

Prediction of solid solute solubility in supercritical CO₂ with cosolvents using the CPA EoS

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ARTICLE INFO

Article history:

Received 6 September 2018

Received in revised form

16 October 2018

Accepted 22 October 2018

Available online 23 October 2018

Keywords:

Thermodynamic modeling

Prediction

Cubic plus association

Solubility

Supercritical carbon dioxide

Cosolvent

ABSTRACT

Supercritical carbon dioxide (scCO₂) is widely used in separation processes applied to the food, chemistry, pharmaceutical and material industries. The knowledge of the solubility of solid solutes in scCO₂, with or without cosolvents, is essential for the design and optimization of extraction, fractionation and purification processes. This work evaluates the accuracy of Cubic Plus Association equation of state (CPA-EoS) to predict the solubility of solutes in ternary and/or quaternary systems from the binary interaction parameters. The solubility of 12 solid solutes in scCO₂ in presence of different organic cosolvents was investigated, totalizing 19 systems at pressures between 8 and 40 MPa, temperatures ranging from 308 K to 353 K and concentrations of cosolvent varying from 0.73 to 10 mol%. The overall average logarithmic deviation (ALD) between experimental and calculated data with CPA-EoS was 0.47, which is better than that obtained with PR + COSMOSAC previously reported in the literature. Furthermore, the effects of temperature, pressure and of cosolvent type and concentration on the solubility were well estimated with the CPA-EoS.

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1. Introduction

In recent years, fast progress has been made toward using the supercritical technology in industrial separation processes. Apart from a green extraction process that replaces organic solvents, applications involving supercritical fluids include supercritical fluid fractionation [1–3], supercritical fluid chromatography [4–6], use as anti-solvent for micro- and nanoparticle formation [7,8] and reaction in supercritical medium [9–11]. Thus, chemical, petroleum, pharmaceutical, food, biotechnology, biomedical, nuclear, material and polymer processing industries are examples of application areas for separation processes using this technology [12].

Carbon dioxide is the gas most commonly applied for supercritical fluid extraction due to its low cost, high purity, safety and low critical properties. Since pure supercritical carbon dioxide (scCO₂) is a lipophilic solvent, mixtures with organic solvents, especially alcohols, are used to increase the polarity of the fluid mixture.

Solubility data of solutes in scCO₂ in presence of cosolvents are an essential for design and optimization of separation processes using scCO₂. Besides the experimental measurements, thermodynamic models are useful and low cost alternatives to obtain phase equilibrium information. For that purpose, the use of reliable thermodynamic models, able to accurately predict the phase equilibria as a function of temperature, pressure, and composition of a specific system, is crucial.

Several semi-empirical equations have also been proposed to describe the solubility of solutes in scCO₂ with [13–15] or without [16–18] entrainer. Due to its easy handling and good results, the cubic equations of state, such as Peng-Robinson (PR-EoS) and Soave-Redlich-Kwong (SRK-EoS), are the models most used to correlate the solubility data under high pressures. Despite these thermodynamic models being able to describe the binary system data with satisfactory results, in most cases the fitted binary interaction parameters are not suitable to estimate the phase equilibrium in multicomponent systems (with cosolvents), since the strong interactions that can occur between the molecules of solute and the cosolvent are not taken into account in the cubic equations of state [19–21].

The solubility of different solutes in scCO₂ and cosolvent

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mixtures was predicted using the Statistical Associating Fluid Theory (SAFT) [22] and PR + COSMOSAC [23] models. In addition, Bitencourt et al. [24] have recently reported good results for caffeic acid solubility in CO₂/ethanol mixtures using the Cubic Plus Association Equation of State (CPA-EoS) from binary interaction parameters. CPA-EoS consists of the combination of a physical term derived from SRK-EoS and an association term as proposed by Wertheim perturbation theory [25] and widely used in SAFT-type equations. The need to accurately describe systems containing strongly polar compounds was one of the main motivations behind the development of this EoS. This type of system forms hydrogen bonds and often presents an unusual thermodynamic behavior because of strong interactions, either between molecules of the same species (self-association) or between molecules of different species (cross-association).

Compared to SAFT, CPA-EoS is a simpler model for associating mixtures, which keeps the well-known advantages of cubic equations of state, while still presenting a high performance for associating compounds. Although CPA has been widely investigated for several application in the academic community, its use in the industry is far from being widespread. Nevertheless, diverse applications in the oil and gas industry are benefitting from the use of this EoS, as well as, diverse companies having in-house versions of the model. Therefore, this work will evaluate the accuracy of the CPA equation of state for the solubility prediction of 12 solid solutes in scCO₂ in presence of different organic cosolvents, for a total of 19 systems at pressures between 8 and 40 MPa, temperatures ranging from 308 K to 353 K and concentrations of cosolvent varying from 0.73 to 10 mol%.

2. Thermodynamic modeling

2.1. Solid-fluid equilibrium

The solubility of a solid solute was described through the equality of fugacities for the solute i in its pure solid phase and in the fluid phase. Considering a pure solid phase with no solid-solid phase transitions and neglecting the Poynting term and the effect of pressure on the melting temperature (T_{fus}) and enthalpy ($\Delta_{fus}H$), the fugacity of the solute i in its pure solid phase at a given temperature T and pressure P is obtained from the fugacity of its hypothetical liquid under the same conditions, requiring information on the T_{fus} and $\Delta_{fus}H$ of the solute [26]. Thus, when an equation of state is selected, the following expression for the mole fraction solubility of the solute (y_i) is used:

$$y_i = \frac{\phi_i^{pure\ liquid}}{\phi_i^{liquid}} \exp \left[-\frac{\Delta_{fus}H}{R} \left(\frac{1}{T} - \frac{1}{T_{fus}} \right) \right] \quad (1)$$

where T is the absolute temperature, R is the gas constant and ϕ are the fugacity coefficients which were calculated by the Cubic Plus Association equation of state (CPA-EoS) in this work.

