

Solubility of Irgacure[®] 2959 photoinitiator in supercritical carbon dioxide: Experimental determination and correlation

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Abstract

CIBA photoinitiator Irgacure[®] 2959 is a highly efficient radical photoinitiator for UV curing systems. Furthermore, and due to its proven low cellular toxicity, this photoinitiator can also be employed in the photopolymerization of polymers and copolymers intended for biomedical and tissue engineering applications, not only in conventional pharmaceutically accepted liquid solvents, but also in supercritical CO₂ (scCO₂). In this work we report the experimental measurement and correlation of the solubility of Irgacure[®] 2959 in scCO₂. Results were obtained using a static analytical method, at 308.2, 318.2 and 328.2 K, and in a pressure range from 10.0 up to 26.0 MPa. Experimental data were correlated with three density-based models (Chrastil, Bartle and Méndez-Santiago–Teja models) and with an equation-of-state (EOS) model: the Peng–Robinson cubic equation of state (PR-EOS) together with the conventional van der Waals mixing and combining rules. Several different sets of solid properties, estimated by different methods available in literature, were used in EOS correlations. The importance of the estimation methods used for the determination of solid properties (namely sublimation pressure) was discussed in terms of correlation results quality.

To the best of our knowledge, these are the first experimental scCO₂ solubility results for this class of initiators and the obtained solubility results indicate the feasibility of using this photoinitiator in free radical polymerization reactions carried out in scCO₂ like, for example, dispersion and precipitation polymerizations, or in the development of interpenetrating polymer networks (IPN's).

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1. Introduction

Despite other inherent advantages, the potentialities of supercritical fluid-based technologies as environmental friendly alternatives to several traditional processes commonly implemented at industrial scale have already been demonstrated [1]. Carbon dioxide (CO₂), in a near critical or in a critical state, is undoubtedly the most investigated and employed supercritical fluid (SCF), mainly due to its relatively low critical temperature and critical pressure ($T_c = 304.15$ K, $P_c = 7.38$ MPa) as well as to other advantageous properties such as its mass and heat transfer properties, non-toxicity, non-flammability and low cost.

In recent years supercritical carbon dioxide (scCO₂) has also become an attractive media solvent for polymer processing and for several types of polymerization reactions [1–3].

Despite the fact that scCO₂ is normally a poor solvent for high molecular weight polymers, it can be considered as an ideal solvent for free-radically initiated polymerization reactions mainly because it does not support chain transfer to the solvent and it is inert towards polymer-based free radicals [3]. Because most vinyl polymers show poor solubility in scCO₂, heterogeneous polymerizations, and particularly dispersion and precipitation polymerizations, have been the most extensively studied polymerization methods in scCO₂ media [1,3]. In these processes, the initiator must be soluble in a certain extent in the initial homogeneous mixture (also containing the vinyl monomer) and it is usually an oil-soluble thermal initiator such as an organic azo-compound (e.g., 2,2'-azobis-isobutyronitrile, AIBN) or a peroxide (e.g., benzoyl peroxide, BPO) [1,3]. Another possible application of these scCO₂-based free radical polymerization methods can be on the development of interpenetrating polymeric networks (IPN's) in which, for example, a second free radical polymerization reaction is carried out inside another previously formed and CO₂-swelled polymeric matrix. In this case, scCO₂ is not just the foaming/swelling agent but also the

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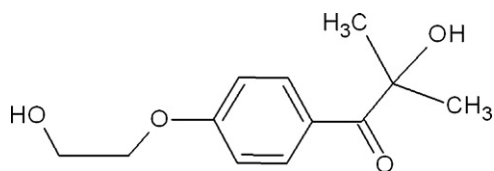


Fig. 1. Chemical structure of Irgacure® 2959 (CAS 106797-53-9, 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone).

carrier/infusion agent for the second vinyl monomer and/or the initiator [3].

However, and when thermal initiators are used, high temperatures (usually above 60 °C) are normally required to initiate free radical polymerization reactions. Therefore, in some cases and for several reasons especially when thermo-labile substances or devices are involved in the reaction or process, it would be preferable to use a different type of oil-soluble initiator, like a photoinitiator, which will avoid the use of high initiation and polymerization temperatures.

Photochemical (ultraviolet or visible light) initiated polymerization reactions are a well-established technology for many industrial applications like offset lithographic and flexographic inks, screen printing, metal decoration, wood coatings, pigmented coatings for textile applications and pigmented primary and secondary optical fiber coatings [4]. Photopolymerization is also commonly used in a broad range of biomedical applications such as dentistry, implants, scaffolds, bioadhesives and drug delivery systems [5,6].

The commercially available CIBA photoinitiator, Irgacure® 2959 (2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Fig. 1) is a highly efficient radical Type I photoinitiator for UV curing systems (comprised by unsaturated monomers and/or pre-polymers), which is also suitable for use in water-borne systems. Furthermore, and mostly due to its properties and to its low cellular toxicity [5], this photoinitiator can also be employed in the photopolymerization of polymers and copolymers intended for biomedical and tissue engineering applications in conventional pharmaceutically accepted liquid solvents [6]. Because of the recognized advantages of polymeric supercritical fluid technology, a dif-

ferent and attractive alternative could be the use of this photoinitiator in polymerization processes carried out in scCO₂ media.

However, for the design of any process based in supercritical fluid technology (like polymerization reactions in scCO₂), it is necessary to have a precise knowledge of the solubility data, at different conditions of temperature and pressure, between all the involved compounds and the SCF solvent. If not completely determined experimentally, the solid solubility in SCFs must then be obtained and extended (interpolated) through correlations based on theoretical or empirical models applied to the existing experimental data [7]. The most common models used to correlate solid-supercritical phase equilibria are cubic equations-of-state (EOS's) belonging to the van der Waals family, like the Peng and Robinson [8] or the Soave-Redlich-Kwong [9] EOSs. As a frequent alternative, several empirical correlations, such as the density-based correlations of Chrastil and co-workers [10–12] are also broadly used.

