

**Molecular diffusion coefficients of phenylmethanol,
1-phenylethanol, 2-phenylethanol, 2-phenyl-1-propanol,
and 3-phenyl-1-propanol in supercritical carbon dioxide.**

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Abstract

The Taylor-Aris chromatographic technique was employed for the determination of the diffusion coefficients of phenylmethanol, 1-phenylethanol, 2-phenylethanol, 2-phenyl-1-propanol, 2-phenyl-1-propanol and 3-phenyl-1-propanol at infinite dilution in supercritical carbon dioxide from 313.16 to 333.16 K and pressures between 15.0 and 35.0 MPa. Diffusivities were correlated with temperature, pressure, solvent density and solvent viscosity, and 12 predictive equations were compared with experimental data: Wilke-Chang, Lulis-Ratcliff, Tyn-Calus, Kooijman, Lai-Tan, Catchpole-King, Eaton-Akgerman, He, He-Yu, Liu-Silva-Macedo, Dariva-Coelho-Oliveira and Rah-Kwak-Eu-Laffleur. Considerations regarding the diffusion coefficients of the isomers were also made.

Keywords: Diffusion; Supercritical; Carbon dioxide; Chromatography; Isomer

1. Introduction

Recent studies have shown that the use of supercritical fluid as an extraction medium provides a powerful alternative to traditional extraction methods. A supercritical fluid can have properties which are intermediate between those of a liquid and those of a gas. These properties such as density (related to solvating power), viscosity (related to flow rate), and diffusion coefficients (related to mass transfer within the fluid) can be controlled by pressure and temperature. Knowledge of these properties is of vital importance to aid the design and optimization of extraction.

Use of fluids with low critical temperatures enables extraction to be conducted under mild thermal conditions ensuring that thermally labile compounds do not decompose. The use of carbon dioxide as the solvent is the main attraction. Some of the reasons for the increased interest in supercritical carbon dioxide include environmental problems associated with liquid solvents, the increasing cost of energy separation techniques and the inability of traditional techniques to design new materials with specific characteristics. Supercritical carbon dioxide has characteristics that allow it to solvate numerous compounds ranging in polarity from nonpolar to moderately polar. For the separation of moderate to polar compounds, organic solvent-modified CO₂ has been used to introduce selectivity to the separation as well as to increase extraction efficiencies [1, 2].

Over the last few decades, the diffusion coefficients of different solutes in supercritical fluids have been measured over a wide range of pressure and temperature. Several correlations have been developed in order to correlate and extrapolate diffusion coefficient data at various pressures and temperatures. Some of these correlations are highly empirical, while others have a strong fundamental basis. They need a reliable measurement of the diffusion coefficient at a given pressure and temperature. However, even when the solute parameters are available, the models often fail to represent the diffusion coefficient accurately. Therefore, more experimental measurements are required.

There exist several experimental techniques for the measurement of diffusion coefficients at supercritical conditions: the solid dissolution technique, the nuclear magnetic resonance technique, the Stefan tube, and the Taylor-Aris dispersion technique. Of these, the latter, the Taylor-Aris method, is the most widely employed [3]. This method is adequate for measuring diffusion coefficients for non and weakly polar compounds. Diffusion coefficients can be determined from supercritical fluid chromatography experiments according to the peak broadening method using a long void column. For polar compounds or high molecular weight

compounds, the method leads to a significant error due to peak tailing caused by adsorption onto the column wall. To overcome this problem, Funazukuri et al. [4] have developed the chromatographic impulse response method by replacing an uncoated capillary column with a polymer-coated capillary column. The response curve is nearly symmetrical and the determined value is reliable.

The objective of the present work was to measure the diffusion coefficients of phenylmethanol, 1-phenylethanol, 2-phenylethanol, 2-phenyl-1-propanol, and 3-phenyl-1-propanol in supercritical carbon dioxide and correlate them with appropriate equations. Diffusion coefficients have been measured at 313, 323, and 333 K over the pressure range from 15.0 to 35.0 MPa. The dependence of temperature, pressure, density and viscosity on the diffusion coefficient is discussed. The validity of several available equations commonly used to describe diffusion in supercritical carbon dioxide was also investigated.

2. Experimental Section

All measurements were performed using a Hewlett-Packard G1205A supercritical fluid chromatograph. A detailed description of the apparatus and calibration of the method have been previously reported [5, 6]. The apparatus mainly consists of a CO₂ cylinder, a pumping module, a mass flow sensor, a column oven, an injection valve, a choice of detectors and SFC ChemStation software.

The HP SFC introduces the sample into the column through a heated manual injection valve. A Rheodyne model 7520 injector of ultralow dispersion with a 0.2 μ l loop was used. Samples are injected as liquids at room temperature, and looped directly into the supercritical stream. The oven module can accommodate capillary and standard HPLC columns. The HP SFC uses both gas and liquid-phase detectors. In the present work, this unit uses a multiple wavelength UV detector (MWD).

The HP SFC uses an electrothermally cooled reciprocating pump to supply supercritical fluids to the system. The pump has feedback control, which compensates for fluid compressibility, minimizes pressure ripple, and provides for more reproducible results. In addition, the use of a reciprocating pump eliminates the inconvenience associated with refilling syringe pumps. Measurements were carried out at carbon dioxide flow rates ranging from 0.12 to 0.14 g/min. Under these circumstances, the flow rate was found to be slow enough to ensure a fully laminar flow of the supercritical carbon dioxide. The variable

restrictor is a programmable, backpressure control device located inside the pump module. The variable restrictor consists of a pressure transducer and nozzle, which opens and closes accordingly, releasing mobile phase to control pressure. Flow rate and column outlet pressure are independently controlled by the system. The mass flow sensor is a device located inside the pumping module.

