.04 ± 0.081 2.08 ± 0.042 729 10.83 ± 0.216 5.59 ± 0.111 653 23.09 ± 0.462 19 818 5.06 ± 0.101 2.61 ± 0.052 748 13.70 ± 0.274 7.07 ± 0.141 675 28.71 ± 0.574 20 831 5.07 ± 0.101 2.62 ± 0.052 765 15.50 ± 0.310 8.01 ± 0.160 696 37.40 ± 0.748 21 844 5.59 ± 0.112 2.89 ± 0.057 780 17.68 ± 0.354 9.14 ± 0.182 714 43.92 ± 0.878 22 856 6.65 ± 0.133 3.43 ± 0.069 794 19.77 ± 0.395 10.21 ± 0.204 732 48.00 ± 0.960 23 867 6.68 ± 0.133 3.44 ± 0.069 808 20.05 ± 0.401 10.36 ± 0.207 747 58.02 ± 1.160 24 877 7.16 ± 0.143 3.70 ± 0.074 820 21.83 ± 0.436 11.28 ± 0.225 762 67.20 ± 1.343 25 887 8.25 ± 0.165 4.26 ± 0.085 832 26.40 ± 0.528 13.64 ± 0.273 775 73.97 ± 1.479 26 896 8.22 ± 0.164 4.25 ± 0.084 843 28.35 ± 0.567 14.65 ± 0.293 788 75.47 ± 1.509 0.82 ± 0.016 1.81 ± 0.036 2.97 ± 0.059 5.24 ± 0.105 6.89 ± 0.138 9.51 ± 0.190 11.93 ± 0.239 14.84 ± 0.297 19.33 ± 0.386 22.70 ± 0.454 24.80 ± 0.496 29.98 ± 0.599 34.72 ± 0.694 38.22 ± 0.764 38.99 ± 0.780 342 1.60 ± 0.032 390 3.67 ± 0.073 436 8.13 ± 0.162 478 7.50 ± 0.290 515 21.18 ± 0.423 549 31.54 ± 0.631 578 47.20 ± 0.944 604 55.84 ± 1.117 628 77.93 ± 1.559 649 89.25 ± 1.785 669 117.6 ± 2.351 687 124.2 ± 2.485 704 160.0 ± 3.200 719 166.5 ± 3.330 734 206.7 ± 4.133 0.83 ± 0.016 1.89 ± 0.038 4.20 ± 0.084 7.50 ± 0.150 10.94 ± 0.219 16.30 ± 0.325 24.39 ± 0.488 28.86 ± 0.577 40.27 ± 0.805 46.12 ± 0.922 60.76 ± 1.215 64.20 ± 1.284 82.68 ± 1.654 86.03 ± 1.721 106.8 ± 2.136 a P ±0.01 MPa and T ±1 K. n 1/2 b y is mole fraction. The standard uncertainty is estimated using standard deviation of the mean, u(xi) = n(n 1 −1) (Xi,k − ¯ Xl)2 . (k=1 ∑) 223 224 F.E. Soetaredjo et al. / Fluid Phase Equilibria 358 (2013) 220–225 Fig. 6. Chrastil correlation (wire mesh) and experimental solubility data of (+)- catechin (•). good as expected, then the first trial is that the association number should be varied linearly with density (k = e0 + e1 1, where e0 and e1 are constant). And in the extreme case, the association number can be in a quadratic (k = e0 + e1 1 + e2 21, where e0, e1 and e2 are constant). González et al.

6**[24] derived an equation for** solubilization **of** a **solute in**

SC-CO2 modified with co-solvent based on Chrastil equa- tion. They assumed that each

1**molecule of solute (A) associates with k molecules of** carbon dioxide **(B)**

and molecules of co-solvent (C). González equation has the form y1 = km exp T + b a (7) where a = ? Hto(tal/R, b)= q − k ln MB − k ln − k ln Mc + ln(MA + kMB + Mc) = constant, k is the association number of carbon diox- ide and is the association number of co-solvent. The estimation of constants for the semi-empirical

16**density based correlations (Chrastil, del Valle and Aguilera, Adachi and Lu**

and González) was done using multivariable non-linear regression analysis. The quality of all data correlations was quantified by the sum of squared errors (SSE), defined as follows: 1/2 SSE = (y1(exp) − y1(cal))2 ( ) (8) ∑ N where y1(exp)

