

New Correlation of the binary interaction factor for polar solutes in supercritical carbon dioxide

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Abstract

Recently a number of investigators have emphasized the need of obtaining reliable measurements of the solubility of a solute in a supercritical fluid. It is the most important thermophysical property that needs to be determined and modelled as a first step to develop any supercritical fluid applications.

The contribution is focalised on very dilute solutions of many polar solutes in carbon dioxide (nonpolar solvent) when the molar polarization of the solute at infinite dilution is accurately known. A database containing experimental solubility data for many solutes was used in this study where isotherms were comprised between 308 and 343 K.

This research was undertaken to develop a mathematical model to compute the solubility of solids in supercritical fluids, particularly in the carbon dioxide. As a result, a new correlation of binary interaction (k_{ij}) is proposed. The new relationship considers the binary interaction term k_{ij} as a function of the dipole moment, the solute carbon number and the reduced temperature.

1. Introduction

Solubility data are essential for the assessment and development of new applications of supercritical fluids. One of the great advantages of supercritical fluids is that a solute's solubility may be adjusted through changing the operating conditions of pressure and temperature. The high-pressure level may be used to increase the solubility to extract, for example, a specified solute from vegetable matrices. Then, a drop in pressure may be used to recover the solute and regenerate the supercritical fluid for reuse. A large solubility database must be generated for each solute, as the solubility is a function of the temperature, the pressure and the presence of other constituents.

Historically, Hannay and Hogarth [1] studied the solubility of solids (inorganic salts) in supercritical solvents (ethanol). By the early 1900s, Buchner [2] discovered that the solubility of organic compounds such as naphthalene in supercritical carbon dioxide is a function of the pressure.

In this work we present firstly phase equilibrium equations and then the followed optimisation technique which can determine precisely the binary interaction factor. Finally we depict the accuracy of the developed correlation by comparing with estimated values of binary interaction coefficient for many isotherms.

2. Solubility Optimization

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 binary systems' solubility data. These models are those of Chrastil [3] and, deduced from equations of state Redlich- Kwong -Soave and Peng -Robinson.

The solute properties necessary to effectively correlate solubilities based on an EOS include the molar volume and the saturated vapour pressure (as a function of temperature). The prediction of solubility using the chosen EOS model assumes that the solute phase remains pure. This assumption is thought to be quite reasonable for solid solutes. However, in the case of liquid solutes, it is likely that carbon dioxide will dissolve into the liquid solute at the same time as the liquid is dissolving in the supercritical carbon dioxide. Indeed, McHugh and Krukoni [4] provide the necessary equations to handle these phase equilibrium of the liquid solute within the supercritical fluid.

The solubility can be expressed by equating fugacity terms of the solute (2) at each state as written:

$$f_i^{(V)}(T, P, y_i) = f_i^{(S)}(T, P, x_i) \quad (1)$$

y_i and x_i denote the mole fraction of vapour and solid phases respectively, and i the considered substance of the solution.

$$f_i^s = P_i^{sat} \varphi_i^{sat} \exp \int_{P_i^{sat}}^P \left(\frac{V_i^s}{RT} \cdot dP \right) \quad (2)$$

$$\text{And } f_i^f = \varphi_i \cdot y_i \cdot P \quad (3)$$

Therefore we obtained the expression of the solute mole fraction as a function of the pressure and the temperature:

$$y_i = \frac{P_i^{sat} \cdot \varphi_i^{sat}}{\varphi_i^f \cdot P} \exp \left(\frac{V_i^s (P - P_i^{sat})}{RT} \right) \quad (4)$$

Where φ_i^{sat} and φ_i^f are the fugacity coefficients of the saturated pure vapour and the supercritical state of the solute, respectively. The coefficient φ_i^{sat} is equal to 1, and the second one is calculated using the chosen EOS.