The SFC ChemStation consists of a PC and HP SFC software. The SFC ChemStation enables instrument control and data handling on a Microsoft® Windows-based platform.

The diffusion column was a stainless steel tube with an inner diameter of 0.762 mm and a length of 30.48 m. The accuracy of the temperature measurement was ± 1 K, and for pressure ± 0.1 MPa. The measurements were repeated at least 7 times with an error within 2%, indicative of the reliability of the method used and the expected accuracy of experimental results obtained.

The chemicals used in the present work were purchased from commercial suppliers: phenylmethanol (>99%), 1-phenylethanol (>98%), 2-phenylethanol (>99%), 2-phenyl-1-propanol (>98%), and 3-phenyl-1-propanol (>98%), were obtained from Merck (synthesis grade). They were used as received without further purification. Carbon dioxide (>99.998%) was obtained from Air Liquide.

The diffusion coefficients were calculated by absorbance measurements at three wavelengths for each compound. The wavelengths of 257, 259 and 261 nm were employed for phenylmethanol; 258, 260, and 262 nm for 1-phenylethanol and 2-phenylethanol; 252, 258 and 265 nm for 2-phenyl-1-propanol; and, 256, 261, and 266 nm for 3-phenyl-1-propanol.

The adsorption of the solute by the inner walls may determine and appreciable asymmetry of the peaks and discrepancies in the elution time of different solvents. Fortunately, no tailing was observed, and the peaks were symmetrical in all the runs. Peaks that have an asymmetric factor greater than 1.05 have been rejected for analysis.

3. Predictive equations

These can be divided into two groups: those based on the Stokes-Einstein formula (compiled in Table 1) and those inspired by the Rough-Hard-Sphere model (shown in Table 2). The Stokes-Einstein theory (SE) assumes that limiting binary diffusivities are a function of

the absolute temperature T , the solvent viscosity η_B , and the molecular diameter of the solute σ_A [7, 8].

$$D_{AB} = \frac{kT}{3\pi\sigma_A\eta_B} \quad (1)$$

The Rough-Hard-Sphere theory (RHS) supposes that the hard-sphere model of Enskog-Thorne [9, 10] can be applied to real fluids introducing an attractive parameter, h_{AB} and temperature dependence diameters [11]:

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

where F_{AB} is a correction function obtained from computer molecular simulations [9, 10], ρ_B is the number density of the solvent, $g(\sigma_{AB})$ the radial distribution function [9, 12], σ_{AB} the solute-solvent mean diameter, $0.5(\sigma_A + \sigma_B)$, and m_{AB} the molecular mean mass of the system, $2m_A m_B / (m_A + m_B)$. The superscript *eff* indicates that the diameter is temperature dependent. As in Eq. (1), k is the Boltzmann constant (1.380658×10^{-23} J K⁻¹).

The free-volume model of Dymond is a particular case of the RHS-type equations [13, 14]. According to this author, molecular movements cease when the molar volume of the solvent, V_B reaches a minimum value $(V_B)_0$

$$D_{AB} = C_D T^{1/2} [V_B - (V_B)_0] \quad (3)$$

being C_D a proportionality constant.

The meaning of all the symbols and their units are compiled in the notation at the end of the paper.

4. Results and discussion

Experimental diffusivities and their errors are presented in Table 3, together with the experimental conditions, molar volumes and viscosities of carbon dioxide. V_B and η_B have been taken from references [26, 27], respectively. Table 4 compiles several properties of the five solutes and of the solvent. It can be seen that phenylmethanol is the lightest and smallest substance, and so has the highest diffusion coefficient. Phenylpropanols, which are bigger and heavier than phenylethanols are the substances that diffuse more slowly. With regard to isomeric differences, Fig. 1 shows that, within experimental error, 1-phenylethanol diffuses faster than, or equal to 2-phenylethanol. 3-Phenyl-1-propanol moves better in CO₂ than 2-phenyl-1-propanol. Neither size nor branching can explain these values of D_{AB} at first glance.

In Table 4, van der Waals size parameters were calculated with the software ChemDraw 3D, the parachors using a group contribution method [15] and volumes at boiling point by means of the equation of Tyn and Calus [15], except for carbon dioxide, whose value is available [28]. Critical properties were taken from the Korea Thermophysical Properties Data Bank ([http://infosys.korea.ac.kr/kdb/.](http://infosys.korea.ac.kr/kdb/)) (carbon dioxide), from the software HYSYS (phenylmethanol and 2-phenylethanol) or calculated with the methods of Joback [15] and Wen-Qiang [29] (1-phenylethanol, 2-phenyl-1-propanol, 3-phenyl-1-propanol). Boiling temperatures are taken from Lide [30] and acentric factors estimated using the equation of Lee-Kesler [15] when these are unknown. Lack of knowledge of the true critical properties for the three solutes is probably the reason why the diffusivities of the isomers can not be explained.