Prior study of the solubility prediction of caffeic acid in mixtures of scCO₂ + ethanol used equilibrium equation similar to Equation (1), however not neglecting the variations on heat capacity and molar volume between solid and liquid phases [24]. CPA prediction was not significantly influenced by these values. Besides that, the requirement of the less data about the solute was crucial for choosing to use the simplified form.

2.2. Cubic Plus Association

CPA-EoS consists of the combination of a physical (cubic) term with an association contribution term. Although there are

variants, the term which consider physical interactions, such as attraction and repulsion forces, is the one from the SRK-EoS. The association contribution, originally proposed by Wertheim, accounts for intermolecular hydrogen bonding and solvation effects. Thus, the CPA-EoS is expressed in terms of the compressibility factor as:

$$\begin{aligned} Z^{CPA} &= Z^{SRK} + Z^{assoc} \\ &= \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2} \left(1 + \rho \frac{\partial(\ln g)}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \end{aligned} \quad (2)$$

where i is the component index, A indexes the bonding sites on molecule i , a is the pure component energy parameter, b is the co-volume pure component parameter, ρ is the molar density, x_i is the molar fraction of component i , g is the function of radial distribution and X_{A_i} is the molar fraction of component i not bound to site A , i.e. represents the free site fraction.

The pure component energy parameter (a) has a Soave-type temperature dependency:

$$a = a_0 \left[1 + c_1 \left(1 - \sqrt{T/T_c} \right) \right] (T)^2 \quad (3)$$

X_{A_i} is calculated from the association strength between two sites belonging to two different molecules ($\Delta^{A_i B_j}$) through the resolution the following set of equations:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} \Delta^{A_i B_j}} \quad (4)$$

where:

$$\Delta^{A_i B_j} = g(\rho) \left[\exp \left(\frac{\epsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (5)$$

The simplified hard-sphere radial distribution function (g) was used [27]:

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad (6)$$

$$\eta = \frac{1}{4} b\rho \quad (7)$$

Therefore, apart from the three pure component parameters (a_0 , c_1 , and b) for non-associating components, two more parameters related to the associative contribution of the components are required: the energy of association between the sites of molecules (ϵ) and the parameter of association volume (β).

When dealing with mixtures, the energy and co-volume parameters of the physical term were calculated employing the conventional van der Waals one-fluid mixing rules (Equations (8)–(10)), fitting a binary interaction parameter (k_{ij}). For the parameters from the associative contribution several combining rules have been suggested [28]. The Elliot combining rule and CR-2 [29] are the most used, because both provide accurate descriptions of the phase equilibria for many mixtures. In this work the CR-2 (Equations (11) and (12)) was used.

$$a = \sum_i \sum_j a_{ij} y_i y_j, \quad (8)$$

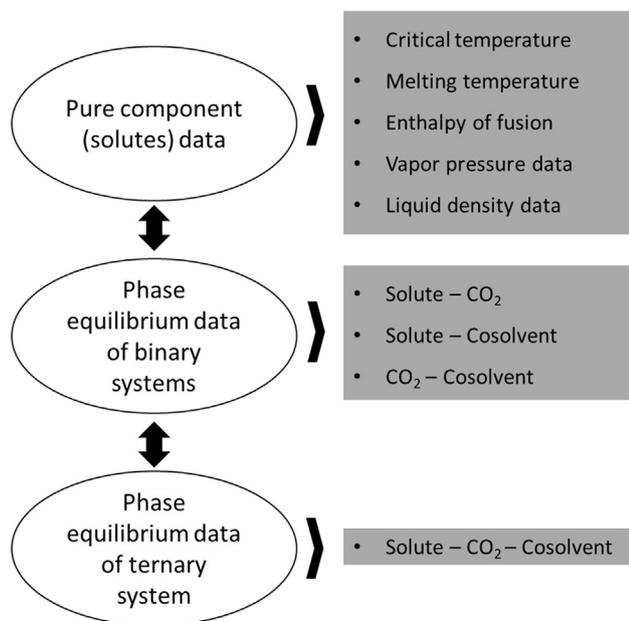


Fig. 1. Set of data required to evaluate the prediction of ternary systems data using CPA model.

$$a_{ij} = \sqrt{\bar{a}_i \bar{a}_j} (1 - k_{ij}) \quad (9)$$

$$b = \sum_i b_i y_i \quad (10)$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i} \beta^{B_j}} \quad (11)$$

$$\epsilon^{A_i B_j} = \frac{1}{2} (\epsilon^{A_i} + \epsilon^{B_j}) \quad (12)$$

3. Selection of data

The solutes were selected based on the set of data needed to evaluate the CPA-EoS for prediction of their solubility in CO₂ + cosolvent, as shown in Fig. 1. Critical temperatures, melting temperatures and enthalpies of fusion of the solutes are required, as shown in Equations (1) and (3). Experimental data for vapor pressure and liquid density at different temperatures are used to fit CPA pure component parameters (a_0 , c_1 , b , ϵ and β). Phase equilibrium data of the binary systems of the components present in the ternary mixtures are relevant to obtain the binary interaction parameters (k_{ij}). Finally, ternary system data were only used for the comparison between the experimental and predicted data.