1**is the** actual **solubility of** (+)-catechin **in** SC **-CO2,** y1(cal) **is the calculated solubility, and N is the number of experimental data. The**

multivariable non-linear regression technique involved an iterative curve fitting procedure. An initial estimation for each parameter was provided, and then calculation of a point by point sum of squares (Eq. (8)) for each iteration was conducted until convergence criteria were fulfilled. Figs. 6–9 show the results of multivariable non-linear regression calculations for the correlation

3**of Chrastil, del Valle and Aguilera, Adachi and Lu, and**

González, respectively. Table 4 summarizes the constants resulted from the calculations. The association num- ber obtained by

3**Chrastil and del Valle and Aguilera** correlation is **the** sum of **association**

number of carbon dioxide and ethanol which indicates that each catechin molecule associates with 5.3 molecules of carbon dioxide and ethanol. The association num- ber obtained from González correlation shows that each catechin molecule associates with 3.37 molecules of carbon dioxide and 1.97 Fig. 7. del Valle and Aguilera correlation (wire mesh) and experimental solubility data of (+)-catechin (•). of co-solvent ethanol molecule. The associate number in Adachi and Lu correlation is presented

3**as a linear function of density**

(Table 4). The constant a is directly related to

3**the enthalpy of solvation and vaporization**

(a = ?H/R); except for the correlation of

3**del Valle and Aguilera. The** value **of**

total enthalpy calculated from del Valle and Aguilera equation is similar to the other correlations (Table 4). This shows that the variation of temperature in the range of these exper- iments is not affecting the enthalpy of vaporization. Méndez-Santiago and Teja [25] proposed a semi-empirical cor- relation

6**based on** the **theory of dilute** solution. **Méndez-Santiago and Teja equation** is a density based model and requires knowl- edge

8**of the sublimation pressure of the solid solute.** This **equation**

8**demonstrates that** the **solubility data for a binary system over a significant range of temperatures and pressures can be plotted on a single straight line:**

T In E = A+B (9) Fig. 8. Adachi and Lu correlation (wire mesh) and experimental solubility data of (+)-catechin (•). F.E. Soetaredjo et al. / Fluid Phase Equilibria 358 (2013) 220–225 225 Table 4 Semi-empirical density based correlation constants. Model k a b d H (kJ/mole) SSE

20**Chrastil Del Valle and Aguilera Adachi and Lu**

González 5.35 5.34 1.9049 + 0.0007 3.37 −21,424.35 −22,315.73 −21,725.75 −21,424.35 14.7716 – 16.0853 151,185.56 34.7191 – 24.4236 – – – – 1.97 −178.12 −(177.50 to 178.20) −180.63 −178.12 0.142 0.141 0.140 0.143 Fig. 9. González correlation (wire mesh) and experimental solubility data of (+)- catechin (•). where E = y1P/P1sub is the enhancement factor. P is pressure, P1sub is sublimation pressure A and B are constants independent of tem- perature. Since the sublimation pressure of (+)-catechin is very low (Table 2) and the mass loss rate below 423 K was undetectable using the existing micro balance, therefore, the

18**Clausius–Clapeyron type expression for the sublimation pressure was** introduced **and** the derivation of **semi-empirical relation**

18**for the solid solubility** becomes: **T In(**

y1P) A′ B′ 1 + C′T = + (10) Fig. 10. Méndez-Santiago and Teja correlation (wire mesh) and experimental solu- bility data of (+)-catechin (•). where A′, B′ and C′ are constants, which are independent of tem- perature and pressure. Fig. 10 shows the results of multivariable non-linear regression calculations. The obtained values of A′, B′ and C′ are −20818, 3.650 and 46.050, respectively. The sum of squared errors (SSE) of this calculation is 0.145. Based on the SSE, the semi-empirical density based equations were fitted very well to the experimental data of (+)-catechin solubility. 4. Conclusion

5**The solubility of** (+)-catechin **in SC-CO2** with ethanol as **the**

co- solvent

2**was measured at several temperatures (313.15, 323.15, 333.15 and 343.15 K) and pressure in the range of 12–26 MPa.**