In this work the solubility of Irgacure® 2959 in scCO₂ was measured between 10.0 and 26 MPa, and at 308.2, 318.2 and 328.2 K, using a static analytical experimental method. Experimental data were correlated using several semi-empirical density-based models (Chrastil, Bartle and Méndez-Santiago-Teja) and the Peng–Robinson cubic equation of state, together with the conventional van der Waals mixing and combining rules. Several different sets of solid properties, which were estimated by different methods available in literature, were used in EOS-based correlations.

2. Experimental

2.1. Materials

Carbon dioxide (CAS 124-38-9, purity >99.998%) was purchased from praxair and ethanol (CAS 64-17-5, purity >99.5%) was obtained from Panreac Quimica SA. Irgacure® 2959 (2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone, CAS 106797-53-9, purity = 97–99.5%) was kindly supplied by Ciba Specialty Chemicals, Switzerland.

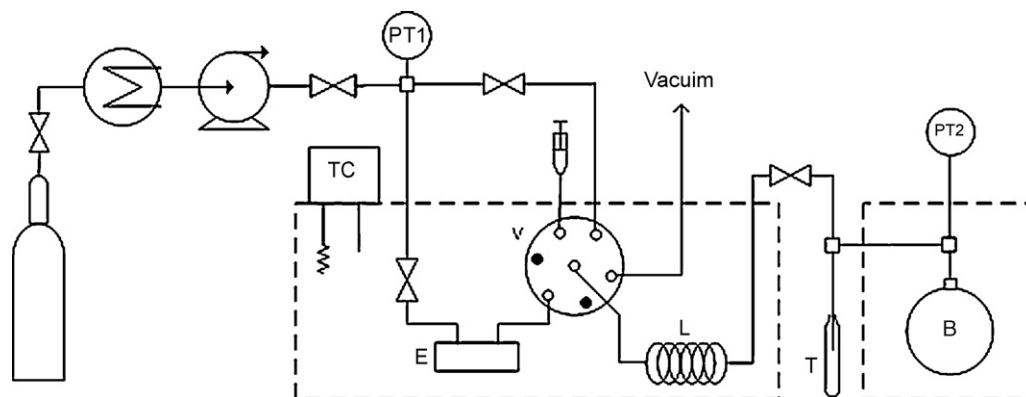


Fig. 2. Schematic diagram of the supercritical solid solubility experimental apparatus. PT1, high pressure transducer; PT2, low pressure transducer; TC, temperature controller; E, equilibrium cell; V, six-port sampling valve; L, sampling loop; T, glass trap; B, expansion balloon.

2.2. Apparatus and procedure

The experimental solubility of Irgacure® 2959 in scCO₂ was measured using the static equilibrium apparatus schematically represented in Fig. 2. A detailed description of the apparatus and its validation were given in previous works [13,14]. A typical experimental procedure is described below.

A high-pressure equilibrium cell, equipped with sapphire windows and with an internal volume of approximately 30 cm³, is loaded with an excess amount of the solid to be studied and a magnetic stirrer. The cell is connected to the apparatus lines and immersed in a water bath, equipped with a temperature controller that maintains the temperature within ± 0.1 K. Carbon dioxide is liquefied in a cooling unit and compressed using a high-pressure liquid pump. When the water bath reaches the experiment temperature, the cell is pressurized with CO₂ until the desired experimental pressure is attained. Pressure is measured with a high-pressure transducer (Setra, model 204, 0–34.40 \pm 0.04 MPa). After pressure and temperature stabilization, the magnetic stirring plate, positioned under equilibrium cell, is switched on and the solid + CO₂ mixture is left to stir for 1 h (the period of time found to be necessary to attain equilibrium and fluid phase saturation), followed by a 20 min period, without stirring, to allow mixture stabilization. An homogeneous mixture sample is then removed from the cell, using a six-port sampling valve (Rheodyne, model 7060), into a sampling loop of 0.456 cm³. This sample is then quickly depressurized and expanded into previously calibrated volumes, composed by a glass trap (15.9 cm³), immersed in ice, and a stainless steel balloon (1735.05 cm³) immersed in a water bath, at room temperature, and previously brought into sub-atmospheric pressure using a vacuum pump. The resultant pressure increase is measured using a calibrated high precision low-pressure transducer (Setra, model 204, 0–0.175 \pm 1.9 $\times 10^{-4}$ MPa). During expansion, the formerly dissolved solid precipitates in the glass trap. To recover all the precipitated solid, a cleaning solvent (ethanol) is injected through the sample loop and expansion lines and re-collected in the glass trap. The lines are also cleaned with fresh CO₂ smoothly pressurized.

The amount of solubilized solid was determined by UV spectrophotometric analysis. The collected samples containing the solid are diluted to a convenient volume with ethanol and the absorbance of the resulting solutions is measured at a fixed wavelength (275 nm) using a UV–vis spectrophotometer (JASCO V-530). A calibration curve was obtained by UV analysis of previously prepared standard solid samples with concentrations between 2 and 25 μ g/ml.

The amount of CO₂ in the sample loop is calculated using the Virial EOS (applied to pure CO₂) and considering the values of the pre-calibrated expansion volumes, the resulting sub-atmospheric pressure increase due to expansion, the temperature of water bath where the expansion balloon is immersed, and the temperature of the ice-immersed glass trap (which is considered to be 273.15 K).

All operations involving Irgacure® 2959 were performed avoiding all possible contact with light. The overall uncertainty, taking in consideration the random uncertainties (statistical,

associated to Beer–Lambert's calibration curve and to the average of the experimental solubility measurements) and the systematic uncertainties (uncertainties due to the preparation of standard calibration solutions and to pressure and temperature measurements) was found to be less than 3.7×10^{-6} (in y, mole fraction of Irgacure® 2959).

3. Correlation of experimental solubility data

Semi-empirical and empirical correlations, based in the density of the pure SCF, are widely used for the correlation of solid/SCF equilibrium mainly due to their simplicity and easy application. In this work we correlated the experimental data with three frequently employed density-based models: the Chrastil model [10], the Bartle et al. model [11] and the Méndez-Santiago–Teja model [12].