Numerous equations of state are proposed in the literature, their use is strongly related to the domains of the operating parameters and the nature of the chemical components. The best known EOS for pure compounds are the cubic equations of state, such as Redlich - Kwong - Soave (RKS) EOS (1972) and Peng - Robinson (PR) EOS (1976). These two PVT relationships can accurately describe the supercritical phase of the carbon dioxide. Valderrama [5] has summarized the use of cubic equations of state, especially RKS EOS for supercritical fluid and mixtures. These equations can be written respectively as:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \quad (5)$$

$$P = \frac{RT}{(V - b)} - \frac{a(T)}{V(V + b) + b(V - b)} \quad (6)$$

The phase equilibrium calculation for a given mixture involves both suitable EOS and mixing rules which define the EOS corrective terms (a, b) of the solution. The most used are those of Van der Waals (VDW), where k_{ij} is the binary interaction parameter:

$$a = \sum_i \sum_j y_i \cdot y_j \cdot a_{ij} \quad (7)$$

$$\text{and } b = \sum_i y_i \cdot b_i \quad (8)$$

Where b_i and a_{ij} are constants depending on the substance nature. The term a_{ij} is defined as:

$$a_{ij} = (a_{ii} \cdot a_{jj})^{0.5} (1 - k_{ij}) \quad (9)$$

The knowledge of the vapour pressure P^{sat} of the solute is also an essential step in the calculation of solubility. If the model is not available as a function of temperature, it is still possible to attempt to fit the solubility data, but the quality of fitting is likely to be poor.

Indeed, several works yield accurate vapour pressure from the triple point up to the critical point. Rogalski et al. [6] give adequate representations of both the saturated vapour pressure expression and the molar volume estimation for different ranges of operating conditions. Using mathematical relationships of vapour tension given in the literature depends highly on the state of the solute state at ambient conditions. Generally, these equations are based on the Clausius - Clapeyron model is given as a logarithmic function of the temperature:

$$\text{Log}_{10}(P^{\text{sat}}) = A - \frac{B}{T} \quad (10)$$

A and B are two constants depending on the chemical structure of the solute. Two kinds of models depending of the acentric factor are summarized in the following:

$$\frac{P^{\text{sat}}}{P} = \exp(f_0 + W(2) \cdot f_1) \quad (11)$$

$$\text{and } \frac{P^{\text{sat}}}{P} = \exp(f_0 + W(2) \cdot f_1 + W(2)^2 \cdot f_2) \quad (12)$$

The most used functions f_0 and f_1 of equation (11) are given by Schreiber and Pitzer [7]:

$$f_0 = 0.90387412 - \frac{3.8754024}{T_r} - 10.021469 \times 2.3 \text{Ln}(T_r) + 2.9715283T_r, \quad (13)$$

$$f_1 = 2.0095293 - \frac{8.66162}{T_r} - 30.391841 \times 2.3 \text{Ln}(T_r) + 6.6520983T_r,$$

According to the second model, equation (12), Ambrose and Walton [8] gave expressions of f_0 , f_1 and f_2 as follows :

$$f_0 = \frac{1}{T_r} \left(-5.97616(1 - T_r) + 1.29874(1 - T_r)^{1.5} - 0.60394(1 - T_r)^{2.5} - 1.068415(1 - T_r)^5 \right)$$

$$f_1 = \frac{1}{T_r} \left(-5.03365(1 - T_r) + 1.11505(1 - T_r)^{1.5} - 5.41217(1 - T_r)^{2.5} - 7.46628(1 - T_r)^5 \right) \quad (14)$$

$$f_2 = \frac{1}{T_r} \left(-0.64774(1 - T_r) + 2.41539(1 - T_r)^{1.5} - 4.26979(1 - T_r)^{2.5} + 3.25259(1 - T_r)^5 \right)$$

3. k_{ij} correlation

As can be seen, the EOS corrective coefficients (a, b) require the interaction parameters for phase behaviour description. Many papers, such as Bartle et al. [9] have given averaged values of this binary interaction. They have used numerous couples of supercritical solvent and solute presented

in the literature, and then by linear fitting, they have obtained empirical correlations for the binary interaction factor. k_{ij} . The last one is estimated as a function of physical properties of the solution such as molecular polarity, weight... We notice that these correlations are valid just for a few kinds of solutes and cannot be extended for large application domains.

Moreover, the binary interaction parameter is fitted numerically from experimental solubility data by Ksibi [10]. The numerical calculation of this parameter is based on the modified Peng-Robinson EOS and the Van der Waals (VDW) mixing rules. The “golden section search” optimization technique is suitable to determine the interaction parameter k_{ij} by a number of iterations [11].

