Solubility of Diisopropoxititanium Bis(acetylacetonate) in Supercritical Carbon Dioxide

Irene Montequi, Esther Alonso,* Angel Martín, and María José Cocero

Departamento Ingeniería Química y Tecnología del Medio Ambiente, Universidad de Valladolid, Prado de la Magdalena s/n, Valladolid 47005, Spain

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The solubility of diisopropoxititanium bis(acetylacetonate) (DIPBAT) in supercritical carbon dioxide was measured using a dynamic method. Measurements were performed at (353, 423, and 473) K over the pressure range from (10 to 20) MPa. The measured mass fraction solubility varies between $5 \cdot 10^{-4}$ and $7.4 \cdot 10^{-2}$. In the range of pressures and temperatures of the measurements, the solubility increases at higher pressures and decreases at higher temperatures. Results were correlated by the Chrastil equation and the Peng–Robinson equation of state.

Introduction

The properties of supercritical fluids, mainly H_2O or CO_2, and the possibility of varying these properties with operational parameters are very attractive for particle generation and precipitation processes.[1] In particular, supercritical carbon dioxide (sc-CO_2) has been used as the reaction medium for the synthesis of micro- or nanoparticles or films.[2–4] In a previous work,[5] we have presented a process for synthesizing anatase TiO_2 nanoparticles by hydrolysis of the organometallic precursor diisopropoxititanium bis(acetylacetonate) (DIPBAT) in sc-CO_2, according to the global following reaction

$$Ti(OC_3H_7)_2(C_5H_7O_2)_2 + 2H_2O \rightarrow 2C_3H_7OH + 2C_5H_7OOH$$

H_2O required by this reaction was obtained by 2-propanol decomposition in the sc-CO_2 medium. For the development and optimization of this process, it is essential to have information about the solubility of DIPBAT in sc-CO_2 because it determines the maximum throughput of the process. The present investigation was undertaken to determine the solubility of DIPBAT in sc-CO_2, in the range of pressures and temperatures of operation of the TiO_2 nanoparticle synthesis process.

Experimental Section

Materials. Carbon dioxide of purity higher than 99.9 % in mass was obtained from Carburos Metalicos (Spain) and was used without further purification. DIPBAT was purchased from Sigma Aldrich (Spain) as a solution in 2-propanol with a concentration of DIPBAT of 75 wt %. The 2-propanol was removed from this solution by evaporation at 343 K under a vacuum in a rotary evaporator filled with 3 mm Raschig Rings. The Raschig Rings impregnated with DIPBAT (which is a viscous liquid) were collected after the evaporation and used to fill the equilibrium cell, as described in the Apparatus and Procedure section.

Apparatus and Procedure. A schematic diagram of the apparatus is shown in Figure 1. This apparatus allowed determination of the solubility by the dynamic method.[6] CO_2 taken from a cylinder and condensed in heat exchanger E-101 was fed by a diaphragm pump P-102 (Dosapro Milton Roy Milroyal D) to the equilibrium cell C-110. The equilibrium cell was made of stainless steel and has a volume of 110 mL. It was placed inside an oven to maintain a constant temperature. Pressure was kept constant by the back-pressure regulation valve V-3 (GO Regulator, Inc.). The filter K-108 with a pore size of 0.5 μm protected the valve from particles swept by the fluid. After depressurization, the extract was collected in a crystal vial S-112, and CO_2 was vented. Another diaphragm pump P-111 allowed rinsing of the downstream part of the equipment with an organic solvent. Pressure was measured with a membrane pressure transmitter PI-107 (DESIN Instruments TPM-18, Spain), which had an accuracy of ± 0.2 MPa. Temperature was measured with a Pt100 thermoresistance TIC-106, with an accuracy of ± 0.1 K. This thermoresistante was calibrated with an HP 2804A Quartz thermometer, with an accuracy of 0.01 K, which was calibrated with the triple point of water. The thermoresistance was connected to a PID controller, which maintained a constant temperature inside the oven. The maximum fluctuations in pressure and temperature during an experiment were ± 0.3 MPa and ± 2 K, respectively. The amount of CO_2 fed to the equilibrium cell during the experiment was measured with the Coriolis mass flow meter FI-104 (Sensor MICRO Motion Elite CMF010 NB, Transmitter MICRO Motion Elite RFT9739), with an accuracy ± 0.10 % of the flow rate ($kg \cdot h^{-1}$).

