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Solid Solubilities in Supercritical Phases : New Apparatus, Measurements and Modeling

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A new apparatus for the measurement of solid solubilities in supercritical fluids is described in detail. It is based on an analytical (the composition of the phase is obtained by analyses) open flow method (the solvent flows continuously through the solid solute). Solubilities of naphthalene in supercritical CO₂ in the pressure range 8-30 MPa are reported along the isotherm 308.15 K. The solubility data are correlated using the Chrastil model.

Introduction.

Supercritical fluids (SCF) are widely used for a broad field of applications. Particle generation is generally handled with RESS (Rapid Expansion of a Supercritical Solution) and SAS (Supercritical Anti-Solvent) processes, which are of particular interest. To develop them, the knowledge of the solubility of the solid compounds in the corresponding involved medium is the basic information required at first. Solubility is a good measurement of the interaction between species. The accurate determination of the influence of pressure and temperature on the solubility level provides insight onto the influence of these variables on extraction behavior.

Several experimental techniques have been developed to investigate high-pressure equilibria¹. It is possible to propose two types of methods according to the way the composition is measured, the synthetic methods and the analytical methods. Synthetic methods involve indirect determination of equilibrium composition without sampling^{2, 3}. They require preparing systems of given total composition according to each point in the (T,x) or (P,x) diagrams, and therefore, are time consuming. In analytical methods, the composition of the phases in equilibrium is obtained by analyses after sampling. These methods are most widely used to determine solid-fluid equilibrium. Two types of

analytical methods can be distinguished according to the way equilibrium is obtained: closed circuit method and open circuit method. In the closed circuit method subgroup, there are the pure static methods where the system is allowed to attain an equilibrium state in appropriately stirred conditions^{4, 5}, and the phase recirculation static methods where at least one phase circulates, provoking the agitation necessary to achieve the thermodynamic equilibrium. In the open circuit method group, either one of the phase is circulated, stripping by one gas⁶ or the whole mixture is circulated⁷. In both cases, it is necessary that the residence time of the flowing phase, in the experimental conditions, is longer than the time needed to reach the equilibrium.

An original apparatus has been developed to measure solubilities in pure and mixed solvents. It is based on a open circuit analytical method. The equilibrium cell was designed to achieve efficient stirring and efficient mass transfer in order to have the exiting supercritical mixture at the thermodynamic equilibrium. A Back Pressure Regulator (BPR) allows a constant pressure in the line. At the outlet, where the supercritical fluid is expanded, a liquid solvent stream is used to collect the solute. The apparatus is conceived to avoid solid precipitation and potential plugging, a problem encountered with most of the open circuit techniques used to measure solubilities in supercritical fluid. The solubility of the solid in supercritical fluid is calculated from the measured data.

Experimental.