In this work the attention is focalised on the dependency of the binary interaction on the temperature seen before and, the dipole moment of the solute as the carbon dioxide is a non polar molecule. The binary interaction is implemented via numerous data base of solubility and several models of vapour pressure eqs (11) and (12) where the numerical code chooses the adequate one by judging a convergence criterion.

The performance of the correlations is quantified by a squared absolute average relative deviation (SAARD). This approach is the most widely used assessment for evaluating the success of the numerical model. An SAARD is calculated according to equation (15):

$$SAARD \% = \frac{1}{N} \sum \left(\frac{Y_{calc} - Y_{exp}}{Y_{exp}} \right)^2 \times 100 \quad (15)$$

4. Results and discussions:

The supercritical solution of limonene and carbon dioxide at equilibrium is studied numerically by using both PR and RKS EoS coupled with VDW mixing rules. The solubility computation using k_{ij} optimisation from experimental data is shown in Figure (1).

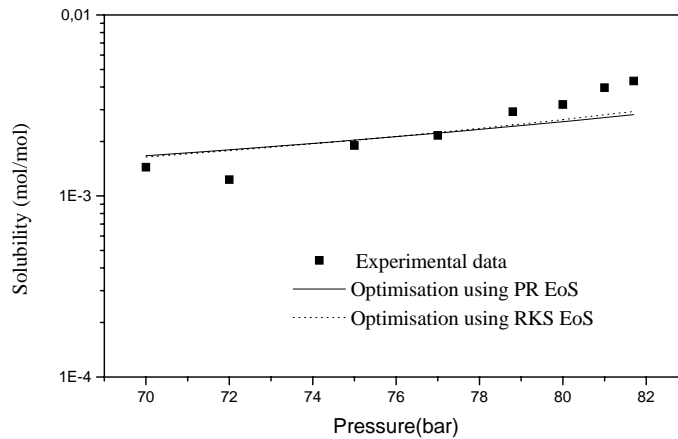


Figure 1: Solubility of limonene in supercritical CO₂: Comparison between calculated and experimental values at 313 K.

The solid line depicts the solubility at equilibrium estimated from relation (4). Therefore, a good agreement with solubility measurements can be noticed and averaged relative deviation of experimental points is less than 7 %. Here we note that at high pressure, the estimated solubility value is strongly altered by the k_{ij} model and error increases enormously.

As a second example of solute, the solubility of naphthalene in supercritical carbon dioxide is calculated as a function of the pressure. The thermodynamic description is based on PR and RKS EoS and the Van der Waals mixing rules. Figure 2 shows the mole fraction for the isotherm (308K) at different pressures. The numerical fitting used the experimental data given by several works. A good agreement of the calculated solubility is noticed when it is compared with the experimental value at the same pressure and temperature.

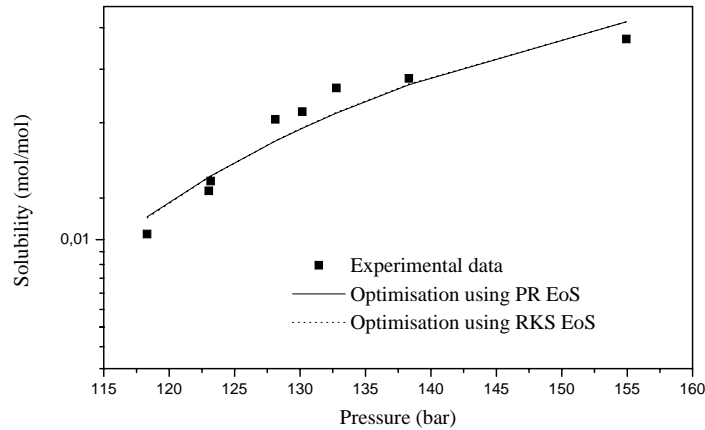


Figure 2: Solubility of naphthalene in supercritical CO₂: Comparison between calculated and experimental values at 308 K.

After calculating different data of k_{ij} and correlating them for several temperature ranges, this parameter is studied as a function of the variable x which reflects the size of the solute molecule (carbon number N_c) and its dipole moment μ . This parameter is expressed as: $x = \mu/N_c^3$.

