

Diffusion coefficients of 2-fluoroanisole, 2-bromoanisole, allylbenzene and 1,3-divinylbenzene at infinite dilution in supercritical carbon dioxide

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Abstract

The Taylor-Aris chromatographic technique was employed for the determination of diffusion coefficients of 2-fluoroanisole, 2-bromoanisole, allylbenzene and 1,3-divinylbenzene at infinite dilution in supercritical carbon dioxide from 313.16 to 333.16 K and pressures between 15 and 35 MPa. As expected, the diffusivities rise when temperature increases and pressure decreases. Numerous predictive equations are compared with experimental data: Lai-Tan, Liu-Ruckenstein cluster formula, Woerlee, Hipler-Schubert-Troe, Catchpole-King, Eaton-Akgerman, He, He-Yu, Liu-Silva-Macedo, Funazukuri and coworkers, Dariva-Coelho-Oliveira, Zhu-Lu-Zhou-Wang-Shi and the Liu-Ruckenstein RHS formula. The equations of He, He-Yu and Catchpole-King are the best of all, but can not be used in the whole range of temperatures and solvent densities.

Keywords: Carbon dioxide; Chromatography; Diffusion; Predictive equation; Supercritical fluid

1. Introduction

Binary diffusion in dilute gases is easier to estimate than in liquids or compressed gases. When a Lennard-Jones (LJ) intermolecular potential is selected and only binary collisions between particles are considered, diffusivities (D_{AB}) can be estimated by the well-known Chapman-Enskog formula [1]:

$$D_{AB}^0 = \frac{3}{8\rho_m (\sigma_{AB}^{LJ})^2} \sqrt{\frac{kT}{\pi m_{AB}}} \frac{1}{\Omega_{AB}^{(1,1)}} \quad (1)$$

where T is the absolute temperature, k the Boltzmann constant, ρ_m the mixture numerical density, σ_{AB} the mean diameter of solute and solvent, calculated as $0.5(\sigma_A + \sigma_B)$ and m_{AB} the molecular mass of the binary system, equal to $2m_A m_B / (m_A + m_B)$. The collision integral, $\Omega^{(1,1)}$ is a function of $T_{AB}^* = kT / \varepsilon_{AB}^{LJ}$, where $\varepsilon_{AB}^{LJ} = \sqrt{\varepsilon_A^{LJ} \varepsilon_B^{LJ}}$. σ^{LJ} and ε^{LJ} are the two characteristic Lennard-Jones parameters.

Nevertheless, low-density gases are of little interest in industry, where liquids or supercritical gases are employed. Among the latter, carbon dioxide plays a very important role [2], thus knowledge of binary diffusion coefficients in pure supercritical CO₂ is necessary for the design of mass transfer operations involving this special fluid [3-9]. Through the Taylor-Aris chromatographic dispersion technique these diffusion coefficients (at infinite dilution of solute in the solvent) can be measured, but the experiments are always time-consuming. Therefore, predictive equations like Eq.(1) should be available, but the models proposed for estimating diffusivities at infinite dilution are not so rigorous, and many of them have limited applicability. The equations considered in this work can be roughly classified

into two groups: Stokes-Einstein type (SE) and Rough-Hard-Sphere type (RHS). The first class includes Lai-Tan [10], Hipler-Schubert-Troe [11,12], Woerlee [13] and Liu-Ruckenstein cluster formula [14]. In the second class there are more equations, related to Dymond free-volume and molecular simulations: Liu-Silva-Macedo [15], Dariva-Coelho-Oliveira [16,17], Liu-Ruckenstein RHS formula [18], Zhu-Lu-Zhou-Wang-Shi [19], Catchpole-King [20], Eaton-Akgerman [21], He of 1997 [22], He of 1998 [23], He-Yu of 1997 [24], He-Yu of 1998 [25], Funazukuri-Hachisu-Wakao [26], Funazukuri-Ishiwata-Wakao [27], Funazukuri-Wakao [5] and Funazukuri-Kong-Kagei [5].

2-Fluoroanisole, 2-bromoanisole, allylbenzene and 1,3-divinylbenzene are simple aromatic molecules and can be employed to evaluate the results of these equations: they do not form intra-molecular hydrogen bonds and can not interact with the carbon dioxide. In this work, the diffusivities of the four compounds were measured from 313.16 to 333.16 K at five pressures between 15 and 35 MPa by the Taylor-Aris technique.

