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Modelling solutions of hydrocarbons in dense CO_2 gas

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Abstract

Shaping of advanced ceramic parts generally requires the use of organic additives which, obviously, have to be removed prior to sintering. In order to obtain free defect green pieces in a short time, an alternative technique to the classical thermal debinding, based on the unique properties of dense gases such as supercritical fluids, has proven to be very efficient. Supercritical extraction of organic additives from a green ceramic part involved both solubilisation and diffusion. The debinding treatment has to be conducted to remove a high amount of the organic phase but in such a way that the cohesion of the green part was maintained. Then, the capillary migration of a molten organic additive has to be avoided and a low amount of binder has to remain in the green part after the debinding treatment. This residual organic phase could be easily removed during the sintering treatment because the porosity is, at this stage, entirely open and interconnected. In this context, extraction was performed using carbon dioxide, (i) at low temperature (lower than 80°C) for which the organic additives used, i.e. paraffin waxes composed of *n*-alkanes, remain in a solid state and, (ii) under experimental conditions of extraction (pressure, temperature, time) chosen to maintain a non soluble part of the binder. It is then necessary to be able to predict the solubility of organic binders in supercritical CO_2 to define a suitable organic formulation (appropriate paraffin waxes) and an adapted debinding treatment. A review of existing models of solubility of organic molecules in supercritical fluids and an analysis of the principal concepts of modelisation are exposed. The choice of an equation of state for solubility prediction of n-alkanes in supercritical CO_2 was made on the basis of (i) the values of average errors between calculations using models of solubility and experimental values of solubility measured in this study and, (ii) the facility of equation employment. Then, calculated values of solubility, using this equation of state, were compared to experimental values (FT–IR) for an alkane (*n*-C_{28}).

Keywords: Alkanes; CO_2; Modelling; Solubility; Supercritical extraction

1. Introduction

Since the first discoveries of critical properties of fluids,[1,2] many applications of dense fluids have been developed. For instance, supercritical solvents are used for extraction of natural compounds (caffeine[3], spices [4–6] and other compounds[7–12]) and for fossil fuel processing.[13,14] More recently, promising studies using supercritical fluids have been performed in the domain of materials:[15] ceramics debinding,[16,17] depollution, polymer processing,[18,19] impregnation of tissues, woods or ceramics,[15] synthesis of powders.[20] Several fluids, such as N_2O, methane and even water, may be industrially used in the supercritical conditions,[21,22] but carbon dioxide is the most convenient due to its low critical point ($T_c = 31°C$, $P_c = 7.4$ MPa), to its low cost and to its absence of toxicity and flammability.

Advanced ceramic processing like dry-pressing, tape-casting, injection or extrusion-moulding requires the use of organic compounds such as dispersants, binders, plasticizers to confer such properties as cohesion, flexibility and workability in the green state. Obviously, these organic additives have to be removed from ceramic green parts prior to sintering and this stage remains one of the most critical in ceramic processing. The use of the unique dissolving characteristics and transport properties of supercritical fluids allows the removal of binders from ceramic green pieces without melting and without any thermal degradation.[15] This original

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technique offers great advantages in comparison to the classical technique of pyrolysis: absence of deformation and of stresses in the green part, absence of residues of pyrolytic degradation, high debinding rate. Supercritical debinding, indeed, requires organic compounds soluble in supercritical fluid, keeping in mind that they have to confer suitable rheological properties to the feedstock for the forming stage. We have previously defined formulations based on paraffin wax binders, with melting temperatures between 42 and 62°C, which are both soluble in supercritical CO_2 and suitable for low and middle pressure injection moulding.[23] These paraffin waxes used are mainly composed of *n*-alkanes. Two phenomena control supercritical extraction of the paraffin waxes debinding: solubilisation of soluble organic additives and diffusion of dissolved paraffin species. A semi-empirical model was developed[24] that allows the determination of the solubility of the paraffin waxes, once their *n*-alkanes distribution has been measured. For paraffins in liquid state and in the pressure range tested (12 to 28 MPa), this simple model is in good agreement with experimental results. This first approach allows a rather good estimation of the evolution of the composition of the paraffin binder in the green part during treatment and to define an adapted debinding cycle. However, we see that this model is not valid for temperature and pressure conditions for which the paraffin wax is solid because it drastically deviates from experimental results, principally in the domain of high pressures (Fig. 1).

