

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

**Using supercritical fluid chromatography to determine
diffusion coefficients of 1,2-diethylbenzene, 1,4-diethylbenzene,
5-tert-butyl-m-xylene and phenylacetylene in
supercritical carbon dioxide.**

Consuelo Pizarro, Octavio Suárez-Iglesias, Ignacio Medina*, Julio L. Bueno

Departamento de Ingeniería Química y T. M. A., Universidad de Oviedo

33071 Oviedo, Spain

Tel: + 34 985 103510

Fax: + 34 985 103434

e-mail: medina@uniovi.es

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36

Abstract

The binary diffusion of 1,2-diethylbenzene, 1,4-diethylbenzene, 5-*tert*-butyl-*m*-xylene and phenylacetylene at infinite dilution in supercritical carbon dioxide were measured between 15 and 35 MPa and in the temperature range of 313.16 to 333.16 K by the Taylor-Aris chromatographic method. The effect of temperature, pressure, viscosity and density was discussed. In the case of temperature dependence, additional measurements were done for 5-*tert*-butyl-*m*-xylene from 308.16 to 398.16 K at 35 MPa. The measured diffusivities of the four solutes were compared with the calculated ones by several predictive formulas.

Keywords: Binary diffusion; Carbon dioxide; Chromatograph; Dispersion technique; Supercritical.

1 **1. Introduction**

2
3 During the past decades, the application of supercritical fluids to several separation
4 processes has been a matter of intensive research, specially those processes that use carbon
5 dioxide as the extracting solvent. This interest has been followed by changes in environmental
6 regulations. Conventionally used solvents are being replaced by green solvents. An example
7 of this, in the food and pharmaceutical industries, where the toxicity of the extraction medium
8 is of concern, carbon dioxide has been especially useful. The advantages of supercritical
9 carbon dioxide are that it can be recycled, it is inexpensive, essentially nontoxic, and
10 nonflammable; and it has easily accesible critical conditions. Moreover, the solvent properties
11 of CO₂ can vary by changing either the pressure or the temperature near its critical conditions.
12 Apart from these advantages, it has some limitations resulting from its lack of polarity and
13 associated lack of capacity for specific solvent-solute interactions. For most high molecular
14 weight compounds, their solubility is quite low requiring high temperatures and pressures for
15 substantial loadings. To improve solvent polarity, small amounts of a highly polar co-solvent
16 can be added to carbon dioxide in order to increase its solvating power.

17 The supercritical fluid extraction requires dissolution and transport of the product as
18 solute. Thus, the solubility and transport properties of a component in a supercritical fluid can
19 provide a basic indication of the technical feasibility of any supercritical fluid extraction
20 process. For this reason a considerable amount of solubility data has appeared in the literature,
21 whereas data for transport properties are scarcer. One of the most important transport
22 properties is the diffusion coefficient since this type of mass transfer is often the rate-
23 determining step. A well-know advantage of supercritical fluids compared to ordinary liquids
24 is that diffusion coefficientes in supercritical fluids are higher than in liquid. This together
25 with the elimination of interphases results in significantly enhanced mass transfer under
26 supercritical conditions. In contrast to other properties, the number of reliable reported
27 diffusion coefficients is limited.

28 Several techniques exist to measure the diffusion coefficient of a solute in supercritical
29 fluids. Precise measurements can be made by the Taylor dispersion method. The principle for
30 this method is that when a sharp pulse is injected into a pure solvent flowing in a slow laminar
31 flow, it broadens into a peak as a result of the combined effects of convection along the tube
32 axis and molecular diffusion in the radial direction. The broadening of the peak gives the
33 molecular diffusion coefficient. Supercritical fluid chromatography can be used to determine

1 binary diffusion coefficients at infinite dilution by this method [1–3]. A review of Roth [4]
2 summarises the measurements of thermodynamic data by supercritical fluid chromatography

3 The present study describes the experimental determination of the molecular diffusion
4 coefficients for 1,2-diethylbenzene, 1,4-diethylbenzene, 5-*tert*-butyl-*m*-xylene, and
5 phenylacetylene in supercritical carbon dioxide at 313.16, 323.16, and 333.16 K over the
6 pressure range from 15.0 to 35.0 MPa. The solutes were chosen in an attempt to give an
7 insight into different types of molecular-scale interactions in solution. The effect of
8 temperature, pressure, carbon dioxide density and viscosity was studied. The applicability of
9 mass transport equations that are commonly used to describe the diffusion in supercritical
10 carbon dioxide was also investigated.

