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The Sanchez–Lacombe lattice fluid model for the modeling of solids in supercritical fluids

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The Sanchez–Lacombe equation of state is known to describe the thermodynamic properties of molecular fluids of arbitrary size, especially polymer–solvent phase behavior. However, it is rarely used for modeling solid–supercritical fluid equilibria. In this work, it is shown that a proper estimation of the EoS characteristic parameters together with a thermodynamically consistent expression of fugacity coefficients allows a satisfactory correlation of the solubility of solids in the supercritical phase. Binary mixtures containing carbon dioxide, ethane, ethylene and xenon were considered for this purpose. In a first step, the consistency of experimental data was checked using variance analysis. Then, different mixing rules were considered and results compared with those obtained with the Peng–Robinson equation. Finally, the lower and upper boundaries of the solid–liquid–vapor regions (LCEP and UCEP) were also determined and compared with experimental values.

Keywords: Model; Equation of state; Solid–fluid equilibria; Mixture

1. Introduction

Due to technical extractive supercritical fluid improvements, a good understanding of solid-supercritical fluid equilibrium is necessary for the development and design of separative processes [1]. The solubility of the solute in the supercritical solvent is one of the most important equilibrium properties, since it provides the extractability limit or solute concentration, which can be used as a basis for the design of the extractive process.

Taking into account the high range of pressures involved in these chemical processes, the estimation of the solubility of low volatile compounds in supercritical fluids (SFC) should be performed by means of an equation of state. Extensive studies were developed in literature for the modeling of the solubility of solids using cubic equations of state (EoS) since they offer the best compromise between accuracy, reliability,

simplicity and efficiency of computation. Two main topics were widely considered according to the nature of the solid compound involved in the process: for complex molecules, such as those of biological interest, the major problem discussed in literature is the estimation of the pure component properties, like sublimation pressures [2] or critical parameters [3,4]; in the case of simpler molecules for which thermodynamic properties can be easily measured, literature studies are mainly concerned with the choice of the best EoS [5–7] and corresponding mixing rules [8,9].

The form of mixing rules that extend the use of EoS developed for pure fluids to mixtures is, as reported by Anderko [6], more important than the particular relationship $P(T, v)$ characterizing each EoS. The most commonly used mixing rules are the conventional van der Waals rules, but they fail in describing highly non-ideal mixtures. Several attempts have been made in literature to overcome these limitations, by introducing composition dependence [10, 11] or density dependence [9] of the EoS parameters. In a previous work, Ashour et al. [8] have shown that incorporating additional parameters

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in the cubic EoS does not significantly improve the prediction of the solubility of the solid in the SCF. However, this study did not take into account the dependence of the interaction EoS parameters with respect to temperature.

The purpose of this work is to check the capability of the Sanchez–Lacombe equation of state [12] for modeling solid–supercritical fluid equilibrium. This equation derives from the “lattice fluid theory” and is known to describe thermodynamic properties of molecular fluids of arbitrary size, mainly polymer–solvent phase behavior. However, this equation is scarcely used for industrial purposes. For instance, concerning the modeling of solids in SCF, Mc Hugh et al. [13] provided a first attempt to correlate binary mixtures using a single mixing rule with temperature independent parameters; in that work, EoS parameters were fitted to the UCEP of the naphthalene–xenon system, so that a poor prediction of the solubility was observed.

The main problem encountered with the Sanchez–Lacombe EoS is the lack of characteristic parameter values available in literature, which constitutes a serious limitation for its technical use. To overcome this limitation, predictive methods [14–16] were developed for the EoS parameter estimation. In addition, it was shown [17] that chemical potentials for mixtures proposed in literature are not thermodynamically consistent; hence, expressions of fugacity coefficients were established for the Sanchez–Lacombe equation allowing a consistent calculation of phase equilibrium occurring in mixtures.

In this work, different mixing rules associated with the Sanchez–Lacombe EoS were considered and results compared with those obtained with the Peng–Robinson equation [18]. For this purpose, binary mixtures of solids with supercritical carbon dioxide, ethane, ethylene and xenon were investigated. In order to provide a reliable comparison of models, the consistency of experimental data was preliminary checked by means of variance analysis [19,20]. Isothermal data sets were first correlated separately, in view of comparing the various mixing rules independently on temperature. The influence of temperature was then investigated by

correlating solubility data by means of temperature dependent parameters. Finally, the lower and upper boundaries of the solid–liquid–vapor regions were also estimated and compared with experimental values.

2. Modeling by means of equations of state

The modeling of the solubility y_2 of a solid component (2) in a supercritical phase requires solving the following equilibrium condition:

$$y_2 = \frac{\varphi_2(T, P_2^{\text{sub}})P_2^{\text{sub}}(T)}{P\varphi_2(T, P, y_2)} \exp\left(\frac{v_2^s(P - P_2^{\text{sub}}(T))}{RT}\right) \quad (1)$$

where $P_2^{\text{sub}}(T)$ is the sublimation pressure of component (2) and v_2^s its molar volume at temperature T ; it is assumed that v_2^s is independent on pressure P . The fugacity coefficients $\varphi_2(T, P_2^{\text{sub}})$ and $\varphi_2(T, P, y_2)$ are respectively those of component (2) as a pure species at $P_2^{\text{sub}}(T)$ and in the supercritical mixture at pressure P ; they should be estimated thanks to an equation of state.

As shown in Fig. 1, which represents the phase equilibrium diagram for a solid-SCF binary mixture, Eq. (1) is valid in the whole range of molar fractions and pressures only for temperatures T_B between the lower and upper critical end points (LCEP and UCEP); at these temperatures, the P - x curves are still influenced by the vapor–liquid equilibria occurring at temperatures $T_A < T_{\text{LCEP}}$ or $T_C > T_{\text{UCEP}}$, which exhibit a critical point with a zero slope of the pressure. Efficient algorithms were proposed in literature [21,22] to determine the LCEP and UCEP temperatures characterized by the equality of the fugacities of all components in the solid (S), liquid (L) and gas (G) phases.

