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## **Diffusion coefficients of solids in supercritical carbon dioxide: Modelling of near critical behaviour**

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### **Abstract**

Most of the models proposed in literature for binary diffusion coefficients of solids in supercritical fluids are restricted to infinite dilution; this can be explained by the fact that most of experimental data are performed in the dilute range. However some industrial processes, such as supercritical fluid separation, operate at finite concentration for complex mixtures. In this case, the concentration dependence of diffusion coefficients must be considered, especially near the upper critical endpoint (UCEP) where a strong decrease of diffusion coefficients was experimentally observed. In order to represent this slowing down, a modified version of the Darken equation was proposed in literature for naphthalene in supercritical carbon dioxide. In this paper, the conditions of application of such a modelling are investigated. In particular, we focus on the order of magnitude of the solubility of the solid and on the vicinity of the critical endpoint. Various equations proposed in literature for the modelling of the infinite dilution diffusion coefficients of the solutes are also compared. Ten binary mixtures of solids with supercritical carbon dioxide were considered for this purpose.

Keywords: diffusion coefficient, model, infinite dilution, Darken equation, critical behaviour

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### **1. Introduction**

The use of supercritical fluids in extraction or separation processes was widely developed during the last twenty years. For this purpose, accurate information about the transport properties of the solutes at finite concentration is required; indeed, mass transfer coefficients, such as diffusion coefficients, allow determining the time required for processing and therefore govern the equipment design. Numerous experimental data were reported in literature for the diffusion coefficients of liquids and solids in supercritical solvents [1]-[3]; however, in most cases, especially for solid solutes, the experimental set ups only allow measurements at infinite dilution [1]. As a consequence, most of the correlations proposed in literature are limited to this range of concentration; it is also the reason why they fail in representing experimental data near the upper critical endpoint (UCEP). Figure 1 recalls the phase diagram pressure - temperature, as proposed by Scott and van Konynenburg [4] for a solid (2) in a supercritical fluid (1); the diagrams pressure

- mole fraction and mole fraction - pressure are those obtained at the UCEP temperature. In this range of temperature and pressure, a strong decrease of diffusion coefficients was observed experimentally [5]-[9]. Taking into account the dependence of diffusion coefficients with respect to the concentration becomes necessary to ensure more accurate calculations in this region. For this purpose, as suggested by Higashi et al. [7] for solid naphthalene in supercritical carbon dioxide, a modified version of the Darken equation [10] involving a thermodynamic factor can be used.

The aim of this work is to study the applicability of this modified Darken equation. For this purpose, ten binary mixtures of solids in supercritical carbon dioxide covering a large range of concentration were considered. The Sanchez-Lacombe equation [11] which derives from the lattice fluid theory was considered for the modelling of the thermodynamic factor. The EoS parameters were determined from the correlation of solubility data as was suggested in a previous work [12].

For each mixture, various models proposed in literature for the calculation of infinite dilution diffusion coefficients of solid solutes were compared. The influence of the concentration and the vicinity of the critical point on the thermodynamic factor and its capability of representing the slowing down in the critical range were carefully checked.

## 2. Critical behaviour of binary diffusion coefficients in supercritical fluids

As many other transport properties, the diffusion coefficient  $D_{21}$  exhibits a singular behaviour at a mixture critical point. More precisely, it decreases to zero, leading to the so-called “critical slowing down” of diffusion properties. Its behaviour is related to that of the Onsager kinetic coefficient  $\alpha$  by the formula:

$$D_{21} = \frac{\alpha}{\rho} \left( \frac{\partial y_2}{\partial \mu} \right)_{P,T}^{-1} \quad \text{with} \quad \mu = \mu_2 - \mu_1 \quad (1)$$

where  $\rho$  is the density of the mixture,  $\mu_1$  and  $\mu_2$  are respectively the chemical potentials of the solvent and the solute and  $y_2$  is the mole fraction of the solute. The derivative  $(\partial y_2 / \partial \mu)_{P,T}$  is the osmotic susceptibility which diverges at a mixture critical point. At this point [13], the Onsager coefficient satisfies the following equation:

$$\alpha = \alpha_c + \alpha_b \quad \text{with} \quad \alpha_c = \frac{kT\rho\omega_\alpha}{6\pi\eta\xi} \left( \frac{\partial y_2}{\partial \mu} \right)_{P,T} \quad (2)$$

where  $\alpha_c$  refers to the asymptotic critical behaviour and  $\alpha_b$  is the background, or regular, contribution;  $\omega_\alpha$  is the crossover function;  $\eta$  and  $\xi$  are respectively the dynamic viscosity and the correlation length. The crossover function  $\omega_\alpha$  is equal to 1 near a critical point and approaches zero far away; it allows a smooth transition between the asymptotic critical behaviour and the regular one.