The equilibrium cell was filled with 3 mm Raschig Rings impregnated with DIPBAT. The impregnation was done during the elimination of 2-propanol from DIPBAT solutions by evaporation in a rotary evaporator, filled with the Raschig Rings. The sampling procedure was started by establishing constant pressure and temperature conditions in the equilibrium cell and setting a constant CO_2 mass flow rate of 100 $g \cdot h^{-1}$. This flow rate was checked by preliminary experiments to be sufficiently low to obtain a completely saturated solvent at the equilibrium cell outlet. These experiments consisted of operating with CO_2 flow rates decreasing down to the final value of 100 $g \cdot h^{-1}$ until it was found that the variation in the obtained solubility with a variation in the flow rate was below the estimated accuracy of data (3 %). After 500 g of CO_2 had passed through the equilibrium cell, flow was stopped. The effluent pipes and metering valve were then rinsed with ethanol to collect all

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* Corresponding author. E-mail address: ealonso@iq.uva.es.

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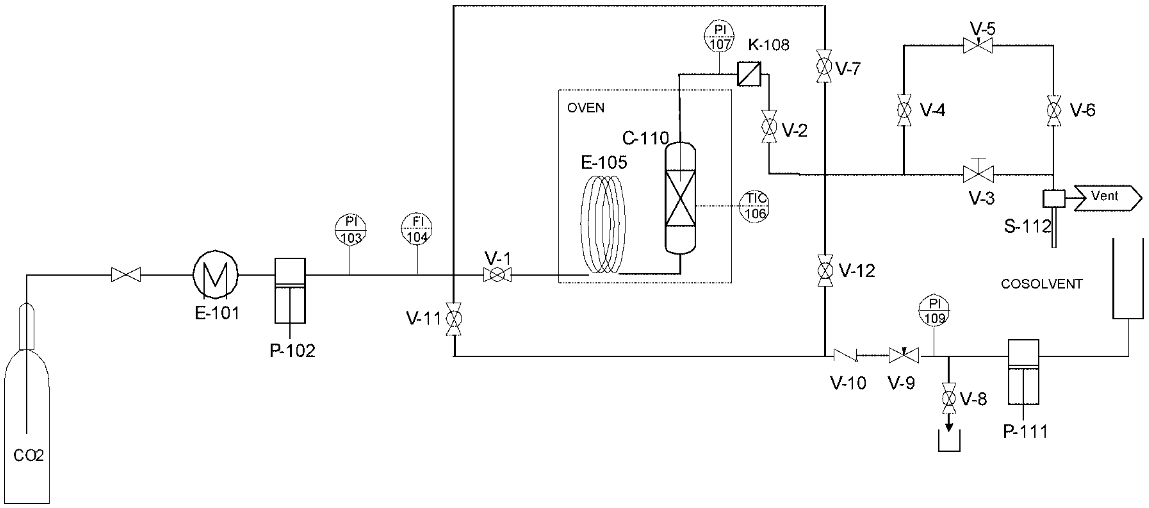

Figure 1. Schematic diagram of the apparatus: E-101, CO_2 condenser; P-102, CO_2 pump; E-105, preheater; C-110, equilibrium cell; K-108, filter; V-3, back pressure valve; S-112, separator and sampling vial; P-111, organic solvent pump.

Table 1. DIPBAT Mass Fraction Solubility *w* (g of DIPBAT·g^{-1} of CO_2) and Molar Fraction Solubility *y*

	$T = 353$ K		$T = 423$ K		$T = 473$ K	
P/MPa	$10^3\ w$	$10^4\ y$	$10^3\ w$	$10^4\ y$	$10^3\ w$	$10^4\ y$
10.0	3.60 ± 0.01	4.35 ± 0.01	1.70 ± 0.02	2.06 ± 0.02	0.50 ± 0.01	0.60 ± 0.01
12.5	10.6 ± 0.2	12.8 ± 0.2	5.1 ± 0.1	6.2 ± 0.1	1.10 ± 0.02	1.33 ± 0.02
15.0	24.2 ± 0.1	29.3 ± 0.1	13.5 ± 0.1	16.3 ± 0.1	4.5 ± 0.1	5.4 ± 0.1
17.5	40.0 ± 0.7	48.4 ± 0.8	22.8 ± 0.4	27.6 ± 0.5	6.9 ± 0.2	8.3 ± 0.2
20.0	74.0 ± 0.8	89.0 ± 1.0	45.0 ± 1.0	54.0 ± 1.0	13.0 ± 0.3	15.7 ± 0.4