13 **2. Experimental**

15 *2.1. Materials*

17 Carbon dioxide (minimum purity of 99.998%) was purchased from Air Liquide. The
18 1,2-diethylbenzene (90%), 1,4-diethylbenzene (98%), 5-*tert*-butyl-*m*-xylene (98%), and
19 phenylacetylene (97%) were obtained from Merck (synthesis grade) and no further
20 purification was done before use.

22 *2.2. Apparatus and operation*

24 The experimental diffusion coefficients of 1,2-diethylbenzene, 1,4-diethylbenzene, 5-
25 *tert*-butyl-*m*-xylene, and phenylacetylene in supercritical carbon dioxide were measured using
26 a commercially available Hewlett-Packard G1205A supercritical fluid chromatograph (HP
27 SFC). This HP SFC system consists of a pumping module, a column oven, a manual injection
28 valve, a multiple wavelength UV detector (MWD), a modifier pump, a mass flow sensor, a
29 HP Vectra PC and a HP printer [5, 6].

31 The HP SFC uses an electrothermally cooled reciprocating pump to supply
32 supercritical fluids to the system. Electrothermal cooling provides a clean, self-contained,
33 quiet and reliable operation. The pump has feedback control, which compensates for fluid
34 compressibility, minimizes pressure ripple, and provides with more reproducible results. In
addition, the use of a reciprocating pump eliminates the inconvenience associated with

1 refilling syringe pumps. The second pump is for the addition of the modifier to the
2 supercritical fluid to create modified mobile phases. The HP SFC provides programmable
3 online mixing of mobile phase from 0 to 100%. By eliminating the need of multiple modifier
4 tanks, the modifier pump reduces method development time and cost, and yields a more
5 reproducible mobile phase composition.

6 The oven module can accommodate capillary and standard HPLC columns. The oven
7 has a temperature range from -80 to + 450°C. The temperature was measured with an
8 accuracy of 1 K. The pressure was measured with an accuracy of 0.1 MPa. The diffusion
9 column consists of a stainless steel tube with an id of 0.762 mm and a length of 30.48 m. The
10 HP SFC introduces the sample into the column with the aid of a heated manual injection
11 valve. A Rheodyne model 7520 injector of ultralow dispersion with a 0.2 µl loop was used.
12 Samples are injected as liquids at room temperature, and looped directly into the supercritical
13 stream. The injection of samples is carried out at intervals of 12-15 min (based on the time
14 between two subsequent injections, which is chosen in order to prevent overlapping of the
15 solute peaks).

16 The mathematical model may be applied to coiled columns with only a few
17 restrictions in the hydrodynamics and mass transfer throughout the column, which may be
18 summarized by the condition $(De)(Sc)^{1/2} < 10$, where De and Sc are the Dean and Schmidt
19 numbers. The measurements were carried out in coiled tubing where the centrifugal forces
20 acting on the solute molecules in radial direction can increase the radial mass transport. This
21 effect is known as secondary flow effect and it can be neglected at low flow rates. In a
22 previous work [7], two figures show the observed binary diffusion coefficient as a function of
23 the mobile phase velocity. The diffusion coefficient should be independent of the mobile
24 phase velocity.

25 During the measurements, the flow rate of carbon dioxide was regulated to
26 approximately 0.12-0.14 g/min. Under these circumstances, the flow rate was found to be
27 slow enough to ensure a fully laminar flow of the supercritical carbon dioxide. The retention
28 time for all experimental conditions was 100-120 min. To obtain diffusion coefficients at
29 temperatures above 333.16 K it is necessary to use very low flow rates (<0.10 g/min) and this
30 is very difficult. This can only be reached at 35.0MPa.

31
32 The HP SFC uses both gas and liquid-phase detectors. In the present work, this unit
33 uses a multiple wavelength UV detector (MWD). The detector has a heat exchanger installed.
34 The heat exchanger compensates for baseline noise wander caused by thermal effects. The

1 diffusion coefficients were determined by absorbance measurements at suitable wavelength
2 for each compound. The wavelengths were 257, 264, and 271 nm for 1,2-diethylbenzene; 259,
3 265, and 273 for 1,4-diethylbenzene; 263, 265, and 267 for 5-*tert*-butyl-*m*-xylene; and 273,
4 275, and 277 for phenylacetylene. Fortunately, no tailing was observed, and the peaks were
5 symmetrical in all the runs.