To vary this variable we need to diversify the dipole moment and the carbon number that means to study phase equilibria of different solutes in the supercritical carbon dioxide.

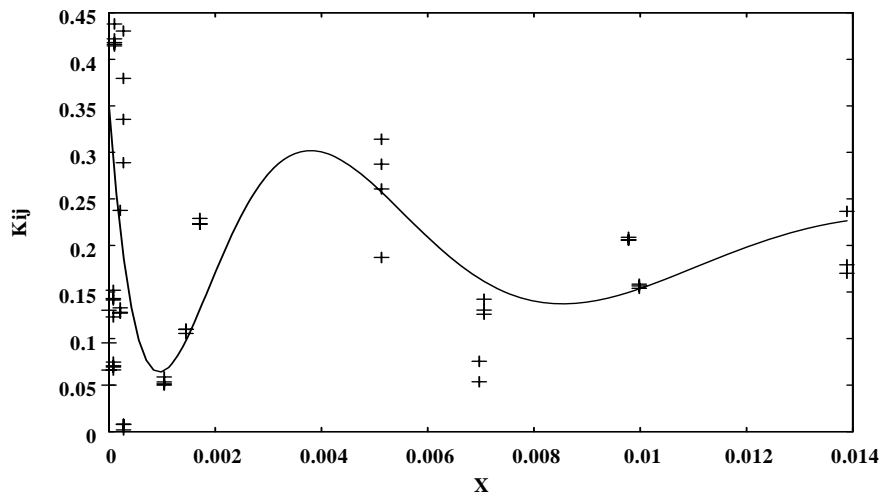


Figure 3: Variation of binary interaction coefficient as a function of x : (+ values of k_{ij} estimated from solubility experimental data, — correlation 15).

Solute	n_c	μ	T	k_{ij}
Naphthalene	10	0	300	$1.30410 \cdot 10^{-1}$
Acetone	10	2.29		$3.34000 \cdot 10^{-2}$
Vanillin	8	3.37		$7.36779 \cdot 10^{-2}$
phenanthrene	14	1.228		$0.74700 \cdot 10^{-1}$
Cholesterol	27	2.01		$4.38000 \cdot 10^{-1}$
Salicylic Acid	7	1.76		$2.14000 \cdot 10^{-1}$
β -naphthol	40	5.20		$1.51832 \cdot 10^{-1}$
Anthracene	14	0.573		$2.37729 \cdot 10^{-1}$
Aquilar	9	7.13		$1.00000 \cdot 10^{-1}$
Fluorene	13	0.6		$0.00000 \cdot 10^{-1}$
Limonene	10	0.27	313	$2.88774 \cdot 10^{-1}$
Tetraethylene glycol	6	2.01		$2.28640 \cdot 10^{-1}$
Cholesterol	27	2.01		$4.14300 \cdot 10^{-1}$
Salicylic Acid	7	1.76		$2.87200 \cdot 10^{-1}$
Anthracene	14	0.573		$1.26189 \cdot 10^{-1}$
DDT	8	0.74		$1.09700 \cdot 10^{-1}$
Nepesone	14	4.69		$2.23000 \cdot 10^{-1}$
Benzoic Acid	7	1.7	312	$1.30610 \cdot 10^{-1}$
Caffeine	8	3.11		$1.36340 \cdot 10^{-2}$
Naphthalene	10	0		$0.33400 \cdot 10^{-2}$
Limonene	10	0.27		$4.30435 \cdot 10^{-1}$
Aquilar	13	2.29		$0.48900 \cdot 10^{-1}$
Vanillin	8	3.37		$3.36146 \cdot 10^{-2}$
phenanthrene	14	1.228		$0.69300 \cdot 10^{-1}$
Cholesterol	27	2.01		$4.16100 \cdot 10^{-1}$
Salicylic Acid	7	1.76		$1.60737 \cdot 10^{-1}$
Anthracene	14	1.573		$1.27203 \cdot 10^{-1}$
Aquilar	9	7.13		$2.03600 \cdot 10^{-1}$
Naphthalene	10	0	323	$6.61626 \cdot 10^{-2}$
Limonene	10	0.27		$3.79439 \cdot 10^{-1}$
phenanthrene	14	1.228		$0.66200 \cdot 10^{-1}$
Tetraethylene glycol	6	2.01		$1.79198 \cdot 10^{-1}$
Cholesterol	27	2.01		$4.10000 \cdot 10^{-1}$
DDT	8	0.74		$1.10000 \cdot 10^{-1}$
Nepesone	14	4.69		$2.23000 \cdot 10^{-1}$
Benzoic Acid	7	1.7	320	$1.26104 \cdot 10^{-1}$
Caffeine	8	3.11		$1.33849 \cdot 10^{-1}$
Naphthalene	10	0		$4.99390 \cdot 10^{-2}$
Aquilar	13	2.29		$0.51400 \cdot 10^{-1}$
phenanthrene	14	1.228		$0.70700 \cdot 10^{-1}$
Salicylic Acid	7	1.76		$1.87047 \cdot 10^{-1}$
Limonene	10	0.27	333	$3.33310 \cdot 10^{-1}$
Tetraethylene glycol	6	2.01		$1.70091 \cdot 10^{-1}$
Cholesterol	27	2.01		$4.21900 \cdot 10^{-1}$
DDT	8	0.74		$1.05400 \cdot 10^{-1}$
Nepesone	14	4.69		$2.20000 \cdot 10^{-1}$
Benzoic Acid	7	1.7	343	$1.40388 \cdot 10^{-1}$
Aquilar	13	2.29		$0.38700 \cdot 10^{-1}$
β -naphthol	40	5.20		$1.23254 \cdot 10^{-1}$
Fluorene	13	0.6		$0.01900 \cdot 10^{-1}$