Extraction of paraffin in solid state is nevertheless necessary in a first stage of the debinding treatment to confer a sufficient granular cohesion to the green part and to avoid its deformation due to capillary migration of a molten phase. In order to obtain a good evaluation of the solubility of paraffin wax binders in the solid state, then to be able to define a suitable formulation (grade of the paraffin wax) and an appropriate debinding parameter to maintain the cohesion of the piece, an adequate model has to be found. In this respect, a review of existing models able to predict long chains carbons solubility in supercritical fluids, essentially supercritical CO_2, under our debinding conditions (40–50°C, 15 to 25 MPa), is performed. The objective is to find the most appropriate model that permits to take into account molecule length, chemical interactions and physical state of the organic processing additives.

2. Simple explicit solubility models

As noticed by Chrastil,[25] solubility of a solid in a supercritical fluid has strong dependence on pressure and temperature. Such a dependence seems difficult to model using an empirical approach based on very simple assumptions.

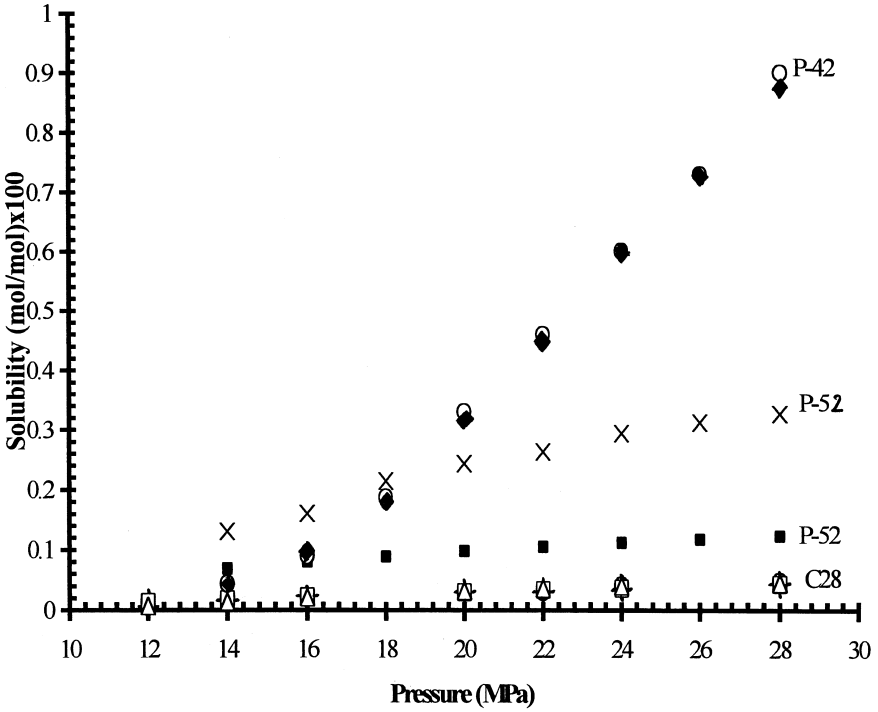

Fig. 1. Comparison of theoretical values of solubility (semi-empirical model[28] and PR-EOS[32]) with experimental values measured with a FT–IR spectroscopy (Ref. 28 and this work). Calculated values using the semi-empirical model for solid *n*-C_{28} ($T=40$°C) (△), liquid paraffin with a melting point of 42°C ($T=70$°C) (◆) and solid paraffin with a melting point of 52°C ($T=40$°C) (■). Calculated values using PR EOS for solid *n*-C_{28} (+). Experimental values for solid *n*-C28 ($T=40$°C) (□), liquid paraffin with a melting point of 42°C ($T=70$°C) (○) and solid paraffin with a melting point of 52°C ($T=40$°C) (×).