2. Experimental section

The experimental apparatus and the procedure have been reported elsewhere [6, 28]. As in these previous studies, a Hewlett-Packard G1205A supercritical fluid chromatograph (HP SFC) was employed. The HP SFC system consists in a pumping module, a column oven, an injection valve, a mass flow sensor, a multiple-wavelength UV detector and the SFC ChemStation software. The Taylor-Aris dispersion technique is based on the changes undergone by a pulse of solute *A* injected in a solvent *B* flowing in laminar regime through a capillary tube or column. After a long residence time, the pulse of solute becomes a Gaussian curve, whose width can be considered a measure of the molecular diffusivity.

$$D_{AB} = \frac{v_0}{4} \left[H \pm \sqrt{H^2 - \left(\frac{r_0^2}{3} \right)} \right] \quad (2)$$

$$H = \frac{LW_{1/2}^2}{5.545t_R^2} \quad (3)$$

D_{AB} is the diffusion coefficient at infinite dilution, v_0 the average velocity of solvent, r_0 the radius of the capillary tube and H a chromatographic parameter termed "height equivalent to a theoretical plate". For liquids and supercritical fluids, only the negative root of Eq.(2) is meaningful [29]. H is directly proportional to the square of Gaussian curve-width at half-height, $W_{1/2}$, in time dimensions. The calculation of H also needs the knowledge of tube length (L) and residence time (t_R). Our equipment automatically measures $W_{1/2}$ and t_R .

Eqs. (2) and (3) may be applied to coiled pipes with the following restriction [30-34]

$$De Sc^{1/2} < 10 \quad (4)$$

where De and Sc are the Dean and Schmidt numbers, respectively, and are defined as

$$De = Re \sqrt{\frac{r_0}{r_{coil}}} \quad (5)$$

$$Sc = \frac{\eta}{m\rho D_{AB}} \quad (6)$$

η and ρ are the viscosity and density of the supercritical carbon dioxide, Re is the Reynolds number and r_{coil} is the coil radius. Tube coiling has practical importance in chemical engineering, because the capillary pipes employed in the Taylor-Aris technique are very long and if coiling was not possible, the experimental apparatus would be enormous. The

chromatographic column is a coiled stainless steel pipe of dimensions 0.762 mm i.d. x 30.48 m length. The diameter of the coil is 0.26 m. The injection valve is a Rheodyne model 7520 injector of ultralow dispersion with a 0.2 μl loop.

The solutes injected in the supercritical chromatograph were purchased from Merck. All had a minimum purity of 98%. The carbon dioxide, supplied by Air Liquide had a minimum purity of 99.998%. The experiments were carried out at 313.16, 323.16 and 333.16 K and pressures of 15, 20, 25, 30 and 35 MPa (which entails densities between 936.1 and 607.1 kg m^{-3}).

3. Results and discussion

Table 1 presents binary diffusion for the four compounds studied, together with density and viscosity of carbon dioxide. Each value is the mean of 7-10 measurements. Density was calculated with the equation of state of Pitzer and Schreiber [35] and viscosity was taken from Stephan and Lucas [36]. At constant temperature, the diffusivity falls when pressure rises, because the molecules are more densely packed and can not move easily. On the other hand, when pressure is constant and temperature rises, the diffusivities increase, because the thermal energy of the molecules increases. The experimental diffusivities ranged from 15.11×10^{-9} to $7.15 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

Table 2 shows the molar mass and van der Waals parameters of the four solutes [37]. As R^{vdW} and Q^{vdW} are proportional to molecular volume and area, respectively, the ratio in the

sixth column of this table is a measure of molecular sphericity, molecules with low values of this ratio being less spherical than the others with high values.

Table 1 shows that 2-bromoanisole is the substance that diffuses more slowly. It is the heaviest molecule, but not the biggest, which is in contradiction to the SE approach. Neither it is the most spherical.

At pressures equal to or higher than 25 MPa, allylbenzene has the highest mobility. It is the lightest substance of the four, but at 15 MPa it is not the substance with the highest values of D_{AB} , which implies that the mass is not the only variable that controls diffusion in the density range studied in this work.

Diffivities of 1,3-divinylbenzene and 2-fluoroanisole are very similar, although at 15 MPa, divinylbenzene is faster than fluoroanisole, and the difference increases at higher temperatures. This is strange because divinylbenzene is larger, heavier and less spherical than the halogenated anisole.

3.1. Models based on Stokes-Einstein formula

3.1.1. Lai-Tan [10]

It is clear in the literature that the SE equation, in which the group $(D_{AB} \eta_B \pi \sigma_A / kT)^{-1}$ is a constant equal to 2 or 3 is not valid in supercritical fluids [32,34,38-42], but the power law of Hayduck and Cheng [43] has proven to work well for correlating experimental data. Lai and

Tan generalized this for diffusion in supercritical carbon dioxide only, and developing it with 141 data points of eight solutes.

$$D_{AB} = \frac{2.77 \times 10^{-14} T \sqrt{M_B}}{\eta_B^{0.688} V_{cA}^{0.284}} \quad (7)$$

3.1.2. Hippler-Schubert-Troe [12,13]

These authors proposed an empirical interpolation between the kinetic theory of dilute gases and the SE formula.

$$\frac{kT}{\eta_B D_{AB}} = \left(\frac{kT}{\eta_B D_{AB}} \right)^{SE} \left[1 - \exp \left(- \frac{\frac{\rho_B kT}{\eta_B^0 (\rho_B D_{AB})^0}}{\left(\frac{kT}{\eta_B D_{AB}} \right)^{SE}} \right) \right] \quad (8)$$

Mathematical expressions for the collision integrals $\Omega^{(1,1)}$ and $\Omega^{(2,2)}$ are available in the literature [44].