4.1. Pressure and temperature dependence of diffusion coefficients

D_{AB} decreases with increasing pressure, as can be seen in Fig. 1. This is due to the fact that pressure packs the solvent molecules more densely and the solute particle can not move between them easily. When temperature increases at constant pressure, D_{AB} increases as well, because temperature increases the kinetic energy of molecules, so the molecules move faster. Liong et al. [31] studied the diffusion of several fatty acid esters in supercritical carbon dioxide and proposed that the following correlations could be employed:

$$\ln D_{AB} = a_T + b_T \ln P \quad \text{at constant temperature} \quad (4)$$

$$\ln D_{AB} = a_P + b_P \ln T \quad \text{at constant pressure} \quad (5)$$

being b_T a negative value and b_P a positive one. The first parameter decreased when temperature increased and the second parameter followed the same tendency with pressure. Nevertheless, for the five solutes used in this work we have obtained nearly constant values of b_T and b_P , so the following formula can be employed for correlating experimental data

$$\ln\left(\frac{D_{AB} \times 10^9}{m^2 s^{-1}}\right) = c_0 + c_1 \ln\left(\frac{T}{K}\right) + c_2 \ln\left(\frac{P}{MPa}\right) \quad (6)$$

Fitting constants of Eq. (6) are given in Table 5. The proposed expression captures the decrease of the pressure dependence at high pressures and the marked increase in the diffusion coefficient as the temperature rises isobarically. The average absolute deviation (AAD) of the correlation is always lower than 3%.

4.2. Viscosity dependence

The Stokes-Einstein relation has been widely employed in the literature for studying diffusion coefficients at infinite dilution in liquids [15-18]. From Fig. 2, in which D_{AB}/T for phenylmethanol is represented against the inverse value of solvent viscosities, it can be observed that this relation is not strictly applicable. The free linear fitting predicts a finite diffusivity when the solvent viscosity is infinite. Nevertheless, the correlation with the SE formula does not give very large errors, as could be thought, except at 15.0 MPa and 333.15 K. Table 6 shows the correlation parameters and AAD for both procedures: for the free fitting, $AAD < 2\%$ in all cases, but for the enforced fitting, the deviations have values between 2.09 and 4.30%.

The Stokes-Einstein equation is only valid for predicting diffusion coefficients in supercritical carbon dioxide over a certain range of the carbon dioxide density. At higher densities, the hydrodynamic behavior is approached. The failure of this equation is especially evident in regions of low density, where the compressibility is large. A considerable amount

of clustering around the solutes occurs in the supercritical region, and the degree of clustering depends on density.

Some authors have proposed that, instead of a linear relation between D_{AB} and the inverse value of η_B , a better correlation can be obtained with an empirical exponential expression [32-34]

$$\ln\left(\frac{D_{AB} \times 10^9}{m^2 s^{-1}}\right) - \ln\left(\frac{T}{K}\right) = \theta_1 + \theta_2 \ln\left(\frac{\eta_B \times 10^6}{kg \cdot m^{-1} s^{-1}}\right) \quad (7)$$

whose parameters θ_1 and θ_2 are given in Table 7. For all solutes, AAD<1.7%, and the values of θ_2 are very similar for four of the five substances.

4.3. Density dependence

The effect of solvent molar volume on the diffusion coefficient of 2-phenyl-1-propanol at 323.16 K is illustrated in Fig. 3. For $V_B < 63 \text{ cm}^3/\text{mol}$ there is a linear relation between molar volume and the group $D_{AB}/T^{1/2}$, which is a proof of the fulfilment of Eq. (3).

$(V_B)_0$ should be only solvent dependent [31, 35-38], but Liu et al. [22] found that $(V_B)_0$ also varies from solute to solute. In Table 8 we can see the results of a free fitting of the two parameters and an “enforced fitting” taking $(V_B)_0 = 24.67 \text{ cm}^3/\text{mol}$. This value was calculated applying Eq. (3) to CO_2 self-diffusivities [39]. The deviations are very similar, and in all cases lower than 3%. The most considerable worsening occurs in 2-phenyl-1-propanol. A plot of $D_{AB}/T^{1/2}$ versus V_B for this substance, together with the results of the free and the enforced fitting can be found in Fig. 3.

4.4. Predicting the experimental data

Table 9 presents the results for the 12 equations compiled in Tables 1 and 2. According to these, the RHS expressions are much better than the SE models for representing diffusion

in supercritical carbon dioxide. Of the SE formulas, Lusis-Ratcliff, Kooijman and Lai-Tan yield the highest errors (from 25 to 47%). Only Tyn-Calus gives deviations lower than the two formulas based on the Rough-Hard-Sphere theory for the five solutes: He and Rah-Kwak-Eu-Lafleur. The best predictions are obtained with Eaton-Akgerman, with errors lower than 4.2% for the five solutes.

5. Conclusions

Binary diffusivities of phenylmethanol, 1-phenylethanol, 2-phenylethanol, 2-phenyl-1-propanol, 2-phenyl-1-propanol and 3-phenyl-1-propanol 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 peak-broadening method. As was expected, phenylmethanol has the highest values of D_{AB} and phenylpropanols the lowest. Concerning predictions, the Rough-Hard-Sphere equation of Eaton-Akgerman gives the best results.

