Ind. Eng. Chem. Res. **2011**, *50*, 207–212

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New Apparatus for Solubility Measurements of Solids in Carbon Dioxide

Octavio Elizalde-Solis[†] and Luis A. Galicia-Luna*,[‡]

Departamento de Ingeniería Química Petrolera, E.S.I.Q.I.E., Instituto Politécnico Nacional, UPALM, Edif. 8, 2° piso, Lindavista, C.P. 07738, México D. F., México, and Laboratorio de Termodinámica, SEPI-E.S.I.Q.I.E., Instituto Politécnico Nacional, UPALM, Edif. Z, Secc. 6, 1ER piso, Lindavista, C.P. 07738, México D. F., México

The aim of this work is to present a new experimental apparatus based on the static-analytic method suitable to perform solubility measurements of solids in sub- and supercritical carbon dioxide. Mole fractions of dissolved solids are determined online via high-performance liquid chromatography. The studied binary mixtures are capsaicin in carbon dioxide from 298 to 328 K, hexadecanoic acid in carbon dioxide at 313 and 318 K, β-carotene in carbon dioxide at 298 and 313 K, and acetaminophen in carbon dioxide at 313 K. The experimental apparatus is also tested by circulating the fluid phase to measure the solubility of capsaicin in carbon dioxide at 298 K. Experimental solid solubilities in carbon dioxide are found to be in agreement with the solubility data reported in the literature. The Méndez-Santiago and Teja and the modified Chrastil models are used to correlate the experimental data.

1. Introduction

Information about solubility of solids in supercritical fluids is of great importance because supercritical fluids have several advantages over organic solvents about physical properties.[1−4] Accurate experimental solubility data are fundamental to test theoretical, empirical or semiempirical models. Semiempirical models based on density are common approaches used to correlate experimental solid solubilities in supercritical fluids. The optimized parameters of these kinds of models come only from the linear relation between the solvent density and the logarithm of the mole fraction.On the basis of density, several models have been proposed by some authors.[5−11] The correlation developed by Chrastil[5] is the most common model used for this purpose. However, Garlapati and Madras[10] have demonstrated that the original Chrastil model is not dimensionally consistent to be used in terms of mole fraction and have proposed a modification. On the other hand the Méndez-Santiago and Teja[11] correlation is also widely used to test the consistency of the experimental solubility data.

In this work, we present a new static-analytic apparatus with online sampling capable to perform solid solubility measurements in dense and supercritical fluids in a low range of about 7×10^{-8} to 1×10^{-3} mole fraction. For this purpose, carbon dioxide is used as a solvent and the used solids are capsaicin, hexadecanoic acid, β-carotene, and acetaminophen. The CO_2 + solid binary systems are used as references because of their vast information about solubility data in the literature and for the application of these compounds in the food, cosmetic, and pharmaceutical industries.[12−20] The present apparatus is also tested by circulating the fluid phase through the same unit. The solubility of capsaicin in subcritical carbon dioxide is measured with this last configuration at 298 K and was observed that the static-circulation method is less time-consuming. Experimental results are found to be in agreement with the literature data for the four binary mixtures.[12−20] The Méndez-Santiago and Teja[11] and the modified Chrastil correlation[10] fit with low deviations of the experimental solubilities.

2. Experimental Section

Materials. Carbon dioxide research grade with a stated purity of 99.995 mol % was purchased from Air Products-Infra (México). Aldrich Chemical Co. Inc. supplied capsaicin (97% of purity), hexadecanoic acid with a purity of 99%, β-carotene (98% of purity), and acetaminophen with a certified purity of 99.7%. No additional purification was carried out for these compounds. Solids were carefully degassed under vacuum before they were used.