3.1.3. Woerlee [13]

The following expression for the viscosity-diffusivity relation was based on the kinetic theory: the molecular motion in liquids and dense gases is due to an Eyring-type mechanism, and the activation energies for diffusion and viscosity are assumed to be the same.

$$D_{AB} = \frac{3kT \left(1 + \frac{3b_B}{2V_B}\right)}{9\pi^2 \eta_B (\sigma_A^{\text{eff}} \sigma_B^{\text{eff}})^2} \frac{V_B}{N_{\text{av}}} \quad (9)$$

3.1.4. Liu-Ruckenstein cluster formula [14]

This is based on the work of Cussler [45] who studied the binary diffusion coefficients at finite concentration near the consolute points of mixtures. With some variations, Liu and Ruckenstein obtained

$$D_{AB} = \frac{kT}{f\pi\sigma_{AB}\eta_B} \left[\frac{1}{1 + \frac{1}{1.5} \sqrt{1 - \frac{1}{2} \lim_{x_A \rightarrow 0} \left(\frac{\partial \ln \phi_A}{\partial x_A} \right)_{T,P}}} + \frac{\sigma_{AB}}{3\sigma_B} \right] \quad (10)$$

Eq. (10) is only valid when the solvent is carbon dioxide in the ranges $0.9 \leq P_{rB} \leq 4.8$ and $0.9 \leq T_{rB} \leq 1.1$.

3.2. Models based in Rough-Hard-Sphere formula

3.2.1. Liu-Silva-Macedo [15]

By means of the RHS model, Liu, Silva and Macedo developed an equation for correlating self-diffusivities of non-associating liquids with two adjustable parameters, σ_B^{LJ} and $\varepsilon_B^{\text{LJ}}/k$ [46], and extended this to binary diffusion at infinite dilution.

$$D_{AB} = \frac{kT}{\frac{8}{3}\rho_B(\sigma_{AB}^{\text{eff}})^2(\pi m_{AB}kT)^{1/2}} \exp\left[-\frac{0.75\rho_B^*}{1.2588 - \rho_B^*} - \frac{0.27862}{T_{AB}^*}\right] \quad (11)$$

3.2.2. Dariva-Coelho-Oliveira [16,17]

Dariva, Coelho and Oliveira also developed an equation for correlating self-diffusivities, but this only required one adjustable parameter: the molecular diameter, because the sensitivity of correlation to the energetic parameter is low. The equation is extended to binary diffusion

$$D_{AB} = \frac{kT}{\frac{8}{3}\rho_B(\sigma_{AB}^{\text{eff}})^2(\pi m_{AB}kT)^{1/2}} \left(1 - \frac{\rho_B^*}{1.09}\right) [1 + (\rho_B^*)^2(0.4 - 0.83(\rho_B^*)^2)] \quad (12)$$

This formula does not reproduce the Chapman-Enskog limit in dilute gases. It can be simplified in supercritical solvents replacing effective diameters with LJ diameters [47] because repulsive forces are dominant in these fluids: the tedious calculation of solute density in working conditions is then avoided.

3.2.3. Liu-Ruckenstein RHS formula [18]

This is based on the molecular simulation data of Alder et al. for binary diffusion in hard-sphere mixtures [48,49].

$$D_{AB} = \frac{I_D \left(\frac{V_{cA}}{V_{cB}} \right)^{0.14} \left(\frac{m_A}{m_B} \right)^{0.06} kT}{\frac{8}{3} \rho_B (\sigma_{AB}^{\text{eff}})^2 (\pi m_{AB} kT)^{1/2} \left[\frac{g(\sigma_{AB}^{\text{eff}})}{F_{AB}} + \frac{0.4}{(T_{AB}^*)^{1.5}} \right]} \quad (13)$$

3.2.4. Zhu-Lu-Zhou-Wang-Shi [19]

Zhu and coworkers adjusted the molecular simulation data of Rowley and Painter [50] for self-diffusion, and extended the expression empirically to binary diffusion.

$$D_{AB} = \frac{kT}{\frac{8}{3} \rho_B (\sigma_{AB}^{\text{eff}})^2 (\pi m_B kT)^{1/2}} \left(1 - \frac{\rho_B^*}{1.029079 (T_{AB}^*)^{0.165377}} \right) \exp \left(-\frac{\rho_B^*}{2T_{AB}^*} \right) \times \left[1 + (\rho_B^*)^{0.126978} \left(\frac{0.596103(\rho_B^* - 1)}{0.539292(\rho_B^* - 1) + (T_{AB}^*)^{(0.400152 - 0.41054\rho_B^*)}} + 0.68856 \right) \right] \quad (14)$$

3.2.5. Catchpole-King [20]

$$D_{AB} = 5.152 D_{cB} T_{rB} \left(\frac{Y}{X} \right) \left[\rho_{rB}^{-2/3} - 0.4510 \right] \quad (15)$$

This can be applied when $0.4 \leq \rho_{rB} \leq 2.5$ and $0.9 \leq T_{rB} \leq 1.25$.