In equation-of-state (EOS)-based models, the supercritical phase can be treated as a compressed gas phase and the solubility of the solid is then given by an expression derived from the thermodynamic equilibrium conditions between the solid phase and that high-pressure gas phase. Cubic EOS's, together with mixing and combining rules, are the most used models to evaluate the fugacity coefficient of the solid in the compressed phase. These models always require the knowledge of critical properties and Pitzer's acentric factor of the involved compounds and also of the molar volume and the sublimation pressure of the studied solid. However, and for most solids, these properties are usually unknown which constitutes a disadvantage for the application of these correlation models. Usually, these required solid properties are obtained using group contribution estimation methods or other estimation methods available in literature. In this work, the well-known Peng–Robinson cubic equation of state (PR-EOS) [8], together with the conventional van der Waals mixing and combining rules, was used to evaluate the fugacity coefficient of the solid in the compressed fluid phase. The required physicochemical properties of the solid, namely the critical properties and the sublimation pressure, were estimated using different estimation methods proposed in the literature.

3.1. Density-based correlations

3.1.1. Chrastil model

Chrastil [10] derived an equation which relates the solubility of a solid solute in a SCF with the density of the pure SCF and the absolute temperature. This model is based on the supposition that one molecule of solute, A, associates with k molecules of the SCF solvent, B, to form a solvate-complex AB _{k} , in equilibrium with the system. The definition of the equilibrium constant, which is obtained throughout several thermodynamic considerations, leads to the following expression for the solid solubility:

$$\ln S = k \ln \rho + \frac{\alpha}{T} + \beta \quad (1)$$

In this expression, S (kg/m³) is the solubility of the solid in the supercritical phase, ρ (kg/m³) is the density of the pure supercritical fluid, k is the association number, α is a constant, defined as $\Delta H/R$ (where ΔH is the sum of the enthalpies of vaporization and

solvation of the solute, and R is the gas constant) and β is another constant somehow related to the molecular weight of the solute and solvent. The parameters, k , α and β , are obtained performing a multiple linear regression on the experimental solubility data.

3.1.2. Bartle et al. model

Bartle and co-workers [11] proposed a simple density-based semi-empirical model to correlate the solubility of solids in SCFs:

$$\ln \left(\frac{y_2 P}{P_{\text{ref}}} \right) = A + C(\rho - \rho_{\text{ref}}) \quad (2)$$

where

$$A = a_1 + \frac{a_2}{T} \quad (3)$$

$$\ln \left(\frac{y_2 P}{P_{\text{ref}}} \right) = a_1 + \frac{a_2}{T} + C(\rho - \rho_{\text{ref}}) \quad (4)$$

In these expressions, P_{ref} is assumed as a standard pressure of 1 bar, ρ_{ref} is a reference density assumed as 700 kg/m³, and a_1 , a_2 , A , and C are empirical constants, determined in the following way: from the experimental solubility data, each isotherm is fitted using Eq. (2), to obtain the values of A and C . The C values are averaged and these values are then used to recalculate the A values for the various isotherms. The A constants are then plotted against $1/T$ and correlated with Eq. (3), in order to determine constants a_1 and a_2 . Finally, the values a_1 , a_2 and C are used to predict the solubility, applying Eq. (4). In this model, the parameter a_2 is related to the enthalpy of sublimation of the solid solute, ΔH_{sub} , by the expression $\Delta H_{\text{sub}} = -Ra_2$, where R is the gas constant.

3.1.3. Méndez-Santiago–Teja model

Based on the theory of dilute solutions, Méndez-Santiago and Teja [12] developed a simple linear expression to correlate the solubility of solids in a SCF:

$$T \ln(y_2 P) = A' + B' \rho + CT \quad (5)$$

In Eq. (5), A' , B' and C' are constants, considered as temperature independent, and obtained by a multiple linear regression of the solubility experimental data.

3.2. EOS-based models

The solubility of a solid solute (y_2) at equilibrium with a fluid, at high pressure, can be calculated using the following general expression:

$$y_2 = \frac{P_2^{\text{sub}}}{P} \frac{1}{\varphi_2^{\text{SCF}}} \exp \left[\frac{v_2(P - P_2^{\text{sub}})}{RT} \right] \quad (6)$$

This equation is derived from the equifugacity condition between the solid and the fluid phase, under the assumptions that the solubility of the solvent (scCO₂) in the solid phase is negligible, the solid is incompressible and the saturated vapor of the pure solid solute at sublimation behaves like an ideal gas. In Eq. (6), P_2^{sub} is the sublimation pressure of the solid solute, v_2 is

the molar volume of the solid, and φ_2^{SCF} is the fugacity coefficient of the solid in the fluid phase, which expresses the non-ideality of the fluid phase. This parameter is usually evaluated by an equation of state. In this work, the Peng–Robinson cubic equation of state (PR-EOS) [8], described by Eqs. (7)–(10), was used to estimate φ_2^{SCF} :

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \quad (7)$$

$$a = 0.45724 \left(\frac{R^2 T_c^2}{P_c} \right) \left\{ 1 + n \left[1 - \left(\frac{T}{T_c} \right)^{0.5} \right] \right\}^2 \quad (8)$$

$$n = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (9)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (10)$$

To apply the above EOS for the binary solid + scCO₂ mixture, we employed the classical van der Waals (vdW) mixing and combining rules, with one or with two adjustable parameters k_{ij} and l_{ij} :

$$a = \sum_i \sum_j y_i y_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (11)$$

$$b = \sum_i \sum_j y_i y_j \left(\frac{b_i + b_j}{2} \right) (1 - l_{ij}) \quad (12)$$

The optimal binary interaction parameters, k_{ij} and l_{ij} , for each temperature, must be obtained by the correlation of experimental data, through the minimization of the objective function average-absolute-relative-deviation (AARD), defined as

$$\text{AARD}(\%) = \frac{100}{N} \sum_n \frac{|y^{\text{cal}} - y^{\text{exp}}|}{y^{\text{exp}}} \quad (13)$$

In this equation, N is the number of experimental data points for each isotherm, y^{cal} correspond to the calculated solubilities and y^{exp} correspond to the experimental solubility data points.