4. Results

Several works have reported solubility data for solutes in mixtures of CO₂ plus a cosolvent. However, mainly due to the lack of experimental data for vapor pressure and for the binary equilibrium cosolvent – solute, only 12 solutes, shown in Fig. 2 were selected to be here studied. Different classes of compounds were investigated, including aromatic and aliphatic molecules, alcohols and acid substances. Thus, the solubility of 12 solid solutes in scCO₂ in presence of different organic cosolvents was investigated, at pressures between 8 and 40 MPa, temperatures ranging from 308 K to 353 K and concentration of cosolvent varying from 0.73 to 10 mol % (Table 1). Polar and non-polar cosolvents were also analyzed, totaling 19 systems. Among them one is a quaternary system, containing trans-ferulic acid, CO₂, ethanol and water.

In a first step for the modeling with CPA, pure components were parameterized by fitting vapor pressure and liquid density data. Liquid density data were not easily accessible on the scientific literature and databases for the trans-ferulic acid and paracetamol. On other hand, the values available for cholesterol and for salicylic and benzoic acids were not used because the model was unable to fit these data. The bibliographic references for vapor pressure and liquid phase density data were shown in Table 2. Table A1 of the Supplementary data reports the temperature, pressure and density

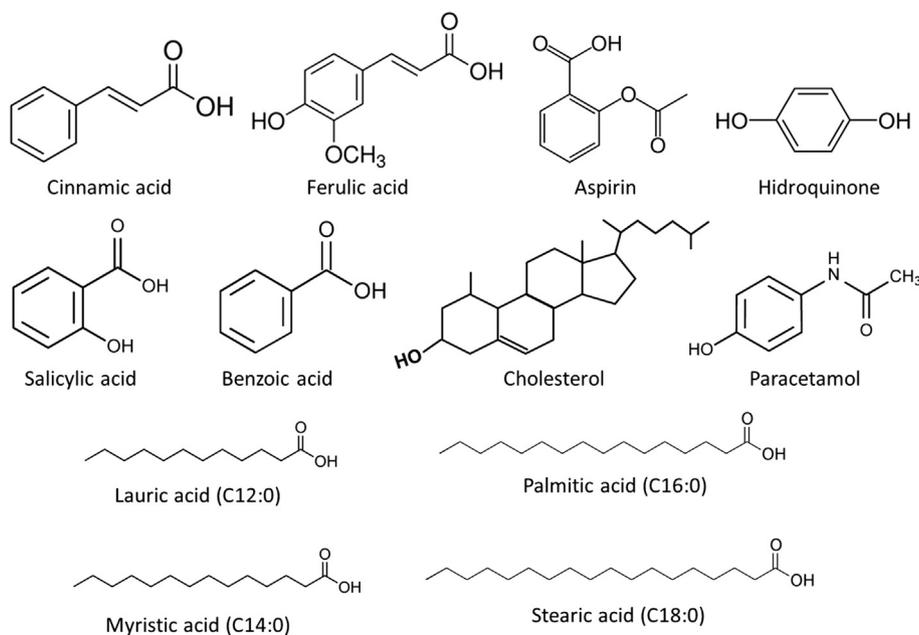


Fig. 2. Chemical structure of the solutes investigated in this work.

Table 1
Ternary and quaternary systems investigated in this work and the average logarithmic deviation between experimental and predicted data using CPA model.

Solute ^a	Cosolvent	Cosolvent (%)	Pressure (MPa)	Temperature (K)	ALD
Trans-cinnamic acid [32]	Ethanol	2–4	10–40	313–353	0.126
Trans-ferulic acid [19]	Ethanol	5–10	20–40	313–333	0.189
	Ethanol/water (90:10 w/w)	2–10	30	323	0.054
Aspirin (acetylsalicylic acid) [33,34]	Ethanol	3	10–20	318–328	0.314
	Acetone	3	10–20	318–328	0.400
Salicylic acid [35,36]	Ethanol	1.47–6.91	8.7–15.7	308–318	0.659
	Methanol	3.5	10.1–20.1	318–328	0.624
	Acetone	3.5	8.6–20.1	318–328	0.453
Benzoic acid [37]	Methanol	3–3.5	10.1–30.4	308–318	0.222
	Hexane	2.2–7	15.2–35.4	308–318	0.105
Hydroquinone [38]	Methanol	2.8	10.3–32.7	308	0.684
Paracetamol [39]	Ethanol	0.85	10–25	313	0.289 ^b
Cholesterol [40,41]	Methanol	3	10–21	318–328	0.059 ^c
	Acetone	3–6	10–22	318–338	0.177 ^c
	Hexane	3.5–6	9–22	318–338	0.193 ^c
Lauric acid [42]	Ethanol	0.5	9.9–22.7	308	1.55
Myristic acid [42]	Ethanol	0.73–4.16	9.9–22.7	308–318	1.32 (0.754)
Palmitic acid [43,44]	Ethanol	0.73–4.16	8.21–22.8	308–318	0.305
Stearic acid [43]	Ethanol	0.73–1.98	12.8–22.6	308–318	0.044

^a Reference for experimental data of ternary or quaternary systems.