The Sanchez–Lacombe EoS [12] (SL), which derives from the lattice fluid theory, is written:

$$P = -RT \left(\frac{r-1}{v}\right) - RT \frac{1}{v^*} \ln\left(1 - \frac{rv^*}{v}\right) - \frac{\varepsilon^* v^* r^2}{v^2} \quad (2)$$

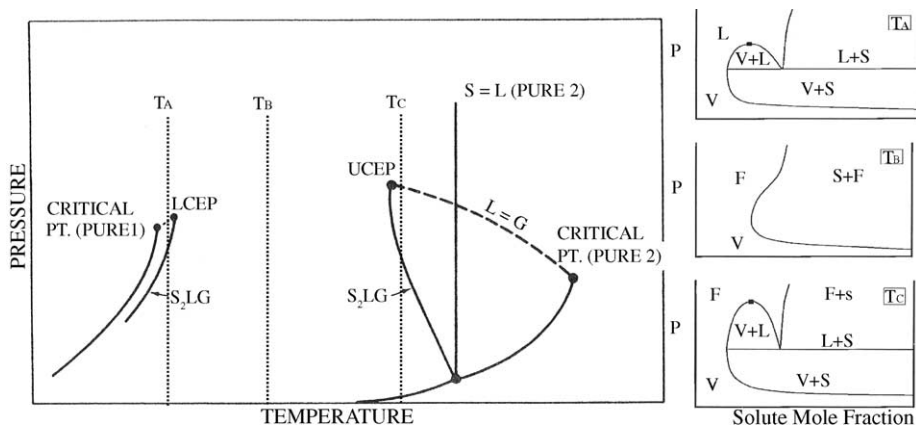


Fig. 1. Phase equilibrium diagram for a solid–SCF binary mixture (from Xu et al. [21]).

where r, v^*, ε^* are the characteristic EoS parameters, respectively, the component segment number, the segment volume and the mer–mer interaction energy.

The fugacity coefficient of a component i in the mixture is expressed by the relation proposed by Neau [17]:

$$\ln \varphi_i(T, v, x) = -\ln z + r_i \left[-2 \frac{\tilde{\rho}}{\tilde{T}} - \ln(1 - \tilde{\rho}) \right] + \left(\frac{z-1}{r} \right) \left[\frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j, T} \right] - \frac{\tilde{\rho}}{\tilde{T}} \left[\frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j, T} \right] \quad (3)$$

where the compressibility factor z is given by

$$z = \frac{Pv}{RT} = r \left[-\frac{1}{\tilde{\rho}} \ln(1 - \tilde{\rho}) - \left(1 - \frac{1}{r} \right) - \frac{\tilde{\rho}}{\tilde{T}} \right], \quad \tilde{\rho} = \frac{rv^*}{v}, \quad \tilde{T} = \frac{RT}{\varepsilon^*} \quad (4)$$

For mixtures, the molar segment number r is defined from the segment fractions ϕ_i as

$$r = \sum x_i r_i, \quad \phi_i = \frac{x_i r_i}{r} \quad (5)$$

The expressions of the partial derivatives in Eq. (3) are given in Table 1 for the different mixing rules considered in this work:

Table 1
Partial derivatives of mixture parameters for the Sanchez–Lacombe EoS

“ k_{ij} ” mixing rule (Sanchez and Panayiotou [23])

$$v^* = \sum_i \phi_i v_{ii}^*, \quad \frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j, T} = \frac{1}{v^*} [r_i (-v^* + v_{ii}^*)], \quad \varepsilon^* = \sum_i \sum_j \phi_i \phi_j \varepsilon_{ij}^*, \quad \frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j, T} = \frac{1}{\varepsilon^*} 2r_i \left(-\varepsilon^* + \sum_j \phi_j \varepsilon_{ij}^* \right), \quad \varepsilon_{ij}^* = \frac{\varepsilon_{ii}^* + \varepsilon_{jj}^*}{2} - \frac{RTk_{ij}}{2} \quad (6)$$

“ k_{ij}, l_{ij} ” mixing rule (Mc Hugh and Krukoni [1])

$$v^* = \sum_i \sum_j \phi_i \phi_j v_{ij}^*, \quad \frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j, T} = \frac{1}{v^*} \left[2r_i \left(-v^* + \sum_j \phi_j v_{ij}^* \right) \right], \quad v_{ij}^* = \frac{(v_{ii}^* + v_{jj}^*)(1 - l_{ij})}{2}, \quad \varepsilon^* v^* = \sum_i \sum_j \phi_i \phi_j \varepsilon_{ij}^* v_{ij}^*, \quad \frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j, T} = \frac{1}{\varepsilon^* v^*} \left[2r_i \left(-\varepsilon^* v^* + \sum_j \phi_j (\varepsilon v)_{ij}^* \right) \right] - \left[\frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j, T} \right], \quad \varepsilon_{ij}^* = (\varepsilon_{ii}^* \varepsilon_{jj}^*)^{1/2} (1 - k_{ij}) \quad (7)$$

“ $k_{ij}^{(0)}, k_{ij}^{(1)}$ ” mixing rule (Neau [24])

$$v^* = \sum_i \phi_i v_{ii}^*, \quad \left[\frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j, T} \right] \text{ (as for Eq. (6)), } \quad \varepsilon^* = \sum_i \sum_j \phi_i \phi_j \varepsilon_{ij}^*(x), \quad \varepsilon_{ij}^*(x) = (\varepsilon_{ii}^* \varepsilon_{jj}^*)^{1/2} (1 - k_{ij}(x)), \quad k_{ij}(x) = k_{ij}^{(0)} + (1 - \delta_{ij}) \sum_m \phi_m (k_{mi}^{(1)} + k_{mj}^{(1)}), \quad \frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j, T} = \frac{1}{\varepsilon^*} \left[2r_i \left(-\varepsilon^* + \sum_j \phi_j \varepsilon_{ij}^*(x) \right) \right] - \frac{1}{\varepsilon^*} \left[r_i \sum_j \sum_l \phi_j \phi_l \left\{ \delta_{jl} \left[(k_{ij}^{(1)} + k_{il}^{(1)}) - \sum_m \phi_m (k_{mj}^{(1)} + k_{ml}^{(1)}) \right] \right\} \right] \quad (8)$$

“ $k_{ij}^{(0)}, k_{ij}^{(1)}, l_{ij}$ ” mixing rule (Neau [24])

$$v^* = \sum_i \sum_j \phi_i \phi_j v_{ij}^*, \quad \left[\frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j, T} \right] \text{ (as for Eq. (7)), } \quad \varepsilon^* = \sum_i \sum_j \phi_i \phi_j \varepsilon_{ij}^*(x), \quad \left[\frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j, T} \right] \text{ (as for Eq. (8))} \quad (9)$$

• *Classical mixing rules.* Two kinds of mixing rules were considered:

- “ k_{ij} ” mixing rule, from Sanchez and Panayiotou [23], which assumes (Eq. (6)) a quadratic expression for the interaction parameter ε^* and a linear relation for the segment volume v^* with respect to the segment fractions ϕ_i .
- “ k_{ij}, l_{ij} ” mixing rule, from Mc Hugh and Krukoni [1], in which both parameters ε^* and v^* have a quadratic dependence with respect to the segment fractions (Eq. (7)).