1- Materials

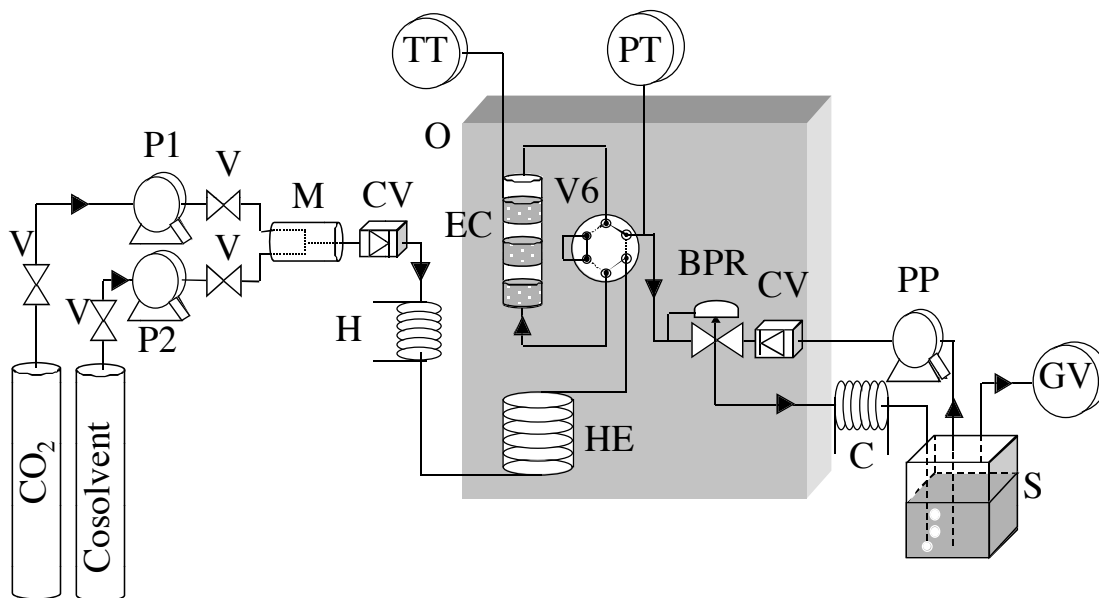
The sources and purities of the various compounds used are given in Table 1. These materials were used without any further purification.

compound	source	purity
Carbon dioxide	Air Liquide S.A.	99.995%
Naphthalene	Aldrich	98%
Hexane	Sds	99%

Table 1. Source and purity of chemicals.

2 – Equipment and procedures

The flow diagram of the apparatus is shown in Figure 1. The main parts of this apparatus are : high-pressure pumps, a mixer, a heater, a heat exchanger, an equilibrium cell, a back pressure regulator and a separator.



V : 2 way valves; P1, P2 : high pressure pumps; M : Mixer; CV : checking valve;
 H : heater; O : thermostated oven; HE : heat exchanger; V6 : 6 way-2 position valve;
 EC : equilibrium cell; TT : temperature transducer; PT : pressure transducer; BPR : back
 pressure regulator; C : cooler; S : separator; PP : peristaltic pump; GV : gas volumeter;

Figure 1. Flow diagram of the apparatus.

Liquid carbon dioxide is compressed at ambient temperature by means of a syringe pump P1 (Isco, model 260D) at the desired pressure. The Isco pump can be operated in either constant flow or constant pressure mode, for flow rates ranging from 0.1 $\mu\text{l}/\text{min}$ to 90 ml/min and pressure up to 50 MPa. The eventual co-solvent is introduced by means of another syringe pump P2, in a parallel flow, at a flow rate depending on the desired composition. To achieve an homogeneous mixing of the two liquid solvents, they circulate through a mixer, M. The mixer is a special device built up for this equipment.

The high-pressure fluid then passes through a heater, H, which consists in a brass body, containing a heating resistance, around which is coiled the solvent circuit (stainless steel tubing). The heater, H, is used to heat rapidly the solvent to temperatures over its critical temperature. The supercritical fluid then enters into an oven (Spame), where the solubility cell is thermo-regulated. The oven can be used up to 400 K, with a temperature regulation within 0.1 K. Due to thermal inertia of the equilibrium cell, its internal temperature is found to be stable within 0.05 K. A heat exchanger, HE, contained in the oven, is used to set the temperature of the solvent at the desired temperature (temperature of the required solubility measurement) before it enters the solubility cell. HE consists in a brass cylinder around which is winded the stainless steel solvent circuit. The cylinder and tubing are covered with a brass radiator. Downstream the heat exchanger, a 6 way-2 position high pressure Valco valve is found in the circuit to either direct the supercritical fluid to the cell or bypass it. This provides a means for removing eventual solid deposits from the line. Cylindrical in shape, the cell EC contains three compartments placed one above the other and fitted at their bottom with stainless steel fritted disks and O'rings. This is equivalent to three different cells connected in series. The solid powder, for which solubility measurements are required, is put inside the three compartments, which have a total volume of about 5 cm³. The fritted disks prevent stripping of the solid during the experiment, and allow a small pressure drop, advantageous to attain the saturation, while a good dispersion of the supercritical solvent is achieved. EC withstands for pressures up to 50 MPa at temperatures up to 400 K. The cap of the cell is sealed in the bottom part using a silicone O'ring. The two parts (cap and bottom) are pressed against each other with a fast connecting mechanical device. The pressure of the supercritical phase is monitored upstream and released downstream through the BPR (Tescom, model 26-1722), which can be either heated or not, to have it at temperatures higher or lower than the extraction temperatures. The BPR allows a pressure constancy to within 0.5 % in the line. It can be used up to 473 K and 70 MPa. At the outlet of the BPR, the mixture pressure is reduced to about the atmospheric pressure, then a recovering liquid solvent (a good solvent at atmospheric pressure) stream is used to get the solute in liquid state for collection. Without the solvent to recover the solute, this latter would precipitate during the pressure drop and lead to potential clogging. Then, a separator S is used to vent off

