1

Prediction of binary interaction coefficient and critical parameters of cholesterol in supercritical carbon dioxide

Hatem Ksibi, Ali Ben Moussa

Istitut Préparatoire aux Etudes d'Ingenieur de Sfax, P. Box 805 Sfax 3018 Tunisia.
Computational Fluid Dynamics & Tranfer Phenomena Resarch Unity, P. Box W.3038
Sfax, Tunisia. hatem.ksibi@ipeis.rnu.tn

Abstract

In this work, the cholesterol concentration in the supercritical (SC) CO_2, under working conditions, is calculated by implementing the modified Peng Robinson equation of state (EoS) combined with the Van Der Waals mixing rules. Here, optimisations of the interaction coefficient (k_{ij}) between solvent and solute and the solute critical parameters (i.e. critical pressure and temperature) are the main issue to get precise calculations of the dissolved mole fraction in SC CO_2.

Keywords

Cholesterol, binary interaction, critical parameters, solubility, supercritical.

1. Introduction

The relatively high supercritical fluid density gives it a good solvent power. Therefore a solute can be extracted at supercritical condition of the solvent, and separated from it by reducing pressure or temperature below the critical parameters of the solvent, yielding a solvent-free extract. By using supercritical solvents having low critical temperatures as carbon dioxide, it is possible to extract thermally labile compounds, especially pharmaceutical and food products. In food industry, the reduction of cholesterol in certain aliments is of crucial importance. The cholesterol can be removed from food products using supercritical solvent resulting in minimal protein degradation [1]. Cholesterol is

a sterol that can be found in many animal tissues. It is the most abundant sterol in human tissues. It is transported in the plasma and is delivered to the tissues in the form of lipoprotein particles. The deposition of cholesterol in tissues can cause the narrowing of blood vessels, known as atherosclerosis. The structure of cholesterol is depicted in figure 1. It is worthwhile to investigate the possibility of applying numerical optimization of the dissolved mole fraction in SC CO_2 when the extraction of these compounds is very difficult and extract analysis requires instrumentations of high performance.
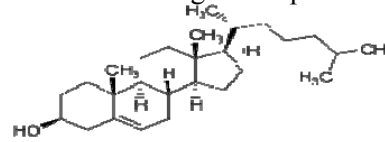

Figure 1 – The structure of Cholesterol molecule

The calculation of the solubility of a compound in the supercritical fluid has included both correlative and predictive approaches. Three models are well used in the literature to establish correlations for solubility data: Chrastil correlation [2] and the cubic EoS such as Redlich-Kwong-Soave (RKS), and the modified Peng-Robinson (PR) introduced by Schmitt and Reid [3].

In the present report, we study the two-parameter equations of state to predict the solubility of cholesterol in supercritical carbon dioxide. These data are computed simultaneously with the binary interaction coefficient by fitting numerically the experimental solubility of cholesterol in carbon dioxide over a wide range of pressure and for a given temperature in the literature [4-6].

2. Problem Statement

To predict the solubility of the cholesterol in supercritical CO_2, the compressed gas model was used. The model requires critical parameters and physical properties of the solute which cannot be measured, because the solute undergoes degradation when treated. In the case of cholesterol group contribution methods (GCM) are used in several works to estimate these properties [7]. Other critical parameters are given in literature for the cholesterol as summarised in table (1).

P_c (bar)	T_c (K)	ω	Ref.
12.20	778.7	-	Hartono et al. [5]
41.55	1168.2	0.950	GCM [7]
12.50	959.0	0.948	Daubert et al. [8]

Table 1- Different critical properties of Cholesterol given in the literature.

P_c, T_c and ω are critical pressure, critical temperature and acentric factor respectively.

3. Paper approach

3.1. Numerical modeling

In predicting the phase equilibrium between a supercritical phase and a condensed phase, the equality of fugacity of each component in each phase is required. The solubility of a condensed (y_2) in a vapor phase at supercritical condition is defined as follow:

$$y_2 = \frac{P_2^{sat}}{\varphi_2^{SF} P} \exp\left(\frac{V_2^S\left(P - P_2^{sat}\right)}{RT}\right) .$$ (1)

Where φ_2^{SF} is the fugacity coefficient of the supercritical state of the solute which is calculated using the chosen EoS.