Apparatus. Solubility measurements of solids in carbon dioxide were performed in an apparatus based on the static-analytic technique. This is mainly constituted by a high-pressure view-cell,[21] a six-port two-way valve (Valco, C-2006E), a high-performance liquid chromatograph (Agilent, 1100 series), a syringe pump (Isco, 100DM), and an air bath (France Etuves, model XL074SP). The schematic diagram of the apparatus is presented in Figure 1. The high-pressure cell was designed to operate at pressures below 30 MPa and contains two sapphire windows in opposite sides to observe the phase phenomena. The air bath regulates the temperature of the cell which is measured using two platinum resistance thermometers (Specitec, 100-Ω) connected to a digital display (Hart Scientific, Chub-E4 1529). Temperature sensors were previously calibrated against a 25 Ω reference probe (Rosemount, 162CE ± 0.005 K certified accuracy) connected to a precision thermometry bridge (Automatic Systems Laboratories, F300S) within an estimated uncertainty of ±0.03 K. A pressure transducer (DRUCK, PDCR 910-1756) connected to the cap of the cell is used to measure pressure through a digital indicator (DRUCK, DPI 145) previously calibrated against a dead weigh balance (D. H. Instruments, 5304). Estimated uncertainty for pressure was found to be within ±0.017 MPa. A gear pump (Micropump, GAH) was used to operate the experimental apparatus in circulating mode of the fluid phase.

Analysis. A high-performance liquid chromatograph (Agilent, 1100 series) was used to quantify the solid in the samples taken from the fluid phase and was previously calibrated. The equipment is constituted by a degassing device, a quaternary pump, a manual injector port of 20 μL, an Alltima C18 (Grace Davison) precolumn 7.5 mm ×4.6 mm, a column 250 mm × 4.6 mm, both of 5 μm and a diode array detector (DAD). These were used to identify the solids. Analytical conditions for the

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* To whom correspondence should be addressed. Tel.: (52) 55 5729-6000 ext 55133. Fax: (52) 55 5586-2728. E-mail: lgalicial@ipn.mx.
[†] Departamento de Ingeniería Química Petrolera, ESIQIE.
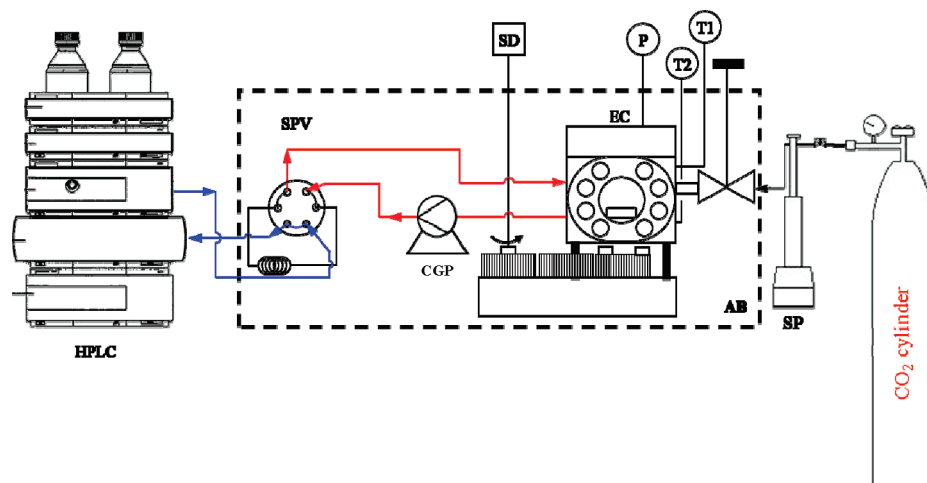[‡] Laboratorio de Termodinámica, SEPI-ESIQIE.

Figure 1. Experimental apparatus for measuring the solubility of solids in carbon dioxide: AB air bath, CGP circulating gear pump, EC equilibrium cell, P pressure transducer, SD stirring device, SP Syringe pump, SPV six-port valve, Ti platinum resistance thermometer i, HPLC high-pressure liquid chromatograph.

Table 1. HPLC Conditions for Calibration and Solubility Measurements

compound	capsaicin	hexadecanoic acid	β-carotene	acetaminophen
mobile phase	acetonitrile/water	acetonitrile	acetonitrile/2-propanol/ methanol/water	methanol/0.05 M KH_2PO_4, pH = 2 H_3PO_4
% volume	70/30	100	39/52/5/4	17/83
flow rate (mL/min)	1.0	1.3	1.0	1.0
wavelength (nm)	280	214	450	280
T (K)	298	318	308	298

calibration and analysis of each solid in the fluid phase depend on the studied system; they are presented in Table 1.