6 The mass flow sensor is a device located inside the pumping module. It gives
7 immediate feedback for flow diagnostics such as if the pump is working correctly, or if the
8 fixed restrictor is plugged. The carbon dioxide stream leaving the capillary column was
9 expanded to atmospheric pressure through the variable restrictor. It is a programmable,
10 backpressure control device located inside the pump module. The variable restrictor consists
11 of a pressure transducer and nozzle, which opens and closes accordingly, releasing mobile
12 phase to control pressure. It ensures that the system pressure is achieved and maintained. For
13 capillary columns, the variable restrictor is located in a recycle loop and controls pressure
14 ahead of the column. The SFC ChemStation consists of a PC and HP SFC software. The SFC
15 ChemStation enables instrument control and data handling on a Microsoft® Windows-based
16 platform.

17 The reported values are obtained from the average of 7-10 replicate measurements
18 with percentage relative standard deviations less than ± 2 %. The reliability and efficiency of
19 the diffusivity measurement technique were previously established by measuring the diffusion
20 coefficient of benzene in supercritical carbon dioxide at 313.16 K and different pressures, as
21 was described before [7, 8].

22

23

24 **3. Results and Discussion**

25

26 The molecular binary diffusivity of solute *A* in a solvent *B* will be the positive root of [9]

27

$$28 \quad D_{AB} = \frac{v_0}{4} \left[\frac{s(x)^2}{L} \pm \sqrt{\left(\frac{s(x)^2}{L} \right)^2 - \frac{r_0^2}{3}} \right] \quad (1)$$

29

1 where v_0 is the mean velocity of the solvent, r_0 the dispersion tube inner radius, L the length
2 of the pipe and $s(x)$ the spatial variance of the chromatographic peak. This variance can be
3 estimated from the peak-width at half-height, $w_{0.5}(x)$ as

$$s(x) = \frac{w_{0.5}(x)}{2.354} \quad (2)$$

6
7 If the experimental apparatus expressed the peak-width in units of time instead of in units
8 of length, $w_{0.5}(t)$, it should be multiplied by the mean velocity to obtain $w_{0.5}(x)$.

9
10 Resulting experimental data are given in Table 1, together with the densities and
11 viscosities of carbon dioxide (taken from Refs. [10] and [11]). As phenylacetylene is the
12 smallest and lightest solute, it has the highest values of D_{AB} while, 5-*tert*-butyl-*m*-xylene has
13 the lowest diffusivities since it is the biggest and heaviest. Between both sets of diffusion
14 coefficients, those of 1,2-diethylbenzene and 1,4-diethylbenzene are found. Within the
15 experimental error and despite the different shapes, the two isomers equally diffuse, as can be
16 seen in Fig. 1.

17 The measured binary diffusivities of these four solutes in supercritical carbon dioxide are
18 of the same order of magnitude that those determined for benzene and alkylbenzenes by many
19 researchers[12], and follow the same temperature and pressure dependence that them. For
20 example, diethylbenzenes and phenylacetylene have molecular masses and volumes close to
21 those of *tert*-butylbenzene [8] and ethylbenzene [12] respectively, and the discrepancies in
22 D_{AB} between our solutes and literature data are always less than 10%.

23 24 *3.1. Temperature and pressure dependence of diffusion coefficients*

25
26 Suárez et al [13] observed that in the ranges of $313.16 < T < 333.16$ and $15 < P < 35$ MPa, D_{AB}
27 linearly increased with the reciprocal of the pressure at constant temperature, and that a same
28 linear tendency was followed when the temperature increased isobarically. Both cases can be
29 taken into account in Eq. (3).

$$D_{AB} = \alpha_1 + \frac{\alpha_2}{P} + \alpha_3 T + \alpha_4 \left(\frac{T}{P} \right) \quad (3)$$

1 Fitting parameters of this formula are listed in Table 2. Diethylbenzenes have been
 2 correlated separately and together, which has made it possible to see the high sensibility of
 3 these parameters to the selected experimental points for the fitting. As an example of this,
 4 experimental and calculated values for phenylacetylene and 5-*tert*-butyl-*m*-xylene are
 5 represented in Figs. 2 and 3.

6
 7 For checking the predictive ability of Eq. (3), we have measured diffusivities of 5-*tert*-
 8 butyl-*m*-xylene in the range of $1.01 \leq T_{rB} \leq 1.31$ at 35 MPa. New data are given in Table 3, and
 9 they are plotted in Fig. 4 with those previously calculated. The maximum deviation is only of
 10 4.6%

11 12 13 3.2. Viscosity dependence

14
 15 In Fig. 5 a logarithmic plot of D_{AB}/T versus viscosity can be seen . If the Stokes-Einstein
 16 model was strictly applicable, the slope of the lines should be one.