^b Assuming paracetamol with one associating site.

^c Assuming cholesterol as a non-associating molecule.

Table 2
Properties and parameters for the pure components.

Compound	T_C (K)	T_{fus} (K)	$\Delta_{fus}H$ (kJ/mol)	Associating Group (AG)	Number of AG	CPA parameters						AARD (%)
						a_0 (J.m ³ /mol)	$b \times 10^5$ (m ³ /mol)	c_1	ϵ (kJ/mol)	$\beta \times 10^{-3}$	P	
Solutes^a												
Trans-cinnamic acid [32,45]	797.3 [32]	406.1 [46]	22.2 [46]	COOH	1	4.45	12.9	1.32	19.1	1.62	3.6	1.1
Trans-ferulic acid [47]	948.0 [48]	443.0 [49]	12.3 [49]	OH and COOH	2	5.12	17.8	1.82	21.4	3.03	1.3	
Acetylsalicylic acid [45,50]	762.9 [34]	408.0 [51]	33.8 [50]	COOH	1	4.99	12.6	0.93	19.4	27.3	2.0	13.0
Salicylic acid [52]	739.0 [45]	431.3 [46]	24.5 [46]	COOH and OH	2	4.25	17.7	1.51	10.0	60.3	0.9	
Benzoic acid [53,54]	755.0 [55]	395.4 [23]	17.1 [23]	COOH	1	4.07	20.9	1.73	19.1	60.5	2.0	
Hydroquinone [45,56]	766.9 [57]	445.1 [23]	27.1 [23]	OH	2	2.19	10.6	1.17	19.2	40.6	3.3	0.5
Paracetamol [58]	828.0 [57]	441.0 [31]	27.7 [31]	OH or NH	1	5.00	13.9	1.84	18.0	16.2	3.3	
Cholesterol [40]	1168.2 [40]	420.2 [23]	27.4 [23]	OH and NH	2	2.77	16.7	3.08	18.0	65.6	3.2	
				non-associating	0	3.83	19.5	1.96			3.5	
Lauric acid [59,60]	743 [61]	316.6 [23]	36.1 [23]	OH	1	3.84	18.1	1.46	21.3	10.1	5.2	
		326.5 [23]	45.0 [23]	COOH	1	6.79	22.4	1.82	17.9	0.226	1.8	1.2
Myristic acid [59,60]	763 [61]	334.7 [23]	53.0 [23]	COOH	1	8.54	25.7	1.58	25.0	0.568	0.4	1.9
Palmitic acid [59,60]	785 [61]	343.0 [23]	61.2 [51]	COOH	1	9.08	29.4	2.02	15.2	4.71	0.4	1.4
Stearic acid [59,60]	803 [61]	343.0 [51]	61.2 [51]	COOH	1	11.88	34.8	1.76	17.9	9.4	4.1	4.7
Solvents^b												
CO ₂ [62]				non-associating	0	0.35	2.72	0.76				
Ethanol [63]				OH	1	0.86716	4.91	0.7369	21.532	8.0		
Methanol [63]				OH	1	0.40531	3.0978	0.43102	24.591	16.1		
Acetone [51]				non-associating	0	1.39	6.14	0.788				
Hexane [64]				non-associating	0	2.3681	10.79	0.8313				
Water [27]				OH	2	0.1228	1.452	0.6736	16.655	69.2		

^a Reference for vapor pressure and/or liquid density experimental data.

^b Reference for the CPA pure component parameters.

ranges and the number of data used for each solute. Therefore, pure component parameters for these solutes were estimated only from vapor pressure data.

For the parameterization of pure compounds it is important to

analyze the nature and number of associating groups, each of these being defined by an association scheme, as proposed by Huang and Radosz [30]. In this work, the two-site (2B) scheme was used for each hydroxyl or carboxyl group contained in the molecule. The

Table 3Binary interaction parameters as function of the temperature: $k_{ij} = A + B \times T/K$.

Solute	Cosolvent	CO ₂ – solute			Cosolvent – solute				
		Reference ^a	k_{ij}		AARD (%)	Reference ^a	k_{ij}		AARD (%)
			A	B			A	B	
Trans-cinnamic acid	Ethanol	[32,65]	-0.384	0.00147	20.4	[66]	-0.145	0.000429	2.5
Trans-ferulic acid	Ethanol	[67]	-0.00764	0.000215	20.3	[19,68]	-0.0675	0.000436	4.8
	Water					[19,46,68]	-0.00198		29.1
Acetylsalicylic acid	Ethanol	[34]	-0.0402		20.6	[69]	-0.0526		6.6
	Acetone					[69]	-0.222	0.000410	0.4
Salicylic acid	Ethanol	[35,70,71]	0.0468		8.8	[72,73]	-0.0567		8.8
	Methanol					[74]	-0.0606		1.2
Benzoic acid	Acetone					[74]	-0.152		1.2
	Methanol	[37,71,75]	-0.0203	0.000286	36.3	[76]	-0.0325		17.5
Hydroquinone	Hexane					[76]	0.00983		35.7
	Methanol	[77,78]	-0.600	0.00163	22.2	[79]	-0.491	0.00131	0.9
Paracetamol ^b	Ethanol	[39,80]	0.0440		39.3	[81,82]	-0.242	0.000552	6.7
Cholesterol ^c	Methanol	[83]	0.201		36.2	[84]	-0.00216		3.0
	Acetone					[84]	0.0528		2.2
Lauric acid	Hexane					[85]	-0.0293	0.000231	2.6
	Ethanol	[42]	0.180		66.2	[86]	-0.00161		10.1
Myristic acid	Ethanol	[42,87]	-0.0929	0.000640	18.1	[88]	-0.264	0.000952	13.0
Palmitic acid	Ethanol	[43,44]	0.0980		11.9	[88,89]	-0.0965	0.000325	17.9
Stearic acid	Ethanol	[90]	-0.0209	0.000348	9.6	[91]	-0.00848	0.00000827	19.3