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TABLES

Table 1

Predictive equations based on the Stokes-Einstein model

| Equation and reference | Mathematical form |
|------------------------|---|
| Wilke-Chang [15] | $D_{AB} = \frac{5.88 \times 10^{-17} T \sqrt{M_B}}{\eta_B V_{bA}^{0.6}}$ |
| Tyn-Calus [16] | $D_{AB} = 8.93 \times 10^{-16} \frac{T}{\eta_B} \left(\frac{V_{bA}^{1/6}}{V_{bB}^{1/3}} \right) \left(\frac{\Gamma_B}{\Gamma_A} \right)^{0.6}$ |
| Lusis-Ratcliff [17] | $D_{AB} = \frac{8.52 \times 10^{-18} T}{\eta_B V_{bB}^{1/3}} \left[1.40 \left(\frac{V_{bB}}{V_{bA}} \right)^{1/3} + \left(\frac{V_{bB}}{V_{bA}} \right) \right]$ |
| Kooijman [18] | $D_{AB} = 1.58 \left(1 - \left 1 - \frac{R_A / Q_A}{1.249} \right \right) \sqrt[3]{1 - \left 1 - \frac{R_B / Q_B}{1.249} \right } \left[1 + \left(\frac{R_B}{R_A} \right)^{1/3} \right] \frac{kT}{3\pi\eta_B\sigma_A}$ $\sigma_A = 6.36 \times 10^{-10} R_A^{1/3}$ |
| Lai-Tan [19] | $D_{AB} = \frac{2.77 \times 10^{-14} T \sqrt{M_B}}{\eta_B^{0.688} V_{cA}^{0.284}}$ |

Table 2

Predictive equations based on the Rough-Hard-Sphere model

| Equation and reference | Mathematical form |
|------------------------|---|
| Catchpole-King [20] | $D_{AB} = 5.152 D_{cB} T_{rB} \left(\frac{Y}{X} \right) \left[\rho_{rB}^{-2/3} - 0.4510 \right]$ $X = \frac{\left[1 + (V_{cB} / V_{cA})^{1/3} \right]^2}{\left[1 + (M_A / M_B) \right]^{1/2}}, \quad Y = 0.664 X^{0.17} \quad D_{cB} = 4.937 \times 10^{-8} \text{ m}^2/\text{s}$ |
| Eaton-Akgerman [21] | $D_{AB} = 1.42 \times 10^{-21} \sqrt{T} \left(\frac{\sigma_A^{eff}}{\sigma_B^{eff}} \right)^{1.7538} \left[\frac{M_A + M_B}{M_A M_B} \right]^{1/2} \left(\frac{(V_B)_0}{(\sigma_{AB}^{eff})^2} \right) \left[\left(\frac{V_B}{(V_B)_0} \right)^e - \frac{\lambda_{AB}}{(V_B)_0} \right]$ $\frac{\lambda_{AB}}{(V_B)_0} = \left[-0.2440 \left(\frac{\sigma_B^{eff}}{\sigma_A^{eff}} \right)^2 + 0.8491 \left(\frac{\sigma_B^{eff}}{\sigma_A^{eff}} \right) + 0.6001 \right] \left(\frac{M_A}{M_B} \right)^{-0.03587}$ $\sigma_i^{eff} = \left(\frac{6V_{ci}}{\pi N_{av}} \right)^{1/3} [0.552803 - 0.0026776 T_{ri}]$ $e = \frac{\sigma_B^{eff}}{\sigma_A^{eff}} - \frac{1}{3}, \quad (V_B)_0 = N_{av} \frac{(\sigma_B^{eff})^3}{\sqrt{2}}, \quad \sigma_{AB}^{eff} = \frac{\sigma_A^{eff} + \sigma_B^{eff}}{2}$ |

Equation and reference

Mathematical form

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

Liu-Silva-Macedo [22]

$$\frac{\varepsilon_{AB}^{LJ}}{k} = \sqrt{\frac{(\sigma_A^{LJ})^3(\varepsilon_A^{LJ}/k)(\sigma_B^{LJ})^3(\varepsilon_B^{LJ}/k)}{(\sigma_{AB}^{LJ})^6}}, \quad \sigma_{AB}^{eff} = 2^{1/6}\left(\frac{\sigma_A^{LJ} + \sigma_B^{LJ}}{2}\right)\left[1 + (1.3229T_{AB}^*)^{1/2}\right]^{-1/6}$$

$$\rho_B^* = \rho_B(\sigma_B^{eff})^3, \quad T_{AB}^* = \frac{kT}{\varepsilon_{AB}^{LJ}}$$

He [23]

$$D_{AB} = 10^{-10}\alpha(V_B^\gamma - 23)\sqrt{\frac{T}{10^3M_A}}$$

$$\alpha = 0.61614 + 3.0902 \exp\left(-2.775 \times 10^9 \frac{\sqrt{M_B V_{cB}}}{P_{cB}}\right)$$

$$\gamma = 1 \quad \text{if } \rho_{rB} \geq 1.2$$
$$\gamma = 1 + (\rho_{rB} - 1.2)\sqrt{0.001/M_B} \quad \text{if } \rho_{rB} < 1.2$$

Equation and reference

Mathematical form

He-Yu [24]

$$D_{AB} = 10^{-10} \beta \sqrt{\frac{T}{10^3 M_A}} \exp\left(\frac{0.3887V_{cB}}{V_B - 0.23V_{cB}}\right)$$
$$\beta = 14.82 + 5.9081\left(\frac{T_{cB}V_{cB}}{M_B}\right) + 2.0821\left(\frac{T_{cB}V_{cB}}{M_B}\right)^2$$