• *Composition dependent mixing rules.* Recently, Neau [24] has suggested to correlate phase equilibria occurring in high dissymmetric systems by using mixing rules depending on binary interaction parameters $k_{ij}(x)$, similar to those used with cubic equations of state [10,11]. Among them, we have considered:

- “ $k_{ij}^{(0)}, k_{ij}^{(1)}$ ” mixing rule, in which ε^* is a quadratic function of the segment fractions, while the segment volume v^* is expressed by a linear relation (Eq. (8)).
- “ $k_{ij}^{(0)}, k_{ij}^{(1)}, l_{ij}$ ” mixing rule, especially suitable for mixtures containing components very different in size, where both ε^* and v^* are quadratic functions (Eq. (9)).

For the comparison with the Peng–Robinson equation [18] (PR), the temperature function proposed by Soave [25] for the interaction energy parameter a was considered. The following mixing rules were investigated:

• *Conventional van der Waals mixing rules*, corresponding to a quadratic expression of parameter a with respect to mole fractions x_i , and:

- a linear covolume b , for the “ k_{ij} ” mixing rule,
- a quadratic dependence of b for the “ k_{ij}, l_{ij} ” mixing rule.
- *Composition dependent mixing rules*, in which the k_{ij} binary interaction parameter of a is considered as a function $k_{ij}(x)$ of the molar fraction of the mixture. The method was originally proposed by Adachi and Sugie [10] and generalized by Hernández-Garduza et al. [11], in order to avoid the *invariance problem* pointed out by Michelsen and Kistenmacher [26]. For binary mixtures studied in this work, the generalized Adachi and Sugie mixing rule was considered:

$$k_{ij}(x) = k_{ij}^{(0)} + (1 - \delta_{ij}) \sum x_m (k_{mi}^{(1)} + k_{mj}^{(1)}),$$

$$k_{ji}^{(0)} = k_{ij}^{(0)}, \quad k_{ji}^{(1)} = -k_{ij}^{(1)} \quad (10)$$

where δ_{ij} is the Kronecker symbol. As for the Sanchez-Lacombe EoS, two versions were studied:

- “ $k_{ij}^{(0)}, k_{ij}^{(1)}$ ” mixing rule associated with a linear covolume b ,
- “ $k_{ij}^{(0)}, k_{ij}^{(1)}, l_{ij}$ ” mixing rule where b is a quadratic function of molar fractions.

It must be recalled that the binary parameters of all above mixing rules have no physical meaning, so that they must be tuned on experimental phase equilibrium data. In addition, these parameters show appreciable temperature dependence; as recommended in a previous work [11] for cubic equations, a satisfactory correlation of data in a wide range of temperatures can be achieved using for k_{ij} , as well as for $l_{ij}, k_{ij}^{(0)}$ and

$k_{ij}^{(1)}$ the following expressions:

$$k_{ij} = k'_{ij} + k''_{ij} \left(\frac{T_0}{T} - 1 \right) \quad (11)$$

where T_0 is a reference temperature, usually chosen in the range of experimental data.

3. Application to binary systems

The binary mixtures of solids with supercritical carbon dioxide, ethane, ethylene and xenon considered in this work are detailed in Table 2. As mentioned in Section 1, the consistency of experimental data was preliminary checked by means of variance analysis [19,20]; the general method is described in the following section. The last section is concerned with the pure component parameter estimation.

3.1. Consistency test of experimental data

The general method is illustrated in the case of carbon dioxide–naphthalene system at 308.15 K, for which numerous measurements were performed in literature (see Table 2). The consistency analysis is performed in two steps:

- *Analysis of each data set measured by one author at a given temperature.* In this first step, experimental errors are estimated and, if necessary, doubtful measurements are eliminated. The method recalled in Appendix A, consists in correlating experimental solubility data y_2^{exp} (Eq. (1)) with

Table 2
Data base for the correlation of solubility data in SCF

| Binary system | Temperature range (K) | N | | | | Reference |
|--|-----------------------|--------|-------|-------|-------|---------------|
| | | Global | 308 K | 318 K | 343 K | |
| CO ₂ –biphenyl | 308–330 | 31 | 15 | 8 | | [31,32] |
| CO ₂ –naphthalene | 308–328 | 175 | 70 | 33 | | [31–42] |
| CO ₂ –2,3- <i>m</i> -naphthalene | 308–328 | 20 | 10 | 5 | | [43–44] |
| CO ₂ –2,6- <i>m</i> -naphthalene | 308–328 | 23 | 9 | 5 | | [43,45] |
| CO ₂ –fluorene | 308–343 | 23 | 6 | | 8 | [46] |
| CO ₂ –phenanthrene | 303–343 | 129 | 7 | 5 | 7 | [34,43,46,47] |
| CO ₂ –anthracene | 308–343 | 118 | 5 | 6 | 9 | [46–48] |
| CO ₂ –pyrene | 308–343 | 119 | 6 | | 8 | [46–47] |
| CO ₂ – <i>n</i> -octacosane | 308–325 | 45 | 10 | 8 | | [49] |
| CO ₂ –benzoic acid | 308–328 | 43 | 9 | 12 | | [43,50] |
| C ₂ H ₆ –biphenyl | 308–318 | 10 | 5 | 5 | | [50] |
| C ₂ H ₆ –naphthalene | 318–328 | 53 | | 20 | | [46,50] |
| C ₂ H ₆ –anthracene | 308–343 | 14 | 4 | | 7 | [46] |
| C ₂ H ₆ – <i>n</i> -octacosane | 308 | 6 | 6 | | | [44] |
| C ₂ H ₆ –benzoic acid | 318–338 | 15 | | 5 | | [43] |
| C ₂ H ₄ –fluorene | 298–343 | 24 | | | | [46] |
| C ₂ H ₄ –phenanthrene | 298–343 | 6 | | 2 | | [46] |
| C ₂ H ₄ –pyrene | 318–343 | 15 | | 8 | | [46] |
| C ₂ H ₄ –benzoic acid | 318–338 | 15 | | 5 | | [43] |
| Xe–naphthalene | 308–318 | 21 | 1 | 17 | | [13] |
| | | 905 | 164 | 144 | 39 | |

N is the number of experimental data respectively, for the global range of temperatures and at 308.15, 318.15 and 343.15 K.