Table 1: Values of k_{ij} for different supercritical solutions

Several experimental works concerning usual solutes in carbon dioxide are implemented and satisfactory comparison between the calculated solubilities and the measured ones is obtained in each case. Therefore we list in table (1) the averaged values of k_{ij} determined for the formed solutions. This table can be represented by graph were the binary interaction factor is shown as a function of x . This correlation is written as follows:

$$K_{ij} = C_1 + C_2 \cdot \exp(-100x) \cos(100\sqrt{x}) \quad (16)$$

Where $C_1 = 0.25$ and $C_2 = 0.15$.

5. Conclusion

This study expresses numerically the effect of the molecular structure and the polarity of the solute dissolved in supercritical carbon dioxide by the means of an optimization of the binary interaction coefficient.

Half of the isotherms were judiciously selected to develop the correlation using several saturation pressure models. The rest of the isotherms were then used to validate the obtained results. Detailed error calculations were carried out for different thermodynamic models that included both Peng-Robinson and Redlich-Kwong-Soave equations of state and Van Der Waals mixing rules.

This work is a significant contribution in the field in two ways. First, it provides a specific correlation that gives excellent values of solubility. Second, it proposes a new formulation that can be extended to other mixing rules and may result in a fully predictive method.

6. References

- [1] Hannay, J. B., Hogarth, J., Proc. Roy. Soc. (London), 29, 1879, p 325.
- [2] Buchner, Z., J. Phys. Chem., 1906, p 56.
- [3] Chrastil, J., J. Phys. Chem. 86, 1982, p 3016
- [4] McHugh, M. A.; Krukonis, V. J., Supercritical Fluid Extraction: Principles and Practice, 1994, eds. Butterworths
- [5] Valderrama, J. O., Ind. Eng. Chem. Res. 42, 2003, p 1603.
- [6] Rogalski, M., Carrier, B., Solimando, R., Peneloux, A., Ind. Eng. Chem. Res., 29, 1990, p 65.
- [7] Schreiber, D. R. Pitzer, K. S., Fluid Phase Equilib. 41, 1995, p 1.
- [8] Ambrose, D. Walton. J., J. Pure & Appl. Chem. 61, 1989, p 1395.
- [9] Bartle, K.D. Clifford, A.A. , Shilstane, G.F., J. of supercritical fluids, 5, 1992, p 220.
- [10] Ksibi, H., Rev. Entropie, 222 1999, p 34.
- [11] Ksibi, H., Int. J. of Thermodynamics, 7, 3 2004, p 131.