the gas and collect the solvent phase. At the end of each experimental run, the liquid solvent line is washed with fresh solvent to recover all the solute. The total volume of used gaseous solvent (extraction solvent), V_1 , is measured by means of a volumeter GV and the concentration of solid in the solute recovering liquid phase C_2^L by a gas or liquid chromatography. From these two data and knowing the total volume of the solute recovering liquid solvent, V_L , the solubility, y_2 , of the solid in supercritical fluid can be calculated through:

$$y_2 = \frac{n_2}{\sum_i n_i} \quad (1)$$

where

$$n_1 = \frac{V_1 \rho_1}{1000 \text{ MW}_1} \quad (2)$$

and

$$n_2 = \frac{C_2^L V_L}{1000 \text{ MW}_2} \quad (3)$$

n is the mole number, ρ the density and MW the molecular weight.

Temperatures of the heater, of the pressure transducer and of the BPR are monitored to better than 0.1 K by a temperature regulator (West Mini, model 6100) fitted with a J-type thermocouple. Temperature in the cell is measured directly in its body through a 4-wires 100 Ω platinum probe, within 0.02 K as a result of a careful calibration, performed against a 25 Ω reference platinum probe. Pressure is measured in the out-stream line of the cell. The pressure transducer (Druck, model PTX611) can measure pressures up to 35 MPa at temperatures up to 400 K, with an accuracy of $4 \cdot 10^{-3}$ MPa as a result of a calibration performed using a dead weight balance (Desgranges et Huot, model 5202S CP). It is thermostated (at a fixed temperature over than solubility measurement temperatures) by a small oven composed of a brass jacket containing a heating resistance (with internal thermocouple) connected to a thermo-regulator (West Mini, model 6100). Two main reasons for the thermal regulation of the pressure transducer: 1- we need to avoid condensation or solid deposit, 2- response coefficient of the pressure transducer is slightly dependent on temperature.

3 – Test of the equipment

An important requirement in the design of the apparatus was to obtain a saturated stream flowing outside the cell. To confirm the efficiency of the equipment on a large range of operating conditions, measurements have been performed at various flow rates. When in a given range of flow rates, no sensitive effect is observed on the measured solubility values, the equilibrium is confirmed. This applicability range is valid for the studied compound but does not stand necessarily for another. Separate experiments are therefore required to confirm operating flow rates for each solute of interest.

The validity of the technique was determined by measuring naphthalene solubility in supercritical CO₂. Corresponding data are very abundant in the literature and provide a good base for quantifying tests.

For this work, hexane was used as the recovering liquid solvent and sample analysis was performed by using a Hewlett Packard gas chromatograph (model 5890) fitted with an HP automatic injector (model 7675) and a SGE capillary column (model 50QC3/BP10 0.5). The extraction solvent flow rate was fixed at 0.75 ml/min. The solubility data are listed in Table 2. Figure 2 is a comparison of our data with those reported in the literature ^{8, 9, 10, 11, 12}. Our solubility measurements are in excellent agreement with previous works.