Nevertheless, a few approaches were successfully attempted, leading to equations mainly justified by an accurate fit to the experimental data. Sometimes it is indeed possible to establish explicit linear relations between logarithm of solubility and density of the supercritical fluid.[25–27] The most significant models are resumed in Table 1. Czubryt[26] and Robin and Vodar[27] models may be regarded as empirical extensions of Hildebrand theory. Of the three models presented here, Chrastil's model is the most theoretically founded, as detailed in Table 1, but its parameters are not generally estimated by theoretical considerations but rather by experimental data regression as in the case of the two other models. Unfortunately, all these equations are not of an easy use for process calculations since they are explicit function of density or δ Hildebrand parameter and not of more convenient variable P. Density or δ should be thus evaluated at temperature and pressure of interest prior to use the solubility model. Furthermore, these models only apply to binary systems and their extension to ternary systems is a priori really not straightforward. However, in the case of liquid paraffin/CO_2 systems, this difficulty may be overcome as shown recently by Chartier et al.[28] A quasi-binary approach was used, total solubility of a paraffin (i.e. a mixture of n alkanes) in supercritical CO_2 was computed directly from the ones of pure individual alkanes in the same fluid and in the same temperature and pressure conditions.

One cannot deny these equations are convenient tools for interpolating data. However, one also notices they have adjustable parameters with no evident physical meaning. The values of these parameters are specific of a given binary system in given experimental conditions. Thus one should not expect that such parameters will allow a realistic extrapolation of solubility at a given pressure and temperature.

3. Solubility and phase equilibrium based on an equation of state (EOS)

3.1. Phase equilibrium treatment and solubility calculation using EOS

There are several ways to define the solubility of a solid species in a gas phase. One of the most correct in applied thermodynamics is to consider the vapour phase mole fraction y_i of the considered species i. The general method for evaluation of y_i starts with the phase equilibrium necessary condition written in terms of equal fugacities of species i in both solid and vapour phase:

$$f_i^{\text{solid}} = f_i^{\text{vapour}} \tag{1}$$

In the case of vapour phase, the mole fraction y_i is often written as follows:

$$y_i = f_i^{\text{vapour}} / \phi_i^{\text{vapour}} \cdot P \tag{2}$$

where ϕ_i^{vapour} is the fugacity coefficient of the species i in the vapour phase and P the total pressure. ϕ_i^{vapour} may be computed from an EOS $P = P(v,T,y_1,\ldots,y_N)$ following:

$$\text{RT}.\ln\phi_i^{\text{vapour}} = \int_V^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,nj\neq ni} - \frac{\text{RT}}{V}\right]\cdot \text{d}V - \text{RT}\,\ln(P.V/n\text{RT}) \tag{3}$$

Table 1
Empirical representation of the solubility

Model authors	Analytical expression	Comments
Chrastil[25]	$y_i = D^k.\exp(A/T + B)$	y_i is the concentration of the solute in the dense gas in g l^{-1} D is the density of the dense gas in g l^{-1} k is a constant $A = \Delta H/R$ where ΔH is the total reaction heat between the molecules of the solute i and the molecules of the dense gas j $B = \ln(M_i + k.M_j) + q\text{-}k\ln M_j$ where M_i and M_j are, respectively, molecular weights of the solute and of the dense gas q is a constant
Czubryt[26]	$\log y_i = \text{C}.\ \delta^2 + \text{D}.\delta + \text{E}$	y_i is the concentration of the solute in the dense gas in g l^{-1} C, D and E are three constants δ is the Hildebrand term for solubility
Robin and Vodar[27]	$\log y_i = \text{F} + \text{G}.d$	y_i is the concentration of the solute in the dense gas in g cm^{-3} F and G are two constants d is the density of the dense gas

where T is absolute temperature, V is the total volume of the vapour phase, R is the gas constant and n_i is the number mole of the component i in the vapour phase.