3.3. Estimation of solid properties

As already mentioned, the correlation of the solubility of a solid in a SCF using an EOS-based model requires the values for the critical properties (T_c , P_c), Pitzer's acentric factor (ω), sublimation pressure and molar volume of the solid. For many pure solid compounds the experimental values of these properties are difficult or even impossible to obtain. For this reason, these properties are commonly obtained employing different estimation methods. For practical reasons, the majority of the predictive methods available in literature were developed based on the behavior of pure components that are gases or liquids at normal temperature and pressure (which is not the case). Thus, the use of these methods to estimate solid compounds properties must be selected and used very carefully. In this work, we estimated the critical properties and the sublimation pressure of Irgacure® 2959 using several different methods available in literature and we employed the obtained different sets of properties

to correlate the experimental solubility data with the PR-EOS. An excellent review on the most important estimation methods for these properties can be found in the recent and well-known book by Poling et al. [15] as well as on its previous editions.

The critical pressure (P_c) and critical temperature (T_c) of Irgacure® 2959 were calculated using three different estimative methods: the Joback method [15], the Wilson–Jasperson method [15] and a group contribution method recently proposed by Marrero and Gani [16]. The Pitzer's acentric factor and the sublimation pressure of the solid were estimated by the Ambrose–Walton corresponding states method [15], according to the following equations:

$$\omega = -\frac{\ln(P_c/1.01325) + f^{(0)}(T_{br})}{f^{(1)}(T_{br})} \quad (14)$$

$$\ln(P^{vp})_r = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + \omega^2 f^{(2)}(T_r) \quad (15)$$

In the above equations, T_{br} is the reduced normal boiling temperature, T_r is the reduced temperature and $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$, are analytical expressions which are functions of T_{br} (for Eq. (14)) or of T_r (for Eq. (15)). In Eq. (15) $(P^{vp})_r$ is the reduced vapor pressure of the pure solid that, in this case, it is assumed to be the solid reduced sublimation pressure, and considering that the solid can be treated has a subcooled liquid.

Another and recent method to predict the vapor pressure of organic solids, proposed by Coutisikos et al. [17], was also employed for the estimation of Irgacure® 2959's sublimation pressure. This procedure, which combines a group contribution method and the concept of a hypothetical liquid, is described by the following equation:

$$\ln P^S = \ln P^L + \frac{\Delta_{fus}S}{R} \left(1 - \frac{T_m}{T}\right) \quad (16)$$

Eq. (16) relates the vapor pressure of the solid, P^S , to the vapor pressure of the referred hypothetical liquid, P^L , at the same temperature, T . P^L is estimated by the Abrams–Massaldi–Prausnitz (AMP) method [18], described by Eq. (17), while the term $\Delta_{fus}S/R$ is determined by a group-contribution method (Eq. (18)):

$$\ln P^L = A + \frac{B}{T} + C \ln T + DT + ET^2 \quad (17)$$

$$\frac{\Delta_{fus}S}{R} = \sum_i n_i \left(\frac{\delta_{fus}S_i}{R} \right) \quad (18)$$

In Eq. (18), $\delta_{fus}S_i$, is the contribution from the group type i , and n_i is the number of groups of type i in a molecule. In Eq. (17), the constants A to E are functions of three fundamental parameters (V_W , s , E_0) which reflect the size and shape, flexibility and intermolecular forces of the molecules, respectively [17,18]. V_W is the van der Waals hard-core volume, E_0 is the enthalpy of vaporization of the hypothetical liquid at $T=0$ K, and s is the number of equivalent oscillators per molecule. In the group-contribution scheme of the AMP equation, these parameters are estimated as

follows:

$$s = \sum_i n_i s_i \quad (19)$$

$$\frac{E_0}{R} = \sum_i n_i \left(\frac{\varepsilon_{0i}}{R} \right) \quad (20)$$

$$V_W = \sum_i n_i V_{Wi} \quad (21)$$

In these equations, s_i , ε_{0i} , and V_{Wi} , are contributions from the group type i and n_i is the number of groups of type i in each molecule. In the Coutisikos' approach, the original parameters s_i and ε_{0i}/R for hydrocarbon molecule groups are reevaluated using mainly sublimation pressure data, while the hard-core van der Waals volume (V_W) is obtained using Bondi's group-contribution increments [19]. In this work, the V_W value for Irgacure® 2959 was estimated using a method proposed by Zissimos and co-workers [20] and based on Bondi's radii.

Finally, the required molar volume of Irgacure® 2959 was estimated using the Fedors group contribution method [21].

4. Results and discussion

4.1. Experimental solubility results

The experimental solubilities of Irgacure® 2959 in scCO₂ were determined at 308.2, 318.2, and 328.2 K, and in the pressure range from 10.0 up to 26.0 MPa, and are reported in Table 1, in terms of solid mole fraction, y_2 , and in terms of concentration of the solid in scCO₂, S (g/l). The solid mole fraction solubility (y_2) varied between 5.17×10^{-6} and 2.83×10^{-4} . Each reported data point is the average of, at least, three replicate measurements with relative standard deviations (RSD) between

Table 1
Experimental solubility of Irgacure® 2959 in supercritical carbon dioxide

T (K)	P (MPa)	ρ (kg/m ³)	y_2 ($\times 10^4$)	S (kg/m ³)
308.2	10.1	713.3	0.431	0.157
	12.7	777.8	0.599	0.237
	15.2	815.1	0.804	0.334
	17.8	843.8	0.916	0.394
	20.4	866.8	1.101	0.486
	22.8	884.6	1.181	0.533
	25.4	901.8	1.263	0.581
318.2	10.1	499.2	0.168	0.043
	12.7	677.9	0.635	0.220
	15.2	742.8	0.972	0.368
	17.8	782.8	1.253	0.500
	20.3	813.0	1.517	0.629
	22.8	836.7	1.664	0.710
	25.6	859.0	1.864	0.816
328.2	10.2	326.9	0.052	0.009
	12.7	540.5	0.412	0.114
	15.2	653.1	1.035	0.345
	17.8	715.1	1.592	0.581
	20.4	756.3	2.160	0.833
	22.9	786.5	2.437	0.977
	25.3	810.6	2.831	1.170