P (MPa)	y ₂
8.05	0.0440
13.43	0.0138
13.52	0.0139
14.85	0.0146
15.05	0.0147
20.03	0.0161
20.08	0.0163
24.82	0.0169
29.76	0.0174
29.92	0.0175

Table 2. Solubility data of naphthalene in supercritical CO₂ (T=308.15 K).

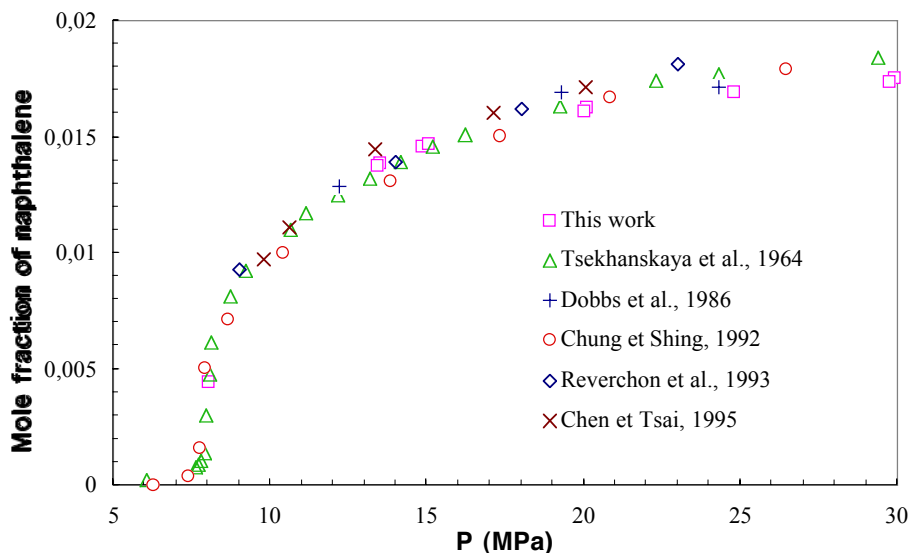


Figure 2. Comparison of our solubility data results with previous works at T=308.2 K.

In the near future work, we will use another compound, for which the solubility is closer to that of the systems relevant to pharmaceutical interest.