^a Reference for experimental data.^b Assuming paracetamol with one associating site.^c Assuming cholesterol as a non-associating molecule.

approach, called group-contribution scheme, should be applied for the association term, as reported in studies on polyfunctional phenolics solubility [31]. Thus ϵ and β parameters were assumed as having unique values for each solute molecule, i.e. they were not fitted for each type of associative group of the molecule but for each molecule. The properties and approaches used for each pure component are presented in Table 2. In addition, the solvents CO₂, hexane and acetone were treated as non-associating components. The section B of Supplementary data exemplifies how the considerations about of number and type of association sites can change the results for prediction of ternary systems.

The binary interaction parameters were then estimated for all the binary systems involved in the ternary or quaternary systems. References for experimental data, the values of k_{ij} fitted and the average absolute relative deviation (AARD) are shown in Table 3. Mainly for the cosolvent – solute systems a good description of the experimental data was achieved.

Finally, the solubility for each solute in the ternary or quaternary system using CPA-EoS was predicted, and the average logarithmic deviation (ALD) was used to evaluate the accuracy of the prediction, as shown below:

$$ALD = \sum_{j=1}^N \frac{1}{N} \left| \log \frac{y_i^{calc}}{y_i^{exp}} \right| \quad (13)$$

where N is the number of experimental points and y_i is the mole fraction solubility of the solute in mixtures of scCO₂ and cosolvent.

In general, accurate results for the prediction of the solubility in scCO₂ + cosolvents using the CPA-EoS were verified. ALD values for each solute (Table 1) varied from 0.04 to 1.5. Few solutes, such as lauric acid, myristic acid, hydroquinone and salicylic acid, presented the highest ALD values. According to Ting et al. [23], higher deviations for carboxylic acids with short chain can be associated to their lower melting temperatures. The melting temperatures for lauric (dodecanoic acid) and myristic (tetradecanoic acid) acids are 316.6 K and 326.5 K, respectively. These values are very close to the temperatures of solubility measurements, indicating that CPA model can not describe these systems at conditions close to the

phase transition region. In this way, excluding the myristic acid solubility data at 318 K, the ALD value decreased from 1.32 to 0.75 (at $T = 308$ K), i.e., when the difference between the melting temperature and the solubility temperature measurement, the CPA prediction significantly improves.

The ALD value obtained by evaluating all the systems simultaneously was 0.47, and excluding lauric and myristic acids the ALD decreased to 0.32. Both values are significantly lower than those reported by Ting et al. [23] (ALD = 0.64), when PR + COSMOSAC equation was used for prediction of the solubility of 23 solutes in scCO₂ and cosolvents. Excluding trans-ferulic acid, all the solutes here evaluated were also investigated by Ting et al. [23] applying the SAFT model to predict solubility of naphthalene, phenanthrene, anthracene, pyrene and benzoic acid in scCO₂ with cosolvents, Yang et al. [22] reported AARD values (between 4.7% and 48.5%) lower than those obtained with a cubic EoS (ranging from 15.0% to 70.8%). This difference was probably due to the fact that these authors have mainly evaluated systems containing non-associating compounds. For instance, to predict the solubility of caffeic acid, which has three association sites, the values estimated using a cubic EoS were more than 100 times lower than the actual experimental data [24]. In addition, the CPA EoS presented good accuracy when predicting the solubility of caffeic acid in scCO₂ + ethanol, with ALD = 0.29 [24].

The dispersion between the experimental and calculated data can be visualized in Fig. 3. Fig. 3 divides the compounds in aromatic acids (●), aromatic alcohols (■), aliphatic acids (▲) and aliphatic alcohols (×). Underestimated prediction of the solubility data was observed in most cases. The solubility of hydroquinone was the only one significantly overestimated. No systematic deviations, by analyzing the different classes of compounds, was identified, since the highest differences between experimental and calculated data were observed for an aromatic acid (salicylic acid), an aliphatic acid (lauric acid) and an aromatic alcohol (hydroquinone).