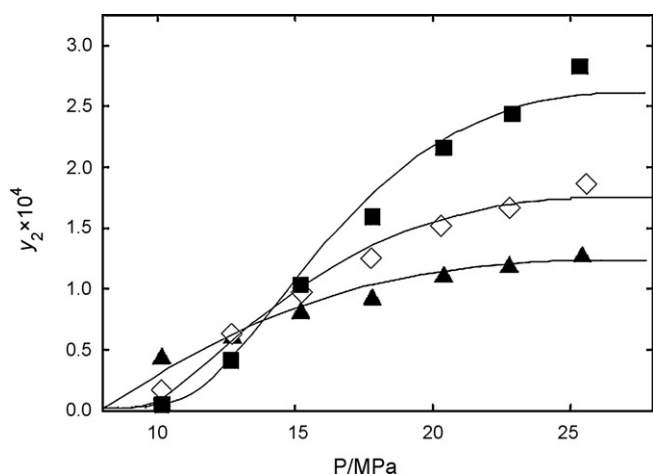


Fig. 3. Solubility of Irgacure® 2959 in scCO₂. Experimental: 308.2 K (▲); 318.2 K (◇); 328.2 K (■); (—) calculated with the PR-vdW2 model using the estimated solid properties of Set 2* (see Table 3).

1.6% ($T = 308.2$ K, $P = 22.9$ MPa, $y_2 = 2.44 \times 10^{-4}$) and 9.5% ($T = 328.2$ K, $P = 10.2$ MPa, $y_2 = 5.17 \times 10^{-6}$), and an overall RSD of 4.2%.

The solubility isotherms of Irgacure® 2959 in scCO₂ follow the typical and expected behavior of a solid/SCF system, with the solubility increase with pressure, due to the increase of scCO₂ density and, consequently, to the enhancement of the scCO₂ dissolving power. The graphic representation of these three experimental isotherms and their corresponding correlation curves (obtained with the PR-EOS-based model described in Section 3.2 and with Set 2* of estimated physical and thermo-physical properties, as we will see further on) can be observed in Fig. 3, where the solid mole fraction solubility is represented as a function of pressure. Isotherms also evidenced the retrograde solubility behavior which is characteristic of most of the solid/SCF systems and which is caused by the opposite effect of temperature on the density of the SCF and on the sublimation pressure of the solid solute. For this system, this so-called “crossover region”, where one can observe the intersection of the solubility isotherms, is located around 14.0 MPa.

A comparison between the magnitude of these solubility results and the experimental scCO₂ solubility data for other free radical initiators is impossible because, to the best of our knowledge, these results were never reported in the literature. For example, some works referred that AIBN and BPO are soluble in some extent in scCO₂ but the corresponding solubility results were never presented [22–25].

4.2. Correlation results

The fitted parameters for the system Irgacure® 2959/scCO₂, obtained with the three investigated density-based correlations, are presented in Table 2, where the corresponding AARD values are also indicated. The graphic representation of these results can be observed in Figs. 4–6, where the experimental data and the fitted curves for the three models are shown. As can be seen, the obtained AARD values were 3.3% (for Chrastil model), 5.3% (for Bartle et al. model) and 4.7% (for Méndez-Santiago–Teja

Table 2

Correlation results obtained with the three employed density-based models

Chrastil model (Eq. (1))	
k	4.5
α (K)	−6460.0
β	−16.7
ΔH (kJ/mol)	−53.7
AARD (%)	3.3
Bartle et al. model (Eq. (4))	
a_1	24.35
a_2 (K)	−9213.8
C (m ³ /kg)	0.010
ΔH_{sub} (kJ/mol)	76.6
AARD (%)	5.3
Méndez-Santiago–Teja model (Eq. (5))	
A' (K)	−11601.2
B' (m ³ /kg)	3.2
C'	24.8
AARD (%)	4.7

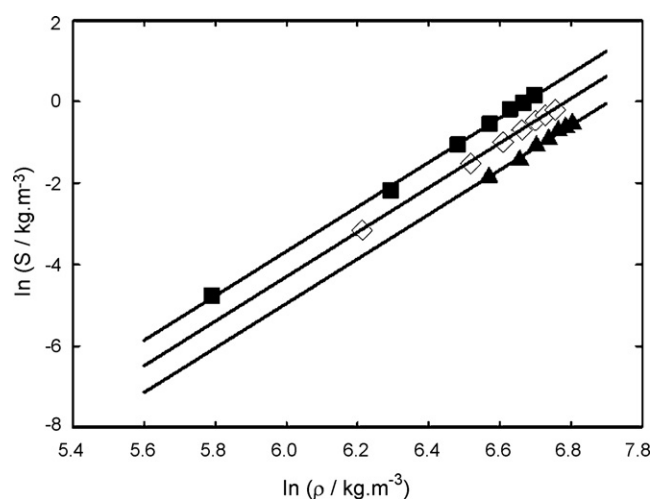


Fig. 4. Logarithmic relationship between Irgacure® 2959 solubility in scCO₂ and the density of pure CO₂. Experimental: 308.2 K (▲); 318.2 K (◇); 328.2 K (■); (—) calculated by Eq. (1), Chrastil's model.

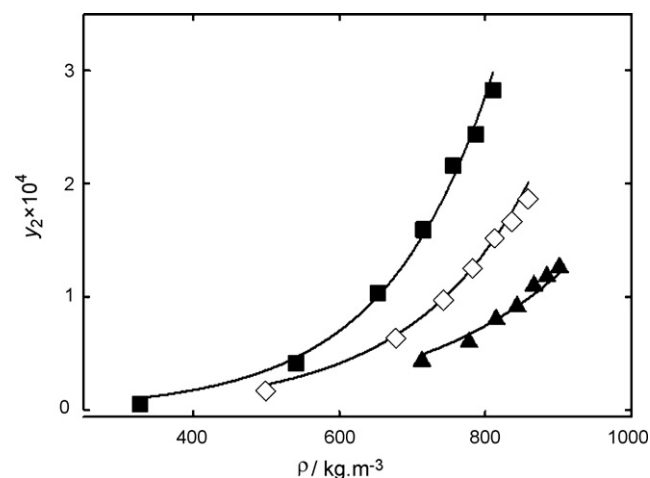


Fig. 5. Solubility of Irgacure® 2959 in scCO₂ as a function of the density of pure CO₂. Experimental: 308.2 K (▲); 318.2 K (◇); 328.2 K (■); (—) calculated by Eq. (4), Bartle's model.