$$17 \quad \ln\left(\frac{D_{AB}}{T}\right) = \ln\left(\frac{k}{3\pi\sigma_A}\right) - \ln(\eta_B) \quad (4)$$

18
 19 Nevertheless, the experimental results suggest a relation of type [14-17]:

$$20 \quad \ln\left(D_{AB} \times 10^9 \text{ (m}^2\text{s}^{-1}\text{)}\right) - \ln(T(\text{K})) = \theta_1 + \theta_2 \ln\left(\eta_B \times 10^6 \text{ (kg m}^{-1}\text{s}^{-1}\text{)}\right) \quad (5)$$

21
 22
 23 The parameters of this equation are given in Table 4. It can be seen that the errors are
 24 very small, and range from 1.03 for phenylacetylene to 2.19 for 1,4-diethylbenzene. θ_2 is
 25 approximately 0.8 for the four solutes.

26 27 28 3.3. Density dependence

29
 30 The simplest models for analyzing the variation of diffusion with density are those based in
 31 the free-volume theory. The free-volume theory was developed for self-diffusion by Cohen
 32 and Turnbull [18] and applied by Dymond [19, 20] to molecular simulations of Alder et al.

1 [21]. Chen et al [22] employed the following Dymond-based formula for correlating binary
2 diffusivities in liquids

$$3 \quad D_{AB}/T^{1/2}=C_1 [V_B-(V_B)_D] \quad (6)$$

4
5
6 where $(V_B)_D$ should be a characteristic parameter of the solvent, and thus solute independent.
7 Some researchers [23-26] have employed this formula with good results, but Liu et al. [27]
8 found that $(V_B)_D$ varies from solute to solute in the same solvent, and sometimes has negative
9 values, which is physically meaningless. Table 5 summarizes the results of free fitting of the
10 two parameters and in Fig. 6 calculated and experimental points are represented. Data at 15.0
11 MPa and 333.16 K have been rejected due to their discrepancy with the linear tendency.

12
13 Another simple model was proposed by Grushka et al. [29]

$$14 \quad D_{AB}/T=C_1 [(\rho_B)_D - \rho_B] \quad (7)$$

15
16
17 Fitting parameters are in Table 6 and the quality of the correlation is shown in Fig. 7.
18 Unlike Eq.(6) no points have to be rejected. Deviations of Eq. (7) are slightly lower than with
19 the Dymond model except for those correlating the solvent self-diffusivities. In both Tables 5
20 and 6 the solvent have been included to determine if $(V_B)_D$ or $(\rho_B)_D$ are solute dependent.
21 Although it seems that these parameters do not vary from solute to solute, it is clear that they
22 are different from those of the pure solvent, being this difference more pronounced in the
23 model of Grushka et al.

24 25 26 **4. Predicting experimental data**

27
28 The properties necessary for calculations were compiled in Table 7. Van der Waals size
29 parameters were calculated with the software ChemDraw 3D, parachors with a group
30 contribution method [30] and volumes at boiling point with the equation of Tyn and Calus
31 [30], except for carbon dioxide, whose value is available [31]. The other six properties were
32 taken from the KDB (diethylbenzenes and carbon dioxide), from the software HYSYS
33 (phenylacetylene) and calculated with the group-contribution methods of Joback [31] and

1 Wen-Qiang [32] (*5-tert-butyl-m-xylene*). Boiling temperatures (required for applying the
2 group-contribution methods) are taken from Lide [33].

3
4 Table 8 presents the results of 21 formulas commonly used for calculating diffusivities in
5 supercritical fluids and in liquids. The first nine are based on the Stokes-Einstein model, and
6 the rest are derived from the Rough-Hard-Sphere theory. The best represented solute is *5-tert-*
7 *butyl-m-xylene* (for which 10 equations give the lowest errors), followed by phenylacetilene
8 (predicted with the lowest AAD by eight equations)

9
10 It must be pointed out that the equations of Woerlee, Tyn-Calus, Liu-Silva-Macedo and
11 Dariva-Coelho-Oliveira tend to subestimate D_{AB} , and the expressions of Scheibel, Reddy-
12 Doraiswamy, Lysis-Ratcliff, Kooijman, Lai-Tan, Liu-Ruckenstein and Funazukuri-Hachisu-
13 Wakao tend to overestimate the diffusivities. The values predicted by Wilke-Chang are lower
14 than the experimental ones for all solutes except for phenylacetilene, for which they are
15 higher. Errors lower than 10% for the four solutes are obtained with the formulas of Wilke-
16 Chang, Catchpole-King, Eaton-Akgerman, He, He-Yu, Funazukuri-Kong-Kagei and Rah-
17 Kwak-Eu-Lafleur.