It follows from Eqs. (1) and (2) that the diffusion coefficient  $D_{21}$  can also be written as:

$$D_{21} = D_{21c} + D_{21b} \quad \text{with} \quad D_{21c} = \frac{kT\omega_\alpha}{6\pi\eta\xi} \quad \text{and} \quad D_{21b} = \frac{\alpha_b}{\rho} \left( \frac{\partial y_2}{\partial \mu} \right)_{P,T}^{-1} \quad (3)$$

Asymptotically near a mixture critical point, the correlation length  $\xi$  diverges as  $\Delta T^{-0.67}$ , where  $\Delta T = (T - T_{cm})/T_{cm}$  is the dimensionless distance to the critical point  $T_{cm}$ . As a

consequence, the diffusion coefficient  $D_{21c}$  vanishes as  $\Delta T^{0.67}$ . However, as was observed experimentally [5]-[9], the behaviour of diffusion coefficients in supercritical fluids is still influenced by this critical decrease in a region much larger than the asymptotic critical region. As stated by Levelt Sengers et al. [14], the extent of this crossover region depends in particular on the concentration of the solute: it is all the smaller as the concentration is low. Indeed, it is related to the asymptotic behaviour of the osmotic susceptibility  $(\partial y_2 / \partial \mu)_{P,T}$  which depends on the mole fraction  $y_2$  of the solute [15]. The more dilute the mixture is the most sudden is the increase of the osmotic susceptibility near the mixture critical point. Therefore, the osmotic susceptibility is the key parameter for the observation of the characteristic decrease of diffusion coefficients in the critical range.

Previous studies reported in literature have shown that models proposed for diffusion coefficients at infinite dilution fail in representing this anomalous decrease near the critical point. They have thus enlightened the need of models taking into account the concentration dependence of the diffusion coefficient. For this purpose, Higashi et al. [7] proposed to model the diffusion coefficient of naphthalene in supercritical carbon dioxide near the upper critical endpoint by using a modified version of the Darken equation [10]:

$$D_{21} = [y_2 D_{11} + (1 - y_2) D_{21}^0] \delta \quad (4)$$

$D_{11}$  and  $D_{21}^0$  are respectively the self diffusion coefficient of the solvent and the infinite dilution diffusion coefficient of the solute;  $\delta$  is the thermodynamic factor:

$$\delta = \left( \frac{\partial \ln f_2}{\partial \ln y_2} \right)_{P,T} = 1 + \left( \frac{\partial \ln \varphi_2}{\partial \ln y_2} \right)_{P,T} \quad (5)$$

where  $f_2$  and  $\varphi_2$  are respectively the fugacity and fugacity coefficient of the solute in the supercritical phase. The mole fraction  $y_2$  of the solid solute is at most equal to the solubility  $y_2^{sat}$  in the supercritical phase; it means that it corresponds to very dilute mixtures for which  $(\partial \ln f_2 / \partial y_2)_{P,T} \approx (\partial \mu / \partial y_2)_{P,T} / RT$ , so that:

$$\delta = \frac{y_2}{RT} \left( \frac{\partial y_2}{\partial \mu} \right)_{P,T}^{-1} \quad (6)$$

Hence, thanks to the thermodynamic factor  $\delta$  (Eq. (6)), diffusion coefficients  $D_{21}$  expressed either from Eq. (4) or Eq. (1) have exactly the same dependence with respect to the osmotic susceptibility  $(\partial y_2 / \partial \mu)_{P,T}$ . The use of the thermodynamic factor in Eq. (4) should therefore allow representing the anomalous decrease of diffusion coefficients in the critical range; this parameter must be calculated by using an equation of state.

### 3. Experimental data of diffusion coefficients in supercritical fluids

Very few experimental data on diffusion coefficients of solids in supercritical fluids are available in literature. Most of them are obtained using the *chromatographic technique*, it means at infinite dilution. In this case, measurements are usually performed at pressures beyond the critical pressure; indeed, as is shown in Table 1 for supercritical carbon dioxide,  $P_{UCEP}$  lies between 74 bars and 77 bars and experimental data are available at higher pressures corresponding to the range of maximum solubility (see Fig. 1). The second source of literature data is provided by the pseudo steady-state *solid dissolution* method which allows investigating the concentration dependence of diffusion coefficients; measurements are usually performed for a solute mole fraction equal to half

of the solubility  $y_2^{sat}$  [7]. It can also be noticed that it is only for naphthalene that measurements were performed at low pressures including the critical pressure range (table 1).

In order to estimate the influence of the concentration dependence of diffusion coefficients in the vicinity of the mixture critical point, the coordinates of the UCEP reported in Table 1 were calculated thanks to the Sanchez-Lacombe equation.

#### 4. Modelling

Different approaches proposed in literature for estimating the parameters of the modified Darken equation are considered in this section. The first part is concerned with the infinite dilution diffusion coefficient of the solid  $D_{21}^0$  and the self-diffusion coefficient of the solvent  $D_{11}$ ; the second one is related to the estimation of the thermodynamic factor  $\delta$  (Eq. (5)).

##### 4.1 Diffusion coefficients $D_{21}^0$ and $D_{11}$

Various equations were proposed in literature for the modelling of the diffusion coefficients  $D_{11}$  and  $D_{21}^0$ . They can be classified in two families: *Homogeneous method* (Schmidt Number Method for  $D_{11}$  and  $D_{21}^0$ ) and *Combined method* (Lee and Thodos model for  $D_{11}$  and Stokes-Einstein type equations for  $D_{21}^0$ ).