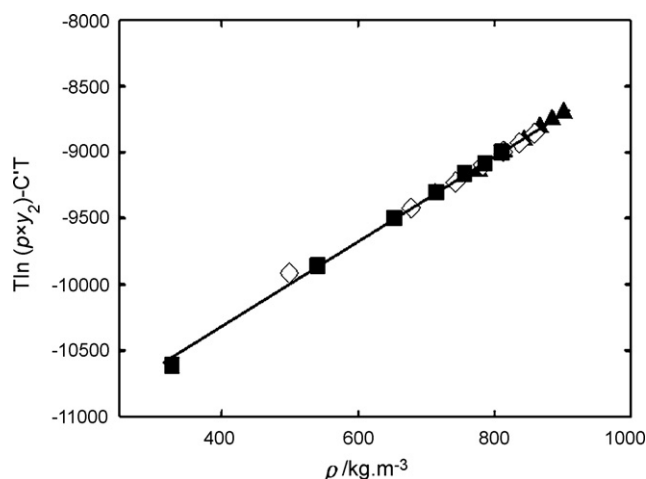


Fig. 6. Relationship between the solubility of Irgacure® 2959 and the density of pure CO₂. Experimental: 308.2 K (▲); 318.2 K (◇); 328.2 K (■); (—) calculated by Eq. (5), Méndez-Santiago-Teja's model.

model). All the employed density-based correlation models fitted almost perfectly the obtained experimental data points, even for low pressure/low density points which normally present larger deviations from the experimental results.

The estimated values for the solid critical properties, acentric factor and sublimation pressure, required for the EOS-based correlation model, as well as the corresponding employed estimation methods (referred in Section 3.3) are presented in the upper part of Table 3. Five different sets of input solid properties (Set 1 to Set 5) were used to correlate the experimental solubility data using the PR-EOS, with the vdW mixing and combining rules with one adjustable parameter (PR-vdW1) or with the vdW mixing and combining rules with two adjustable parameters (PR-vdW2). The solid molar volume was estimated to be 151.1 cm³ mol⁻¹ by the Fedors group contribution method [21]. This value was used in all sets of properties. Experimental values of Irgacure® 2959 normal boiling temperature [26] were also used as indicated in Table 3.

Analyzing the values of upper part of Table 3, it is clear that completely different sets of estimated values were generated for the solid properties, especially for the acentric factor (with values

varying from 0.131 to 1.682) and for solid sublimation pressure (with clearly over- and underestimated values like, for example, 3.08 Pa and 1.43×10^{-13} Pa, at 308.2 K). These discrepancies are not surprising and are related with the different estimation methods employed to calculate ω and P^{sub} , which require the values of solid critical properties and solid normal boiling temperature, which are also estimated values. Thus, depending on the estimated values of these properties, completely different estimated values of ω and P^{sub} will be generated. These aspects were already discussed in previous works [7,14].

The optimal fitted interaction parameters and the corresponding AARD values, obtained by the correlation of experimental solubility data with the PR-EOS model and using the above-referred five sets of properties, are presented in the left side of Table 4. The graphical representation of these correlation results can be observed in Fig. 7, where the molar fraction solubility data of Irgacure® 2959 in scCO₂, at 318.2 K, is plotted against pressure, together with the fitted curves obtained with the PR-vdW1 and PR-vdW2 models. This figure clearly reveals that, for the model with only one adjustable parameter, PR-vdW1 (Fig. 7a), only Set 2 of estimated properties was capable to generate a fair fitting of experimental data (7.5% AARD). The same behavior was observed for the other two isotherms. When correlating with two adjustable parameters (Fig. 7b) and as expected, the correlation results were improved and the discrepancies of fitted curves were attenuated, with Sets 1 to 4 generating also reasonably fittings for all isotherms. The use of Set 5 of estimated properties, in both PR-vdW1 and PR-vdW2 models, failed to fit experimental data for all isotherms.

To have an idea how the different estimated sublimation pressure values used in the models differ from the real sublimation pressure of Irgacure, P^{sub} was also estimated at 298.2 K and the obtained values were compared with the experimental sublimation pressure of Irgacure at the same temperature, taken from literature [26]. These results can be observed in Table 5. As observed, the only estimated P^{sub} value with the same order of magnitude of the experimental sublimation pressure was obtained with the corresponding states method of Ambrose–Walton, using the values of T_b , T_c , and P_c estimated with the group contribution method of Marrero–Gani. This cor-

Table 3
Estimated critical and thermophysical properties of Irgacure® 2959

Set	Estimation method				T_c (K)	P_c (bar)	T_b (K)	ω	P_2^{sub} (Pa)		
	T_c, P_c	T_b	ω	P_2^{sub}					308.2 K	318.2 K	328.2 K
1	M–G	Exp	A–W	A–W	840.6	28.90	604.2	0.600	4.63×10^{-2}	1.34×10^{-1}	3.61×10^{-1}
2	M–G	M–G	A–W	A–W	840.6	28.90	628.6	0.873	7.97×10^{-4}	3.04×10^{-3}	1.05×10^{-2}
3	W–J	Exp	A–W	A–W	822.1	23.10	604.2	0.641	4.54×10^{-2}	1.33×10^{-1}	3.58×10^{-1}
4	Job	Exp	A–W	A–W	959.0	36.25	604.2	0.131	3.08	6.30	12.28
5	Job	Job	A–W	A–W	959.0	36.25	763.0	1.682	1.43×10^{-13}	1.99×10^{-12}	2.26×10^{-11}
1*	M–G	Exp	A–W	Cout	840.6	28.90	604.2	0.600	2.59×10^{-5}	2.95×10^{-4}	2.81×10^{-3}
2*	M–G	M–G	A–W	Cout	840.6	28.90	628.6	0.873	2.59×10^{-5}	2.95×10^{-4}	2.81×10^{-3}
3*	W–J	Exp	A–W	Cout	822.1	23.10	604.2	0.641	2.59×10^{-5}	2.95×10^{-4}	2.81×10^{-3}
4*	Job	Exp	A–W	Cout	959.0	36.25	604.2	0.131	2.59×10^{-5}	2.95×10^{-4}	2.81×10^{-3}
5*	Job	Job	A–W	Cout	959.0	36.25	763.0	1.682	2.59×10^{-5}	2.95×10^{-4}	2.81×10^{-3}

M–G: Marrero–Gani method [16]; A–W: Ambrose–Walton corresponding states method [15]; W–J: Wilson–Jasperson method [15]; Job: Joback method [15]; Cout: Coutsikos method [11]; Exp: experimental [26].