However, the EOS approach cannot be applied to a solid phase. An activity coefficient model must be used. Assuming that the fluid is not adsorbed by the solid, in other words the solid remains pure, we have $a_i^{solid} = 1$ (in the pure compound reference state). The fugacity of the solid species i is then given by:

$$f_i^{solid} = P_i^{sub}.\exp(v_i^{solid}.(P - P_i^{sub})/RT) \quad (4)$$

where v_i^{solid} is the solid molar volume of the solute and P_i^{sub} the sublimation pressure. This leads to the following expression for the solubility:

$$y_i = P_i^{sub}.\exp[v_i^{solid}.(P - P_i^{sub})/RT]/\phi_i^{vapour}.P \quad (5)$$

Since pressure in our system may reach 25 to 30 MPa, vapour phase cannot be regarded as ideal. One has to select an adequate non ideal gas EOS to evaluate ϕ_i^{vapour} and then, subsequently, the solubility y_i. Typical calculations for solubility y_i include several stages which will be described in Section 5 with the solubility calculations for the specific case of solid n-C_{28} in supercritical carbon dioxide. The choice of an EOS appears thus as a primordial step and is discussed in the next section.

3.2. Equations of state (EOS) used for process design

There is no general EOS that allows a satisfactory representation of all phase diagram typologies. Among the numerous EOS that may be found in the literature, some are useful tools to fit accurately the experimental data (both in the subcritical and in the supercritical domains) whereas other ones can be used to make realistic extrapolations within reasonable but nevertheless significant average errors (>5 to 10%) between experimental and theoretical values of solubility. Despite a still increasing number of researches on the subject, no EOS today satisfactorily combines both accurate representation of available data and reliable predictions. The purpose of this section is to provide information that should be useful to determine if EOS are appropriated to our objective, i.e. modelling solubility of organic compounds in supercritical carbon dioxide.

Before the discussion, we have to make an important remark. Since all the equations presented below are mean field models, they cannot represent very accurately the solubility in the immediate vicinity of the critical point. Fortunately, supercritical extractions of binders are performed far from the critical point of carbon dioxide.

3.2.1. Cubic equations of state (cubic-EOS)

The modern cubic equations of state are empirical extensions of original van der Waals EOS (VDW-EOS) to high pressure domain up to several tens MPa. For this reason, they remain rough EOS which may be improved yet, especially for modelling asymmetric systems (mixture of long molecules with small molecules, that is the case of our n-alkanes in supercritical carbon dioxide). This may explain why numerous versions of these equations were proposed in the last three decades (Table 2). For a comprehensive review, see Anderko.[29]

In order to obtain mathematical values of the solubility y_i, the calculations can be made from equations, which may be formally written as follow:

$$P = \frac{RT}{v - b} - \frac{a(T)}{\alpha(b, T) + \beta(b, T).v + v^2} \quad (6)$$

where $\alpha(b,T)$ and $\beta(b,T)$ are functions of the temperature and of the co-volume b of the molecules of solute. The first term in the equation is for the repulsive interactions where co-volume b accounts for the size of the molecules. At $v = b$, this term has an infinite value meaning that the fluid cannot be more compressed. b is commonly supposed independent of the temperature. The second term is attractive and the function of temperature $a(T)$ is assumed to encounter the interaction energy between species. Numerous analytical expressions are proposed for this second term (Table 2). Except in the case of the van der Waals concept, equations cannot be justified by theoretical consideration. The different cubic equations have a comparable fitting capability, which a priori unable to chose one equation in particular for the representation of a given system. In

Table 2
Examples of cubic equations of state (a, b and c are constants dependent on critical pressure and temperature; v is the molar volume of the solute; u and w are mathematical constants)

Authors	Analytical expressions
Redlich and Soave[49]	$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)}$
Peng and Robinson[50]	$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)}$
Patel and Teja[51]	$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + c(v - b)}$
Schimdt and Wenzel[52]	$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + ubv + wb^2}$
Harmens and Knapp[53]	$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + cbv - (c - 1)b^2}$
Kubic[54]	$P = \frac{RT}{v - b} - \frac{a(T)}{(v + c)^2}$
Heyen[55]	$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + (c + b)v - bc}$

fact, only a restricted number of cubic equations are effectively used for process design, namely they are Redlich–Kwong–Soave EOS [RKS, $\alpha(b,T)=0$ and $\beta(b,T)=b$] and Peng–Robinson EOS [PR, $\alpha(b,T)=-b^2$ and $\beta(b,T)=2b$]. These equations were widely applied to a large variety of systems with some success.[30]