Rah-Kwak-Eu-Lafleur [25]

$$D_{AB} = \left(\frac{2}{1 + \sigma_A^{vdW} / \sigma_B^{vdW}}\right)^2 \left[\frac{1}{2} \left(1 + \frac{m_B}{m_A}\right)\right]^{-1/2} D_B$$

Table 3

Experimental conditions, molar volumes, viscosities and binary diffusion coefficients in supercritical carbon dioxide

| T (K) | P (MPa) | $V_B \times 10^6$ (m ³ mol ⁻¹) | $\eta_B \times 10^6$ (kg m ⁻¹ s ⁻¹) | $D_{AB} \times 10^9$ (m ² s ⁻¹) | | | | |
|-----------------|-------------------|--|---|--|-----------------|-----------------|---------------------|---------------------|
| | | | | Phenylmethanol | 1-Phenylethanol | 2-Phenylethanol | 2-Phenyl-1-propanol | 3-Phenyl-1-propanol |
| 313.16 | 15 | 56.34 | 67.2 | 10.98 ± 0.09 | 9.80 ± 0.15 | 9.75 ± 0.28 | 9.44 ± 0.18 | 9.85 ± 0.25 |
| | 20 | 52.33 | 77.2 | 9.48 ± 0.28 | 8.86 ± 0.05 | 8.76 ± 0.08 | 8.31 ± 0.07 | 8.49 ± 0.16 |
| | 25 | 49.96 | 85.0 | 8.81 ± 0.12 | 8.26 ± 0.15 | 8.18 ± 0.04 | 7.52 ± 0.05 | 7.70 ± 0.22 |
| | 30 | 48.29 | 93.1 | 8.18 ± 0.06 | 7.79 ± 0.08 | 7.62 ± 0.13 | 7.27 ± 0.03 | 7.25 ± 0.14 |
| | 35 | 47.00 | 102.3 | 7.89 ± 0.11 | 7.36 ± 0.07 | 7.25 ± 0.05 | 6.90 ± 0.07 | 6.82 ± 0.14 |
| 323.16 | 15 | 62.79 | 57.1 | 12.60 ± 0.21 | 11.98 ± 0.21 | 11.58 ± 0.51 | 10.94 ± 0.21 | 11.75 ± 0.19 |
| | 20 | 56.06 | 68.8 | 11.22 ± 0.11 | 10.31 ± 0.17 | 10.31 ± 0.17 | 9.57 ± 0.12 | 9.61 ± 0.08 |
| | 25 | 52.69 | 77.0 | 10.15 ± 0.18 | 9.40 ± 0.16 | 9.37 ± 0.11 | 8.88 ± 0.06 | 8.71 ± 0.16 |
| | 30 | 50.49 | 85.1 | 9.16 ± 0.08 | 8.76 ± 0.08 | 8.76 ± 0.11 | 7.98 ± 0.07 | 8.13 ± 0.19 |
| | 35 | 48.89 | 91.5 | 8.78 ± 0.10 | 8.19 ± 0.06 | 8.19 ± 0.04 | 7.65 ± 0.18 | 7.32 ± 0.20 |
| 333.16 | 15 | 72.48 | 47.6 | 14.96 ± 0.46 | 13.46 ± 0.43 | 13.74 ± 0.42 | 12.92 ± 0.22 | 13.76 ± 0.22 |
| | 20 | 60.72 | 59.8 | 12.86 ± 0.55 | 12.29 ± 0.29 | 11.97 ± 0.15 | 10.98 ± 0.21 | 11.54 ± 0.19 |
| | 25 | 56.32 | 68.7 | 11.38 ± 0.25 | 10.73 ± 0.18 | 10.73 ± 0.18 | 10.09 ± 0.13 | 10.00 ± 0.29 |
| | 30 | 52.98 | 73.8 | 10.39 ± 0.06 | 9.81 ± 0.07 | 9.78 ± 0.46 | 9.10 ± 0.16 | 9.21 ± 0.17 |
| | 35 | 50.93 | 83.9 | 9.60 ± 0.10 | 9.22 ± 0.07 | 9.14 ± 0.07 | 8.56 ± 0.11 | 8.62 ± 0.14 |

Table 4
Properties of pure substances

| | Phenylmethanol | 1-Phenylethanol | 2-Phenylethanol | 2-Phenyl- 1-propanol | 3-Phenyl- 1-propanol | Carbon dioxide |
|--|----------------|-----------------|-----------------|-------------------------|-------------------------|----------------|
| $M \times 10^3 (\text{g mol}^{-1})$ | 108.14 | 122.17 | 122.17 | 136.2 | 136.2 | 44.01 |
| $A^{vdW} (\text{\AA}^2)$ | 144.7 | 167.56 | 166.79 | 189.59 | 189.29 | 54.06 |
| $V^{vdW} (\text{\AA}^3)$ | 111.72 | 129.12 | 129.05 | 146.48 | 146.45 | 34.12 |
| Parachor ($\text{g}^{0.25} \text{cm}^3 \text{mol}^{-1} \text{s}^{-0.5}$) | 259.4 | 299.4 | 299.4 | 339.4 | 339.4 | 49.0 |
| $V_b \times 10^6 (\text{m}^3 \text{mol}^{-1})$ | 112.426 | 148.862 | 146.813 | 169.244 | 174.137 | 35.019 |
| T_c (K) | 720.21 | 675.30 | 684.01 | 662.02 | 702.30 | 304.10 |
| P_c (MPa) | 4.40 | 4.06 | 3.92 | 3.69 | 3.64 | 7.38 |
| $V_c \times 10^6 (\text{m}^3 \text{mol}^{-1})$ | 300.00 | 392.15 | 387.00 | 443.23 | 455.45 | 93.90 |
| T_b (K) | 478.61 | 478.16 | 492.06 | 476.16 | 508.16 | 194.70 |
| ω | 0.3949 | 0.6708 | 0.7429 | 0.7263 | 0.7589 | 0.2390 |