- *Homogeneous method*

Funazukuri and Wakao [16] proposed the Schmidt number correlation based on the rough hard sphere theory for predicting diffusion coefficients  $D$ :

$$Sc = \eta / \rho D \quad (7)$$

where  $\eta$  and  $\rho$  are respectively the mixture viscosity and density. For the dilute mixtures of solids in supercritical fluids,  $\eta$  is approximated to the pure carbon dioxide viscosity  $\eta_1$ , according to the correlation of Olchoway and Sengers [17]; the density is obtained from the molar volume  $v$  of the mixture estimated by means of the equation of state. The Schmidt number at high pressure,  $Sc$ , is expressed as follows:

$$\frac{Sc}{Sc^*} = 1 + \exp\left(\sum_{i=0}^5 a_i \left(\frac{v_0}{v}\right)^i\right) \quad (8)$$

$Sc^*$  is the Schmidt number at atmospheric pressure defined by:

$$Sc^* = \frac{5}{6} \left[ \frac{\sigma_1 + \sigma_2}{2\sigma_1} \right]^2 \left[ \frac{2M_2}{M_1 + M_2} \right] \quad (9)$$

$v_0$  is the hard-sphere closest-packed volume for the solvent molecules, obtained for carbon dioxide from the polynomial function of temperature proposed by Funazukuri et al. [18];  $\sigma_i$  and  $M_i$  are respectively the hard-sphere diameters and molar weight of the molecules. The ratio of the effective hard-sphere diameters  $\sigma_2/\sigma_1$  is calculated from the van der Waals diameters  $\sigma_{vw,i}$  estimated using the method of Bondi [19]:

$$\frac{\sigma_2}{\sigma_1} = \frac{\sigma_{vw,2}}{\sigma_{vw,1}} \quad (10)$$

The values of  $\sigma_{vw,i}$  for carbon dioxide and the studied solutes are given in Table 2.

- *Combined method*

The self-diffusion coefficient  $D_{11}$  is expressed from Lee and Thodos method [20]:

$$D_{11} = \frac{D_c T_r (\rho_r^{1/3} - 0.4358 \rho_r)}{0.5642 \rho_r} \quad \text{with} \quad T_r = \frac{T}{T_c}, \quad \rho_r = \frac{\rho}{\rho_c} \quad (11)$$

$D_c$  is the value of  $D_{11}$  at the critical point ( $D_c = 4.937 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$  for  $\text{CO}_2$ ).

For the infinite dilution diffusion coefficient  $D_{21}^0$  ( $\text{m}^2 \cdot \text{s}^{-1}$ ) different Stokes-Einstein type equations proposed in literature were considered. All of them assume that the diffusion coefficient depends on the viscosity  $\eta_1$  of the pure solvent and on the molar liquid volumes  $v_{b,i}$  of the solvent and solute at their normal boiling point:

- Wilke and Chang [21]:

$$D_{21}^0 = 7.4 \times 10^{-15} \frac{T M_1^{1/2}}{\eta_1 (v_{b,2})^{0.6}} \quad (12)$$

- Scheibel [22]:

$$D_{21}^0 = 8.2 \times 10^{-15} \frac{T}{\eta_1 v_{b,2}} \left[ 1 + \left( 3 \frac{v_{b,1}}{v_{b,2}} \right)^{2/3} \right] \quad (13)$$

- Hayduk and Minhas [23]:

$$D_{21}^0 = 13.3 \times 10^{-8} \frac{T^{1.47} (10^{-3} \eta_1)^\varepsilon}{(v_{b,2})^{0.71}} \quad \text{with} \quad \varepsilon = 10.2/v_{b,2} - 0.791 \quad (14)$$

In Eqs (12)-(14),  $T$  is the temperature (K) and  $M_1$  is the molar weight ( $\text{g} \cdot \text{mol}^{-1}$ ) of the solvent; the solvent viscosity  $\eta_1$  is expressed in (Pa.s) and the molar volumes  $v_{b,i}$  are given in ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ).

The molar volumes  $v_{b,i}$  of the solutes at the normal boiling point are estimated directly with the group contributions proposed by Le Bas [24]. Other literature methods, such as those of Spencer and Danner [25] or Tyn and Calus [26], turned out to be less precise for these components; indeed, they depend on the critical parameters, usually unknown for complex solute molecules, and therefore estimated thanks to other group contribution methods. On the other hand, for carbon dioxide, the method of Tyn and Calus was considered. Corresponding values are reported in Table 2.

#### 4.2 Calculation of the thermodynamic factor $\delta$

The equation of state considered for the estimation of the thermodynamic factor  $\delta$  (Eq. (5)) is the lattice fluid equation of Sanchez and Lacombe [11]:

$$P = -RT \left( \frac{r-1}{v} \right) - RT \frac{1}{v^*} \ln \left( 1 - \frac{rv^*}{v} \right) - \frac{\varepsilon^* v^* r^2}{v^2} \quad (15)$$

$r$ ,  $v^*$  and  $\varepsilon^*$  are the characteristic EoS parameters: respectively, the component segment number, the segment volume and the mer-mer interaction energy. Their values for the pure components considered in this work are given in Table 2.

The fugacity coefficient  $\varphi_2$  is expressed according to the relation proposed by Neau [27] for mixtures:

$$\ln \varphi_2 = -\ln z + r_2 \left[ -2 \frac{\tilde{\rho}}{\tilde{T}} - \ln(1 - \tilde{\rho}) \right] + \left( \frac{z-1}{r} \right) \left[ \frac{nr}{v^*} \left( \frac{\partial v^*}{\partial n_2} \right)_{n_1, T} \right] - \frac{\tilde{\rho}}{\tilde{T}} \left[ \frac{nr}{\varepsilon^*} \left( \frac{\partial \varepsilon^*}{\partial n_2} \right)_{n_1, T} \right] \quad (16)$$

with:

$$z = \frac{Pv}{RT}, \quad \tilde{\rho} = \frac{rv^*}{v}, \quad \tilde{T} = \frac{RT}{\varepsilon^*} \quad \text{and} \quad r = \sum x_i r_i \quad (17)$$