Experimental Procedure. About 5 g of pure solid was placed in the equilibrium cell to ensure a sufficient amount of this component. The sampling circuit, solvent feeding system, and the cell was degassed for 2 h. Then, the air bath was fixed at a stated temperature and carbon dioxide was fed to the equilibrium cell through a syringe pump; meanwhile the binary mixture (solid + carbon dioxide) was vigorously stirred by means of the stirring device which has a magnetic bar located inside the cell. Pressure in the cell decreased slowly due to the solubilization of the solid in the fluid phase. For that reason, carbon dioxide had to be again loaded to the equilibrium cell continuously. This apparatus was also tested based on the static-circulation principle. In this case, the gear pump was turned on by circulating the fluid phase from the lower side of the cell to the six-port valve and returned to the upper side of the cell. An in-line filter of 7 μm was placed between the gear pump and the six-port valve to avoid the presence of solids in the sample loop.

Equilibrium conditions were reached after 12 h. It was considered when pressure and temperature varied within the uncertainty of the measuring devices. After equilibrium was reached, samples of the fluid phase saturated with the solid were sent online to the HPLC through the six-port valve which has an internal volume of 20 μL. The solubility of the solid in the fluid phase y_2 expressed as a mole fraction was calculated by the following equation:

$$y_2 = \frac{A_{FP} V_{HPLC} M_1}{A_S V_{FP} \rho_1} C_S \qquad (1)$$

where A_{FP} is the chromatographic area of the solid in the fluid phase, A_S is chromatographic area of the solid in the standard solution, V_{HPLC} is the volume of the injector port, and V_{FP} is the sample volume of the fluid phase. M_1 and ρ_1 denotes the

Table 2. Solubility of Capsaicin (2) in Carbon Dioxide (1)

T = 298.18 K		T = 313.54 K		T = 328.31 K	
p (MPa)	$y_2 \times 10^{-5}$	p (MPa)	$y_2 \times 10^{-5}$	p (MPa)	$y_2 \times 10^{-5}$
7.95	6.00 ± 0.05	7.81	0.58 ± 0.07	8.16	1.20 ± 0.08
8.32	6.90 ± 0.09	8.54	1.26 ± 0.05	8.37	1.55 ± 0.09
9.42	7.04 ± 0.06	9.72	3.77 ± 0.06	10.24	5.18 ± 0.06
9.63	7.32 ± 0.09	9.83	4.17 ± 0.06	10.53	6.15 ± 0.05
10.69	7.90 ± 0.07	10.32	4.99 ± 0.07	12.92	8.39 ± 0.06
12.34	8.34 ± 0.08	10.55	5.55 ± 0.07	12.98	8.27 ± 0.07
13.13	9.00 ± 0.09	11.57	7.28 ± 0.08	14.72	9.77 ± 0.08
13.51	8.97 ± 0.09	12.00	7.54 ± 0.09	15.54	9.93 ± 0.09
15.41	9.29 ± 0.08	13.09	9.67 ± 0.09	15.94	11.30 ± 0.13
15.69	9.43 ± 0.09	13.21	9.41 ± 0.09	17.41	14.86 ± 0.18
15.79	9.35 ± 0.09	13.60	10.53 ± 0.11	18.28	16.88 ± 0.20
17.75	10.14 ± 0.09	15.55	12.72 ± 0.15	18.63	16.22 ± 0.20
20.42	10.76 ± 0.10	16.42	14.33 ± 0.17	19.32	19.62 ± 0.23
20.77	10.90 ± 0.12	16.58	14.62 ± 0.17	19.98	20.35 ± 0.24
21.07	11.05 ± 0.10	17.43	14.89 ± 0.18	20.85	22.68 ± 0.27
21.34	11.07 ± 0.10	18.08	15.66 ± 0.18	21.01	22.66 ± 0.27
22.62	11.82 ± 0.11	19.54	17.44 ± 0.21	21.20	23.72 ± 0.28
23.09	12.26 ± 0.11	20.27	17.50 ± 0.21	22.16	27.25 ± 0.32
24.65	12.25 ± 0.11	21.59	19.44 ± 0.23	23.25	27.83 ± 0.33
24.92	12.67 ± 0.11	22.43	20.41 ± 0.24	23.33	27.41 ± 0.32
24.98	12.62 ± 0.11	23.36	21.48 ± 0.25	23.59	27.72 ± 0.33
		24.29	22.31 ± 0.26	24.19	30.01 ± 0.35
		24.66	22.68 ± 0.27	24.34	30.21 ± 0.35
		25.49	22.97 ± 0.27	24.76	30.79 ± 0.36
				24.85	32.47 ± 0.38
				25.62	32.68 ± 0.38