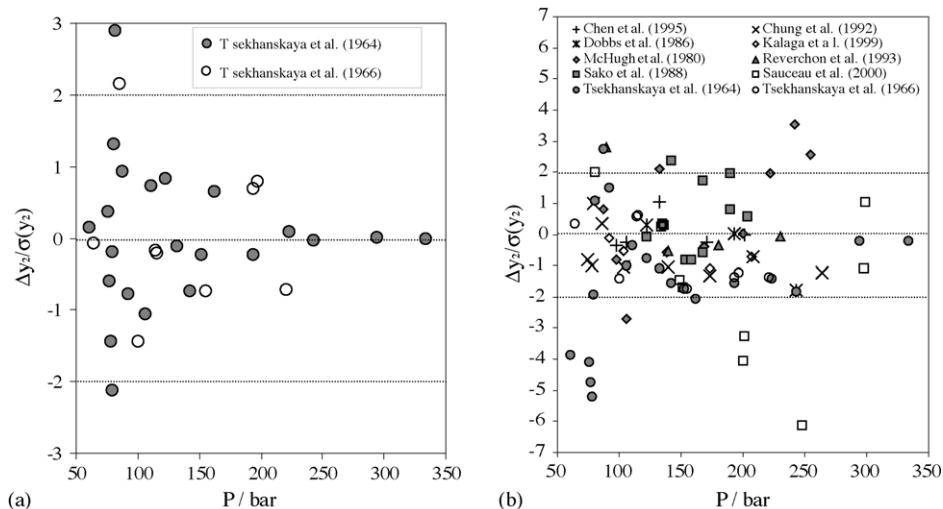


Fig. 2. Carbon dioxide–naphthalene system: deviations $\Delta y_{2i}/\sigma(y_{2i})$ between experimental and estimated values of solubility (Eq. (A.1)). (a) Correlation of single data sets at 308.15 K in step (1). (b) Correlation of the whole data set at 308.15 K in step (2).

respect to pressure P using a polynomial form (Eq. (A.1)), the degree of which, not fixed in advance, should be high enough in order to avoid systematic errors. For each experimental point i , the deviation Δy_{2i} between the measured value y_{2i}^{exp} and the calculated one y_{2i}^{cal} should be of the same magnitude as the resulting error $\sigma(y_{2i})$ (Eq. (A.3)). A value of the ratio $|\Delta y_{2i}/\sigma(y_{2i})|$ greater than 2.0 gives evidence of a systematic error, and this measure should be eliminated. The principle of the method is illustrated in Fig. 2a for the data of Tsekhanskaya et al. [39,40], for which three wrong determinations were detected in this step.

- *Check of the consistency of the whole data set.* In a second step, all data measured by different authors are correlated using a single polynomial form (Eq. (A.1)). In the case of perfectly consistent data, relative deviations $|\Delta y_{2i}/\sigma(y_{2i})|$ should also be smaller than 2.0. This procedure is illustrated in Fig. 2b, where inconsistent data were evidenced and eliminated for the further correlation of this system at this temperature.

3.2. Pure component parameters

The properties of the pure solids considered in this work are described in Table 3. Both the solid volumes v_2^s and sublimation pressures $P_2^{\text{sub}}(T)$ were taken from literature. However, it is worth recalling that these pressures become rapidly unknown for heavy compounds, like biological ones; in that case, $P_2^{\text{sub}}(T)$ can be estimated from the predictive method proposed by Neau et al. [2]; with this method, the sublimation pressure is calculated by means of the Clapeyron equation, in which the characteristic parameters are obtained from the fusion properties and the vaporization curve derived from the equation of state.

The Sanchez–Lacombe EoS parameters used for the correlation of solubility data are also reported in Table 3. They were estimated using the methods proposed by Neau et al. [27] for the light components (supercritical fluids) and by Rigal et al. [15,28] for the heaviest ones (solid components). Other sets of parameters could have been considered: literature values

Table 3
Sanchez–Lacombe EoS parameters and referenced pure solid properties

| Component | ε^* (J/mol) | v^* (cm ³ /mol) | r | v^s (cm ³ /mol) | A^{suba} | B^{suba} |
|------------------------------|-------------------------|------------------------------|--------|------------------------------|-------------------|-------------------|
| Carbon dioxide | 2276.66 | 3.638 | 8.564 | | | |
| Ethane | 2444.62 | 7.865 | 6.653 | | | |
| Ethylene | 2273.34 | 7.238 | 6.518 | | | |
| Xenon | 2943.30 | 11.854 | 3.644 | | | |
| Biphenyl [51] | 5280.12 | 14.985 | 11.708 | 131.0 | 9.4068 | 4262.0 |
| Naphthalene [50] | 5509.75 | 12.407 | 9.600 | 110.0 | 8.5830 | 3733.9 |
| 2,3-Dimethylnaphthalene [51] | 5604.69 | 13.069 | 11.245 | 154.7 | 9.0646 | 4302.5 |
| 2,6-Dimethylnaphthalene [51] | 5540.04 | 13.069 | 11.244 | 139.2 | 9.4286 | 4419.5 |
| Fluorene [51] | 5866.55 | 10.676 | 11.821 | 139.3 | 9.2046 | 4561.8 |
| Phenanthrene [51] | 6354.58 | 13.804 | 11.378 | 151.0 | 9.6310 | 4873.4 |
| Anthracene [51] | 6372.58 | 13.804 | 11.378 | 142.6 | 7.1464 | 4397.6 |
| Pyrene [51] | 6732.91 | 14.733 | 11.980 | 158.5 | 8.3946 | 4904.0 |
| <i>n</i> -Octacosane [44] | 5295.78 | 17.360 | 22.989 | 489.4 | 29.4613 | 12834.4 |
| Benzoic Acid [52] | 4920.81 | 6.196 | 15.431 | 96.5 | 9.4080 | 4618.1 |

^a $\log(P^{\text{sub}})$ (bar) = $A^{\text{sub}} - B^{\text{sub}}/T$.

Table 4

Deviations on saturation pressures ΔP^{sat} (%) and liquid saturated volumes Δv^{sat} (%) using different estimation methods for the Sanchez–Lacombe EoS parameters

| Methods | ΔP^{sat} (%) | | Δv^{sat} (%) | |
|------------------|------------------------------|----------------------------|------------------------------|--------------------------|
| | CO ₂ ^a | Naphthalene ^{b,c} | CO ₂ ^a | Naphthalene ^d |
| This work | 0.90 | 3.85 | 11.46 | 0.92 |
| Gauter–Heidemann | 1.08 | 3.01 | 23.34 | 13.04 |
| Literature | 24.97 | – | 5.04 | – |

^a Angus et al. [53].

^b Fowler et al. [54].

^c Camin and Rossini [55].

^d API [56].

[23], available for a restricted number of components, or estimations derived from the method proposed by Gauter and Heidemann [16]. The EoS parameters were selected taking into account the quality of the saturation properties predicted with the different procedures. As an example, results obtained for carbon dioxide and naphthalene are reported in Table 4. It clearly appears that literature values should be avoided and that the two other methods provide equivalent satisfactory correlations of vapor pressures, so that they will lead to similar solubility estimations. However, it must be noted, even if it has no influence on the present modeling, that the main advantage of the methods considered in this work is the improved representation of saturated liquid volumes.

For the Peng–Robinson equation, the values of T_c , P_c and ω were mainly taken from literature [29]; when no data were available, as it was the case for polycondensed aromatics, EoS parameters were predicted by means of the group contribution method of Avaullée et al. [30] especially efficient for hydrocarbons.