Experimental errors should be analyze since they could justify the deviation between predicted and experimental data. Error experimental for solubility data in ternary and quaternary systems were not reported in detail (for each point) in most solubility data sources used in our work. Excluding the ferulic acid data, the mean

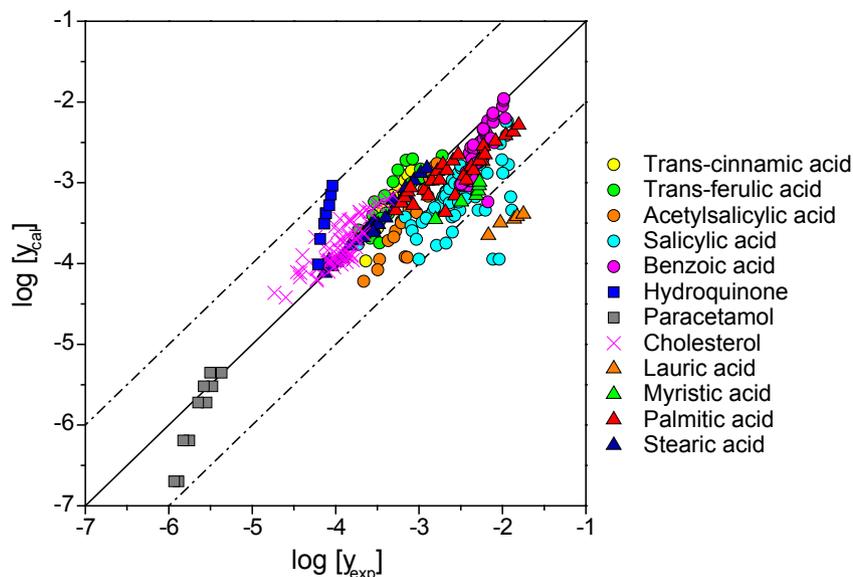


Fig. 3. Comparison between experimental and predicted values of the solubility of 12 solutes in scCO_2 with cosolvent.

deviations values reported ranged from 3 to 15%. The maximum experimental error was verified for the paracetamol solubility [39]. In this way, the error values does not show relevant to justify the deviation between the experimental and calculated data for solubility of the solutes in the CO_2 and cosolvent mixtures.

Because the ternary solubilities of solids in systems containing cosolvents are complex functions of temperature, pressure and cosolvent/cosolute composition [13], it is essential to study the influence of variables, such as temperature, pressure, concentration and type of cosolvent, and number of associating sites of the solute, on the results.

4.1. Temperature and pressure effects

Solubility of solutes in scCO_2 exhibit a typical behavior, as shown by the straight line when plotting the logarithm of solubility versus the logarithm of CO_2 density (which is a function of temperature and pressure). Commonly the solubility increases with pressure at a fixed temperature, and the crossing of solubility isotherms, known as “crossover pressure”, represents the pressure value at which solubility is independent of temperature. Knowledge on this crossing point can be useful when small differences in selectivity are required, such as in the separation of isomers [92]. By adding a cosolvent to the system, the crossover pressure point increases because it promotes an increase in the mixture critical point of the supercritical mixture [93].

Fig. 4a presents the effect of temperature and pressure on the solubility of stearic and palmitic acids in $\text{scCO}_2 + 0.73\%$ ethanol. The highest values of solubility were obtained at higher pressures, however the pressure influence is more relevant at their lower values ($P \leq 15$ MPa). On the other hand, temperature increases the solubility more effectively at higher pressures. These solubility behaviors were also observed for the predicted data obtained using the CPA-EoS, showing the accuracy of this equation to describe the influence of temperature and pressure on solubility data in CO_2 plus cosolvents. No experimental crossover pressure was observed in the range of temperature and pressure here studied, however Fig. 4a indicates that the crossover pressures are probably close to 12 MPa for these carboxylic acids, further confirmed by the CPA prediction.

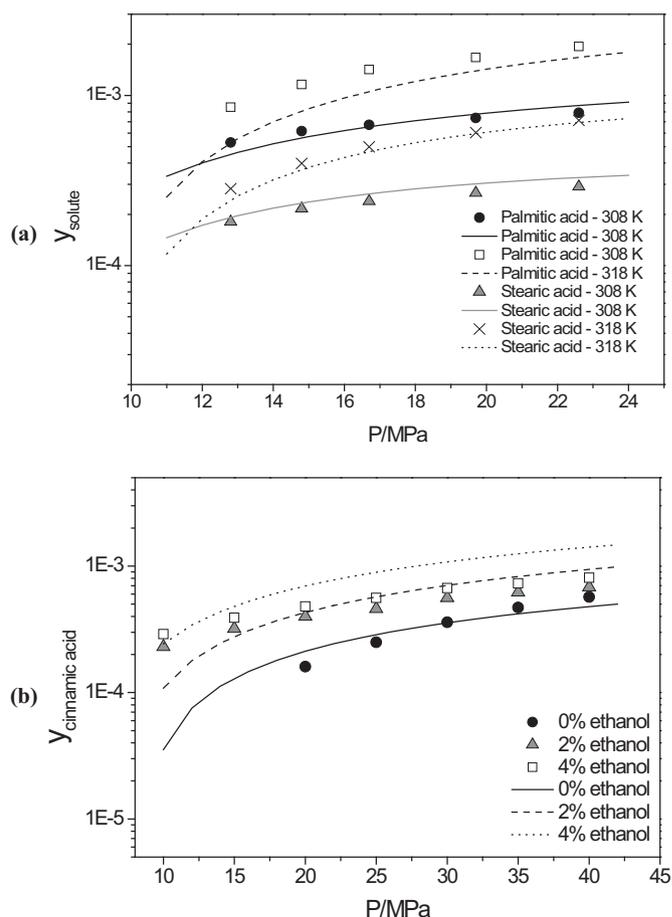


Fig. 4. Effect of the temperature and pressure on: (a) Solubility of stearic and palmitic acids in $\text{CO}_2 + 0.73\%$ ethanol; (b) solubility of trans-cinnamic acid in $\text{CO}_2 + \text{ethanol}$ at 313 K. The lines correspond to predictions of CPA-EoS.