3.2.6. Eaton-Akgerman [21]

This semiempirical equation is based on the molecular simulation data of Eastal and Woolf. The equation is valid in the ranges $0.35 \leq \rho_{\text{rB}} \leq 3.10$ and $0.8 \leq T_{\text{rB}} \leq 1.1$

$$D_{\text{AB}} = 1.42 \times 10^{-21} \sqrt{T} \left(\frac{\sigma_{\text{A}}^{\text{eff}}}{\sigma_{\text{B}}^{\text{eff}}} \right)^{1.7538} \left[\frac{M_{\text{A}} + M_{\text{B}}}{M_{\text{A}} M_{\text{B}}} \right]^{1/2} \left(\frac{(V_{\text{B}})_0}{(\sigma_{\text{AB}}^{\text{eff}})^2} \right) \left[\left(\frac{V_{\text{B}}}{(V_{\text{B}})_0} \right)^e - \frac{b_{\text{AB}}}{(V_{\text{B}})_0} \right] \quad (16)$$

3.2.7. He [22,23]

In 1997, He proposed for $\rho_{\text{rB}} \geq 0.21$ and $0.92 \leq T_{\text{rB}} \leq 1.78$ [22]

$$D_{\text{AB}} = 10^{-10} \alpha (V_{\text{B}}^{\gamma} - b_{\text{B}}) \sqrt{\frac{T}{10^3 M_{\text{A}}}} \quad (17)$$

In 1998, He combined the SE expression with Eq. (17), obtaining [23]

$$D_{\text{AB}} = 10^{-10} \alpha (V_{\text{B}}^{\gamma} - b_{\text{B}}) \frac{T}{\sqrt{10^3 M_{\text{A}}}} \exp \left[c \left(1 - \frac{1}{T_{\text{rB}}} \right) \right] \quad (18)$$

The restrictions are now $0.21 \leq \rho_{\text{rB}} \leq 2.62$, $0.66 \leq T_{\text{rB}} \leq 1.78$ and $0.0581 \leq M_{\text{B}} \leq 0.8854$.

3.2.8. He-Yu [24,25]

A modification of Eq. (17) was made by He and Yu in 1997 [24]. In 1998, they proposed a free-volume-based equation [25] for $0.4 \leq \rho_{rB} \leq 2.5$, $0.66 \leq T_{rB} \leq 1.78$ and $0.0581 \leq M_B \leq 0.8854$

$$D_{AB} = 10^{-10} \alpha \sqrt{\frac{T}{10^3 M_A}} \exp\left(\frac{0.3887V_{cB}}{V_B - 0.23V_{cB}}\right) \quad (19)$$

3.2.9. Funazukuri and coworkers

Three of these equations are based on the Schmidt number, Sc . Funazukuri et al. [26] proposed in 1991 the following empirical equation for the prediction of binary diffusion coefficients in supercritical carbon dioxide

$$\ln\left(\frac{Sc - Sc^0}{Sc^0}\right) = -1.4 \ln\left(\frac{V_B - 1.384(V_B)_0}{1.384(V_B)_0}\right) + 1.48 \quad (20)$$

Funazukuri et al. [27] elaborated in 1992, with more theoretical bases.

$$\frac{Sc}{Sc^0} = 1 + 2.18 \left(\frac{M_A}{M_B}\right)^{-0.089} \left[\frac{\left(\frac{V_B}{1.384(V_B)_0}\right) \Omega_B^{(2,2)}}{\left(\frac{V_B}{1.384(V_B)_0} - 1\right)^2 \Omega_{AB}^{(1,1)}} \right]^{1.12} \quad (21)$$

valid for $V_B/(V_B)_0 > 2.24$. In the case of self-diffusion, the ratio between collision integrals for viscosity and diffusivity is roughly 1.11 in a wide range of reduced temperatures, and the authors took this value for binary diffusion (but this supposition is not necessarily correct).

In 1995, Funazukuri and Wakao [5] developed an empirical RHS equation for diffusion in supercritical carbon dioxide.

$$D_{AB} = \frac{3}{8\rho_B(\sigma_{AB}^{\text{eff}})^2} \sqrt{\frac{kT}{\pi m_{AB}}} \frac{1}{g(\sigma_{AB}^{\text{eff}})} I_D F_{AB} \quad (22)$$

From 2000 to date, Funazukuri and coworkers have been widely using the Funazukuri-Kong-Kagei formula [5,7-9]

$$\begin{aligned} \ln\left(\frac{Sc - Sc^0}{Sc^0}\right) = & -4.92519817 + 54.5529385\left(\frac{(V_B)_0}{V_B}\right) - 245.231443\left(\frac{(V_B)_0}{V_B}\right)^2 + \\ & + 607.893924\left(\frac{(V_B)_0}{V_B}\right)^3 - 708.884016\left(\frac{(V_B)_0}{V_B}\right)^4 + 329.611433\left(\frac{(V_B)_0}{V_B}\right)^5 \quad (23) \end{aligned}$$