molecular weight and the density of the solvent, respectively. C_S is the concentration of the solid in the standard solution for the calibration of the HPLC. The law of propagation of errors[22] and the deviations of each variable associated with eq 1 were considered to calculate mole fraction uncertainties. These results are reported in Tables 2−6 for each system.

Along the measurements at a stated pressure and temperature, the initial samples were used as purge because their compositions were too low neither reproducible. The sampling procedure was stopped when the solubility of the solid in the fluid phase was within 1% of reproducibility at fixed temperature and pressure for the last five consecutive samples. Pressure drop
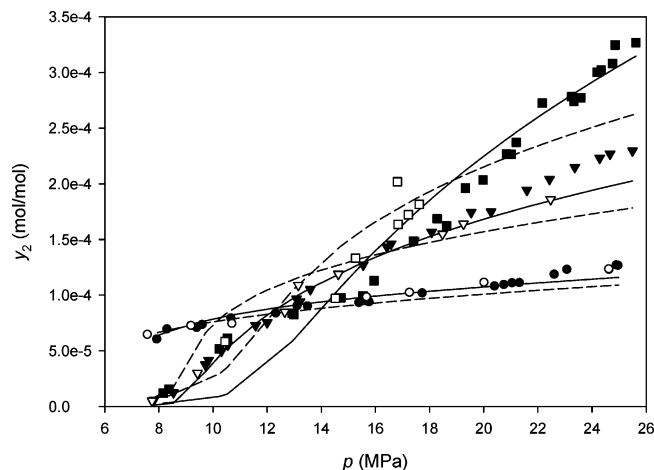
Figure 2. Solubility of capsaicin (2) in carbon dioxide (1). 298 K, ●, this work; ○, Valderrama et al.[12] 313 K, ▼, this work; ▽, Valderrama et al.[12] 328 K, ■, this work; □, Elizalde-Solis and Galicia-Luna.[13] Solid lines represent the calculated values using eq 2, and dashed lines correspond to the values from eq 3.

Table 3. Solubility of Hexadecanoic Acid (2) in Supercritical Carbon Dioxide (1)

$T = 313.16$ K		$T = 318.22$ K	
p (MPa)	$y_1 \times 10^{-4}$	p (MPa)	$y_1 \times 10^{-4}$
9.95	2.08 ± 0.27	10.40	1.73 ± 0.32
15.19	5.35 ± 0.25	12.42	3.17 ± 0.49
19.04	7.03 ± 0.38	15.58	6.10 ± 0.28
19.22	7.25 ± 0.41	17.65	8.00 ± 0.47
19.50	7.44 ± 0.40	20.57	9.03 ± 0.35
25.03	10.15 ± 0.36	20.73	9.28 ± 0.30
		26.09	10.63 ± 0.27

caused by the sampling procedure changed 0.05 MPa. Therefore pressure was increased to the desired value by adding carbon dioxide to the cell after each sampling. Temperature and pressure conditions had to be stable before each sampling. Isothermal solubility measurements were performed at different pressure conditions by adding carbon dioxide to the system.