Table 2. Chrastil Equation Parameters (Equation 1)

T/K	k	c	AARD % (eq 2)
353	3.88	−21.16	4.2
423	5.05	−26.53	4.7
473	5.34	−28.44	5.7

extract that could have been retained in this part of the equipment. Ethanol was removed from the extract by evaporation at 333 K under a vacuum. The amount of DIPBAT extracted was determined by weight with an analytical balance of accuracy ± 0.0001 g. The solubility of DIPBAT was then calculated as the ratio between the mass of DIPBAT extracted and the mass of CO_2 passed through the equilibrium cell. The extract was analyzed by infrared spectroscopy (Tensor 27 Bruker) and thermogravimetry (TGA SDTA 851e, Mettler Toledo, temperature ramp of 20 K·min^{-1} until 1123 K under an N_2 atmosphere) to ensure that DIPBAT had not suffered thermal degradation during the experimental procedure. All samples were repeated five times to check the reproducibility of the results and to estimate the experimental error.

Results and Discussion

Experimental solubilities of DIPBAT in sc-CO_2 are presented in Table 1. The 95 % confidence interval reported together with the solubility take into account both the systematic error derived from the accuracy of instruments and the statistical error estimated from the variation of the results among the five samples collected at each P,T condition, using the standard method of estimation of systematic and statistical experimental errors.[7] It can be seen that the estimated error is lower than 3 % of the solubility in all measurements. Solubility increases at higher pressures and decreases at higher temperatures in the range of pressures and temperatures considered for the measurements. The highest solubility was $7.4 \cdot 10^{-2}$ g of DIPBAT·g^{-1} of CO_2, measured at 20 MPa and 353 K.

The solubility data were correlated as a function of sc-CO_2 density with the Chrastil empirical correlation (eq 1)[8]

$$\ln S = k \cdot \ln \rho_{CO2} + c \qquad (1)$$

where S is the solubility expressed as kilograms of solute·m^{-3} of sc-CO_2 and ρ_{CO2} is sc-CO_2 density (kg·m^{-3}). This density was obtained from NIST chemistry webbook.[9] The Chrastil equation parameters were calculated by minimizing the difference between experimental and calculated solubility, according to the objective function presented in eq 2. Chrastil temperature-dependent parameters are presented in Table 2, and the agreement of the Chrastil equation with experimental data is shown in Figure 2.

$$\text{AARD } \% = \frac{100}{n}\sum_{i=1}^{n}\frac{|S_i^{\text{exptl}} - S_i^{\text{calcd}}|}{S_i^{\text{exptl}}} \qquad (2)$$

Data were also correlated with the Peng–Robinson cubic equation of state (PR-EoS) with quadratic mixing rules (eqs 3 to 5).[10] For the application of this equation, it is necessary to know the critical properties of the substances. Because this information is not available for DIPBAT, the critical properties and acentric factor of DIPBAT were estimated using the Joback group contribution method.[11] For the application of this method, it has been supposed that the contribution of the Ti atom of DIPBAT is equal to the contribution of a C atom, as suggested by Stradi et al.[12] The critical properties of CO_2 and the estimated critical properties of DIPBAT considered for the correlation are presented in Table 3.

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2 - 2b\bar{V} - b^2} \qquad (3)$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij}) \qquad (4)$$

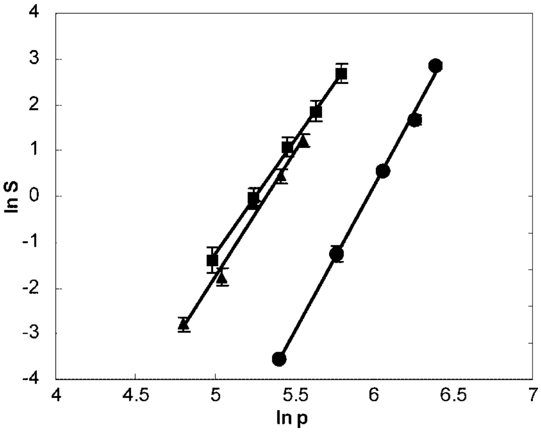

Figure 2. Solubility S of DIPBAT in sc-CO_2 as a function of sc-CO_2 density ρ at three different temperatures: •, $T = 353$ K; ■, $T = 423$ K; ▲, $T = 473$ K; lines calculated with the Chrastil equation (eq 1). The error bars in experimental data correspond with the accuracy of the data points presented in Table 1.