3.3. Comparison of methods

For evaluating all the previous models, the molecular weights, critical properties and acentric factors are required, but these have only been found for divinylbenzene (in the HYSYS database) and carbon dioxide (in the Korea thermophysical properties Data Bank, KDB, at website <http://infosys.korea.ac.kr/kdb/>). So, the arithmetic means of two group contribution methods for estimating these critical properties have been used: Joback [37] and Wen-Qiang [51]. The normal boiling temperatures (necessary for calculating critical

temperatures and acentric factors] were taken from Lide [52] and Merck catalog [53]. The acentric factors were calculated with the formula of Lee-Kesler [37]:

$$\omega_i = \frac{-\ln P_{ci} - 5.92714 + 6.09648(T_{bi}/T_{ci})^{-1} + 1.28862 \ln(T_{bi}/T_{ci}) - 0.169347(T_{bi}/T_{ci})^6}{15.2518 - 15.6875(T_{bi}/T_{ci})^{-1} - 13.4721 \ln(T_{bi}/T_{ci}) + 0.43577(T_{bi}/T_{ci})^6} \quad (24)$$

All the properties are compiled in Table 3. For the formulas of Woerlee, Hippler-Schubert-Troe and Funazukuri, the molecular diameters and/or Lennard-Jones energies for solutes and solvent were calculated from Chung's expressions [37]. On the other hand, in the model of Dariva-Coelho-Oliveira, the parameters obtained for correlating carbon dioxide self-diffusion were employed (3.6283×10^{-10} m of diameter and $\varepsilon/k=195.2$ K). Exactly the same was carried out with Liu-Silva-Macedo (3.26192×10^{-10} m and 500.71 K from ref. [46]) and Liu-Ruckenstein RHS formula (3.4482×10^{-10} m of diameter from ref. [54] and ε/k by Chung). In the Liu-Ruckenstein cluster formula, the recommended values for ξ_{AB} and λ_{AB} were used, except in the case of divinylbenzene, where $\xi_{AB}=0.066$ and $\lambda_{AB}=-0.04$ were assigned, following the literature for fluid phase equilibria of alkylbenzenes+ carbon dioxide [55,56]. The AAD of the studied models are presented in Table 4.

Fig. 1 shows the experimental data of 1,3-divinylbenzene at 323.15 K and the calculated values with the SE type equations. The Woerlee expression underestimates the diffusivities of the four substances, and Liu-Ruckenstein and Lai-Tan overestimate them. The best equation of this group is that of Hippler-Schubert-Troe, but this gives poor results as the pressure decreases, as can be seen in Fig. 1.

Fig. 2 illustrates the experimental diffusivities for 2-fluoroanisole at 323.15 K and the values calculated with the RHS type equations. The predictions of the equation of

Funazukuri-Ishiwata-Wakao and Funazukuri-Wakao are not plotted because of the overestimation of experimental results. Nevertheless, if in Eq. (22) effective diameters are not taken for solute or solvent, the AAD decreases nearly to 10%, and if in Eq. (21) the collision integral for self-diffusion is employed instead of the corresponding integral for binary diffusion, the errors are of the same order.

The equations of He-Yu of 1997 and 1998 yield very similar numerical results and only one of them is represented. It can be observed that the formula of He of 1997 is very similar to these but the expression proposed by this author in 1998 gives higher AAD's for all substances except for 2-bromoanisole. The equations of Catchpole-King and Eaton-Akgerman are also good, with AAD's lower than 10%.

If the parameter values involved in some correlations are adjusted from experimental data, the accuracies become highly improved, as can be seen in Table 5, and the errors are of the same order of magnitude as the previously mentioned formulae.

4. Conclusions

Binary diffusivities of 2-fluoroanisole, 2-bromoanisole, allylbenzene and 1,3-divinylbenzene in supercritical CO₂ were determined at 313.15, 323.15 and 333.15 K and pressures of 15, 20, 25, 30 and 35 MPa by the chromatographic dispersion technique. The 2-bromoanisole, the heaviest of the studied substances, has the lowest values of D_{AB} in all the experimental conditions, but the diffusion coefficients of the other two compounds do not follow this simple mass dependence.

Concerning predictions, the free-volume based equation of Catchpole-King gives the best results: its maximum deviation is 7.03% for allylbenzene. The two equations of He and He-Yu, and the expression of Eaton-Akgerman are also good.

Listo f symbols

AAD	average absolute deviation
b_i	molar excluded volume of the i component ($\text{m}^3 \text{mol}^{-1}$)
c	numerical constant
D_{AB}	binary diffusivity ($\text{m}^2 \text{s}^{-1}$)
De	Dean number
e	parameter of the Eaton-Akgerman equation
F_{AB}	mathematical function related with binary diffusion at infinite dilution
F	corrective factor in the Liu-Ruckenstein cluster formula
$g(\sigma)$	radial distribution function
H	height equivalent to a theoretical plate (m)
I_D	coupling parameter
k	Boltzmann constant = $1,380658 \cdot 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$
L	length of the Taylor-Aris tube, m
LJ	Lennard-Jones
M	molar mass (kg mol^{-1})
m	molecular mass (kg molecule^{-1})