18
19 The equations of Table 8 with an AAD<10% for *5-tert-butyl-m-xylene* have been selected
20 to predict the diffusivities of this solute at 35.0 MPa and $306.16 \leq T \leq 398.16$ K versus the
21 experimental ones. Eaton-Akgerman is limited to $T_r < 1.1$, and Catchpole-King to $T_r < 1.25$, so
22 none of them can be employed in the full range of temperatures. The deviations are compiled
23 in Table 9, and they are all lower than 10% except for He of 1998 and for Funazukuri-Kong-
24 Kagei. Figure 8 shows the comparison between calculated and experimental points for five of
25 the nine formulas. This figure also illustrates the considerable overestimation of Scheibel and
26 He of 1998 at high temperatures, and the subestimation done by the two formulas of
27 Funazukuri et al. The best estimations are due to the model of He-Yu of 1997.

30 5. Conclusions

31
32 This work presents data of infinite dilution binary diffusivities of four alkylated benzenes
33 in CO₂ under supercritical conditions, determined by the chromatographic dispersion

1 technique: 1,2-diethylbenzene, 1,4-diethylbenzene, 5-*tert*-butyl-*m*-xylene and
2 phenylacetylene. As was expected, heavier solutes diffuse slower than lighter ones.

3 The measured points were correlated with temperature, pressure, viscosity and density,
4 and compared with the results of several predictive equations based on the Stokes-Einstein
5 model and on the Rough-Hard-Sphere theory. The formulae developed by He and Yu are the
6 best for calculating the diffusion coefficients of the four solutes (deviations lower than 4%).

7
8
9

10 Nomenclature

11
12

AAD	average absolute deviation
A^{vdW}	van der Waals area ($\text{m}^2\text{molecule}^{-1}$)
C_I	fitting constant of Eq. (6) ($\text{mol s}^{-1}\text{K}^{-0.5}\text{m}^{-1}$)
D_{AB}	binary diffusivity at infinite dilution (m^2s^{-1})
K	Boltzman constant ($\text{J K}^{-1}\text{molecule}^{-1}$)
L	length of the pipe (m)
M	molar mass (kg mol^{-1})
P	pressure (Pa)
r_0	dispersion tube inner radius (m)
$s(x)$	spatial variance of the chromatographic peak (m)
T	absolute temperature (K)
v_0	mean velocity of the solvent (m s^{-1})
V	molar volume ($\text{m}^3\text{mol}^{-1}$)
V^{vdw}	van der Waals volume ($\text{m}^3\text{molecule}^{-1}$)
$(V_B)_D$	limiting volume ($\text{m}^3\text{mol}^{-1}$)
$w_{0.5}$	peak-width at half-height (m)

13

14 Greek symbols

α	fitting constants of Eq. (3)
η	viscosity ($\text{kg m}^{-1}\text{s}^{-1}$)
θ	fitting constants of Eq. (5)
ρ	density (kg m^{-3})

$(\rho_B)_D$	limiting density (kg m^{-3})
σ	molecular diameter (m)
ω	acentric factor
1	
2	
3	<i>Subscripts</i>
<i>A</i>	solute
<i>b</i>	boiling point
<i>B</i>	solvent
<i>c</i>	critical point
<i>r</i>	reduced respect to the critical point

4

5

6

7 **Acknowledgements**

8

9 The authors are grateful to the Ministry of Education and Science of Spain, which support
10 the research with the project PPQ2001-3619

11

12

13

14 **References**

15

16 [1] T. Funazukuri, C.Y. Kong, S.Kagei, J. Chromatogr. A 1037 (2004) 411.

17

18 [2] T. Funazukuri, C.Y. Kong, S.Kagei, J. Chromatogr. A 1150 (2007) 105.

19

20 [3] N. Dahmen, A. Kordikowski, G.M. Schneider, J. Chromatogr. 505 (1990) 169.

21

22 [4] M. Roth, J. Microcol. Separation 3 (1991) 173.

23

24 [5] I. Medina, J.L. Bueno, J. Chem. Eng. Data 45 (2000) 298.

25

26 [6] L.M. González, J.L. Bueno, I. Medina, Ind. Eng. Chem. Res. 40 (2001) 3711.