Semi- empirical density based equations were found to fit the measured solubility data very well. (+)-Catechin is a stable phenolic com- pound with very low sublimation pressure. References [1] C. Garlapati, G. Madras, J. Chem. Eng. Data 53 (2008) 2913–2917. [2] A. Braeuer, S. Dowy, A. Leipertz, R. Schatz, E. Schluecker, Opt. Express 15 (2007) 8377–8382. [3] W.J. Schmitt, R.C. Reid, Fluid Phase Equilib. 32 (1986) 77–99. [4] A. Berna, A. Chafer, J.B. Monton, S. Subirats, J. Supercrit. Fluids 20 (2001) 157–162. [5] A.R.C. Duarte, S. Santiago, H.C. de Sousa, C.M.M. Duarte, J. Chem. Eng. Data 50 (2005) 216–220. [6] C. Garlapati, G. Madras, J. Chem. Eng. Data 53 (2008) 2637–2641. [7] Z. Huang, W.D. Lu, S. Kawi, Y.C. Chiew, J. Chem. Eng. Data 49 (2004) 1323–1327. [8] L.-H. Wang, Y.-Y. Cheng, J. Chem. Eng. Data 50 (2005) 1747–1749. [9] S. Sang, X. Cheng, R.E. Stark, R.T. Rosen, C.S. Yang, C.-T. Ho, Bioorg. Med. Chem. 10 (2002) 2233–2237. [10] S. Sang, S. Tian, H. Wang, R.E. Stark, R.T. Rosen, C.S. Yang, C.-T. Ho, Bioorg. Med. Chem. 11 (2003) 3371–3378. [11] Y. Yilmaz, Food Sci. Technol.: LEB 17 (2006) 64–71. [12] P. Lacopini, M. Baldi, P. Storchi, L. Sebastiani, J. Food Compost. Anal. 21 (2008) 589–598. [13] M. Palma, Z. Pineiro, C.G. Barroso, J. Chromatogr. A 968 (2002) 1–6. [14] C. Passos, R.M. Silva, F.A. Da Silva, M.A. Coimbra, C.M. Silva, Chem. Eng. J. 160 (2010) 634–640. [15] Y. Yilmaz, E.B. Ozvural, H. Vural, J. Supercrit. Fluids 55 (2011) 924–928. [16] I. Ramirez-Sanchez, L. Maya, G. Ceballos, F. Villarreal, J. Food Compost. Anal. 23 (2010) 790–793. [17] S.M. Anthonysamy, N.B. Saari, K. Muhammad, F.A. Bakar, J. Food Biochem. 28 (2004) 91–99. [18] C.-Y. Day, C.J. Chang, C.-Y. Chen, J. Chem. Eng. Data 41 (1996) 839–843. [19] K. Suzuki, H. Sue, J. Chem. Eng. Data 35 (1990) 63–66. [20] S.N. Joung, C.W. Yoo, H.Y. Shin, S.Y. Kim, K.-P. Yoo, C.S. Lee, W.S. Huh, Fluid Phase Equilib. 185 (2001) 219–230. [21] S.E. Guigard, W.H. Stiver, Ind. Eng. Chem. Res. 37 (1998) 3786–3792. [22] M. Skerget, Z. Knez, M. Knez-Hrncic, J. Chem. Eng. Data 56 (2011) 694–719. [23] J. Chrastil, J. Phys. Chem. 86 (1982) 3016–3021. [24] J.C. Gonzalez, M.R. Vieytes, A.M. Botana, J.M. Vieites, L.M. Botana, J. Chromatogr. A 910 (2001) 119. [25] J. Mendez-Santiago, A.S. Teja, Fluid Phase Equilib. 158–160 (1999) 501–510. [26] S.S. Pinto, H.P. Diogo, J. Chem. Thermodyn. 38 (2006) 1515–1522. [27] W. Gückel, R. Kästel, T. Kröhl, A. Parg, Pest. Sci. 45 (1995) 27–31. [28] D.M. Prince, S. Bashir, P.R. Derrick, Thermochim. Acta 327 (1999) 167–171. [29] A. Lahde, J. Raula, J. Malm, E.I. Kauppinen, M. Karppinen, Thermochim. Acta 482 (2009) 17–20. [30] J.P. Elder, J. Therm. Anal. 49 (1997) 897–905. [31] A. Gairola, G.V. Kunte, A.M. Umarji, S.A. Shivashankar, Thermochim. Acta 488 (2009) 17–20. [32] Y. Zuo, H. Chen, Y. Deng, Talanta 57 (2002) 307–316. [33] R. Stryjek, J.H. Vera, Can. J. Chem. Eng. 64 (1986) 323–333. [34] J.M. del Valle, J.M. Aguilera, Ind. Eng. Chem. Res. 27 (1988) 1551–1553. [35] Y. Adachi, B.C.-Y. Lu, Fluid Phase Equilib. 14 (1983) 147–156. [36] D.L. Sparks, L.A. Estevez, R. Hernandez, K. Barlow, T. French, J. Chem. Eng. Data 53 (2008) 407–410.