N_{av}	Avogadro number
P	pressure (Pa)
Q^{vdW}	van der Waals surface parameter
r_{coil}	coil radius
r_0	radius of the Taylor-Aris tube
R	gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
R^{vdW}	van der Waals volume parameter
Re	Reynolds number
Sc	Schmidt number
t_R	retention time (s)
T	absolute temperature
v_0	average velocity of a fluid in the Taylor-Aris pipe (m s^{-1})
V	molar volume (mol m^{-3})
$(V_B)_0$	close-packed volume of the solvent ($\text{m}^3 \text{ mol}^{-1}$)
$W_{1/2}$	curve-width at half-height (s)
x	molar fraction
X	parameter of the Catchpole-King equation
y	packing factor = $(\pi / 6) \rho \sigma^3$
Y	parameter of the Catchpole-King equation

Greek letters

α	parameters of the He and He-Yu equations
ε	molecular energy (J molecule^{-1})
γ	parameters of the He and He-Yu equations

ϕ	Peng-Robinson fugacity
η	viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
λ	interaction parameter in the Peng-Robinson equation
ρ	number density (molecules m^{-3})
σ	molecular diameter (m)
ω	acentric factor
ξ	interaction parameter in the Peng-Robinson equation
$\Omega^{(n,n)}$	collision integral. When $n=1$, this refers to diffusion, and when $n=2$, this refers to viscosity.

Superscripts

eff	Effective
LJ	Lennard-Jones
vdW	van der Waals
0	low-density conditions
*	molecular-reduced property

Subscripts

A	Solute
b	normal boiling point
B	Solvent
c	critical conditions
m	Mixture
r	reduced property with respect to critical conditions

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FIGURES

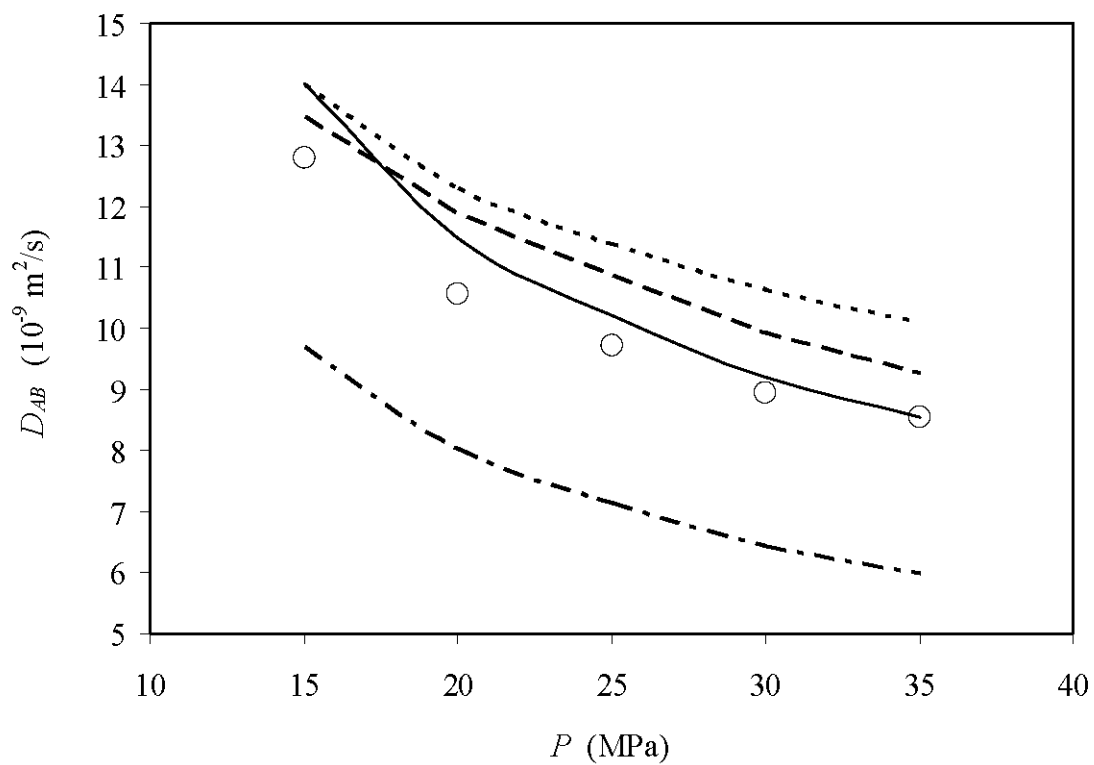


Fig. 1. Binary diffusivities of 1,3-divinylbenzene in carbon dioxide at 323.15 K as a function of pressure. Symbols represent experimental data and lines are the calculated values with the models based on the SE formula: (.....) Lai-Tan, (- - - - -) Woerlee, (-----) Liu-Ruckenstein cluster, (————) Hippler-Schubert-Troe.