Table 4

Correlation results obtained with the Peng–Robinson EOS model

<i>T</i> (K)	Set	PR-vdW1		PR-vdW2			Set	PR-vdW1		PR-vdW2		
		<i>k</i> ₁₂	AARD (%)	<i>k</i> ₁₂	<i>l</i> ₁₂	AARD (%)		<i>k</i> ₁₂	AARD (%)	<i>k</i> ₁₂	<i>l</i> ₁₂	AARD (%)
308.2	1	0.218	19.5	0.313	0.225	2.9	1*	−0.054	23.4	−0.198	−0.325	7.8
	2	0.140	7.5	0.119	−0.051	4.8	2*	0.028	23.5	−0.086	−0.280	7.9
	3	0.220	35.2	0.377	0.352	2.8	3*	−0.034	11.7	−0.074	−0.080	7.9
	4	0.320	47.8	0.564	0.551	3.2	4*	−0.181	27.9	−0.382	−0.420	7.8
	5	−0.238	67.4	−0.816	−1.85	20.5	5*	0.247	28.5	0.121	−0.412	7.9
318.2	1	0.217	24.1	0.305	0.215	2.9	1*	−0.031	30.3	−0.182	−0.350	12.2
	2	0.133	15.7	0.051	−0.205	7.4	2*	0.047	30.5	−0.094	−0.355	12.2
	3	0.225	43.1	0.370	0.344	2.8	3*	−0.011	19.0	−0.072	−0.130	12.2
	4	0.356	75.0	0.583	0.602	16.2	4*	−0.153	34.5	−0.382	−0.500	12.3
	5	−0.254	72.0	−0.982	−2.327	29.2	5*	0.260	35.4	0.122	−0.473	12.2
328.2	1	0.222	43.2	0.352	0.341	12.4	1*	−0.010	30.0	−0.169	−0.385	10.5
	2	0.120	18.1	0.034	−0.225	5.7	2*	0.066	30.2	−0.082	−0.387	10.5
	3	0.230	63.9	0.421	0.479	13.1	3*	0.010	18.5	−0.059	−0.155	10.5
	4	0.574	83.8	0.882	1.279	35.8	4*	−0.126	34.2	−0.344	−0.498	10.5
	5	−0.293	75.1	−1.137	−2.769	36.5	5*	0.292	43.6	0.129	−0.512	10.5

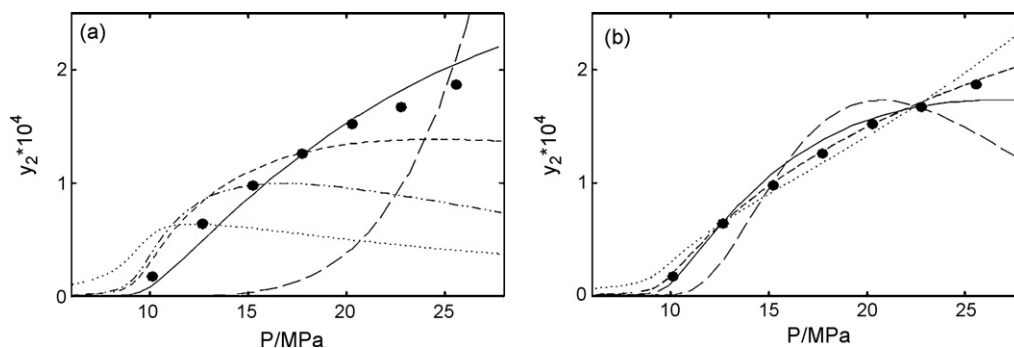


Fig. 7. Experimental solubility of Irgacure® 2959 in scCO₂, at 318.2 K, and correlation results obtained for five different sets of critical and physicochemical properties of the solid. (a) PR-EOS with vdW1 and (b) PR-EOS with vdW2. Set 1 (---); Set 2 (—); Set 3(— · —); Set 4 (·· ·); Set 5 (——).

responds to Set 2 of estimated properties, precisely the one that yielded the best correlation results and the only one for which the PR-EOS model with only one adjustable parameter, PR-vdW1, successfully fitted the data. On the contrary, the obtained P^{sub} values, using the critical properties estimated by the Joback group contribution method, were found to be greatly over- (Set 4) or underestimated (Set 5). It was also with these sets of properties, especially with Set 5, that the PR-EOS models were unable to fit the data, even when two adjustable parameters were used (see Fig. 7 and Table 4). For the remaining sets of properties

(Set 1 and Set 3), the estimated sublimation pressures were overestimated by two orders of magnitude. Finally, the sublimation pressure was also estimated with the Coutisikos method, at 298.2 K, and results indicated that P^{sub} was underestimated just by two orders of magnitude.

To analyze the role of these sublimation pressure input values, five new sets of properties were generated by substituting, in all the original five sets, the different P^{sub} values generated by the Ambrose–Walton corresponding states method by the P^{sub} values estimated with the Coutisikos method. These estimated values, at 308.2, 318.2 and 328.2 K, are presented in the lower part of Table 3 and were designated as Set 1*, Set 2*, Set 3*, Set 4* and Set 5*. The correlation results obtained with the PR-vdW1 and PR-vdW2 models are displayed on the right side of Table 4. The corresponding generated correlation curves are represented in Fig. 8, for the 318.2 K solubility isotherm. As can be seen, the fitted curves are very similar, especially for the model with two adjustable parameters, where all these new property sets generated almost identical curves and AARD values, for the three isotherms (~7.9, ~12.2 and ~10.5% for 308.2, 318.2 and 328.2 K, respectively), despite the considerably different values of T_c , P_c and ω used in those five sets of properties. Once again, these results evidenced the dominant character that solid

Table 5

Relation between the estimated and the experimental sublimation pressure of Irgacure® 2959 at 298.2 K