The segment volume  $v^*$  and the mer-mer interaction energy  $\varepsilon^*$  of mixtures are estimated from the “ $k_{ij}$ ,  $l_{ij}$ ” mixing rules proposed by Mc Hugh and Krukoniš [28]; in this approach, both  $v^*$  and  $\varepsilon^*$  have a quadratic dependence with respect to the mixture composition. Related expressions of partial derivatives in Eq. (16) are given in the original paper [12]. As was suggested in that work, the following dependence of  $k_{ij}$  with respect to temperature should be considered:

$$k_{ij} = k'_{ij} + k''_{ij} (T_0 / T - 1) \quad (18)$$

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

In the present study, parameters  $k'_{ij}$ ,  $k''_{ij}$ ,  $l_{ij}$  were determined by correlating only the solubility data of solids in supercritical carbon dioxide. Values of the fitted parameters are given in Table 2, assuming that  $T_0 = 308.15$  K, it means the lowest experimental temperature close to the UCEP temperature of most studied mixtures.

## 5. Results and discussion

The two first parts of this section are devoted to the evaluation of the methods previously considered for the representation of diffusion coefficients  $D_{11}$  and  $D_{21}^0$ , and the calculation of the thermodynamic factor  $\delta$ . The last one concerns the prediction of the concentration dependence of diffusion coefficients  $D_{21}$  of solid solutes in supercritical carbon dioxide.

### 5.1. Evaluation of models for $D_{21}^0$

Deviations between experimental values of  $D_{21}^0$  measured by the chromatographic technique (Table 1) and those calculated by using Eq. (7) and Eqs. (12)-(14) are reported in Table 3. It can be observed that the Schmidt number method and the Hayduk-Minhas equation give similar mean deviations; but detailed results reveal that, except for pyrene and  $\beta$ -carotene, the Schmidt number method provides a better agreement.

In addition Fig. 2 shows for naphthalene and  $\beta$ -carotene that the behaviour of the two models diverges at low pressures. The lack of experimental values of  $D_{21}^0$  in this pressure range did not allow discriminating between the two methods. Nevertheless, we have considered that the measured values of  $D_{21}$  for naphthalene using the solid technique (Table 1) were representative of  $D_{21}^0$ : indeed, in this pressure range (below 75 bars), the solubility  $y_2^{sat}$  is very low (about  $2.10^{-4}$ ) so that the term in brackets in Eq. (4) tends to  $D_{21}^0$  and, as will be shown in Fig. 4a, the thermodynamic factor  $\delta$  is close to one. Values plotted in Fig. 2 show that the Schmidt number method is the most reliable. Thus, further calculations were performed using the homogeneous method based on the Schmidt number correlation for both  $D_{11}$  and  $D_{21}^0$ .

### 5.2 .Influence of the thermodynamic factor $\delta$

Equation (6) shows that the behaviour of the thermodynamic factor  $\delta$  is directly linked to that of the inverse of the osmotic susceptibility  $(\partial y_2 / \partial \mu)_{P,T}$ . As was shown by Levelt Sengers [15] the behaviour of the osmotic susceptibility in the crossover region depends on the level of the solute concentration and, therefore, on the level of the solubility in the case of solid solutes. In order to check the capability of the Sanchez-Lacombe EoS to represent this effect, the thermodynamic factor obtained for three solutes in carbon dioxide, namely naphthalene, benzoic acid and  $\beta$ -carotene, were considered as representative of different solubility levels (see Table 1). Results presented in Figs. 3 and 4 were obtained by estimating  $\delta$  according to Eq. (5) and using for  $y_2$  the maximum value equal to the solubility  $y_2^{sat}$  predicted from this EoS.

Figures 3 illustrate the effect of temperature at a given pressure ( $P=79$  bars for naphthalene and  $P=75.4$  bars for benzoic acid and  $\beta$ -carotene) close to the UCEP of the mixtures. For all solutes, the thermodynamic factor exhibits a sudden variation near the mixture critical point, exactly like the osmotic susceptibility as described by Levelt Sengers [15]. The more dilute the mixture is, the most sudden is the variation of the thermodynamic factor and the smallest is the extent of this phenomenon.

Figures 4 show, for the same three solutes, the variations of  $(\partial \ln \phi_2 / \partial \ln y_2)_{P,T}$ , it means  $\delta-1$  (Eq. (5)), with respect to pressure at two temperatures; the lowest one, close to the UCEP temperature, belongs to the crossover region ( $T=308.15$  K for naphthalene and  $T=305.15$  K for benzoic acid and  $\beta$ -carotene). Whatever the solubility range,  $\delta-1$  exhibits a strong decrease at the UCEP pressure for the first isotherm. However, the magnitude of this decrease is highly dependent on the level of solubility: it is equal to 0.6 for naphthalene, 0.14 for benzoic acid and only  $10^{-6}$  for  $\beta$ -carotene. As a consequence, for  $\beta$ -carotene, this fall down is totally negligible with respect to 1 in the calculation of the thermodynamic factor  $\delta$ ; this is not the case for other solutes like benzoic acid and naphthalene.