4. Results and discussion

Binary interaction parameters were obtained by minimizing the objective function:

$$F^{\text{obj}} = \sum_{i=1}^N \left[\frac{\Delta y_{2i}}{y_{2i}^{\text{exp}}} \right]^2, \quad \Delta y_{2i} = y_{2i}^{\text{exp}} - y_{2i}^{\text{cal}} \quad (12)$$

where y_{2i}^{exp} and y_{2i}^{cal} are respectively the experimental solubilities of the solids in SCF and those estimated by means of Eq. (1).

Table 5

Global relative deviations Δy_2 (%) obtained at 308.15, 318.15 and 343.15 K with the Sanchez–Lacombe (SL) and the Peng–Robinson (PR) EoS using temperature independent parameters

| Mixing rules | Data at 308.15 K | | Data at 318.15 K | | Data at 343.15 K | |
|--|------------------|-------|------------------|-------|------------------|-------|
| | SL | PR | SL | PR | SL | PR |
| “ k_{ij} ” | 27.79 | 17.86 | 35.68 | 23.83 | 34.29 | 32.22 |
| “ k_{ij}, l_{ij} ” | 10.94 | 8.56 | 10.69 | 8.66 | 19.18 | 19.32 |
| “ $k_{ij}^{(0)}, k_{ij}^{(1)}$ ” | 8.09 | 10.68 | 9.63 | 11.17 | 17.84 | 23.85 |
| “ $k_{ij}^{(0)}, k_{ij}^{(1)}, l_{ij}$ ” | 6.91 | 7.06 | 8.85 | 8.44 | 14.38 | 11.93 |

4.1. Correlation of isothermal data

The comparison of the correlation of isothermal data, respectively at 308.15, 318.15 and 343.15 K, using temperature independent parameters are reported in Table 5 for the Sanchez–Lacombe and Peng–Robinson equations. The interest of this preliminary study is twice. First of all, the deviations given in this table can be considered as the reference level which can be expected, at these temperatures, when correlating in the next section the global data sets with respect to temperature. Second, even if the order of magnitude of the deviations depends on the temperature considered, their evolution gives evidence of the same trend with respect to the different modelings.

The Sanchez–Lacombe EoS fails in correlating solubility data using a single binary interaction parameter “ k_{ij} ”; the same behavior is also observed with the Peng–Robinson EoS, as it was already mentioned by Ashour et al. [8]. For this reason, this simple mixing rule will not be considered for further calculations with respect to temperature.

Both equations, SL and PR, require taking into account, at least two binary interaction parameters. However, the global behavior of the two EoS with respect to the “ k_{ij}, l_{ij} ” or “ $k_{ij}^{(0)}, k_{ij}^{(1)}$ ” mixing rules is somewhat different:

- In the case of the cubic equation and dissymmetric systems, the consideration of a quadratic mixing rule for representing the covolume b is more important than the choice of a complex mixing rule for the interaction parameter a . This remark is illustrated in Table 5, where the “ k_{ij}, l_{ij} ” mixing rule provides better global results.
- On the contrary, the Sanchez–Lacombe equation appears to be more influenced by the choice of a more complex mixing rule for the energy parameter ε^* rather than for the segment volume v^* ; indeed, as shown in Table 5, the “ $k_{ij}^{(0)}, k_{ij}^{(1)}$ ” mixing rule usually leads to a better correlation of solubility data. This behavior is significant of the superiority of this equation in representing liquid volumes, even for dissymmetric systems.

Finally, similar improved results can be obtained with both SL and PR equations using a three binary interaction parameter mixing rule of the type “ $k_{ij}^{(0)}, k_{ij}^{(1)}, l_{ij}$ ”. In many cases, the use of this composition dependent mixing

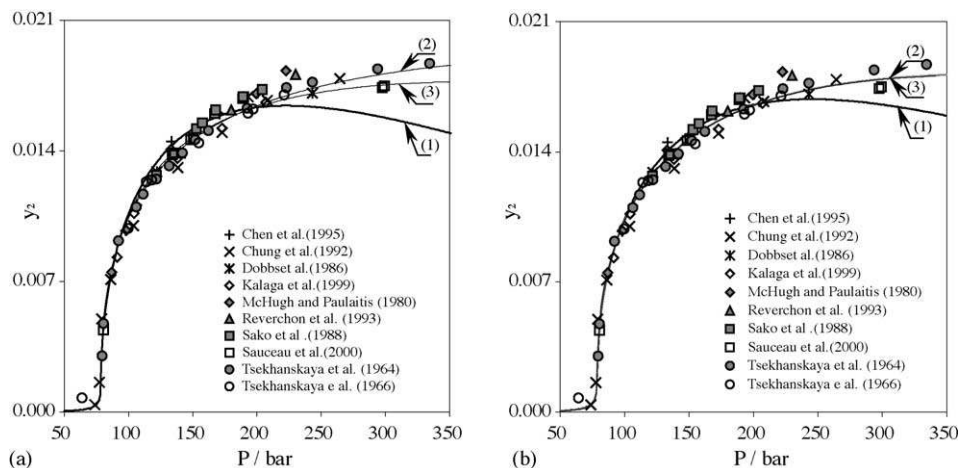


Fig. 3. (a) Carbon dioxide–naphthalene system: correlation of solubility data at 308.15 K. (a) Sanchez–Lacombe EoS and the following parameters: (1) $k_{12} = 0.2120$, $l_{12} = -0.2455$, (2) $k_{12}^{(0)} = 2.1248$, $k_{12}^{(1)} = 2.2787$ and (3) $k_{12}^{(0)} = 1.4979$, $k_{12}^{(1)} = 1.6129$, $l_{12} = -0.0886$. (b) Peng–Robinson EoS and the following parameters: (1) $k_{12} = 0.0396$, $l_{12} = -0.1135$, (2) $k_{12}^{(0)} = 0.4975$, $k_{12}^{(1)} = 0.4270$ and (3) $k_{12}^{(0)} = 0.4850$, $k_{12}^{(1)} = 0.4152$, $l_{12} = -0.0030$.

rule allows to obtain more reliable results by means of the Sanchez–Lacombe equation.

Even if composition dependent mixing rules appear to be globally the best solution for the correlation of solubility data of solids in SCF, especially in the case of the Sanchez–Lacombe equation, their practical use should be restricted to specific cases. Indeed, composition dependent mixing rules are well adapted to the correlation or prediction of data covering a large domain of molar fractions, as is shown in Fig. 3 for the system carbon dioxide–naphthalene. However, in many cases, the range of molar fractions is so narrow, that it is quite illusory to correlate solubility data by means of a complex model; doing that will only lead to unmeaningful $k_{ij}^{(0)}$ and $k_{ij}^{(1)}$ parameters, as is shown in Fig. 4.

