

SOLUBILITY CALCULATION OF AROMATIC COMPOUNDS IN SUPERCRITICAL CO₂ BY GROUP CONTRIBUTION METHODS

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Solubility calculation of aromatic compounds in supercritical CO₂ is presented using Peng-Robinson equation of state applied in a predictive way with UNIFAC group contribution activity coefficient model incorporated in its mixing rules using LCVM procedure. This is an alternative way when no experimental data on solubility is available. Experimental solubility data of naphthalene, 2,3-dimethylnaphthalene, anthracene, biphenyl, diclorobiphenyl, 2-naphthol and benzoic acid in SC-CO₂ is used to validate this methodology. The results show satisfactory agreement between calculated and experimental solubility values.

Keywords: solubility calculation, supercritical CO₂, aromatic compounds, group contribution

INTRODUCTION

Accurate prediction of solid solubility in supercritical fluids is an important requirement for supercritical fluid extraction process development. Despite some experimental data base available for solid solubility in supercritical fluids, in most cases additional experimental efforts are often needed. A promising alternative is the use of predictive group contribution methods to calculate solid solubility without experimental data. Equations of state (EOS) combined with UNIFAC models are used to describe supercritical fluid phase behavior but they are still not capable of being completely predictive across all solute-SCF systems.

Sublimation pressure and molar volume of solute are the key properties to calculate solid solubility in supercritical fluids. In an early work, we show that solid sublimation pressure is more important than molar volume and that it has particularly an important role on the accurate calculation of crossover pressure [1].

In this work, a methodology is proposed to predict solute solubility in supercritical carbon dioxide by Peng-Robinson-LCVM-UNIFAC equation of state. No experimental data of critical properties, acentric factor, sublimation pressure and molar volume of solute are used. These properties are calculated by group contribution methods and corrected during the convergence procedure for solid solubility calculation of a reference compound (naphthalene), that is a compound with experimental solubility data available. This methodology is applied to systems containing supercritical CO₂ and aromatic compounds (naphthalene, 2,3-dimethylnaphthalene, anthracene, biphenyl, diclorobiphenyl, 2-naphthol and benzoic acid). Solute solubility is calculated for several conditions and the obtained results are compared to experimental data. Based upon these satisfactory results, this methodology proves to be applicable to evaluate other systems displaying analogous behavior.

MATERIAL AND METHODS

Solid solubility in supercritical solvents is often modeled assuming that the solvent does not dissolve in the solid phase and the supercritical fluid-rich phase behaves like a dense gas. If the molar volume of the solid is considered independent of pressure and the fugacity coefficient of pure vapor is unity at a given temperature and vapor pressure, the solid solubility in the supercritical solvent may be expressed as

$$y_2 = \frac{P_2^s}{\hat{\phi}_2 \cdot P} \cdot \exp\left[\frac{v_2^s(P - P_2^s)}{RT}\right] \quad (1)$$

where P_2^s , v_2^s and $\hat{\phi}_2$ are the vapor pressure, molar volume and fugacity coefficient of the solid solute in the supercritical solvent-rich phase, respectively.

In this work, Peng-Robinson equation of state [2] with mixing rules from LCVM method coupled with UNIFAC model [3] is used to calculate the fugacity coefficient of some aromatic solutes in supercritical carbon dioxide.

To calculate the solubility of 2,3-dimethylnaphthalene, anthracene, biphenyl, dichlorobiphenyl, 2-naphthol and benzoic acid in SC-CO₂, we use only the experimental data of naphthalene. With the PR-UNIFAC-LCVM model, a new algorithm is proposed to calculate the pure component properties of these solutes (critical pressure and temperature, Pitzer acentric factor, solid molar volume and solute vapor pressure). That is because very often no experimental data of these properties are found in the literature. So, the pure component properties are internally and simultaneously estimated by group contribution using the methodology developed.

These compounds have one, two or three aromatic rings and their molecular structure are shown in figure 1.