For a pure compound, the values of $a(T)$ and b may be correlated to critical coordinates T_C and P_C.[31] To ensure accuracy of the EOS at higher or lower temperature than T_C, $a(T)$ is computed from T_C and P_C through empirical correlation such as the one proposed by Peng and Robinson:[32]

$$a(T) = 0.45724.(R^2.T_C^2/P_C).[1 + (0.37464 + 1.54226.\omega - 0.26992.\omega^2).(1 - T_R^{1/2})]^2 \quad (7)$$

where reduced temperature $T_R = T/T_C$. The acentric factor ω is an empirical correction introduced to extend cubic EOS to slightly non-spherical molecules as long molecules (Pitzer[33]); it accounts for the shape of the molecule and is 0 when the molecule is spherical. This factor may be evaluated from experimental vapour pressures or it is even sometimes adjusted. The values of ω for the small molecules (up to n-C_{20} in the case of the n-alkanes) are available.[33]

In the case of multi-component systems which is the case of paraffin waxes (composed of n-alkanes) used as binders, parameters a and b are related to individual pure component parameters a_i and b_i (each n-alkane) through combining and mixing rules. One of the most simple is the modified van der Waals mixing rules:

$$a = \sum_i \sum_j x_i x_j.(1 - k_{ij}).(a_i a_j)^{0.5} \quad (8)$$

$$b = \sum_i x_i.b_i \quad (9)$$

where x_i is the molar fraction of each compound and k_{ij} is an empirical binary interaction parameter between species i and j, generally assumed symmetrical ($k_{ij}=k_{ji}$). It is set to 0 for i = j. The k_{ij} parameters are adjusted so that the model fits the vapour–liquid equilibrium (VLE) diagram of the corresponding binary systems. The resulting values of a and b depend both on the system and on the EOS used for VLE calculations. In the case of CO_2-n alkanes binary systems, k_{ij} values are available in Prausnitz et al.[34] up to C_{10} (for which k_{ij} is equal to 0.11 ± 0.01 for PR-EOS). Prediction of the solubility in the VLE diagram of CO_2/decane and CO_2/hexadecane binary systems using PR-EOS by fitting k_{ij} for hexadecane (n-C_{16}) with n-C_1 to n-C_{10} values is satisfactory within few percent (1 to 10% average error between experimental and theoretical solubility).

Values of k_{ij} determined on binary systems may fail to predict ternary systems. The numerical values of k_{ij} depend on the chosen mixing rules and are by no means universal. A large number of mixing rules has been developed in recent years. The simplest rules are given in Table 3. In the case of complex mixtures in CO_2 (especially those containing heavy n-alkanes, $n>18$), a more accurate representation may be obtained if one uses the so-called "G^E mixing rules" (excess Gibbs energy mixing rule). These rules were first proposed by Huron and Vidal,[35] using relationship between an activity coefficient model and the EOS. They established their expressions using an activity model for liquid mixtures.

Sato et al.[36] compared different G^E mixing rules combined with RK EOS to model solubility of C_{20}, C_{22}, C_{24} and C_{28} linear alkanes in supercritical CO_2 in the temperature range [50–100°C] up to 40 MPa. They obtained an average error within 20% between experimental and modelled solubility.

As a first approximation, an average error of 10–30% between experimental and theoretical solubility can be expected using an EOS. For instance, Cochran et al.[34] obtained 26.4% average error using Peng–Robinson EOS.

3.2.2. EOS derived from statistical mechanics

Statistical mechanics have been used for several decades as an alternative approach to develop semi-theoretical EOS with an expected better predictive capability. This approach is explicitly based on molecular theory of dense fluid that connects molecular interactions to macroscopic thermodynamic functions.