Relations of RKS EoS (2) and PR EoS (3), could be extended to a solution at equilibrium of a multi-component system by using suitable mixing rules that define the mixture characteristics. They can be written respectively as:

$$P = \frac{RT}{(V - b)} - \frac{a}{V(V + b)} f(T_r)$$ (2)

$$P = \frac{RT}{(V - b)} - \frac{a}{V(V + b) + b(V - b)} f(T_r)$$ (3)

R is the perfect gas constant, *a* denotes the attractive term and *b* is the covolume. They are expressed as functions of the critical coordinates of both the solvent and the solute. The corrective function $f(T_r)$, is a function of both temperature and acentric factor ω. The conventional mixing rules of Van Der Waals for the supercritical solution are defined as:

$$\begin{cases} b = \displaystyle\sum_i y_i b_i \\ a = \displaystyle\sum_i \sum_j y_i y_j a_{ij} \end{cases}$$ (4)

and $a_{i \neq j} = \sqrt{a_i a_j}(1 - k_{ij})$ (5)

The fitting aspect bases on the molecular interaction coefficient as the adjustable solute parameter. The solute properties necessary to effectively correlate solubilities based on the modified PR approach or the RKS EoS include the molar volume and the saturated vapor pressure. The molar volume of cholesterol V^S is given in the literature by various values, which their average value is: $V^S = 373.55$ cm^3/mol.

The knowledge of the vapor pressure of the solute P_2^{sat} is also an essential step in the calculation of solubility.

Its equation is based on the Clausuis-Clapeyron model and given as a logarithmic function of the temperature:

$$\text{Log}_{10}\left(\text{P}^{\text{sat}}\right) = \text{A} - \text{B}/\text{T} \tag{6}$$

For cholesterol, we find in literature constants A and B as: A= 14.418 and B=5633,4. Sometimes, for a complex solute molecule both critical and binary interaction parameters are unknown. Nevertheless, we find in the literature a few measurable data such as the burning temperature and the density. The physical properties such as critical data, vapour pressure, molar volume and acentric factor required for using the PR EoS are not available and are estimated using group contribution methods, see table 1. Estimated values of critical temperature, critical pressure and acentric factor should not be interpreted as "true properties"; in fact, uncertainty in these values probably contributes to fake use of the PR EoS. The critical coordinates and k_{ij} are computed by optimization techniques (gold number algorithm) and compared with the experimental solubility values. When critical pressure of the solute is obtained group contribution methods are used to determine the critical temperature, the critical volume and the acentric factor.

3.2 The Chrastil model

The Chrastil model, although simple, relies much on the knowledge of the thermodynamic behavior of the supercritical solvent rather than of the solute and it is mostly capable of correlating, rather than predicting, the solubility. The Chrastil empirical relation is written as:

$$y_2 = \rho_1^k \exp\left(\frac{a}{T} + b\right) \tag{7}$$

Where y_2 is the solute solubility (mol/mol), ρ_1 is the supercritical fluid density and *a, b* and *k* are empirical fitting parameters. For cholesterol, these constants are set as follows: k= 12.095; a= –9460 ; b= -50.488.
The optimization technique of the solubility is quantified by an absolute average relative deviation (AARD) approach which is the most widely used assessment for evaluating the success of the numerical model and calculated as:

$$\text{AARD}\left(\%\right) = \frac{100}{N}\left|\Sigma\frac{y_e - y_c}{y_e}\right| \tag{8}$$

Where y_c and y_e denote the calculated and the experimental solubilities.

3.2. Results & discussions

The solubility of cholesterol in supercritical carbon dioxide as predicted by PR, RKS equations and the empirical correlation of Chrastil and compared with the experimental data is shown in Figure 2. According to this figure, both the PR and RKS EoS are in good agreement with the experimental data. The solubility of cholesterol calculated using the Chrastil correlation is one order of magnitude

higher than the experimental data. From this calculation, we can underline the limitation of this predictive correlation for cholesterol in carbon dioxide.
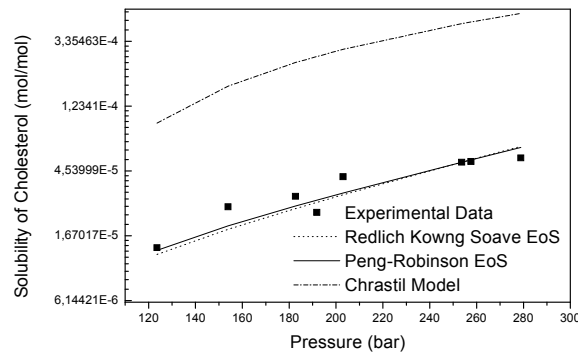