Figures 4 clearly show that the sudden fall of  $\delta-1$  disappears when temperature is increasing. It can also be noticed that, whatever the temperature, the value of  $(\partial \ln \phi_2 / \partial \ln y_2)_{P,T}$  is close to zero at the lowest pressures; it means that the thermodynamic factor is close to one. However, Fig. 4a also shows, for naphthalene which corresponds to the maximum solubility, that  $(\partial \ln \phi_2 / \partial \ln y_2)_{P,T}$  has still an influence at higher pressures.



### 5.3. Modelling of the concentration dependence of diffusion coefficients $D_{21}$

Diffusion coefficients  $D_{21}$  of naphthalene calculated with the modified Darken equation are presented in Figs. 5; experimental data were obtained with the “solid technique” (see Table 1) for the mole fraction  $y_2 = y_2^{sat}/2$ . Curves obtained without taking into account the thermodynamic factor are also plotted in the same figures; two temperatures were considered, the lowest one (Fig. 5a) being very close to the UCEP temperature. It can be seen, that the use of the thermodynamic factor in Eq. (4) really influences the calculated diffusion coefficients: at the lowest temperature, it allows predicting correctly the observed decrease of  $D_{21}$  at the UCEP pressure (Fig. 5a) and at the highest temperature (Fig. 5b), it makes possible representing accurately the diffusion coefficient, especially in the high pressure range. It should be mentioned that such results are obtained thanks to the proper estimation of  $y_2^{sat}$  from the Sanchez-Lacombe EoS.

In the same way, deviations between experimental diffusion coefficients  $D_{21}$  measured with the “solid technique” (see Table 1) and those predicted from the Darken equation (Eq. (4)) are presented in Table 4; the range of experimental solubilities is also given. Results obtained taking into account the thermodynamic factor  $\delta$  estimated from the Sanchez-Lacombe EoS or neglecting it ( $\delta = 1$ ) are compared in this table. It can be noticed that for all these systems the solubility  $y_2^{sat}$  is greater than  $10^{-4}$  and the use of the thermodynamic factor improves the prediction of diffusion coefficients. Obviously the maximum effect is observed for naphthalene due to the presence of experimental data in the crossover region.

The present study leads us to propose the following scheme for predicting diffusion coefficients of solids in supercritical fluids from solubility data:

- Estimation of the UCEP temperature in order to define the domain where experimental processes will involve only biphasic equilibria ( $T > T_{UCEP}$ ). For this purpose, we recommend:
  - First, to correlate experimental solubility data of solids in the supercritical fluid by means of an equation of state, such as the Sanchez-Lacombe EoS, associated with classical “ $k_{ij}$ ,  $l_{ij}$ ” mixing rules. As shown in a previous work [12], the choice of the temperature dependence of  $k_{ij}$  given by Eq. (18) ensures a more satisfactory prediction of solubilities over a wide range of temperatures involving the UCEP.
  - Second, to estimate the UCEP coordinates. The location of  $T_{UCEP}$  can be evaluated by following, for various temperatures, the evolution of the curves  $y_2^{sat}$  with respect to pressure; starting from high temperatures (namely 310 K in the case of solids in supercritical carbon dioxide) the proximity of the UCEP temperature is characterized, at the UCEP pressure by an inflexion point with an infinite slope tangent.
- According to the order of magnitude of the maximum solubility  $y_2^{sat}$  in the domain of experimental processes the calculation of diffusion coefficients  $D_{21}$  should be performed as follows:
  - In the case where the maximum solubility is less than  $10^{-5}$  (as for  $\beta$ -carotene), diffusion coefficients  $D_{21}$  are equivalent to infinite dilution diffusion coefficients  $D_{21}^0$  and their calculation does not require taking into account an equation of state.
  - In the other cases, the modelling must be performed with the modified Darken equation (Eq. (4)).

## 6. Conclusion

The prediction of diffusion coefficients of solids in supercritical carbon dioxide by means of the modified Darken equation proposed by Higashi et al. [7] was studied in this work. For this purpose, ten solid solutes representative of a large range of solubility were considered. As illustrated by Eq. (4) this equation allows representing the dependence of diffusion coefficients with respect to the concentration of the solute in the supercritical fluid; it depends on both infinite dilution diffusion coefficient of the solute and self-diffusion coefficient of the solvent and on the thermodynamic factor. In a first step, we have evaluated the accuracy of four models available in literature for the calculation of infinite dilution diffusion coefficients  $D_{21}^0$ ; the Schmidt number correlation appeared to provide more reliable results, especially in the low pressure range. In the second step, we have checked the capability of the modified Darken equation, associated with the Schmidt number method, for representing the variation of the diffusion coefficient  $D_{21}$  with respect to the solubility of the solute in the supercritical phase. The thermodynamic factor was calculated using the Sanchez–Lacombe EoS which parameters were obtained from the correlation of solubility data. It was observed that, whatever the solubility range, the thermodynamic factor exhibits a sudden variation near the mixture critical point, exactly like the osmotic susceptibility as described by Levelt Sengers [15]. The more dilute the mixture is, the most sudden is the variation of the thermodynamic factor and the smallest is the extent of this phenomenon. We have also shown that, when the solubility is very low, such as for  $\beta$ -carotene, this thermodynamic factor remains equal to one in all the pressure and temperature range, so that diffusion coefficients can correctly be estimated from infinite dilution diffusion coefficient models. On the other hand, when the solubility is not too low, the thermodynamic factor becomes necessary for an accurate representation of experimental data, not only in the vicinity of the critical region, but also in a wide range of pressures and temperatures. Finally, we have proposed a scheme for predicting diffusion coefficients of solids in supercritical fluids according to the magnitude of the solute solubility.