3. Results and Discussion

The reliability of the online static-analytic apparatus to measure solubility data of solids in carbon dioxide was tested by using capsaicin, hexadecanoic acid, β-carotene, and acetaminophen as solids. Solubility measurements of capsaicin in carbon dioxide were performed at 298.18, 313.54, and 328.31 K, and these results are listed in Table 2. Solubility data were compared against the published data by Valderrama et al.[12] and Elizalde-Solis and Galicia-Luna[13] in Figure 2. As can be observed the
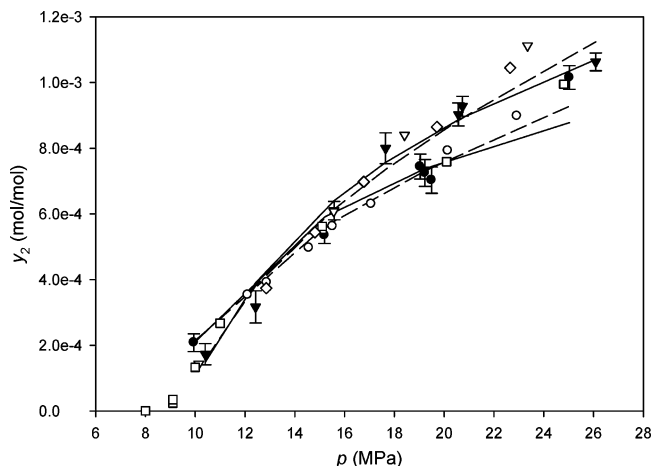

Figure 3. Solubility of hexadecanoic acid (2) in supercritical carbon dioxide (1) at 313 K, □, Bamberger et al.;[14] ○, Brandt et al.;[15] ●, this work. 318 K, ▽, Brandt et al.;[15] ◇, Garlapati and Madras;[16] ▼, this work. Solid lines represent the calculated values using eq 2. Dashed lines correspond to the computed values from eq 3.

experimental data agree with the literature data at 298 and 313 K; the agreement cannot be verified with the reported in ref 13 above 18 MPa at 328 K due to lack of data.

Experimental solubilities for the hexadecanoic acid in supercritical carbon dioxide were obtained at 313.16 and 318.22 K and are listed in Table 3. Solubility isotherms for this system were compared with the data published by Bamberger et al.,[14] Brandt et al.,[15] and Garlapati and Madras[16] in Figure 3. Good agreement can be observed for the two temperatures in the studied range of pressure. A slight deviation is found between the solubilities reported in this work and the data points reported in refs 15 and 16 above 22 MPa at 318 K. Solubility data from both references at these conditions are higher than our obtained solubilities. This deviation could be attributed to the detector saturation of the analytical HPLC equipment used in this work. Therefore, the analytical equipment is not recommended to perform solid solubility measurements in carbon dioxide where the composition is above 1×10^{-3} in the mole fraction.

Isothermal solubility data of β-carotene in carbon dioxide were obtained at 298.30 and 313.43 K and are reported in Table 4 and Figure 4. The experimental solubilities obtained in this work are in the trends with the data reported by Škerget et al.[17] for both temperatures. However, our solubility trend is inconsistent with the data reported by Sakaki[18] and Sovová et al.[19] at 313 K.

Finally, solubility measurements of acetaminophen in supercritical carbon dioxide were carried out at 313.25 K, and data
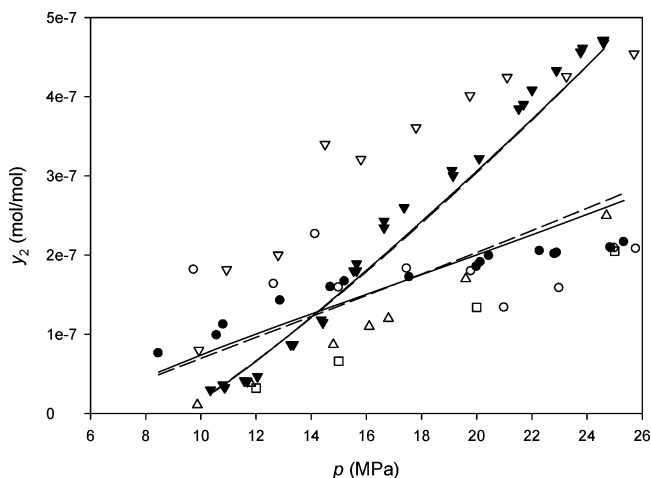
Table 4. Solubility of β-Carotene (2) in Carbon Dioxide (1)