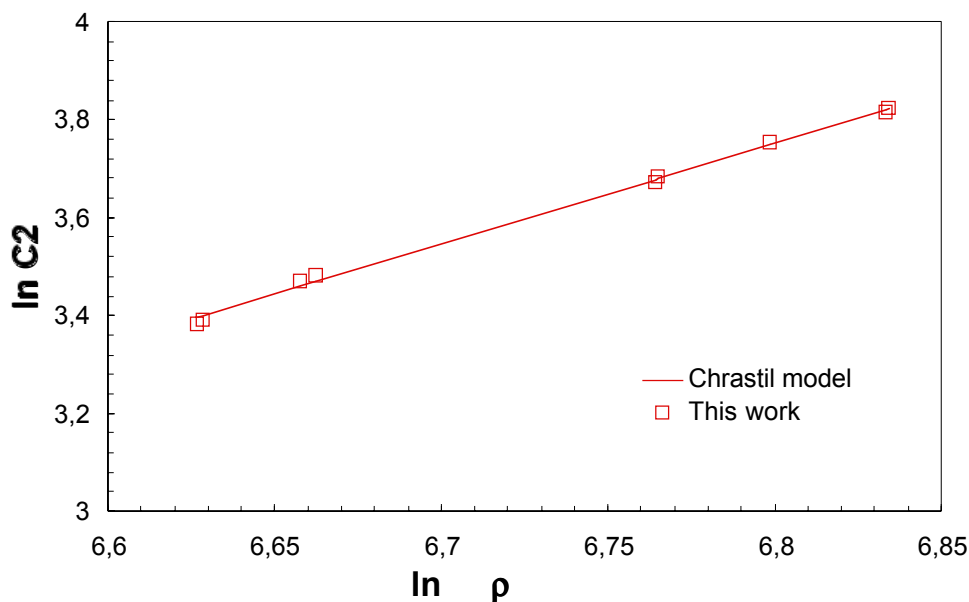
Modeling

Solids solubility in supercritical fluids can be correlated basically through two approaches: the density-based empirical model proposed by Chrastil¹³ and the Peng-Robinson equation of state (PR EoS)¹⁴. We plan to apply the PR EoS. For this option however, the critical parameters of the solute and the solvent must be known. They are obviously available, from the literature, for CO₂ and for most of the classical co-solvents, but this is not true for most of the complex solids related to pharmaceutical industry. At first, the solute critical parameters will be estimated using a group contribution method^{15, 16}. If results are not satisfying, critical parameters will be treated as adjustable parameters of the thermodynamic model (PR-EoS)^{17, 18}.

In the present work, the Chrastil correlation was applied for the naphthalene. This correlation may be regarded as a macroscopic description of the surroundings of the molecules in the fluid phase. Indeed, the Chrastil model assumes that solvation can be described as a complex formation equilibrium between native species of solvent and solute. The definition of the equilibrium constant through thermodynamic considerations leads to the following expression for the solubility:

$$\ln(C_2) = k \ln(\rho_1) + a/T + b \quad (4)$$

where C_2 is the concentration of the solute in the supercritical phase (kg.m^{-3}), ρ_1 is the density of the fluid (kg.m^{-3}). k (association number), a and b are adjusted on solubility experimental data taking into account the total heat of the reaction and the molecular weight of the species. The Chrastil development suggests that plots of $\ln(C_2)$ vs. $\ln(\rho_1)$ are straight lines with slopes equal to k . Experimental results were satisfactorily regressed



using a linear function, with a regression coefficient higher than 0.95 (Figure 3).

Figure 3. Concentration of naphthalene vs. density. Correlation proposed by Chrastil¹³.

The coefficients k obtained by regression on data over 13.5 MPa are listed in table 3.

	k
This work	2.1
Tsekhanskaya <i>et al</i> ⁸	2.4
Dobbs <i>et al</i> ⁹	1.3
Chung and Shing ¹⁰	2.7
Reverchon <i>et al</i> ¹¹	2.8
Chen and Tsai ¹²	2.1

Table 2. Coefficient k (Chrastil model)

We have limited the range of pressures to our investigated range because $\ln(C_2)$ vs. $\ln(\rho_1)$ was not found strictly linear for all data sources. Our k value is consistent with all the others.

Conclusion

A new apparatus for very accurate measurements of solid solubilities in supercritical fluids has been designed, built up and tested. Measurements of the solubility of naphthalene in supercritical carbon dioxide were carried out at 308.15 K over a range of pressures typically encountered in supercritical processes. The comparison with previous works indicates the validity of this apparatus, based on an analytical open circuit method. The data were correlated with a density-based model proposed by Chrastil, which provides an estimation of the number of solvent molecules per molecule of solute engaged in the solvato-complex.

Nomenclature.

a = parameter (Chrastil model)
 b = parameter (Chrastil model)
 C = concentration ($\text{kg}\cdot\text{m}^{-3}$)
 k = association number (Chrastil model)
 MW = molecular weight ($\text{g}\cdot\text{mol}^{-1}$)
 n = mole number (mol)
 P = pressure (MPa)
 T = temperature (K)
 V = volume (m^3)
 y = mole fraction

Greek symbols

ρ = density ($\text{kg}\cdot\text{m}^{-3}$)

Subscripts

L = recovering liquid solvent
 1 = light solvent component
 2 = heavy solute component

Superscripts

L = recovering liquid solvent

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