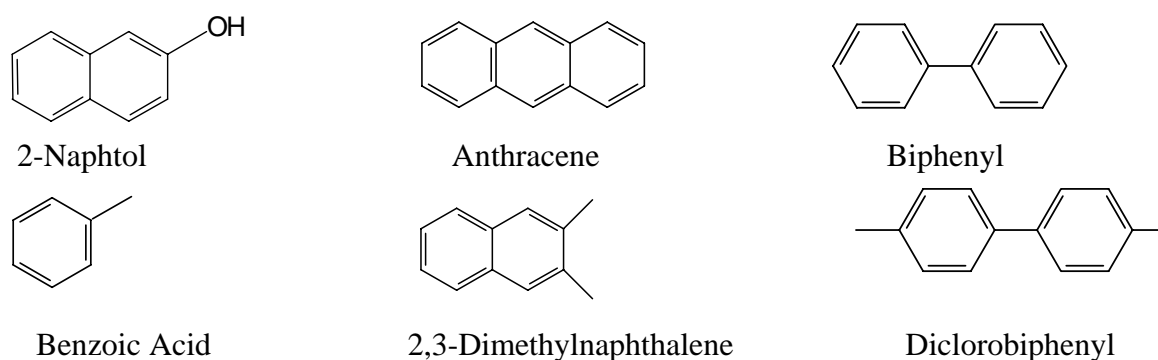


Figure 1. Molecular structures of 2-naphthol, anthracene, biphenyl, benzoic acid, 2,3-dimethylnaphthalene and dichlorobiphenyl.

Critical pressure (P_c) and the ratio of critical temperature to normal boiling temperature ($\theta = T_c/T_b$) is calculated by Lydersen's method and the critical volume (V_c) by Vetere's method. Using the procedure proposed by Subra *et al.* [4] we find the first estimative for T_c . With P_c and θ it is possible to calculate the acentric factor by Edmister's method [5] to obtain the initial guess of T_c , P_c and w for naphthalene.

Initial guess of vapor pressure (P^s) for the aromatic solutes is done by

$$\ln P^s = A - \frac{B}{T} \quad (2)$$

$$B = \frac{\Delta H^{sub}}{R} \quad \text{and} \quad A = \frac{B}{T_f} \quad (3)$$

where ΔH^{sub} is the enthalpy of sublimation estimated by group contribution [6] and T_f is the melting point temperature estimated by Joback's method [5].

The molar volumes (v^s) of these solutes are estimated from a correction factor of van der Waals volume (V_w), calculated by group contribution [6], in which v^s is about 1.5 to 2.0 times the value of V_w , as seen before [1]. After the first estimation of these properties, their values are internally rearranged by the model following a procedure similar to one recommended in literature [4], with the possibility of changing the initial values of all properties estimated. Solubility of naphthalene in SC-CO₂ is the unique experimental data really needed for calculation by the model. Table 1 shows the properties values for naphthalene before and after this procedure.

Table 1. Physical properties of naftaleno.

Solute	T_c (K)	P_c (atm)	w	A	B	v^s (cm ³ /gmol)
Before	698.597	36.215	0.32567	28.9147	7549.07	114.2682
After	698.597	39.1116	0.32567	20.6864	8558.16	114.2682

RESULTS AND DISCUSSION

Solubility calculation of 2,3-dimethylnaphthalene, anthracene, biphenyl, diclorobiphenyl, 2-naphthol and benzoic acid in SC-CO₂ is presented at 308K for pressure in the range from 100 to 500 atm using a predictive method. These calculations are performed using naphthalene as the departure molecule. Table 2 show a comparison between experimental and calculated solubility of naphthalene in supercritical CO₂ at 308K. The average absolute relative deviation (AARD) for naphthalene is 1,52%. For every solute is used the same group contribution method used for the initial estimation of T_c , P_c , w , A , B and v^s for naphthalene. Next, a linear correction factor, obtained from the molecular structure and experimental solubility of naphthalene, is used for all these solutes and the final values of T_c , P_c , w , A , B and v^s are determined for all of them. These final values are used to calculate solute solubility without fitting parameter to experimental data.