$T = 298.30$ K				$T = 313.43$ K			
p (MPa)	$y_2 \times 10^{-7}$	p (MPa)	$y_2 \times 10^{-7}$	p (MPa)	$y_2 \times 10^{-7}$	p (MPa)	$y_2 \times 10^{-7}$
8.47	0.76 ± 0.02	20.45	1.99 ± 0.04	10.35	0.30 ± 0.02	16.64	2.35 ± 0.04
10.58	0.99 ± 0.02	22.29	2.05 ± 0.04	10.80	0.36 ± 0.02	17.37	2.60 ± 0.05
10.82	1.12 ± 0.03	22.83	2.01 ± 0.04	10.87	0.33 ± 0.02	19.10	3.07 ± 0.05
12.88	1.42 ± 0.03	22.86	2.01 ± 0.04	11.58	0.41 ± 0.02	19.14	3.00 ± 0.05
14.71	1.59 ± 0.03	22.91	2.03 ± 0.04	11.68	0.41 ± 0.02	20.09	3.22 ± 0.06
15.21	1.67 ± 0.03	24.85	2.09 ± 0.04	12.05	0.47 ± 0.02	21.52	3.85 ± 0.07
17.57	1.72 ± 0.03	24.88	2.09 ± 0.04	13.26	0.87 ± 0.02	21.70	3.90 ± 0.07
20.00	1.85 ± 0.04	25.34	2.16 ± 0.04	13.36	0.87 ± 0.02	22.00	4.08 ± 0.07
20.14	1.91 ± 0.04			14.37	1.18 ± 0.03	22.89	4.33 ± 0.08
				14.42	1.15 ± 0.03	23.77	4.56 ± 0.08
				15.54	1.80 ± 0.04	23.84	4.61 ± 0.08
				15.65	1.89 ± 0.04	24.56	4.71 ± 0.08
				15.65	1.80 ± 0.04	24.60	4.68 ± 0.08
				16.64	2.43 ± 0.04	24.61	4.72 ± 0.08

Figure 4. Solubility of β-carotene (2) in carbon dioxide (1) at 298 K, ○, Škerget et al.;[17] ●, this work. 313 K, ▽, Škerget et al.;[17] △, Sakaki;[18] □, Sovová et al.;[19] ▼, this work. Solid lines represent the calculated values using eq 2. Dashed lines correspond to the computed values from eq 3.

Table 5. Solubility of Acetaminophen (2) in Supercritical Carbon Dioxide (1)

	T = 313.25 K		
p (MPa)	$y_2 \times 10^{-7}$	p (MPa)	$y_2 \times 10^{-7}$
11.14	4.3 ± 0.2	18.45	10.1 ± 0.4
13.57	7.3 ± 0.3	21.04	12.8 ± 0.5
13.98	8.0 ± 0.3	21.98	13.8 ± 0.5
15.93	9.1 ± 0.4	25.02	15.8 ± 0.5
17.89	9.8 ± 0.4		

points are presented in Table 5. The experimental solubility trends were compared against the two sets of data reported by Bristow and Shekunov[20] in Figure 5. These literature data were measured via a dynamic system with offline and online sampling. An agreement can be found between the three sets of data taking into account the experimental uncertainties reported in this work and from the cited reference.

The last modification of the apparatus was made based on the static-circulation method and was tested by measuring the solubility of capsaicin in dense carbon dioxide at 298.51 K. These results are reported in Table 6. This isothermal solubility trend was in agreement with the data obtained using the static-
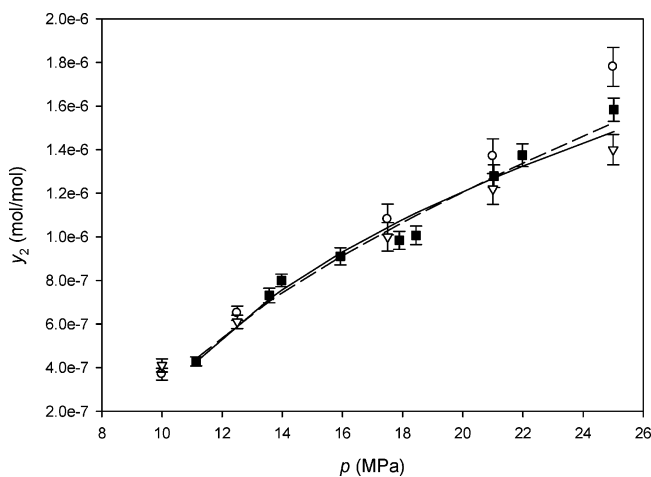