Table 5

Fitting parameters for Eq. (6)

| Substance | c_0 | c_1 | c_2 | AAD (%) |
|---------------------|--------|-------|-------|---------|
| Phenyl methanol | -21.57 | 4.39 | -0.47 | 2.68 |
| 1-Phenyl ethanol | -22.56 | 4.53 | -0.42 | 2.33 |
| 2-Phenyl ethanol | -23.59 | 4.71 | -0.43 | 1.52 |
| 2-Phenyl-1-propanol | -22.08 | 4.44 | -0.44 | 1.56 |
| 3-Phenyl-1-propanol | -23.19 | 4.69 | -0.53 | 2.83 |

Table 6

Linear fitting of D_{AB}/T versus the inverse value of the solvent viscosity

| Substance | Free fitting | | | Enforced fitting | |
|---------------------|--|--|---------|--|---------|
| | Intercept $\times 10^{12}$ ($\text{m}^2\text{s}^{-1}\text{K}^{-1}$) | Slope $\times 10^9$ ($\text{m}^2\text{kg}^{-1}\text{K}^{-1}$) | AAD (%) | Slope $\times 10^9$ ($\text{m}^2\text{kg}^{-1}\text{K}^{-1}$) | AAD (%) |
| Phenyl methanol | 6.8882 | 1.8472 | 1.52 | 2.3286 | 3.61 |
| 1-Phenyl ethanol | 7.7783 | 1.6282 | 1.93 | 2.1722 | 4.30 |
| 2-Phenyl ethanol | 7.2696 | 1.6490 | 1.77 | 2.1572 | 4.22 |
| 2-Phenyl-1-propanol | 6.7954 | 1.5485 | 1.42 | 2.0235 | 4.02 |
| 3-Phenyl-1-propanol | 3.3422 | 1.8400 | 1.56 | 2.07362 | 2.09 |

Table 7

Fitting parameters for Eq. (7)

| Substance | θ_1 | θ_2 | AAD (%) |
|---------------------|------------|------------|---------|
| Phenyl methanol | -5.5244 | -0.7992 | 1.49 |
| 1-Phenyl ethanol | -5.4916 | -0.7609 | 1.76 |
| 2-Phenyl ethanol | -5.5244 | -0.7719 | 1.67 |
| 2-Phenyl-1-propanol | -5.5880 | -0.7704 | 1.35 |
| 3-Phenyl-1-propanol | -5.8778 | -0.8877 | 1.61 |

Table 8

Fitting parameters for Eq. (3)

| Substance ^a | Free fitting | | | Enforced fitting with (V_B) ₀ =24.67×10 ⁶ m ³ mol ⁻¹ | |
|------------------------|--|---|------------|---|------------|
| | $C_D \times 10^9$ (m ² s ⁻¹ K ^{-1/2}) | (V_B) ₀ × 10 ⁶ (m ³ mol ⁻¹) | AAD (%) | $C_D \times 10^9$ (m ² s ⁻¹ K ^{-1/2}) | AAD (%) |
| Phenyl methanol | 17542 | 21.212 | 1.69 | 19706 | 1.54 |
| 1-Phenyl ethanol | 16497 | 21.289 | 1.93 | 18491 | 2.08 |
| 2-Phenyl ethanol | 15672 | 19.953 | 2.55 | 18311 | 2.39 |
| 2-Phenyl-1-propanol | 14622 | 19.785 | 1.84 | 17172 | 2.35 |
| 3-Phenyl-1-propanol | 17336 | 24.614 | 1.31 | 17370 | 1.30 |
| Carbon dioxide | 38593 | 24.670 | 1.12 | 38593 | 1.12 |

^aData at 15.0 MPa and 333.16 K have been rejected due to discrepancy with the linear tendency.

Table 9

Average absolute deviations (%) of the predictive equations of Tables 1 and 2

| Equation | Phenylmethanol | 1-Phenylethanol | 2-Phenylethanol | 2-Phenyl-1-propanol | 3-Phenyl-1-propanol |
|----------------------------------|----------------|-----------------|-----------------|---------------------|---------------------|
| Wilke-Chang | 22.10 | 10.31 | 12.09 | 9.73 | 6.21 |
| Lusis-Ratcliff | 38.81 | 29.47 | 31.33 | 30.05 | 27.16 |
| Tyn-Calus | 7.14 | 5.60 | 5.22 | 4.35 | 3.81 |
| Kooijman | 44.63 | 44.86 | 45.40 | 46.41 | 43.91 |
| Lai-Tan | 26.54 | 25.32 | 26.79 | 30.06 | 27.20 |
| Catchpole-King | 7.15 | 4.03 | 4.60 | 5.28 | 2.79 |
| Eaton-Akgerman | 2.73 | 3.82 | 3.72 | 4.11 | 5.67 |
| He | 7.15 | 7.79 | 8.63 | 9.68 | 7.98 |
| He-Yu | 5.60 | 6.23 | 7.06 | 8.09 | 6.39 |
| Liu-Silva-Macedo | 9.49 | 4.74 | 5.26 | 1.79 | 5.48 |
| Dariva-Coelho-Oliveira | 3.61 | 5.97 | 5.14 | 5.13 | 5.74 |
| Rah-Kwak-Eu-Lafleur ^a | 7.44 | 6.56 | 7.41 | 7.22 | 5.55 |