Table 2. Comparison between experimental and calculated solubility of naphthalene in supercritical CO₂ at 308K.

P (atm)	85.7	96.9	105.1	131.3	166.8	196.9	219.5	239.3	252.0
y_{exp}	7.5×10^{-3}	9.75×10^{-3}	10.7×10^{-3}	14.1×10^{-3}	16.0×10^{-3}	17.1×10^{-3}	18.3×10^{-3}	19.1×10^{-3}	19.2×10^{-3}
y_{cal}	7.3×10^{-3}	9.75×10^{-3}	11.0×10^{-3}	13.8×10^{-3}	16.2×10^{-3}	17.5×10^{-3}	18.3×10^{-3}	18.8×10^{-3}	19.1×10^{-3}

Group contribution prediction of the other solid solubilities were compared with experimental data taken from [7] and [8]. Comparison between calculated and experimental solubility data can be seen in figures 2 to 7. The model reproduces quite well the experimental solubilities.

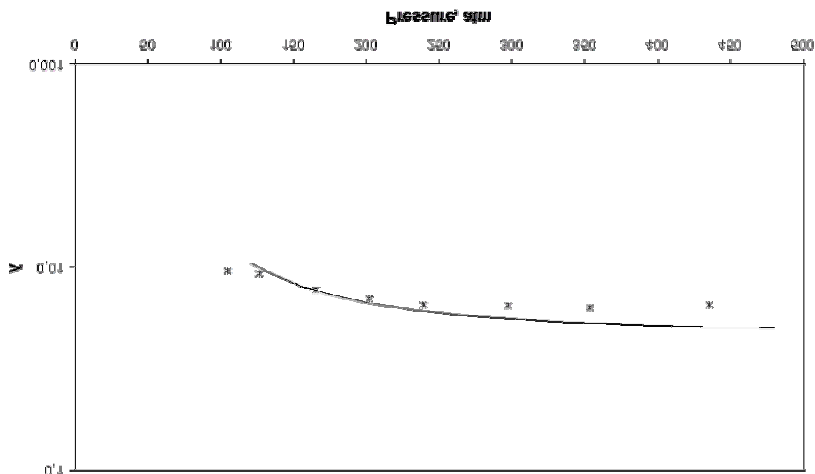


Figure 2. Experimental solubility data of biphenyl in SC-CO₂ at 308 K, taken from Schmitt and Reid (1986). Continuous line represents the solubility isotherm calculated with the PR-LCVM-UNIFAC equation of state.

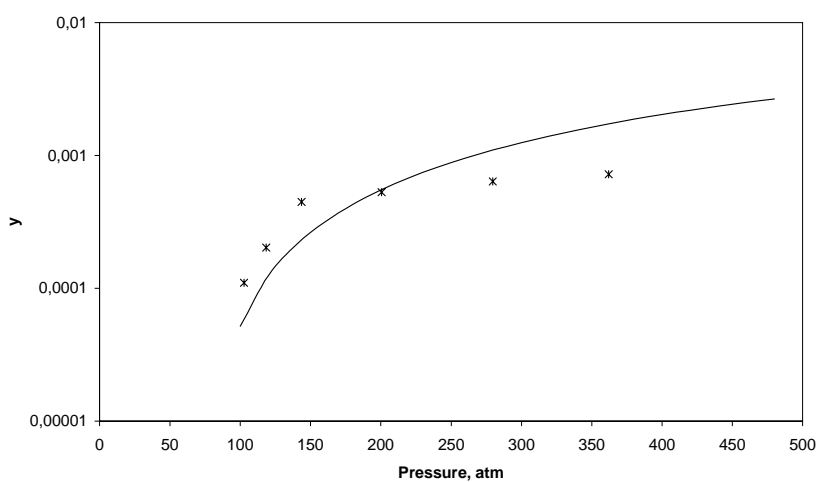


Figure 3. Experimental solubility data of 2-naphthol in SC-CO₂ at 308 K, taken from Schmitt and Reid (1986). Continuous line represents the solubility isotherm calculated with the PR-LCVM-UNIFAC equation of state.