Figure 5. Solubility of acetaminophen (2) in supercritical carbon dioxide (1) at 313 K, ■, this work; ○, Bristow and Shekunov (offline dynamic);[20] ▽, Bristow and Shekunov (online dynamic);[20] solid line represents the calculated values using eq 2; dashed line corresponds to the computed values from eq 3.

Table 6. Solubility of Capsaicin (2) in Carbon Dioxide (1) by Using the Online Static-Circulation Apparatus

			T = 298.51 K		
p (MPa)	$y_2 \times 10^{-5}$	p (MPa)	$y_2 \times 10^{-5}$	p (MPa)	$y_2 \times 10^{-5}$
8.14	5.92 ± 0.06	11.71	8.16 ± 0.08	21.95	11.43 ± 0.11
8.18	5.90 ± 0.06	11.77	8.09 ± 0.08	22.50	11.90 ± 0.12
8.81	6.54 ± 0.07	11.95	8.27 ± 0.09	23.38	12.02 ± 0.13
8.84	6.56 ± 0.07	13.70	9.00 ± 0.09	23.33	12.15 ± 0.13
10.64	7.84 ± 0.07	14.60	9.07 ± 0.09	25.03	12.22 ± 0.13
10.86	7.89 ± 0.07	14.98	9.31 ± 0.09	25.18	12.23 ± 0.13
10.86	7.81 ± 0.08	16.36	10.23 ± 0.10		
10.88	7.94 ± 0.08	16.98	10.44 ± 0.10		

analytic apparatus as can be observed in Figure 6. The main difference between the static-analytic and the static-circulation apparatus is that the circulation mode is less time-consuming. Then, static-circulation option can be considered a useful technique to perform solubility measurements of this kind of systems.

Density-Based Correlation. Two density-based semiempirical models were used to correlate the experimental results. The equation proposed by Méndez-Santiago and Teja[11] based on the theory of dilute solutions:

$$T \ln(y_2 P) = A' + B'\rho_1 + C'T \tag{2}$$

In this model, the solubility of the solid in the supercritical carbon dioxide y_2 in terms of mole fraction is calculated by optimizing the parameters A', B', and C', which are independent of temperature T. p is the pressure of the system, and ρ_1 is the density of the solvent (carbon dioxide) because the concentration of the solid in the fluid phase is considered too low as shown previously.[13]

The second density-based model is the proposed by Garlapati and Madras,[16] which consist of a modification to the Chrastil model.[5] This correlation is dimensionally consistent to calculate the experimental solubilities:

$$y_2 = \left(\frac{RT\rho_1}{M_1 f^{\bullet}}\right)^{\kappa-1} \exp\left(\frac{\alpha}{T} + \beta\right) \tag{3}$$

where y_2 is the solid mole fraction in the fluid phase, T is the temperature (K), the universal gas constant R is set to 0.08205 (atm L/mol K), the fugacity of the gas is considered as 1 (atm), and ρ_1 and M_1 are the density and the molecular weight of the
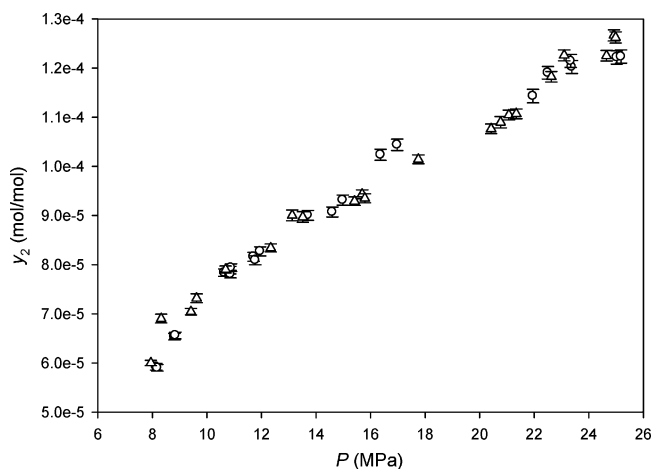