Temperature and pressure effects on the solubility can also be influenced by the concentration of cosolvent. Fig. 4b shows the pressure effect on the solubility of trans-cinnamic acid at different concentrations of ethanol (0, 2 and 4 mol%). Experimental data

indicates that the pressure effect becomes less important when higher concentration of cosolvent are used, as described in other studies [19,20,24]. Although CPA has shown a good accuracy in the description of this mixture, the decrease on the pressure effect when the cosolvent was added to scCO_2 was not well estimated. It is worth mentioning that CPA correctly predicted the effect of pressure on the solubility data for the other systems for which the pressure effect remained relevant at high concentrations of cosolvent.

4.2. Effect of the cosolvent nature

It is important to evaluate the effect of either the cosolvent or co-solute on the experimental ternary solubilities of solids as well as on the prediction of phase equilibria data. Although there are few studies using non-polar solvents as entrainers, the polar solvents such as methanol, ethanol and acetone are the most used. The solubility of solid solutes in scCO_2 in presence of a cosolvent, and consequently the choice of a cosolvent, is influenced by the ability of the solute to form hydrogen bonds with the cosolvent and by the structure (size) and polarity of the molecule [94]. Therefore, there is not a specific cosolvent that should be used for all solutes, since the increase in the solubility of solids in ternary systems (CO_2 + cosolvent) should be attributed to the increase in solvent density, to dipole-dipole interactions and also to hydrogen bonds formed between the solute and the molecules of cosolvent [33].

In this section, two examples are presented aiming to show the ability of CPA-EoS to predict the increase in solubility data when

adding different cosolvents. Fig. 5a presents the solubility of the aspirin (acetyl salicylic acid) in scCO_2 + ethanol and scCO_2 + acetone. Both experimental data and model predictions show that the use of ethanol as cosolvent increases aspirin solubility more than acetone. This is probably related with ethanol's polarity and with the fact of ethanol being an associating compound, unlike acetone.

The enhancement of the cholesterol solubility in scCO_2 with the addition of methanol and acetone as cosolvents was very similar (Fig. 5b). At 328 K the acetone promotes a slightly higher increase in solubility of cholesterol when compared to methanol, however there was no visible difference for the experimental data at 318 K. In contrast to the aspirin solubility behavior (Fig. 5a), the temperature showed to be more important than the cosolvent type to improve the solubility of cholesterol in scCO_2 + cosolvent. Although different behaviors were observed, the estimation of solubility by CPA-EoS was suitable for both systems presented in Fig. 5, mainly at pressures removed from the critical point.

It is worth mentioning that the prediction of the solubility behavior in presence of cosolvents through thermodynamic models is also an important stage in order to select a cosolvent in the initial steps of design and optimization of processes.

4.3. Effect of the cosolvent concentration

To evaluate the quality of predictions using CPA, when analyzing the effect of cosolvent concentration on the solubility, systems with

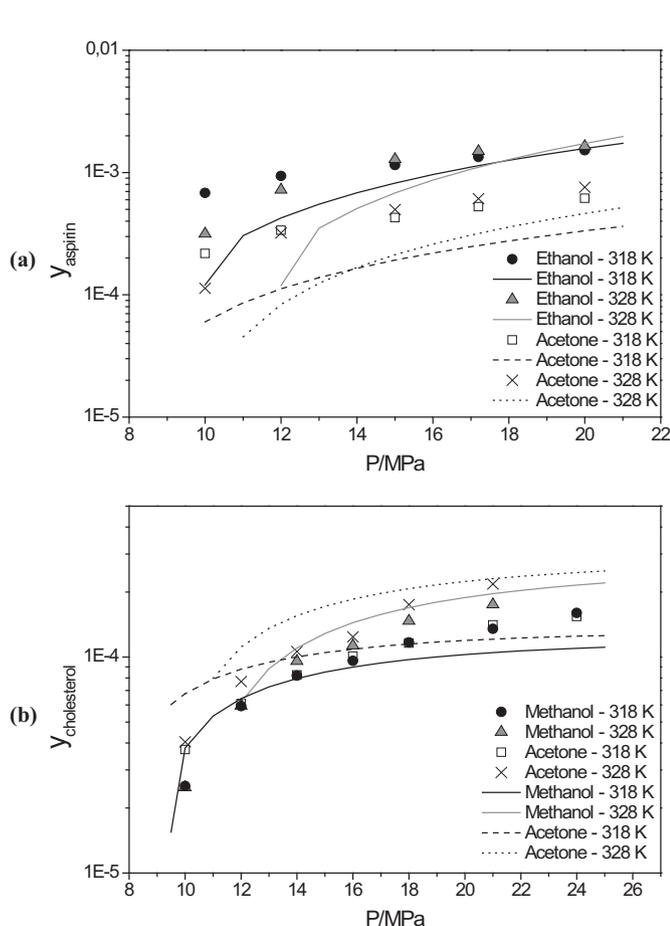


Fig. 5. Effect of cosolvent type on: (a) aspirin solubility in CO_2 + 3% cosolvent; (b) cholesterol solubility in CO_2 + 3% cosolvent. The lines are the model predictions.