^a D_B taken from Groß et al.[39]

FIGURES

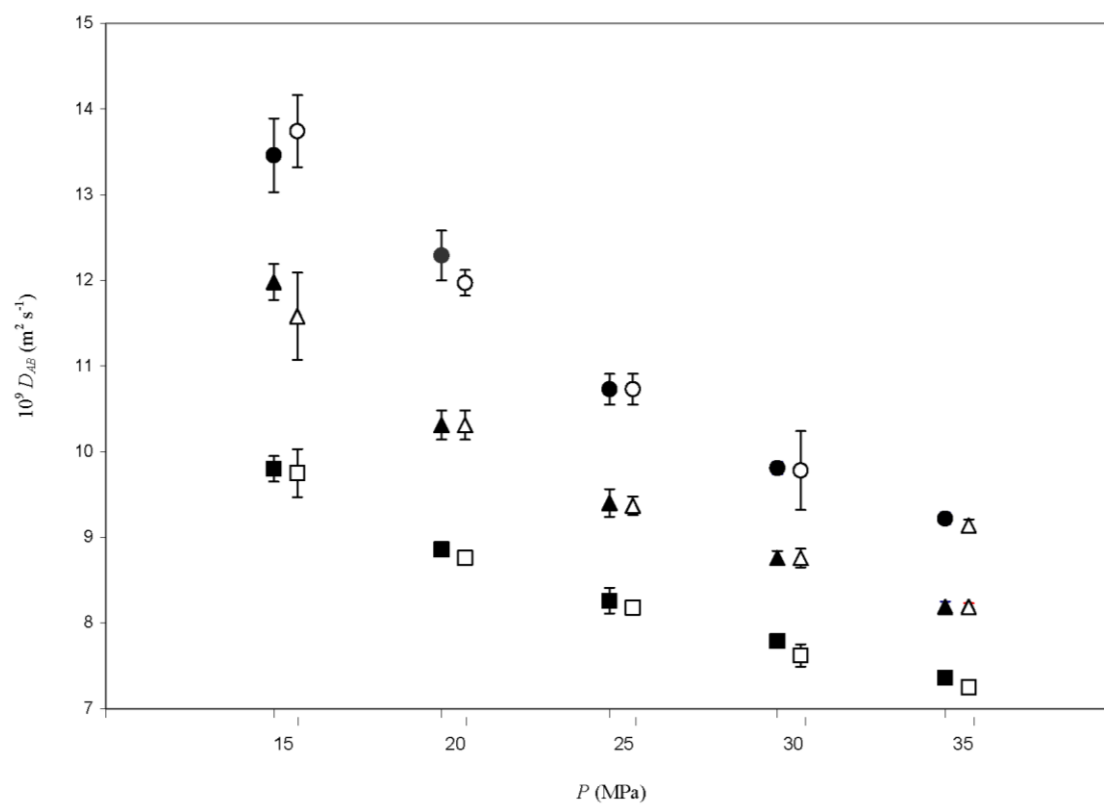


Fig. 1. Binary diffusivities of phenylethanols as a function of pressure: (\diamond) at 313.15 K, (\square) at 323.15 K, (\triangle) at 333.15 K. White symbols represent 2-phenyl ethanol and black ones represent 3-phenyl ethanol.