- 1
- 2 [7] J.L. Bueno, J.J. Suárez, J. Dizy, I. Medina, *J. Chem. Eng. Data* 38 (1993) 344.
- 3
- 4 [8] L.M. González, J.L. Bueno, I. Medina, *J. Supercrit. Fluids* 24 (2002) 219.
- 5
- 6 [9] K.K. Liong, P.A. Wells, N.R. Foster, *J. Supercrit. Fluids* 4 (1991) 91.
- 7
- 8 [10] K.S. Pitzer, D.R. Schreiber, *Fluid Phase Equilib.* 41 (1988) 1.
- 9
- 10 [11] K. Stephan, K. Lucas, *Viscosity of dense fluids*, Plenum.Press, New York, 1979.
- 11
- 12 [12] J.J. Suarez, I. Medina, J.L. Bueno, *Fluid Phase Equilib.* 153 (1998) 167.
- 13
- 14 [13] J.J. Suarez, J.L. Bueno, I. Medina, J.L. Martinez, *Afinidad* 51 (1994) 132.
- 15
- 16 [14] C.Y. Kong, N.R.W. Withanage, T. Funazukuri, S. Kagei, *J.Chem. Eng. Data.* 50 (2005)
- 17 1635.
- 18
- 19 [15] T. Funazukuri, C.Y. Kong, S. Kagei, *Fluid Phase Equilib.* 219 (2004) 67.
- 20
- 21 [16] T. Funazukuri, C.Y. Kong, T. Kikuchi, S. Kagei, *J. Chem. Eng. Data* 48 (2003) 684.
- 22
- 23 [17] C.Y. Kong, N.R.W. Withanage, T. Funazukuri, S. Kagei, *J. Supercrit. Fluids* 37 (2006)
- 24 63.
- 25
- 26 [18] M.H. Cohen, D. Turnbull, *J. Chem. Phys.* 31 (1959) 1164.
- 27
- 28 [19] J.H. Dymond, *J. Chem. Soc., Faraday Tran.s II* 68 (1972) 1789.
- 29
- 30 [20] J.H. Dymond, *J. Chem. Phys.* 60 (1974) 969.
- 31
- 32 [21] B.J. Alder, D.M. Gass, T.E. Wainwright, *J. Chem. Phys.* 53 (1970) 3813.
- 33
- 34 [22] S.H.Chen, H.T.Davis, D.F. Evans, *J. Chem. Phys.* 77 (1982) 2540.

- 1
- 2 [23] H.C. Chen, S.H. Chen, *Chem. Eng. Sci.* 40 (1985) 819.
- 3
- 4 [24] M.A. Matthews, J.B. Rodden, A. Akgerman, *J. Chem. Eng. Data* 32 (1987) 317.
- 5
- 6 [25] M.A. Matthews, J.B. Rodden, A. Akgerman, *J. Chem. Eng. Data* 32 (1987) 319.
- 7
- 8 [26] C.A. Filho, C.M. Silva, M.B. Quadri, E.A. Macedo, *J. Chem. Eng. Data* 47 (2002)
- 9 1351.
- 10
- 11 [27] H. Liu, C.M. Silva, E.A. Macedo, *Ind. Eng. Chem. Res.* 36 (1997) 246. Correction in
- 12 37 (1998) 308.
- 13
- 14 [28] Groß, T.; Buchhauser, J.; Lüdemann, H.-D. *J. Chem. Phys.* 109 (1998) 4518.
- 15
- 16 [29] E. Grushka, E. Kikta Jr., H.T. Cullinan Jr., *J. Phys. Chem.* 80 (1976) 757.
- 17
- 18 [30] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The properties of gases and liquids*, 4th ed.,
- 19 McGraw-Hill Inc., New York, 1987.
- 20
- 21 [31] Perry, R.H.; Green, D.W. *Chemical Engineer's Handbook* (Spanish edition), 7th ed.,
- 22 McGraw-Hill, Madrid, 2001.
- 23
- 24 [32] X. Wen, Y. Qiang, *Ind. Eng. Chem. Res.* 40 (2001) 6245.
- 25
- 26 [33] R.D. Lide, *CRC Handbook of Chemistry and Physics*, 80th ed., CRC Press, Boca Raton,
- 27 1999.
- 28
- 29 [34] K.A. Reddy, L.K. Doraiswamy, *Ind. Eng. Chem. Fundam.* 6 (1967) 77.
- 30
- 31 [35] M.A. Lysis, G.A. Ratcliff, *Can. J. Chem. Eng.* 46 (1968) 385.
- 32
- 33 [36] M.T. Tyn, W.F. Calus, *J. Chem. Eng. Data* 20 (1975) 106.
- 34