### List of symbols

$D_{11}$	self-diffusion coefficient of the solvent
$D_{21}$	diffusion coefficient of the solid in the supercritical fluid
$D_{21}^0$	diffusion coefficient of the solid in the supercritical fluid at infinite dilution
$f$	fugacity
$k$	Boltzmann constant
$k_{ij}, l_{ij}$	binary EoS parameters
$M$	molar weight
$P$	pressure
$r$	segment number
$T$	absolute temperature
$v$	molar volume
$v^*$	segment volume
$v_o$	hard-sphere closest-packed volume
$y_2$	mole fraction of the solute

### Greek letters

$\alpha$	Onsager kinetic coefficient
$\delta$	thermodynamic factor
$\varepsilon^*$	interaction energy
$\eta$	dynamic viscosity
$\mu$	chemical potential
$\rho$	density
$\xi$	correlation length
$\sigma_{vw}$	van der Waals diameter
$\varphi$	fugacity coefficient
$\omega_\alpha$	crossover function

### Subscript

$b$	background
$c$	critical
$i$	component i
$m$	mixture
$r$	reduced property

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## FIGURE CAPTIONS

Fig. 1. Phase diagram of a solid (2) in a supercritical fluid (1) according to Scott and van Konynenburg.

Fig. 2. Correlation of infinite dilution diffusion coefficients  $D_{21}^0$  at 308.15K using the Schmidt number method (naphthalene: —,  $\beta$ -carotene: ---) and the Hayduk–Minhas method (naphthalene: - - - -,  $\beta$ -carotene: - - - -) and experimental data reported in literature [6, 7, 44].

Fig. 3. Variations of  $\log(\delta)$  with respect to temperature at pressures close to the  $P_{UCEP}$ : (a) naphthalene  $P=79$  bars, (b) benzoic acid,  $P=75.4$  bars and (c)  $\beta$ -carotene,  $P=75.4$  bars.

Fig. 4: Isothermal variations of  $(\partial \ln \phi_2 / \partial \ln y_2)_{P,T} = \delta - 1$  with respect to pressure in the crossover region (—) and at  $T = 318.15$  K (- - - -) for: (a) naphthalene, (b) benzoic acid and (c)  $\beta$ -carotene.

Fig. 5. Correlation of diffusion coefficients  $D_{12}$  of naphthalene using the modified Darken equation with the thermodynamic factor  $\delta$  (————) and without  $\delta$  (- - - -) at: (a)  $T = 308.15$  K and (b)  $T = 318.15$  K with experimental data reported in literature [6, 7, 30].

Table 1. Data base for diffusion coefficients together with estimated UCEP coordinates.

<i>Solute</i>	<i>Chromatographic technique</i>			<i>Solid technique</i>			<i>UCEP</i>		
	<i>T(K)</i>	<i>P (bar)</i>	<i>Ref.</i>	<i>T(K)</i>	<i>P(bar)</i>	<i>Ref.</i>	<i>T(K)</i>	<i>P(bar)</i>	$y_2^{sat}$
Biphenyl	308 - 323	80 – 200	[29]	-	-	-	305.7	75.7	$7.1 \cdot 10^{-4}$
Naphthalene	308 - 328	100 - 1000	[31,34,36]	308 - 328	70 - 300	[6,7,30]	306.6	76.4	$2.0 \cdot 10^{-3}$
2,3-dimethyl Naphthalene	-	-		308	100 - 200	[7]	304.9	74.7	$2.5 \cdot 10^{-4}$
2,6-dimethyl Naphthalene	-	-		308	90 - 200	[6,7]	304.8	74.5	$2.7 \cdot 10^{-4}$
2,7-dimethyl Naphthalene	-	-		308	100 - 200	[6,7]	305.1	74.9	$3.4 \cdot 10^{-4}$
Phenanthrene	308 - 333	100 - 300	[34,36,40,41]	-	-	-	304.5	74.2	$3.6 \cdot 10^{-5}$
Pyrene	313	250	[36]	-	-	-	304.3	73.9	$4.5 \cdot 10^{-5}$
Benzoic acid	308 - 328	80 – 300	[29,39,40,41]	318 - 319	100 - 150		304.4	74.0	$6.7 \cdot 10^{-5}$
$\beta$ -Carotene	308 - 333	90 – 300	[42,43,44]	-	-	-	304.3	73.9	$8.9 \cdot 10^{-10}$
Vanillin	308 - 318	100 - 200	[45]	-	-	-	304.9	74.3	$1.9 \cdot 10^{-4}$

Table 2. Pure component parameters and binary interaction parameters used with the Sanchez-Lacombe EoS.