Table 3
Principal mixing rules (a, a′, b and c are the mixture constants for the EOS; a_i and b_i are the solute constants; a_{ij}, b_{ij}, a'_{ij} and c_{ij} are the binary constants; x_i is the molar fraction of the solute i; k_{ij} and l_{ij} are binary interaction parameters)

Authors	Mixing rules
van der Waals[56]	$a = \sum_i \sum_j x_i.x_j.a_{ij}$
	$a_{ij} = (1-k_{ij})(a_i a_j)^{0.5}$
	$b = \sum_i x_i.b_i$
Mansoori[56]	$a = \sum_i \sum_i x_i.x_j.a_{ij}$
	$a_{ij} = (1-k_{ij})(a_i.a_j)^{0.5}$
	$b = \sum_i \sum_j x_i.x_j.b_{ij}$
	$b_{ij} = (1-l_{ij})(b_i.b_j)^{0.5}$
	$a = [\sum_i \sum_j x_i x_j a_{ij}^{2/3} / \sum_i \sum_j x_i.x_j b_{ij}]^{0.5}$
	$b = \sum_i \sum_j x_i.x_j b_{ij}$
	$a' = \sum_i \sum_j x_i x_j a'_{ij}$
	$b = \sum_i \sum_j x_i.x_j b_{ij}$
	$c = \sum_i \sum_j x_i.x_j c_{ij}$

Simplified interaction potentials are generally used to achieve an analytical development. Consequently, such EOS also own adjustable parameters. However, these parameters generally have well defined physical meanings (potential depth, coordination number, chain length, molecular weight) which allow to accurately estimate their order of magnitude. Despite the simplifications, the resulting analytical expressions of these EOS are more complex than in the case of cubic equations. So, they should preferably be used for prediction, extrapolation in temperature or pressure and for treatment of compound families (*n*-alkanes, 1-alkanols for instance).

A brief presentation of the principal kind of models is given below. More details can be found in a recent review.[37]

The simplest models were developed by Flory[38] and by Sanchez and Lacombe.[39] They assumed that the fluid structure is solid-like: molecules are located on a lattice and interact with their immediate neighbours either through a constant bonding energy or through a constant interaction energy. Such attempts were successful to qualitatively model polymer systems.

A better quantitative agreement with experimental data may be obtained using a more realistic description of the fluid structure. One may consider that molecules are found in a spatially continuous mean field of interaction potential, neglecting local density fluctuations. perturbed anisotropic chain theory (PACT),[38] perturbed hard chain theory (PHCT),[40] perturbed soft chain theory (PSCT) EOS[38] and statistical associating fluid theory (SAFT)[41] fall in this category. These models take into account both repulsive and attractive (dispersive, polar, associative) interactions using various theories (Carnahan–Starling for example) as well as molecule "length" (chain model). They appear thus appropriated for the representation of systems containing small and large molecules (like paraffins which contain light a heavy *n*-alkanes).

For instance, in the SAFT concept, a given molecule is constituted of identical spheres interacting one with another through a dispersive energy. The CO_2/*n*-alkane binary systems were represented up to C_{44} using original SAFT-EOS. Average error between experimental solubility[42] and calculated values are within 8%.[43] Regarding the restrictive hypothesis made, the computations are in satisfactory agreement with experimental data (Fig. 2). Nevertheless, this representation is slightly worse compared to Peng–Robinson calculations. Especially, representation of the solubility of *n*-alkanes in supercritical carbon dioxide with SAFT fails close to the mixture critical point.

4. Solubility from fluctuation solution theory

Another approach to model the solubility of polymers in supercritical fluids was developed by Kirkwood and Buff.[44] They established a direct relation between the solubility of the solute and fluctuations of solvent concentration in the vicinity of molecules of solute in terms of fluctuation integrals:

$$\ln y_2 = \ln\frac{P_2^{\text{sat}}}{P} + \frac{v^s}{\text{RT}}(P - P_2^{\text{sat}}) + \ln Z^0 + \int_{P_2^{\text{sat}}}^{p} \frac{G_{12}}{kT}.dP \quad (10)$$

where

$$G_{12} = \int_o^{\infty} [g_{12}(r) - 1].4\pi r^2.dr \quad (11)$$

where subscript (1) refers to solvent molecule, (2) refers to solute, $g_{12}(r)$ is the radial distribution function of the solvent molecules around solute molecules, r is the distance between solvent and solute molecules and Z^0 is the compressibility factor at infinite dilution.