Table 3. Critical Properties of Pure Substances[a]

component	T_c/K	P_c/MPa	ω
CO_2	304.2	7.38	0.225
DIPBAT	944	1.29	0.439

[a] The properties of DIPBAT have been estimated with the Joback group contribution method.[11]

Table 4. PR-EoS Interaction Coefficients between CO_2 and DIPBAT

T/K	k_{ij}	l_{ij}	AARD % (eq 2)
353	0.1289	0.2620	35
423	0.0129	0.0554	17
473	0.2930	−0.3475	69

$$b = \sum_i \sum_j x_i x_j \frac{(b_i + b_j)}{2}(1 - l_{ij}) \tag{5}$$

The interaction parameters k_{ij} and l_{ij} have been calculated correlating the experimental solubility data minimizing the difference between experimental and calculated data (eq 2). The obtained interaction parameters are presented in Table 4, and the calculations with the PR-EoS are compared with experimental data in Figure 3. It can be seen that the deviations between experimental data and calculations with the PR-EoS are larger than with the Chrastil equation, especially at low pressures [(10 to 12.5) MPa]. Performing a sensitivity analysis to study the influence of the different parameters of the PR-EoS model on the calculated solubility, it was found that a variation of 10 % in the critical temperature T_c of DIPBAT causes a variation of over 200 % on the calculated solubility, while a variation of 10 % on the critical pressure P_c or acentric factor ω only causes a variation of about 20 % on the solubility. The same variation on the interaction coefficients k_{ij} and l_{ij} has a negligible influence on the calculated solubility. Therefore, it can be concluded that the main reason for the low accuracy of the PR-EoS model for the correlation of DIPBAT solubility is the lack of information about the critical properties of this component, especially the critical temperature.

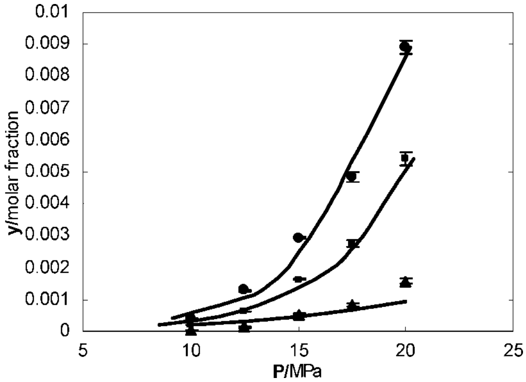

Figure 3. Solubility of DIPBAT y (molar fraction) in sc-CO_2 as a function of pressure P (MPa) at three different temperatures: •, $T = 353$ K; ■, $T = 423$ K; ▲, $T = 473$ K; lines calculated with the PR-EoS (eqs 3 to 5). The error bars in experimental data correspond with the accuracy of the data points presented in Table 1.

Conclusions

The solubility of diisopropoxititanium bis(acetylacetonate) (DIPBAT) in supercritical carbon dioxide has been measured with the continuous flow method. The obtained solubilities range from $5 \cdot 10^{-4}$ g_{DIPBAT}/g_{CO2} at $P = 10$ MPa and $T = 473$ K to $7.4 \cdot 10^{-2}$ g_{DIPBAT}/g_{CO2} at $P = 20$ MPa and $T = 353$ K. The solubility data have been correlated with the Chrastil equation with good results. Data have also been correlated with the Peng–Robinson equation of state (PR-EoS) with worse results, especially in the pressure range (10 to 12.5) MPa. The reason for the poor accuracy of the PR-EoS probably is the lack of experimental data about the critical properties of DIPBAT, especially the critical temperature, which had to be estimated with a group contribution method.

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