As a consequence, in the next section, the comparison of EoS for the correlation of global data sets will be restricted to the “ k_{ij}, l_{ij} ” mixing rule.

4.2. Correlation of global data sets

Results obtained by correlating the global data sets presented in Table 2 are described in Table 6 and in Figs. 5 and 6. For the selected “ k_{ij}, l_{ij} ” mixing rule the correlation of experimental data was performed assuming: first, independent binary interaction parameters, as is usually done in literature, then temperature dependent functions. In this work, different “ $k_{ij}(T), l_{ij}$ ”, “ $k_{ij}, l_{ij}(T)$ ” and “ $k_{ij}(T), l_{ij}(T)$ ” mixing rules were considered. The reference temperature T_0 in Eq. (11) was 318.15 K, it means the middle temperature range for most systems (Table 2). In order to check the influence of the parameter temperature dependence, results obtained for the prediction of data sets at the extreme temperatures, 308.15 and 343.15 K selected in Table 5, are also recalled in Table 6.

Whatever the EoS considered, reliable correlations of solubility data at different temperatures cannot be obtained

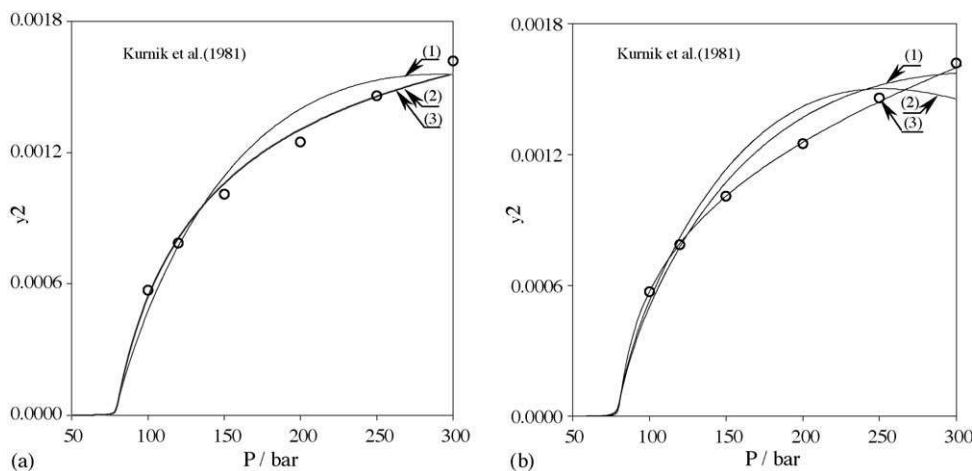


Fig. 4. (a) Carbon dioxide–phenanthrene system: correlation of solubility data at 308.15 K. (a) Sanchez–Lacombe EoS and the following parameters: (1) $k_{12} = 0.2542$, $l_{12} = -0.2671$, (2) $k_{12}^{(0)} = 25.1721$, $k_{12}^{(1)} = 25.3514$ and (3) $k_{12}^{(0)} = 26.5314$, $k_{12}^{(1)} = 26.7182$, $l_{12} = 0.0156$. (b) Peng–Robinson EoS and the following parameters: (1) $k_{12} = 0.1697$, $l_{12} = -0.0701$, (2) $k_{12}^{(0)} = -1.4596$, $k_{12}^{(1)} = -1.6048$ and (3) $k_{12}^{(0)} = 47.2160$, $k_{12}^{(1)} = 46.6878$, $l_{12} = 1.3422$.

Table 6

Correlation of global data sets using different mixing rules with the Sanchez–Lacombe (SL) and the Peng–Robinson (PR) EoS: relative deviations Δy_2 (%) obtained for the correlation of the global data sets and the prediction of data at 308.15 and 343.15 K

| Mixing rules | N | Global data sets | | Prediction at 308.15 K | | Prediction at 343.15 K | |
|---|-----|------------------|-------|------------------------|-------|------------------------|-------|
| | | SL | PR | SL | PR | SL | PR |
| Temperature independent “ k_{ij}, l_{ij} ” | 2 | 22.09 | 15.34 | 19.77 | 14.79 | 44.92 | 35.30 |
| Temperature dependent “ $k_{ij}(T), l_{ij}$ ” | 3 | 11.92 | 11.31 | 11.04 | 9.28 | 22.13 | 21.55 |
| “ $k_{ij}, l_{ij}(T)$ ” | 3 | 12.36 | 11.47 | 11.97 | 9.14 | 22.94 | 22.89 |
| “ $k_{ij}(T), l_{ij}(T)$ ” | 4 | 12.39 | 11.00 | 11.10 | 8.97 | 22.19 | 21.68 |
| Reference deviations obtained by correlating isothermal data (Table 5) | | | | 10.94 | 8.56 | 19.18 | 19.32 |

N is the number of parameters.

considering temperature independent binary parameters. This conclusion is in agreement with the results obtained by Ashour et al. [8] who observed mean deviations merely around 20% for different mixing rules associated with cubic EoS. From this point of view, the Sanchez–Lacombe EoS appears to be more sensible to the influence of temperature; indeed, the prediction of data at 308.15 and 343.15 K obtained with these independent parameters is considerably deteriorated: respectively, 19.77% and 44.92%, instead of 10.94% and 19.18% obtained by correlating isothermal data.

Thanks to the temperature dependence considered in Eq. (11) for interaction parameters, the correlation of global solubility data is highly improved; which allows predicting at 308.15 and 343.15 K solubilities quite similar to those obtained by the isothermal correlation. Results given in Table 6 show that the use of three parameters with the “ $k_{ij}(T), l_{ij}$ ” or “ $k_{ij}, l_{ij}(T)$ ” mixing rules is sufficient for providing a satisfac-

tory correlation and prediction of solubility data in a wide range of temperatures. The consideration of four parameters with the “ $k_{ij}(T), l_{ij}(T)$ ” mixing rule does not improve significantly the results.

In Table 7, the deviations on solubility data obtained with the Sanchez–Lacombe EoS using the “ $k_{ij}(T), l_{ij}$ ” mixing rule are reported for all systems considered. The values of the corresponding binary interaction parameters are also given.