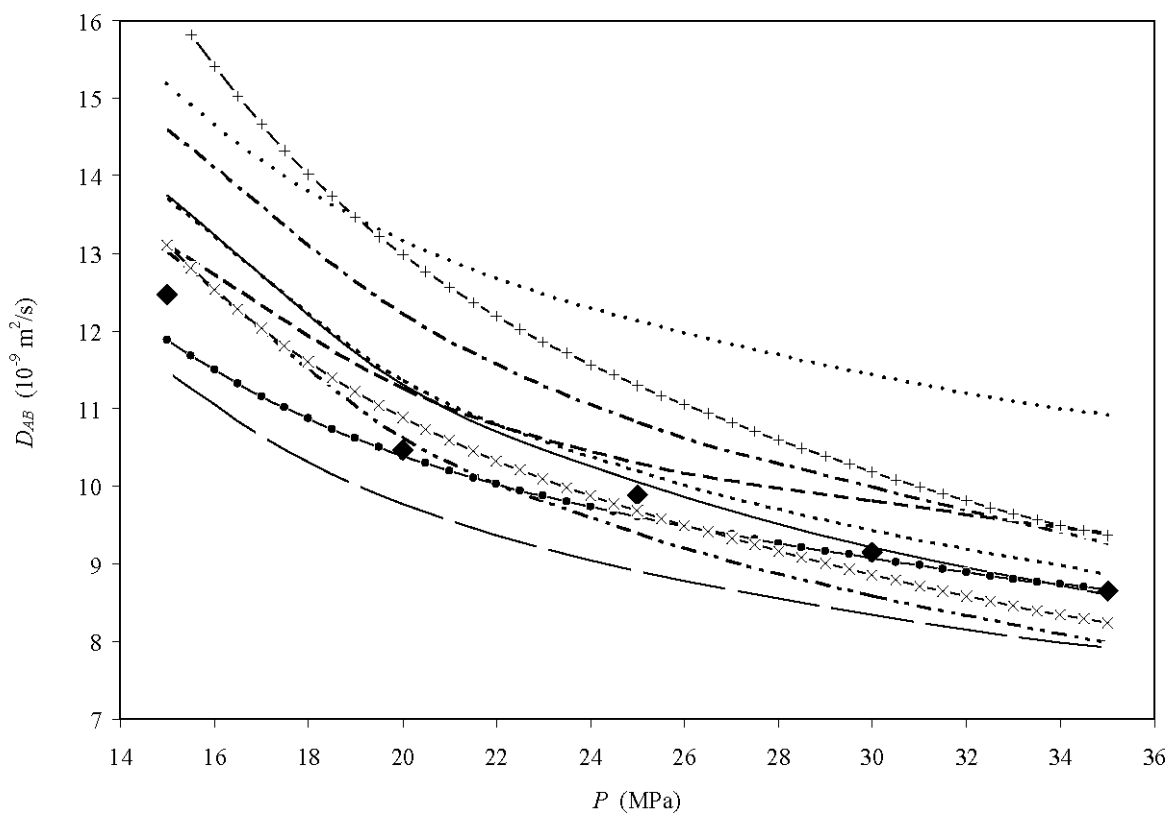


Fig. 2. Binary diffusivities of 2-fluoroanisole in carbon dioxide at 323.15 K as a function of pressure. Symbols represent experimental data and lines are the calculated values with the models based on the RHS model: (————) Catchpole-King, (-●-●-) Eaton-Akgerman, (-x-x-) He-Yu of 1997, (- - - -) Funazukuri-Hachisu-Wakao, (-·-·-·-·) Funazukuri-Kong-Kagei, (.....) Liu-Ruckenstein RHS, (—— ———) Liu-Silva-Macedo, (-,+,-,+,-) Zhu-Lu-Zhou-Wang-Shi, (-----) He of 1998, (-·-·-·-·) Dariva-Coelho-Oliveira.

TABLES

Table 1

Experimental D_{AB} values ($10^{-9} \text{ m}^2\text{s}^{-1}$) and wavelengths at which the data were measured

P (MPa)	T (K)	ρ (kg m^{-3})	η ($10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$)	2-fluoroanisole (236 nm)	2-bromoanisole (250 nm)	allylbenzene (260 nm)	1,3-divinylbenzene (309 nm)
15.0	313.16	781	0.0672	10.20 ± 0.12	9.46 ± 0.13	10.29 ± 0.10	10.26 ± 0.27
15.0	323.16	700.8	0.0571	12.47 ± 0.29	11.52 ± 0.32	12.25 ± 0.30	12.79 ± 0.72
15.0	333.16	607.1	0.0476	14.30 ± 0.17	12.76 ± 0.42	14.11 ± 0.36	15.11 ± 0.94
20.0	313.16	840.8	0.0772	9.27 ± 0.14	8.66 ± 0.24	9.11 ± 0.12	9.44 ± 0.34
20.0	323.16	784.9	0.0688	10.47 ± 0.28	10.15 ± 0.25	11.15 ± 0.32	10.56 ± 0.45
20.0	333.16	724.6	0.0598	12.26 ± 0.26	11.90 ± 0.29	12.22 ± 0.17	12.07 ± 0.42
25.0	313.16	880.7	0.085	8.69 ± 0.09	7.92 ± 0.18	8.93 ± 0.14	8.69 ± 0.27
25.0	323.16	835	0.077	9.89 ± 0.11	9.08 ± 0.19	10.02 ± 0.17	9.71 ± 0.39
25.0	333.16	781.2	0.0687	10.97 ± 0.12	10.64 ± 0.15	11.46 ± 0.22	11.11 ± 0.36
30.0	313.16	911.2	0.0931	8.01 ± 0.10	7.48 ± 0.07	8.29 ± 0.14	8.07 ± 0.19
30.0	323.16	871.4	0.0851	9.14 ± 0.06	8.52 ± 0.23	9.35 ± 0.16	8.94 ± 0.09
30.0	333.16	830.5	0.0738	10.33 ± 0.08	9.45 ± 0.18	10.51 ± 0.45	9.95 ± 0.27
35.0	313.16	936.1	0.1023	7.68 ± 0.08	7.15 ± 0.05	7.67 ± 0.16	7.69 ± 0.16
35.0	323.16	900	0.0915	8.65 ± 0.15	7.98 ± 0.16	9.01 ± 0.14	8.54 ± 0.12
35.0	333.16	864	0.0839	9.67 ± 0.14	8.98 ± 0.20	9.87 ± 0.10	9.47 ± 0.25