<i>Component</i>	$v_b$ ( $cm^3/mol$ )	$\sigma_{pw}$ ( $\text{\AA}$ )	$\epsilon^*$ ( $J/mol$ )	$v^*$ ( $cm^3/mol$ )	$r$	$k'_{ij}$	$k''_{ij}$	$l_{ij}$
Carbon dioxide	33.32*	3.97	2276.66	3.638	8.564			
Biphenyl	184.6	6.63	5280.12	14.985	11.708	0.1840	0.1580	0.0067
Naphthalene	147.6	6.17	5509.80	12.407	9.600	0.2047	0.2609	-0.2036
2,3-dimethyl Naphthalene	192.0	6.74	5604.69	13.069	11.245	0.2259	0.0914	-0.2530
2,6-dimethyl Naphthalene	192.0	6.74	5540.04	13.069	11.245	0.2341	0.2374	-0.3054
2,7-dimethyl Naphthalene	192.0	6.74	5548.13	13.069	11.245	0.2375	0.1911	-0.3311
Phenanthrene	199.2	6.81	6354.58	13.804	11.378	0.2697	0.1867	-0.3502
Pyrene	213.0	7.02	6732.91	14.733	11.980	0.2853	0.1779	-0.2971
Benzoic acid	130.2	5.79	4920.81	6.196	15.431	0.1231	0.2774	-0.3991
$\beta$ -Carotene	799.2	10.49	5565.85	23.080	24.722	0.2894	-0.5490	0.4347
Vanillin	164.4	7.23	4199.16	5.766	20.787	0.2075	0.2032	-1.0415

\* Liquid molar volume calculated using the Tyn and Calus expression [26]

Table 3. Comparison of literature models for the prediction of infinite dilution diffusion coefficients. Deviations  $\Delta D_{21}^0\%$  between data measured with the chromatographic technique and calculated values.

<i>Solute</i>	<i>N</i>	<i>Schmidt Number</i>	<i>Stokes-Einstein</i>		
			<i>W-C</i>	<i>SCH</i>	<i>H-M</i>
Biphenyl	15	14.98	19.40	33.48	20.05
Naphthalene	59	13.74	16.72	23.18	14.35
Phenanthrene	28	11.68	15.01	19.39	12.14
Pyrene	2	8.65	11.93	1.44	5.71
Benzoic acid	21	22.86	26.05	37.82	27.98
$\beta$ -Carotene	90	13.30	11.02	16.44	5.59
Vanillin	15	6.94	27.51	42.62	33.63
Mean deviation	230	13.74	15.97	23.17	13.45

Table 4. Influence of the thermodynamic factor  $\delta$  for the calculation of diffusion coefficients using the modified Darken equation. Deviations  $\Delta D_{21}\%$  between data measured with the solid technique and calculated values; minimum and maximum experimental solubilities  $y_2^{sat}$ .

<i>Solute</i>	<i>N</i>	<i>with <math>\delta</math></i>	<i>without <math>\delta</math></i>	$y_2^{sat}$	
				<i>minimum</i>	<i>maximum</i>
Naphthalene	79	11.20	32.34	$2.0 \cdot 10^{-4}$	$5.5 \cdot 10^{-2}$
2,3-dimethyl Naphthalene	3	10.26	14.36	$1.3 \cdot 10^{-3}$	$9.0 \cdot 10^{-3}$
2,6-dimethyl Naphthalene	6	12.11	14.88	$4.8 \cdot 10^{-4}$	$7.0 \cdot 10^{-3}$
2,7-dimethyl Naphthalene	6	10.05	12.18	$7.4 \cdot 10^{-4}$	$1.2 \cdot 10^{-2}$
Benzoic acid	2	8.49	11.59	$1.2 \cdot 10^{-4}$	$9.0 \cdot 10^{-3}$
Mean deviation	96	11.10	28.29		