4.3. Prediction of LCEP and UCEP temperatures

Binary interaction parameters determined previously using the “ $k_{ij}(T), l_{ij}$ ” mixing rule (Table 7) were considered for the prediction of the LCEP and UCEP of naphthalene in carbon dioxide, ethane and xenon. Results obtained with

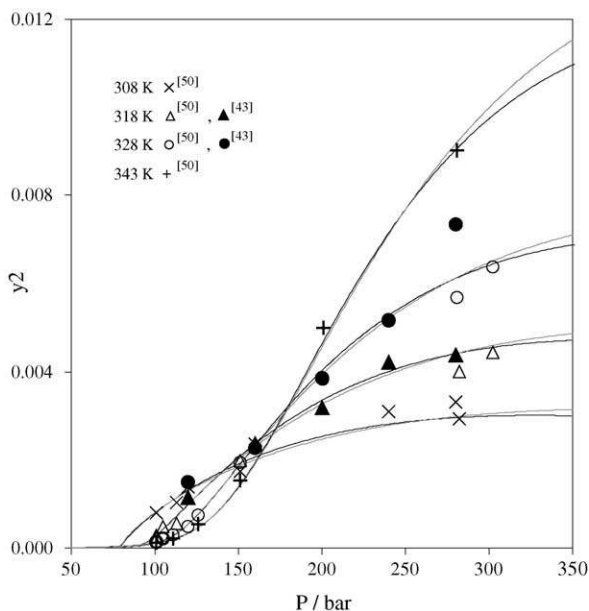


Fig. 5. Solubility of benzoic acid(2) in carbon dioxide. Correlation using “ $k_{ij}(T), l_{ij}$ ” mixing rule with: – Sanchez–Lacombe EoS (Table 7), ... Peng–Robinson EoS ($k_{12}' = -0.0722$, $k_{12}'' = 0.3570$, $l_{12} = -0.2096$).

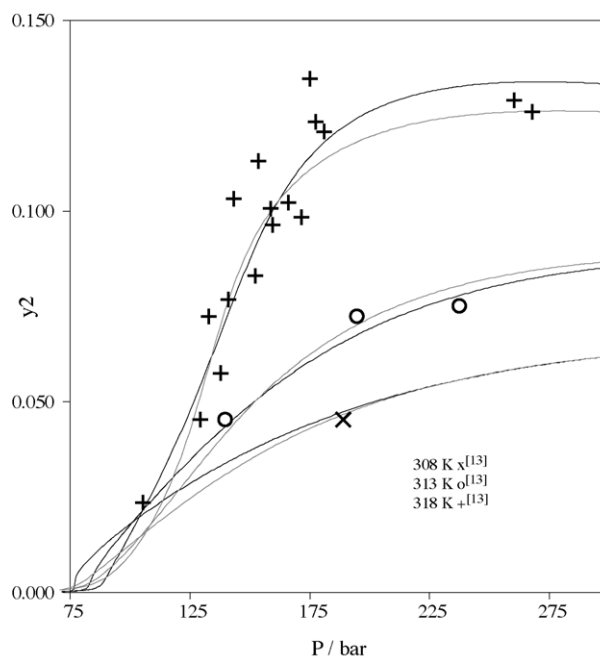


Fig. 6. Solubility of naphthalene(2) in xenon. Correlation using “ $k_{ij}(T), l_{ij}$ ” mixing rule with: – Sanchez–Lacombe EoS (Table 7), ... Peng–Robinson EoS ($k_{12}' = 0.0087$, $k_{12}'' = 0.1192$, $l_{12} = -0.0292$).

Table 7

Relative deviations Δy_2 (%) obtained with the Sanchez–Lacombe EoS and the “ $k_{ij}(T), l_{ij}$ ” mixing rule, together with the binary interaction parameters

| Binary system | N | Δy_2 (%) | k'_{12} | k''_{12} | l_{12} |
|--|-----|------------------|-----------|------------|----------|
| CO ₂ –biphenyl | 31 | 10.51 | 0.1840 | 0.1580 | 0.0067 |
| CO ₂ –naphthalene | 175 | 9.43 | 0.1985 | 0.2509 | −0.2162 |
| CO ₂ –2,3- <i>m</i> -naphthalene | 20 | 10.88 | 0.2259 | 0.0907 | −0.2729 |
| CO ₂ –2,6- <i>m</i> -naphthalene | 23 | 27.47 | 0.2285 | 0.1858 | −0.3110 |
| CO ₂ –fluorene | 23 | 12.63 | 0.2279 | 0.1722 | −0.4510 |
| CO ₂ –phenanthrene | 129 | 11.50 | 0.2434 | 0.0959 | −0.2301 |
| CO ₂ –anthracene | 118 | 11.39 | 0.2471 | 0.2755 | −0.1589 |
| CO ₂ –pyrene | 119 | 10.43 | 0.2615 | 0.1518 | −0.2040 |
| CO ₂ – <i>n</i> -octacosane | 45 | 10.05 | 0.2711 | 0.0465 | −0.3562 |
| CO ₂ –benzoic acid | 43 | 8.65 | 0.1191 | 0.2753 | −0.4264 |
| C ₂ H ₆ –biphenyl | 10 | 14.26 | 0.0740 | 0.1496 | −0.1069 |
| C ₂ H ₆ –naphthalene | 53 | 19.30 | 0.0678 | 0.2893 | −0.2188 |
| C ₂ H ₆ –anthracene | 14 | 10.69 | 0.1197 | 0.2430 | −0.1998 |
| C ₂ H ₆ – <i>n</i> -octacosane | 6 | 32.36 | 0.1249 | 0.0101 | −0.4677 |
| C ₂ H ₆ –benzoic acid | 15 | 13.32 | −0.1455 | 0.1563 | 0.1817 |
| C ₂ H ₄ –fluorene | 24 | 24.66 | 0.0759 | 0.1801 | −0.3545 |
| C ₂ H ₄ –phenanthrene | 6 | 1.96 | 0.2020 | −0.1635 | −0.0330 |
| C ₂ H ₄ –pyrene | 15 | 14.21 | 0.1457 | 0.1632 | −0.3614 |
| C ₂ H ₄ –benzoic acid | 15 | 3.83 | 0.0340 | 0.2542 | −0.4361 |
| Xe–naphthalene | 21 | 9.36 | 0.0283 | −0.0214 | −0.0372 |

 N is the number of experimental data for each binary system.

the Sanchez–Lacombe and the Peng–Robinson EoS are compared with literature values in Table 8.

Both equations provide quite similar results for the temperatures and pressures of both LCEP and UCEP. Concerning the agreement with experimental values:

The prediction of critical temperatures is rather satisfactory, with a general tendency of predicting slightly lower T_{LCEP} and higher T_{UCEP} . For a practical point of view, both equations extend the domain of temperatures where the two solid and SCF phases are in equilibrium in the whole range of molar fractions and pressures.

For critical pressures, the prediction of P_{LCEP} seems to be consistent, which is not the case of the P_{UCEP} which is greatly underestimated.

The case of the system xenon–naphthalene is especially interesting, since the UCEP was previously correlated by Mc

Hugh et al. [13] with the Sanchez–Lacombe equation. In that work, temperature independent interaction parameters k_{ij} and l_{ij} were tuned on the UCEP of this system, so that a poor prediction of the solubility was observed. Indeed, as was discussed in the previous section and is shown in Table 6, temperature independent parameters cannot provide a good prediction of solubility data over a wide range of temperatures. On the contrary, results presented in Table 8 show that a satisfactory prediction of both UCEP and solubility data can be achieved with the same SL equation, but using temperature dependent parameters determined from solubility data.