- 1 [37] C.-C. Lai, C.-S. Tan, *Ind. Eng. Chem. Res.* 34 (1995) 674.
2
- 3 [38] H.A. Kooijman, *Ind. Eng. Chem. Res.* 41 (2002) 3326.
4
- 5 [39] H.Liu, E. Ruckenstein, *Ind. Eng. Chem. Res.* 36(1997) 888. Correction in 37 (1998)
6 3524.
7
- 8 [40] G.F. Woerlee, *Ind. Eng. Chem. Res.* 40 (2001) 465.
9
- 10 [41] O.J. Catchpole, M.B. King, *Ind. Eng. Chem. Res.* 33 (1994) 1828. Correction in 36
11 (1997) 4013.
12
- 13 [42] A.P. Eaton, A. Akgerman, *Ind. Eng. Chem. Res.* 36 (1997) 923.
14
- 15 [43] C.-H. He, *AIChE J.* 43 (1997) 2944.
16
- 17 [44] C.-H. He, *Fluid Phase Equilib.* 147 (1998) 309.
18
- 19 [45] C.-H. He, Y.-S. Yu, *Ind. Eng. Chem. Res.* 36 (1997) 4430.
20
- 21 [46] C.-H. He, Y.-S. Yu, *Ind. Eng. Chem. Res.* 37 (1998) 3793.
22
- 23 [47] T. Funazukuri, S. Hachisu, N. Wakao, *Ind. Eng. Chem. Res.* 30 (1991) 1323.
24
- 25 [48] H. Higashi, Y. Iwai, Y. Arai, *Chem. Eng. Sci.* 56 (2001) 3027.
26
- 27 [49] C. Dariva, L.A.F. Coelho, J.V. Oliveira, *Brazilian J. Chem. Eng.* 16 (1999) 213.
28
- 29 [50] C. Dariva, L.A.F. Coelho, J.V. Oliveira, *Fluid Phase Equilib.* 158 (1999) 1045.
30
- 31 [51] L.A.F. Coelho, A. Marchut, J.V. Oliveira, P.B. Balbuena, *Ind. Eng. Chem. Res.* 39
32 (2000) 227.
33
- 34 [52] Y. Zhu, X. Lu, J. Zhou, Y. Wang, J. Shi, *Fluid Phase Equilib.* 194 (2002) 1141.

1

2 [53] K. Rah, S. Kwak, B.C. Eu, M. Lafleur, J. Phys. Chem. A 106 (2002) 11841.

3

4 [54] R.N. Occhiogrosso, J.T. Igel, M.A. McHugh, Fluid Phase Equilib. 26 (1986) 165.