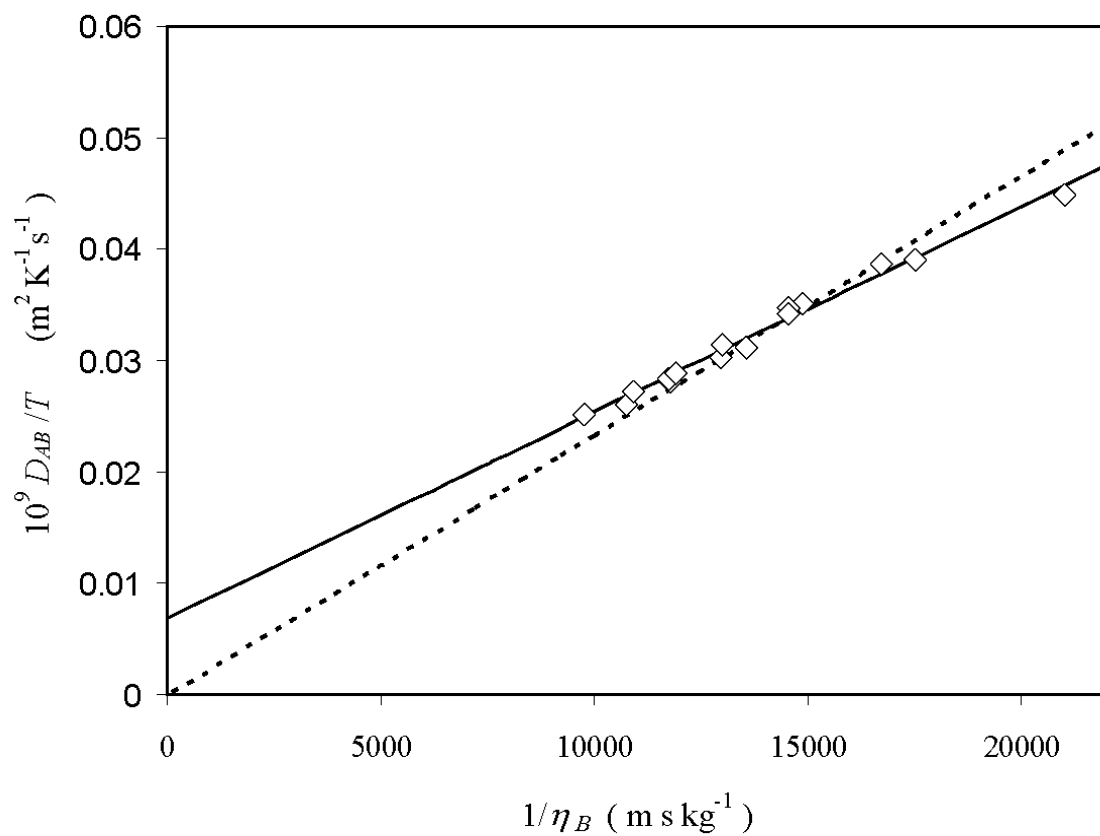


Fig. 2. Influence of the viscosity of carbon dioxide on the group D_{AB}/T in phenyl methanol. Solid line represents the free fitting and broken line represents the enforcing fitting.

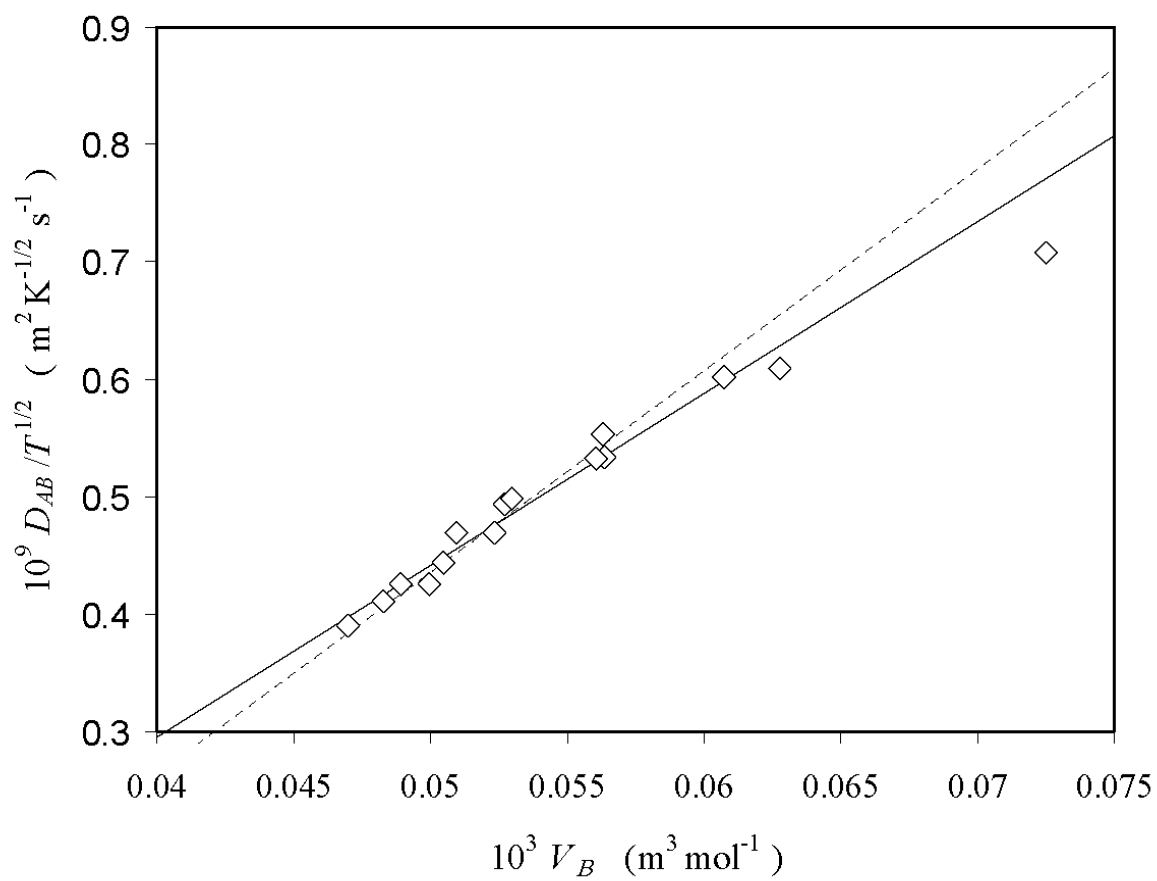


Fig. 3. Free volume plot of the diffusion coefficients in carbon dioxide for 2-phenyl-1-propanol (\diamond). The solid line is the free fitting to eq 3, and the broken line is the enforced fitting.