5. Conclusion

The purpose of this work was to check the Sanchez–Lacombe equation for the correlation of the solubility of solids in supercritical fluids, using a proper estimation of EoS parameters and a consistent expression of fugacity coefficients [17]. The Peng–Robinson equation was considered as a reference equation for this study.

Several mixing rules were considered, among which classical “ k_{ij}, l_{ij} ” and composition dependent “ $k_{ij}^{(0)}, k_{ij}^{(1)}, l_{ij}$ ” ones. It was shown that, in many cases, the range of solubility data is too narrow to allow estimating meaningful $k_{ij}^{(0)}$ and $k_{ij}^{(1)}$ values. The correlation of data in a large range of temperatures by means of classical mixing rules requires taking into account a temperature dependence of binary interaction parameters. It was observed that, with the proposed temperature function, only three parameters associated with the “ $k_{ij}(T), l_{ij}$ ” or “ $k_{ij}, l_{ij}(T)$ ” mixing rules allow to predict solubility data with an accuracy comparable to that of isothermal correlation. Results obtained in the same conditions with the Peng–Robinson EoS

Table 8

Comparison between experimental and calculated LCEP and UCEP by means of the Sanchez–Lacombe (SL) and the Peng–Robinson (PR) EoS

| Systems | Experimental | SL | PR |
|--|--------------|--------|-------|
| CO ₂ –naphthalene | | | |
| T_{LCEP} (K) | 307.65 [57] | 304.20 | 306.0 |
| P_{LCEP} (bar) | – | 72.0 | 76.0 |
| T_{UCEP} (K) | 333.25 [1] | 347.0 | 341.0 |
| P_{UCEP} (bar) | 256.0 [1] | 52.0 | 51.0 |
| C ₂ H ₆ –naphthalene | | | |
| T_{LCEP} (K) | 309.95 [49] | 305.0 | 305.0 |
| P_{LCEP} (bar) | 52.2 [49] | 49.0 | 49.0 |
| T_{UCEP} (K) | 329.65 [49] | 338.0 | 327.0 |
| P_{UCEP} (bar) | 124.1 [49] | 83.0 | 87.0 |
| Xe–naphthalene | | | |
| T_{UCEP} (K) | 319.50 [13] | 320.0 | 321.0 |
| P_{UCEP} (bar) | 136.8 [13] | 128.0 | 120.0 |

are of the same accuracy, under the condition that a temperature dependence of EoS parameters should be considered.

The lower and upper boundaries of the solid–liquid–vapor regions (LCEP and UCEP) were also calculated, using the temperature dependent EoS parameters preliminary determined from the correlation of solubility data. Both the Sanchez–Lacombe and the Peng–Robinson EoS provide the order of magnitude of these temperatures.

List of symbols

| | |
|------------------|--|
| a | attractive parameter in cubic equation of state |
| b | covolume |
| F^{obj} | objective function |
| k_{ij} | binary interaction parameter for the parameters a or ε^* |
| l_{ij} | binary interaction parameter for the covolume b or characteristic volume v^* |
| P | pressure |
| r | segment number in Sanchez–Lacombe equation of state |
| R | ideal gas constant |
| T | temperature |
| T_0 | reference temperature |
| v | molar volume |
| v^* | segment volume in Sanchez–Lacombe equation of state |
| y_2 | solubility of the solid component in the supercritical phase |
| z | compressibility factor |

Greek letters

| | |
|-----------------|---|
| ε^* | interaction energy in Sanchez–Lacombe equation of state |
| φ | fugacity coefficient |
| ϕ | segment fraction |
| ρ | density |
| σ | resulting error |
| σ_e | experimental error |

Subscript

| | |
|-----|-------------------|
| W | weighted function |
|-----|-------------------|

Superscript

| | |
|-----|--------------|
| cal | calculated |
| exp | experimental |
| s | solid state |
| sat | saturation |
| sub | sublimation |

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Appendix A

Solubility data y_2 were correlated with respect to pressure P , using the polynomial form especially adapted to the variance analysis [19,20]:

$$y_2 = \sum_{j=1}^m A_j Y_j, \quad (A.1)$$

$$Y_j = 2XY_{j-1} - \frac{4(j-2)^2}{4(j-2)^2 - 1} Y_{j-2} \quad (j > 2)$$

where Y_j is a function of the reduced centered variable X defined between the minimum and maximum pressure values P_{\min} and P_{\max} :

$$X = \frac{2P - (P_{\max} + P_{\min})}{P_{\max} - P_{\min}}, \quad Y_1 = \frac{1}{2}, \quad Y_2 = X \quad (A.2)$$

For a given value of the polynomial degree m (Eq. (A.1)), the resulting error $\sigma(y_{2i})$ on each experimental solubility data y_{2i}^{exp} is expressed by the error propagation law of Gauss:

$$\sigma^2(y_{2i}) = \sigma_e^2(y_{2i}) + \left(\frac{\partial y_2}{\partial P} \right)_i^2 \sigma_e^2(P_i) \quad (A.3)$$

where $\sigma_e(y_{2i})$ and $\sigma_e(P_i)$ are respectively the experimental errors on the measured solubility and pressure. According to Eq. (A.1), the partial derivative is

$$\frac{\partial y_2}{\partial P} = \sum_{j=1}^m A_j \left\{ 2 \left[X \left(\frac{\partial Y_{j-1}}{\partial P} \right) + Y_{j-1} \left(\frac{\partial X}{\partial P} \right) \right] - \frac{4(j-2)^2}{4(j-2)^2 - 1} \left(\frac{\partial Y_{j-2}}{\partial P} \right) \right\} \quad (A.4)$$

with

$$\left(\frac{\partial X}{\partial P} \right) = \frac{2}{P_{\max} - P_{\min}}, \quad \frac{\partial Y_1}{\partial P} = 0, \quad \frac{\partial Y_2}{\partial P} = \frac{\partial X}{\partial P} \quad (A.5)$$

For a satisfactory estimation of the absolute or relative experimental errors on solubility and pressure, the weighted objective function F_W^{obj} calculated from N experimental data:

$$F_W^{\text{obj}} = \sum_{i=1}^N \left[\frac{\Delta y_{2i}}{\sigma(y_{2i})} \right]^2, \quad \Delta y_{2i} = y_{2i}^{\text{exp}} - y_{2i}^{\text{cal}} \quad (A.6)$$

should be around $N-m$, according to the properties of the Chi-square distribution. Starting from estimations given by the authors, a corrective factor can be introduced in order to fulfill this condition.

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