$(P_2^{\text{sub}})_{\text{cal}}/\text{Pa}$		$(P_2^{\text{sub}})_{\text{cal}}/(P_2^{\text{sub}})_{\text{exp}}$
Estimation method	Value	
Ambrose–Walton (Set 1)	1.46×10^{-2}	$2.1 \times 10^{+2}$
Ambrose–Walton (Set 2)	1.86×10^{-4}	2.7
Ambrose–Walton (Set 3)	1.42×10^{-2}	$2.0 \times 10^{+2}$
Ambrose–Walton (Set 4)	1.42	$2.0 \times 10^{+4}$
Ambrose–Walton (Set 5)	8.51×10^{-15}	1.2×10^{-10}
Coutisikos	1.86×10^{-6}	2.7×10^{-2}

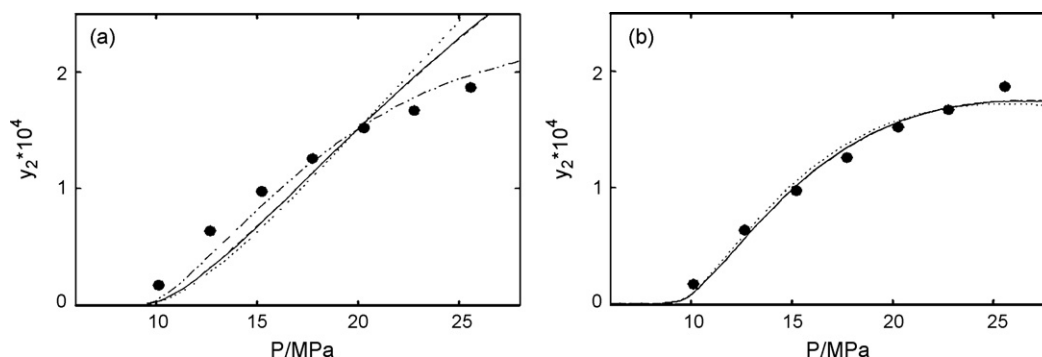


Fig. 8. Experimental solubility of Irgacure® 2959 in scCO₂, at 318.2 K, and correlation results obtained for five different sets of critical and physicochemical properties of the solid. (a) PR-EOS with vdW1 and (b) PR-EOS with vdW2. Set 1* (---); Set 2* (—); Set 3* (— · —); Set 4* (···); Set 5* (— — —).

sublimation pressure has over all other estimated properties in the solid/SCF correlation capacity of EOS models, especially when only one adjustable parameter is used.

From the presented results we can draw some conclusions and general helpful guidelines for the correlation of solid-scCO₂ solubility using classic cubic EOS's (like PR-EOS) and the traditional van der Waals mixing and combining rules:

- It is clear that solid sublimation pressure is a key property to achieve a successful EOS-based correlation result. However, special attention must be paid on the chosen estimation methods and the obtained results must be cautiously analyzed. If possible, the recent method proposed by Coutisikos et al. should be employed since this method was developed specifically to predict the sublimation pressure of organic solid compounds and, unlike other estimation methods, it does not require any of the solid critical properties (which should be estimated by other methods).
- Without a fair estimate of P^{sub} or without any reliable experimental sublimation pressure data, the PR-EOS (or any other common cubic EOS) with one adjustable interaction parameter (vdW1) will probably fail to correlate experimental data. Thus, in these cases an EOS model with two adjustable parameters must be employed to successfully correlate experimental solubility data. These adjustable parameters can be the two interaction parameters of the van der Waals combining and mixing rules (vdW2, k_{ij} and l_{ij}) or, alternatively, sublimation pressure can be also an adjustable parameter in the correlation procedure, together with the k_{ij} interaction parameter on the one adjustable interaction parameter model (vdW1) [7].
- The fitted binary interaction parameters obtained are intrinsically connected with the estimated solid properties values, which in many cases are just very rough estimations of the real properties. For this reason, it's usually unrealistic to consider that these fitted parameters may have a trustworthy physical meaning.
- Also because of the uncertainties associated to the estimated critical and thermophysical properties, these EOS models should be seen and employed just as pure correlative models and should not be used to compute solubility values out of experimental solubility temperature and pressure ranges.

In conclusion, and despite some known limitations of these cubic EOS models, following the general guidelines indicated above it is possible to obtain fairly good experimental solubility correlations using simple cubic equation of state models like the PR-EOS (or the Soave-Redlich-Kwong EOS), together with the simple van der Waals mixing and combining rules.

5. Conclusions

The experimental solubilities of Irgacure® 2959 (4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone) in scCO₂ were determined at 308.2, 318.2, and 328.2 K, and in the pressure range from 10.0 up to 26.0 MPa. The solid mole fraction solubility (y_2) varied between 5.17×10^{-6} and 2.83×10^{-4} .

Experimental data were correlated using three semi-empirical density-based models (Chrastil, Bartle et al. and Méndez-Santiago-Teja). All the employed density-based models fitted effectively the obtained experimental data points, even for low pressure/low density points which normally present larger deviations from the experimental results. The corresponding AARD values were around 5%, which indicates the internal consistency of obtained experimental data. These simple-to-use models proved their capacity to correlate the solubility of solids in scCO₂, based only in the density of the pure SCF and without the necessity of estimating any of the solid's critical or thermophysical properties.

Correlation was also performed employing the Peng-Robinson cubic EOS together with the conventional van der Waals mixing and combining rules. Several different sets of solids' properties, which were estimated by different methods available in literature, were used in these correlations. Results showed that solid sublimation pressure is a key property to successfully apply EOS based models to solid/scCO₂ equilibrium data. However, special attention must be paid on the selected estimation methods. A recent method, proposed by Coutisikos et al., was successfully employed for solid sublimation pressure estimation. This method was developed specifically for organic solid compounds and it does not require any of the solid critical properties. Without a fair estimative of P^{sub} or without any reliable experimental sublimation pressure data, the PR-EOS with

two adjustable parameters must be employed to successfully correlate experimental solubility data.

To the best of our knowledge, these are the first experimental scCO₂ solubility results for this class of initiators and the obtained solubility results indicate the feasibility of using this compound in free radical polymerization reactions carried out in scCO₂ medium.

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