Figure 6. Solubility of capsaicin (2) in dense carbon dioxide (1) at 298 K obtained in this work with the online sampling apparatus: ○, static-circulation; △, static-analytic.

Table 7. Correlated Results for the Solubility of Solids in Carbon Dioxide Using the Méndez-Santiago and Teja[11] and the Modified Chrastil[5] Models

system	carbon dioxide + capsaicin	carbon dioxide + hexadecanoic acid	carbon dioxide + β-carotene	carbon dioxide + acetaminophen
N	93	13	45	9
T	298.18, 298.51, 313.54,	313.16	298.30	313.25
(K)	328.31	318.22	313.43	
p (MPa)	7.81−25.62	9.95−26.09	8.47−25.34	11.14−25.0
Méndez-Santiago and Teja Parameters				
$A1$	−10 153.8	−9947.5	−15 043.0	−3944.7
$B4$	3.100	2.910	5.185	3.363
$C3$	18.407	19.770	22.121	−7.048
AARD (%)	11.37	5.76	14.12	4.50
Modified Chrastil Parameters				
$k4\ 3$	3.5466	5.3322	10.5339	6.0413
α (K)1 1	−3234.5	−3862.9	−4637.6	441.1
$\beta3\ 2$	−14.2107	−21.6863	−59.2643	−46.2661
AARD (%)	15.46	5.66	15.40	4.19

solvent, respectively. The parameters κ, α, and β are adjusted from experimental data.[16]

The absolute average relative deviation AARD (%) for the correlated solubility results is calculated as follows:

$$AARD(\%) = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{y_2^{\text{exptl}} - y_2^{\text{calcd}}}{y_2^{\text{exptl}}} \right| \qquad (4)$$

where N is the number of data points. The experimental and calculated solubility data are denoted with the superscripts exptl and calcd, respectively. The optimal parameters and the AARD (%) from the semiempirical models proposed by Méndez-Santiago and Teja and the modified Chrastil model using the experimental data of this work are reported in Table 7 for each system over the entire range of pressure and temperature.

Experimental solid solubilities in carbon dioxide are satisfactory correlated with the two density-based models. Similar deviations in terms of the AARD were obtained with both correlations as can be observed from Figures 2−5. Because of scarce data points, the lower deviations were obtained for the solubility of hexadecanoic acid and acetaminophen in carbon dioxide systems of 5.76%, 5.66% and 4.5%, 4.19%, respectively. The major difference between the Méndez-Santiago and Teja and the modified Chrastil models can be observed at the computed solubility of capsaicin in carbon dioxide. In consequence, the Méndez-Santiago and Teja model provides slightly a better fit than the modified Chrastil model with a lower AARD for the experimental data. Therefore it can be assumed that the experimental solubilities satisfy the self-consistent test of the Méndez-Santiago and Teja model.

4. Conclusions

Solid solubility measurements in carbon dioxide were performed in a new experimental apparatus which is capable of measuring up to 28 MPa from 298 to 328 K. This apparatus is based on the static-analytical method. The studied solids were capsaicin, hexadecanoic acid, β-carotene, and acetaminophen to cover a wide range of composition. The solubility of capsaicin in dense carbon dioxide was also measured by using the apparatus as a static-circulation unit at 298 K. The main advantage of the second option is that measurements can be carried out with timesaving because the fluid phase is circulated within the apparatus. The analytical equipment is suggested to perform solubility measurements of solids in supercritical fluids at composition above 1×10^{-7} and below 1×10^{-3} mole fraction. Experimental solubility data are self-consistent ac-

cording to the Méndez-Santiago and Teja model. This model supplies lower deviation (AARD) compared with the modified Chrastil model.

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