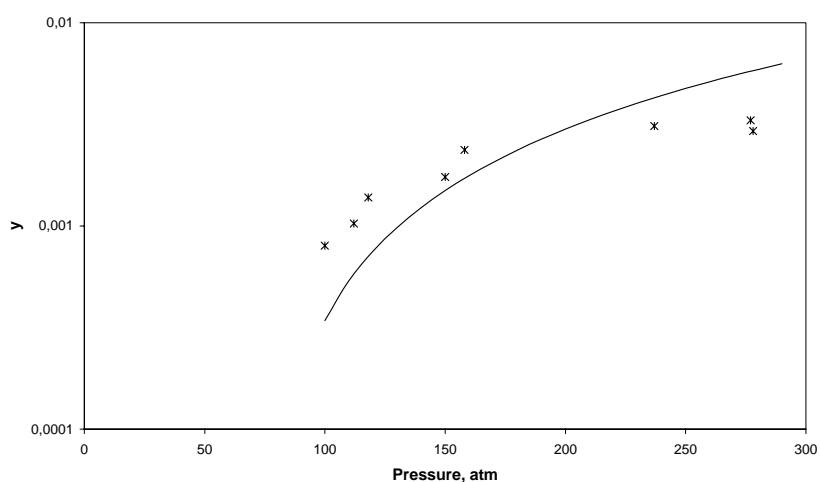


Figure 4. Experimental solubility data of benzoic acid in SC-CO₂ at 308 K, taken from Schmitt and Reid (1986). Continuous line represents the solubility isotherm calculated with the PR-LCVM-UNIFAC equation of state.