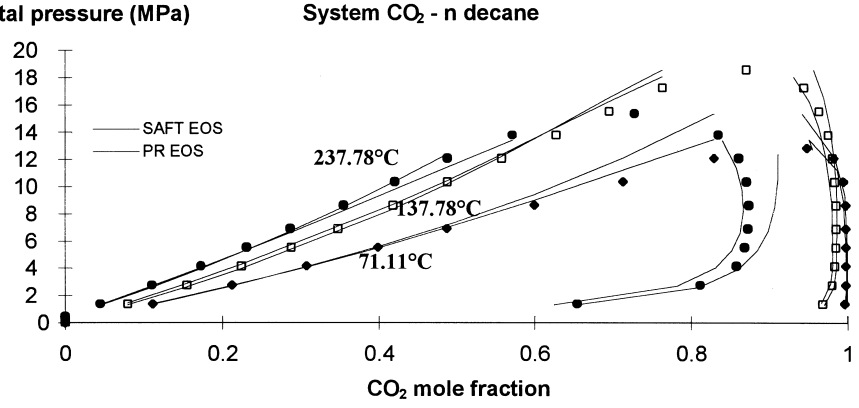

Fig. 2. Modelling CO_2/*n*-decane system using PR and SAFT models (experimental points from Reamer et al[42]: ●, 237.78°C; □, 137.78°C; ◆, 71.11°C).

Various versions of this approach[45,46] were tested for computing solubility of solids in supercritical fluid. Average errors on solubility between experimental and theoretical values with the Kirkwood–Buff theory of solutions[45] is within 22.6% and a modified version ("exclude volume model"[45]) is within 18.4%. Kwong and Mansoori[46] coupled hard sphere theory with Kirkwood–Buff theory of solutions (Table 4). They improved the representation significantly with only 12.88% mean error between experimental values of solubility and their calculations.

5. Application of an EOS to *n*-alkane solubility calculations

As a consequence of the above discussion, the use of a cubic equation of state seems the most suitable for our purpose, i.e. giving a good prediction of the solubility of a solid paraffin binder in supercritical CO_2 by using the simplest equation as possible. For example, let us consider here the case of solid n-C_{28} which enters in the composition of the paraffin (12 wt.%) with a melting point of 52°C. As shown by FT–IR experimental measurements (Fig. 1), its solubility in supercritical CO_2 at 313.15 K is low enough (lower than 10^{-3} mol/mol) to consider that n-C_{28} is infinitely diluted in the vapour phase. Then, the fugacity coefficient of n-C_{28} may be computed from Peng–Robinson equation (Section 3.2.1):

$$\ln\phi_2 = \frac{b_2}{b_1}(Z_1 - 1) - \ln[Z_1 - (b_1.P)/(\mathrm{RT})] - \frac{a_1}{2\mathrm{RT}\sqrt{2}b_1}.[[2(a_1a_2)^{0.5}/a_1).(l - k_{12})] - b_2/b_1].\ln[(Z_1 + (1+\sqrt{2}).(b_1P/\mathrm{RT})]/[Z_1 + (1-\sqrt{2}).(b_1P/\mathrm{RT})] \quad (12)$$

Table 4
Comparison of the average errors between calculations of the authors, made with the principal cited models, and their experimental values of solubilities (for alkanes molecules C_{20} to C_{32} in supercritical carbon dioxide for pressure up to 30 MPa and temperatures between 50 and 100°C)