Table 2

Mass and van der Waals parameters of the studied substances

Substance	Formula	M (10^{-3} kg mol $^{-1}$)	R^{vdW}	Q^{vdW}	$\frac{(R^{vdW} / Q^{vdW})}{(R^{vdW})^{1/3}}$
2-fluoroanisole	C ₇ H ₇ FO	126.13	4.3302	3.332	0.7973218
2-bromoanisole	C ₇ H ₇ BrO	187.04	4.9498	3.760	0.7724504
allylbenzene	C ₉ H ₁₀	118.18	5.0415	3.836	0.7664690
1,3-divinylbenzene	C ₁₀ H ₁₀	130.19	5.5464	4.192	0.7474569

Table 3

Properties of the studied substances

Substance	T_c (K)	T_b (K)	P_c (MPa)	V_c (10^{-6} m 3 mol $^{-1}$)	ω
2-fluoroanisole ^a	644.81	427.66	3.811	328.87	0.3199
2-bromoanisole ^a	737.58	489.16	4.004	378.05	0.3371
allylbenzene ^a	639.86	429.16	3.350	419.80	0.3188
1,3-divinylbenzene ^b	692.06	472.66	3.120	440.00	0.3734
carbon dioxide ^c	304.14	216.55	7.375	94.00	0.2390

^a Average of values estimated from group contribution methods.^b HYSYS data base.^c KDB.

Table 4
AAD (%) in pure carbon dioxide

Equation	2-fluoroanisole	2-bromoanisole	allylbenzene	1,3-divinylbenzene
Lai-Tan	26.66	30.69	16.33	16.58
Liu-Ruckenstein cluster	17.53	19.33	7.74	10.43
Woerlee	9.94	13.19	24.13	26.04
Hippler-Schubert-Troe ^a	17.60	19.54	7.56	6.69
Catchpole-King	5.18	4.30	7.03	6.10
Eaton-Akgerman	2.71	4.32	9.13	9.00
He of 1997	3.41	10.91	4.64	1.83
He of 1998	6.50	8.20	8.37	5.00
He-Yu of 1997	4.04	11.91	4.67	3.09
He-Yu of 1998	3.63	11.93	4.25	2.81
Funazukuri-Hachisu-Wakao	7.49	17.33	9.81	5.33
Funazukuri-Ishiwata-Wakao ^b	20.23	39.05	22.30	20.05
Funazukuri-Wakao ^c	60.69	60.87	54.92	52.61
Funazukuri-Kong-Kagei	11.86	9.23	5.61	2.87
Liu-Ruckenstein RHS	25.32	26.65	11.67	9.08
Liu-Silva-Macedo	7.54	10.69	11.60	17.20
Zhu-Lu-Zhou-Wang-Shi	18.73	15.73	10.57	8.73
Dariva-Coelho-Oliveira	5.33	7.31	12.57	13.16

^a $\left(\frac{kT}{\eta_B D_{AB}}\right)^{SE} = 3\pi\sigma_A^{LJ}$. If the value of 2 is used instead of 3, the AAD rises above 60%.

^b If $\Omega_B^{(1,1)}$ is used instead of $\Omega_{AB}^{(1,1)}$ the AAD is roughly reduced to the half.

^c If σ_{AB}^{eff} is replaced by σ_{AB}^{vdW} , AAD is six times lower.

Table 5

Fitted parameters of some equations and AAD (%) of the new formulae

Equation	Change	2-fluoroanisole	2-bromoanisole	allylbenzene	1,3-divinylbenzene
Lai-Tan	2.27×10^{-14} instead of 2.77×10^{-14}	3.91	7.22	4.63	4.35
Liu-Ruckenstein cluster	$f = \text{constant} = 2.28$	3.96	3.24	6.58	6.31
Liu-Ruckenstein RHS	$I_D = \text{constant} = 0.821$	6.32	7.66	5.39	6.87
Funazukuri-Hächisu-Wakao	-1.399 and 1.593 instead of -1.4 and 1.48	3.80	7.11	3.88	4.44