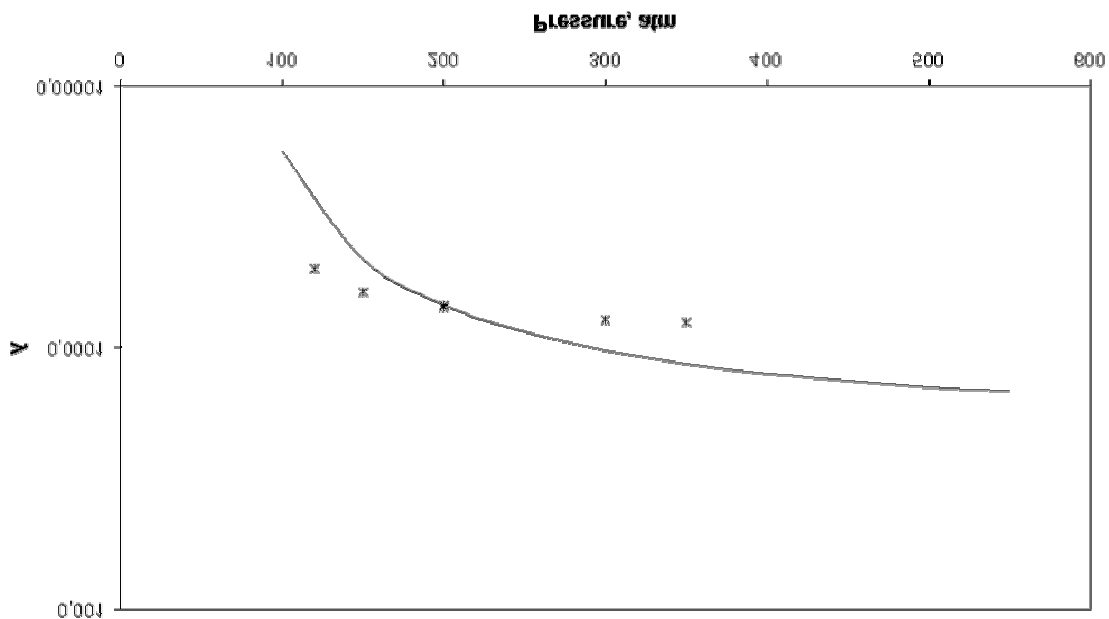


Figure 5. Experimental solubility data of anthracene in SC-CO₂ at 308 K, taken from Garnier *et al.* (1999). Continuous line represents the solubility isotherm calculated with the PR-LCVM-UNIFAC equation of state.

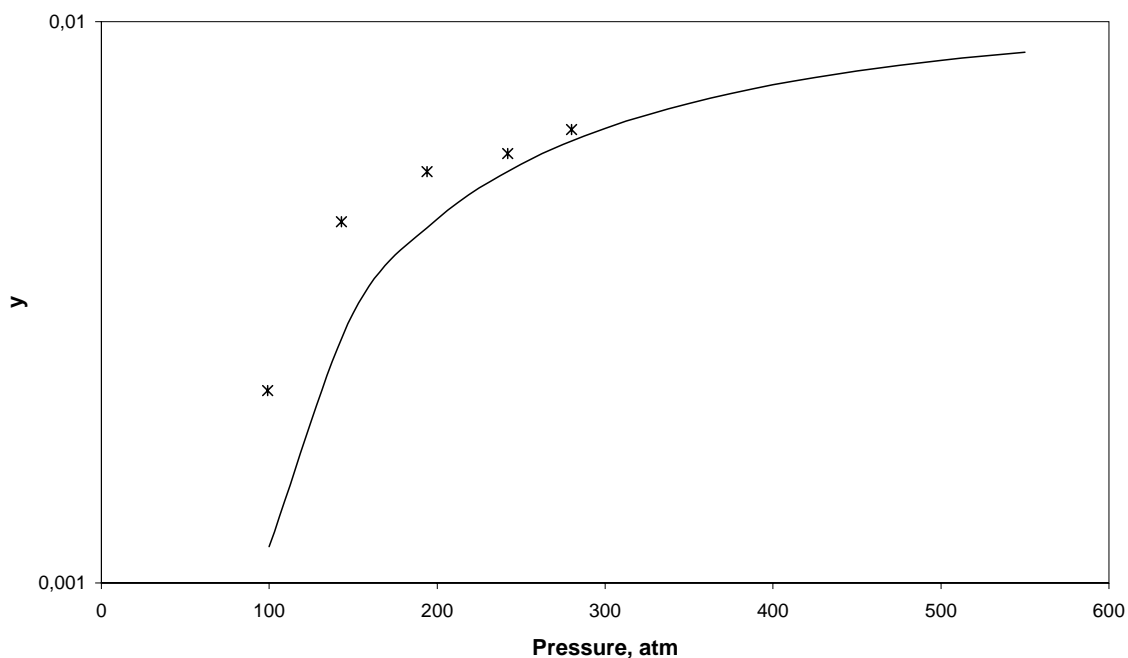


Figure 6. Experimental solubility data of 2,3-dimethylnaphthalene in SC-CO₂ at 308 K, taken from Garnier *et al.* (1999). Continuous line represents the solubility isotherm calculated with the PR-LCVM-UNIFAC equation of state.