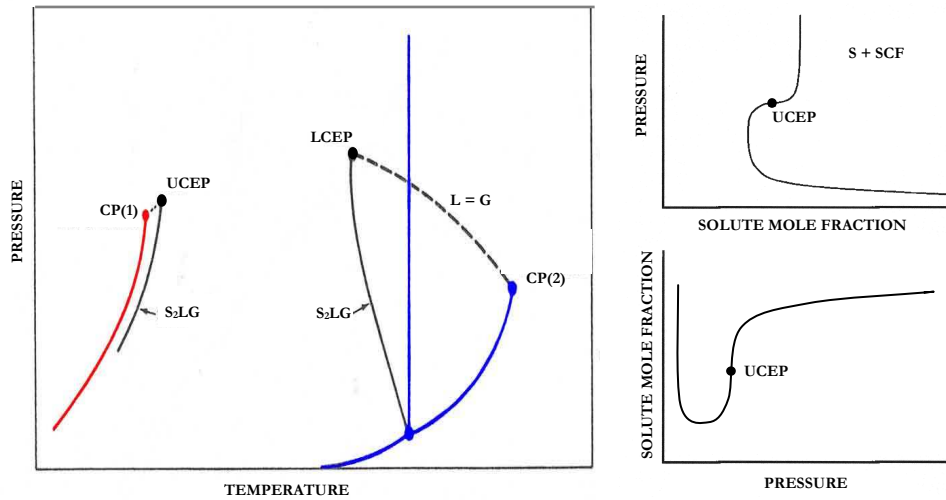


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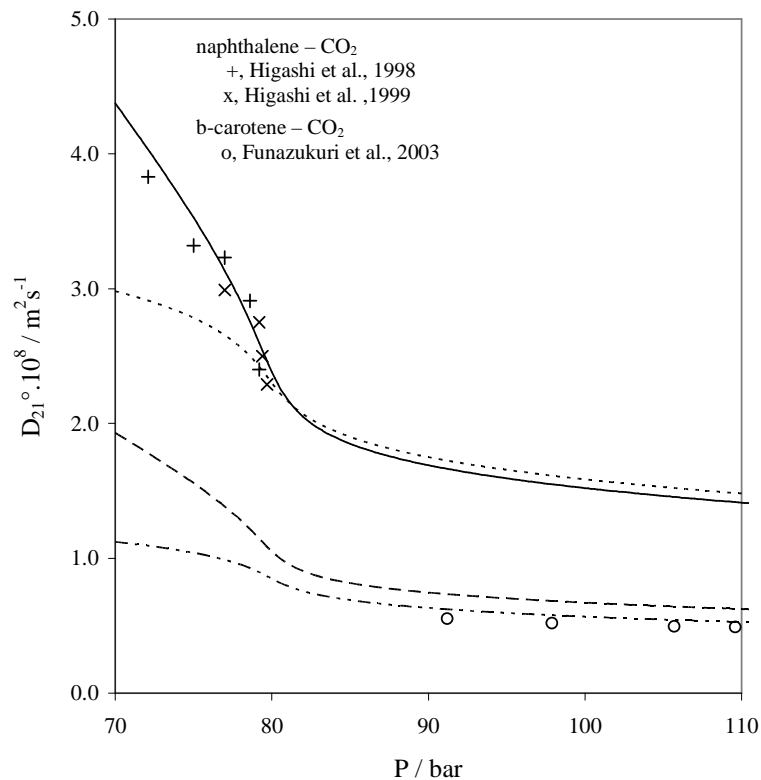


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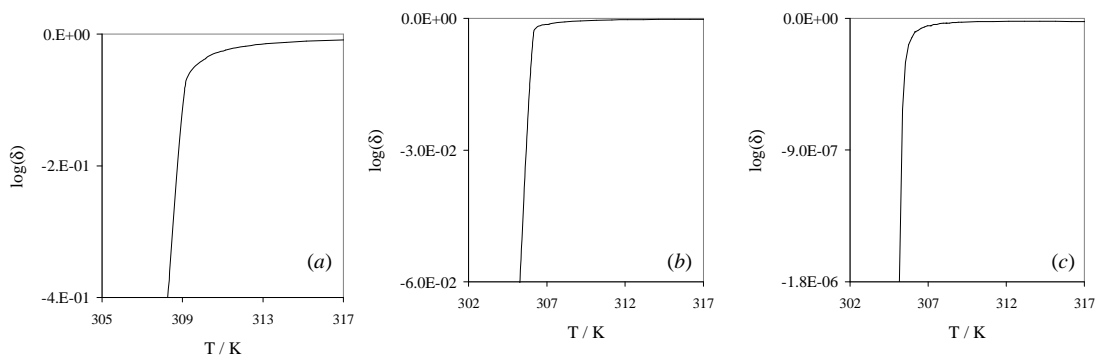


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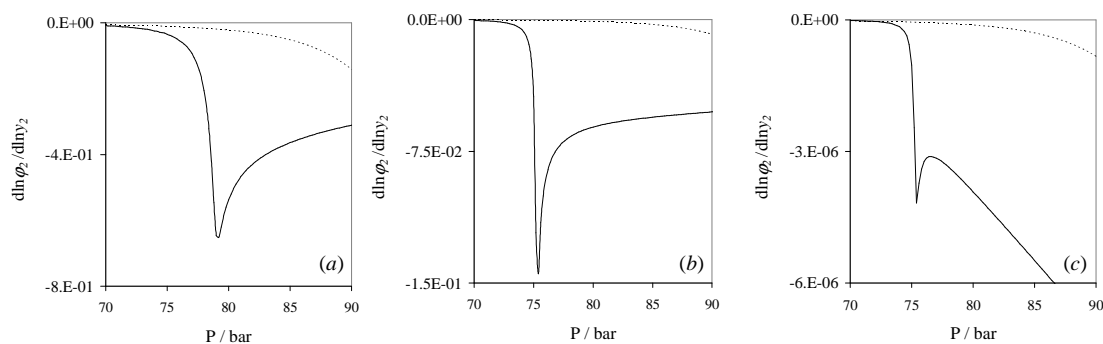


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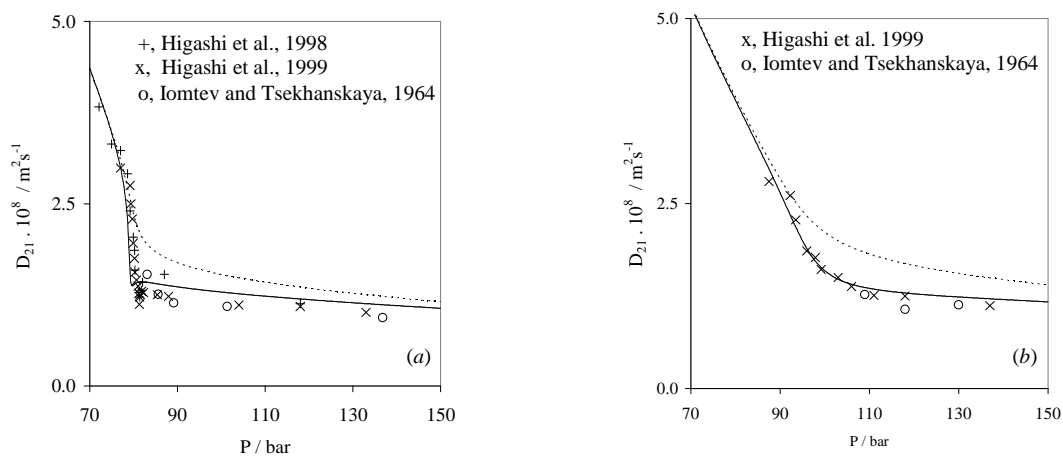


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