Figure 2 – Comparison between experimental data [4] and several numerical optimisation of the cholesterol solubility at T=308.15 K

At temperature T=318,15 K, we compare the calculated solubilites using the PR EoS for different critical properties given in the literature as presented in table (1). We find that values of cholesterol solubility are strongly altered by these parameters. For example, critical data of [8] give the lowest value at every pressure when it is compared to the experimental measurements.
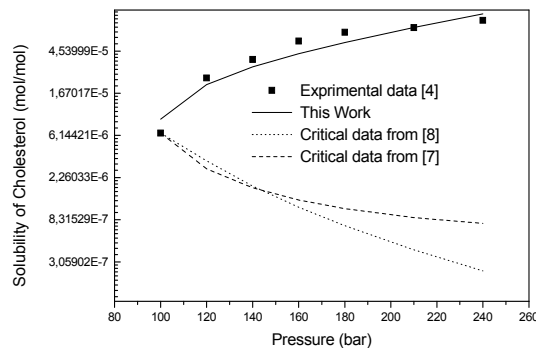

Figure 3 – Cholesterol solubility calculated through several critical coordinates optimizations comparison with experimental data of [4] at T=318.15 K

A tiny amelioration is given by implementing the solubility using critical properties given in [7], but error exceeds many orders of magnitude. The present critical values give the best fitting of the experimental data. These critical coordinates are summarized as follows: P_c = 43 bars; T_c= 875 K and ω = 0,949. We notice that the new value of critical temperature is close to the average value of critical temperatures given in table 1, whereas the critical pressure is near to that estimated by Daubert et al. [8].
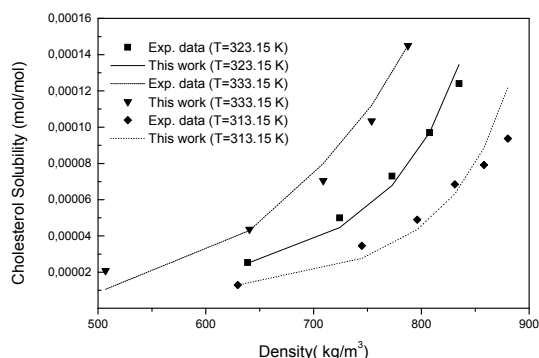
Figure 4 – Isotherm network of cholesterol solubility – comparison between experimental data given in [4-6] and numerical computations of this work

In figure (4), the experimental solubilites given in references [4-6] are fitted using new critical parameters and an optimized binary interaction factor. A good agreement between both calculated and experimental data of the cholesterol solubility is obtained for several isotherms.

4. Conclusion

We present in this work a numerical model for estimating the solubility of high molecular weight compound in supercritical carbon dioxide. Different comparisons of the obtained results with both experimental data and other numerical predictions of the solubility at equilibrium are shown. The accuracy of the present numerical technique is noticed by giving new critical coordinates data of the cholesterol and an accurate binary interaction coefficient for the system Cholesterol / carbon dioxide.

References

1. Zeidler, G., Pasin, G. and King, A.J. (1996) `Supercritical Fluid Extraction of Cholesterol from Liquid Egg Yolk'. US Patent 5,514,401
2. J. Chrastil, J. Phys. Chem. 86, 15, (1982) 3016
3. W. J. Schmitt, R. C. Reid, Fluid Phase Equilibria 32,1 (1986), 77
4. J.M. Wong, K.P. Johnston, Biotech. Prog., 2 (1986) 29
5. R. Hartono, G. A. Mansoori , A. Suwono, Chem. Eng. Sc. 56,24 (2001) 6949
6. S. L. J Yun, K. K. Liong, G. S. Gurdial, N. R. Foster, Ind. Eng. Chem. Res. 30 (1991) 2476
7. R.C. Reid, J.M. Prausnitz, B.E. Poling, Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York (1987)
8. T. E. Daubert, R. P. Danner, H. M. Sibul, C. C. Stebbins, Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation; Taylor & Francis: London (1996)