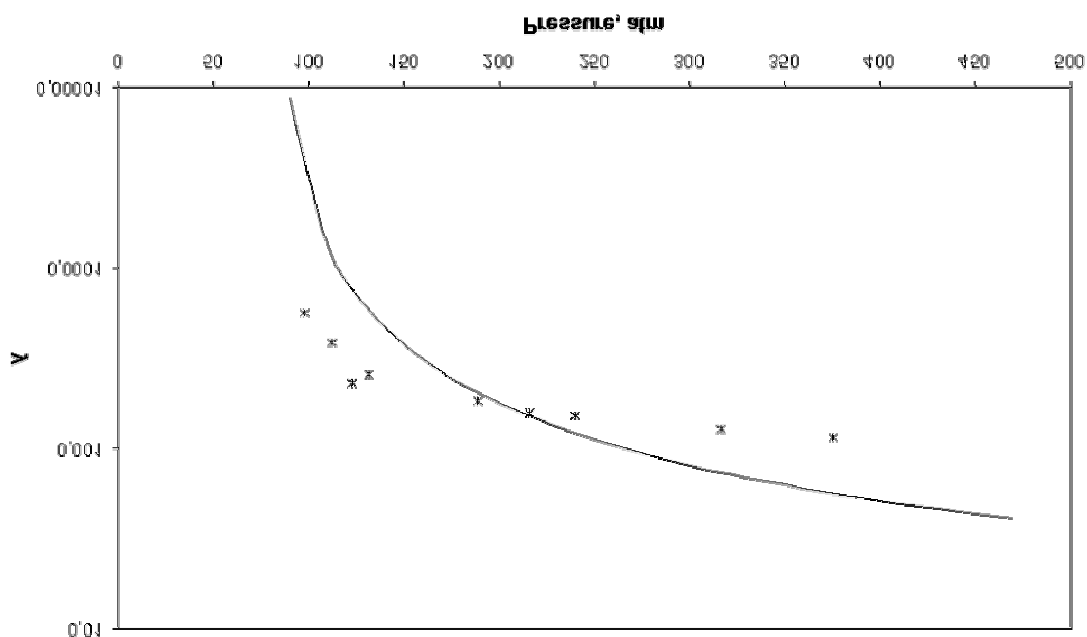


Figure 7. Experimental solubility data of diclorobiphenyl in SC-CO₂ at 308 K, taken from Garnier *et al.* (1999). Continuous line represents the solubility isotherm calculated with the PR-LCVM-UNIFAC equation of state.

CONCLUSIONS

In this paper prediction of the solubility of some aromatic compounds in supercritical CO₂ is done by the Peng-Robinson equation of state in a predictive way with UNIFAC group contribution activity coefficient model incorporated in its mixing rules using LCVM procedure. Experimental solubility data of naphthalene in SC-CO₂ is used to validate this methodology. Results show an alternative way to evaluate the possibility of supercritical fluid extraction of a solute when no experimental data is available. Further study is extending this methodology to other class of compounds in order to generalize the proposed method.

REFERENCES

- [1] COSTA, G.M.N., VIEIRA DE MELO, S.A.B., PESSOA, F.L.P., CAMPOS, A.M., *Chemical Engineering Transactions*, vol. 2, **2002**, 321-326.
- [2] PENG, D. Y.; ROBINSON, D. B., *Ind. Eng. Chem. Fundam.*, 15, **1976**, 58-64.
- [3] BOUKOUVALAS, C.; SPILIOIS, N.; COUTSIKOS, N.; TASSIOS, D., *Fluid Phase Equilibria*, 92, **1994**, 75-106.
- [4] SUBRA, P., CASTELLANI, S., KSIBI, H., GARRABOS, Y., *Fluid Phase Equilibria*, 131, **1997**, 269-286.
- [5] REID, R. C., PRAUSNITZ, J. M., POLING, B. E. *The Properties of Gases & Liquids*, McGraw-Hill, 4th. ed., Singapore, **1989**.
- [6] BONDI, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*, John Wiley & Sons Inc., New York, **1968**.
- [7] SCHMITT, W.J.; REID, R.C., *J. Chem. Eng. Data*, 31, **1986**, 204-212.
- [8] GARNIER, S.; NEAU, E.; ALESSI, P.; CORTESI, A.; KIKIC, I., *Fluid Phase Equilibria*, 158-160, **1999**, 491-500.