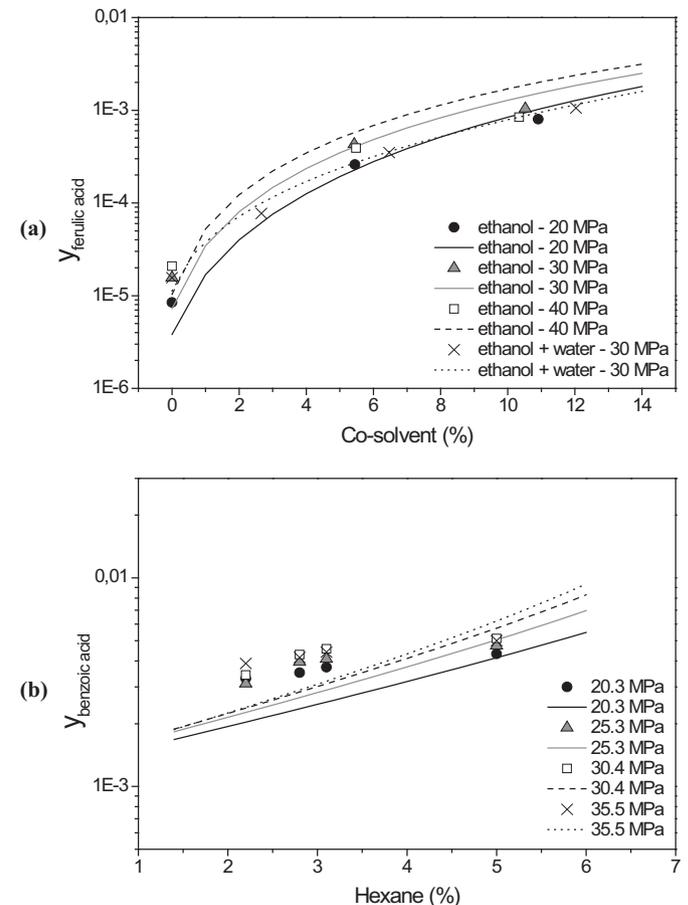


Fig. 6. Effect of cosolvent concentration on: (a) trans-ferulic acid solubility in CO_2 + cosolvent at 323 K; (b) benzoic acid solubility in CO_2 + hexane at 308 K. The lines correspond to predictions of CPA-EoS.

diverse cosolvents, were selected, which presented quite different behaviors of the solubility as a function of the cosolvent concentration.

In general, the solute solubility increases at higher concentrations of cosolvent. However, while the solubility of trans-ferulic acid increases following an exponential behavior, with values up to 100 times higher than its solubility in pure scCO₂ when using 10 mol% of ethanol (Fig. 6a), the increase on benzoic acid solubility by increasing the hexane concentration is minor (Fig. 6b). In both cases, the model predictions followed the tendency of the experimental data.

The predictions for the quaternary system investigated in this work are presented in Fig. 6a. The excellent description obtained with CPA indicates the possibility of applying this model to estimate the phase equilibrium in multicomponent systems. Furthermore, since there was good prediction in the quaternary system, it emphasizes that some faulty predictions for ternary systems may eventually occur due to the reliability of both the solubility data in CO₂ + cosolvent and/or the pure components and the binary phase equilibrium data.

5. Conclusions

The CPA-EoS was here shown to present a good ability for the description and prediction of solute solubilities in supercritical carbon dioxide in presence of organic cosolvents. These results were obtained for systems containing different classes of compounds, both for solute and cosolvent. Furthermore, the effects of temperature, pressure, type and concentration of the cosolvent on the solubility of solids in carbon dioxide were calculated with reasonable accuracy. It must be emphasized, however, that the EoS to properly perform requires the definition of a suitable molecular model, including the number of association sites for solute and cosolvent molecules, a reliable data source for the vapor pressure and liquid density of pure components, as well as phase equilibria of binary systems.

Acknowledgments

The authors acknowledge KBC Advanced Technologies Limited for providing Multiflash software used for the CPA modeling and Dr. Antonio. J. Queimada for fruitful discussions. Raphaela G. Bitencourt and André M. Palma are grateful respectively to CNPq (140345/2014-0) and KBC for their grants.

In Brazil, this work was financially supported by CAPES, FAEPEX (Project number 2781/2017, 519.292), FAPESP (Project number 2010/16665-3 and 2014/21252-0) and CNPq (Project numbers 406856/2013-3, 305870/2014-9, 303734/2016-7 and 406963/2016-9).

In Portugal, this work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.

Nomenclature

Abbreviations

AG	association group
ALD	Average logarithmic deviation
CPA	Cubic Plus Association
COSMO-SAC	Conductor-like Screening Model - Segment Activity Coefficient

EoS	Equation of State
PR	Peng-Robinson
SAFT	Statistical Associating Fluid Theory
SRK	Soave-Redlich-Kwong
scCO ₂	supercritical carbon dioxide

List of symbols

a	energy parameter in the physical term
a_0c_1	parameters for calculating a
b	co-volume parameter in the physical term
g	radial distribution function
H	enthalpy
k_{ij}	binary interaction parameter
N	number of experimental data
P	pressure
R	gas constant
T	temperature
X_{Ai}	fraction of molecule not bonded at site A
x, y	mole fractions

Greek symbols

β	association volume
ϵ	association energy
Δ	association strength
ρ	molar density
η	reduced fluid density
ϕ	fugacity coefficient

Sub and superscripts

AB	molecules sites indexes
C	critical property
cal	calculated
exp	experimental
i, j	pure component indexes
fus	fusion
vap	vapor

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fluid.2018.10.020>.

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