Authors	Type of models	Average error on y_i (%)
Prausnitz[34]	Peng and Robinson (EOS)	1–10
Sato[36]	RK/G^E "mixing rules" (EOS)	20
Cochran et al.[44]	Kirkwood–Buff theory (Statistical mechanics)	22.6
Cochran et al.[45]	"Exclude volume model" (Statistical mechanics)	18.4
Kwong and Mansoori[46]	Kirkwood–Buff theory combined with hard sphere theory (statistical mechanics)	12.88

where subscripts 1 and 2 refer, respectively, to CO_2 and to n-C_{28}. Parameters a_i, b_i and k_{ij} have been defined in Section 3.2.1. Z_1 is the compressibility factor of pure supercritical carbon dioxide at the same temperature and pressure as the mixture. We computed y_2 from Eq. (5) using the values of P_2^{sub} (T) and v_2^{solid} provided by Moradinia and Teja.[37] k_{12} is set to 0.11 as suggested in Section 3.2.1. Since there is no general agreement on critical pressure and temperature values of n-C_{28}, the parameters a_2 and b_2 were adjusted. Indeed, according to Moradinia and Teja[37] $T_C = 838.3$ K and $P_C = 0.892$ MPa, Magoulas and Tassios[47] proposed $T_C = 829.9$ K and $P_C = 0.807$ MPa and Gasem and Robinson[48] suggested $T_C = 827.4$ K and $P_C = 0.661$ MPa. After data regression, we obtained $a = 64.12$ kg m^3 s^{-2} and $b = 4.59$ 10^{-4} m^3/mol. Average error between our experimental FT–IR values of solid n-C_{28} solubility and calculated values of solubility of n-C_{28} are within 14.6% (Fig. 1).

6. Discussion and conclusions

The knowledge of the n-alkane solubility in supercritical CO_2 is necessary to choose a suitable paraffin binder and an adapted debinding treatment to extract the organic phase in a short time and to avoid the generation of defects in the green part. A first approach to evaluate the solubility of a compound in a fluid is the application of a mathematical equation to the studied system. In this context, a review of existing models for solubility predictions of organic compounds in supercritical carbon dioxide allows to choose the appropriate equation. The Peng–Robinson equation of state allows a good prediction of the solubility of alkanes, constituting the paraffin binder, in supercritical CO_2. The calculated value of solubility of solid n-C_{28} alkane, equal to 0.4 10^{-3} mol/mol at 40°C under 28 MPa, is in good agreement with experimental value. For each n-alkane present in the paraffin composition, the same calculation can be performed. However, if we consider the solubility of a paraffin, one must take into account interactions between each n-alkane molecule.

The n-alkanes up to n-C_{28} are soluble in supercritical CO_2 at 40°C and under high pressures (higher than 25 MPa). However, the solubility drastically decreases when the carbon atom number is higher than 28 (n-C_{36} is not soluble in supercritical CO_2). Then, a paraffin wax composed of alkanes could be partially soluble in supercritical CO_2, that is confirmed by FT–IR measurements.

The partial solubility of paraffin waxes presents the advantage to maintain a low amount (1 to 3 wt.% based on the mass of powder) of binder (non soluble high molecular weight alkanes) to ensure the cohesion of the green part during extraction of the major part of the binder (soluble low molecular weight alkanes) and after

the debinding treatment. A non soluble paraffin with a high molecular weight distribution can also be mixed with a soluble paraffin with a low molecular weight distribution. Then, injection moulding formulations could be either based on a partially soluble paraffin binder or on a mixture of a soluble paraffin with a non soluble one.

An example of the first case is a paraffin binder (melting point equal to 52–54°C) with a large molecular weight distribution (C_{19} to C_{34}) centred on C_{26}. The major part (70 wt.% of the binder), corresponding to alkane from C_{19} to C_{28}, was dissolved. The non-soluble, high molecular weight, part of the binder, which represents 3% of the mass of powder, allows maintaining the ceramic cohesion. A previous work[23] showed that 50 to 70 wt.% of the binder can be evacuated after 2 h treatment at 28 MPa. An example of the second case is a mixture of a soluble low molecular weight paraffin (melting point equal to 42–44°C with a composition centred on C_{24}) and an insoluble crystallised paraffin wax.

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