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

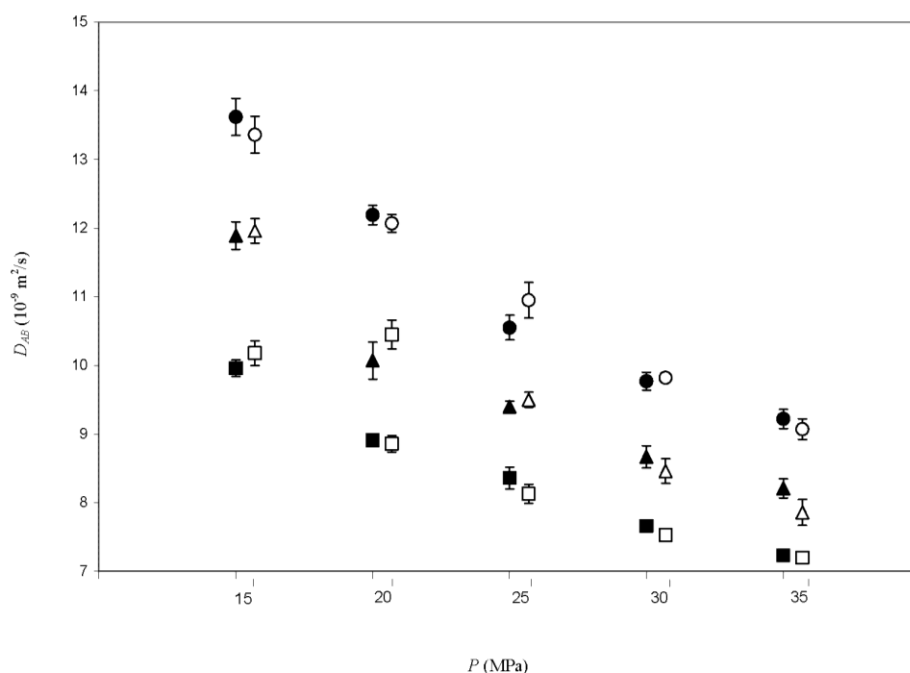
31

32

33

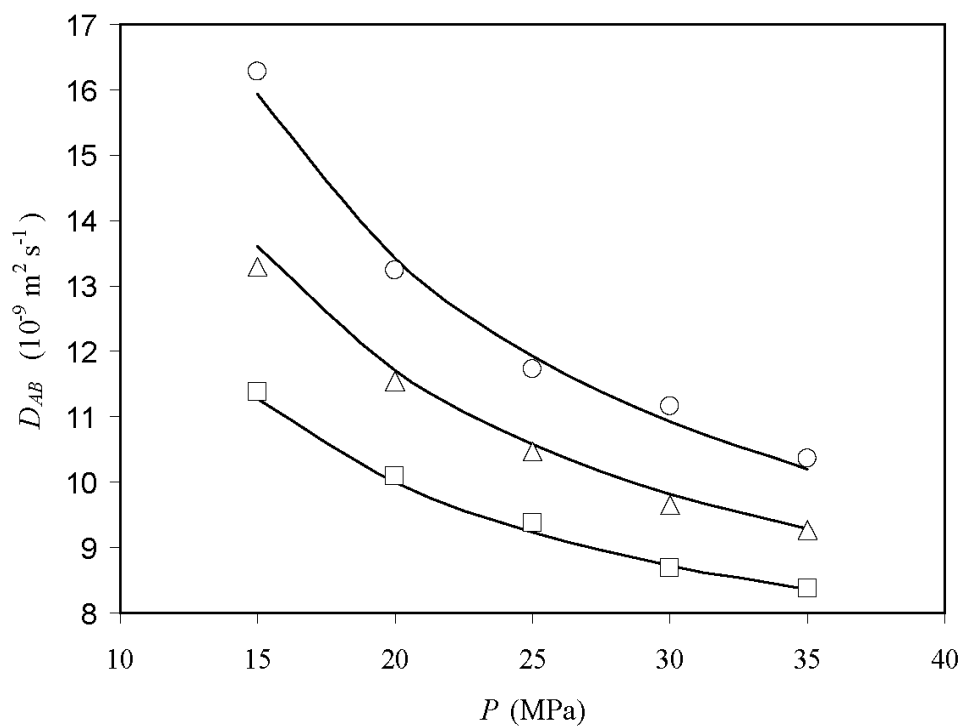
34

1 LIST OF THE CAPTIONS



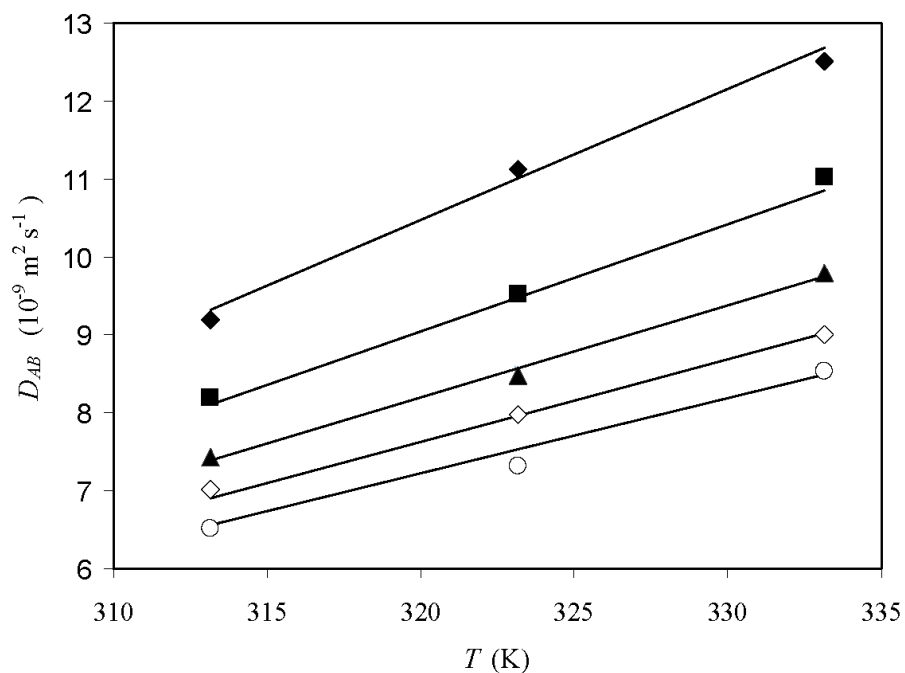
2

3 Fig.1. Experimental diffusivities of 1,2-diethylbenzene (black symbols) and 1,4-
 4 diethylbenzene (white symbols) with the error bars at 313.16 K (squares), 323.16 K
 5 (triangles) and 333.16 K (rhombi)

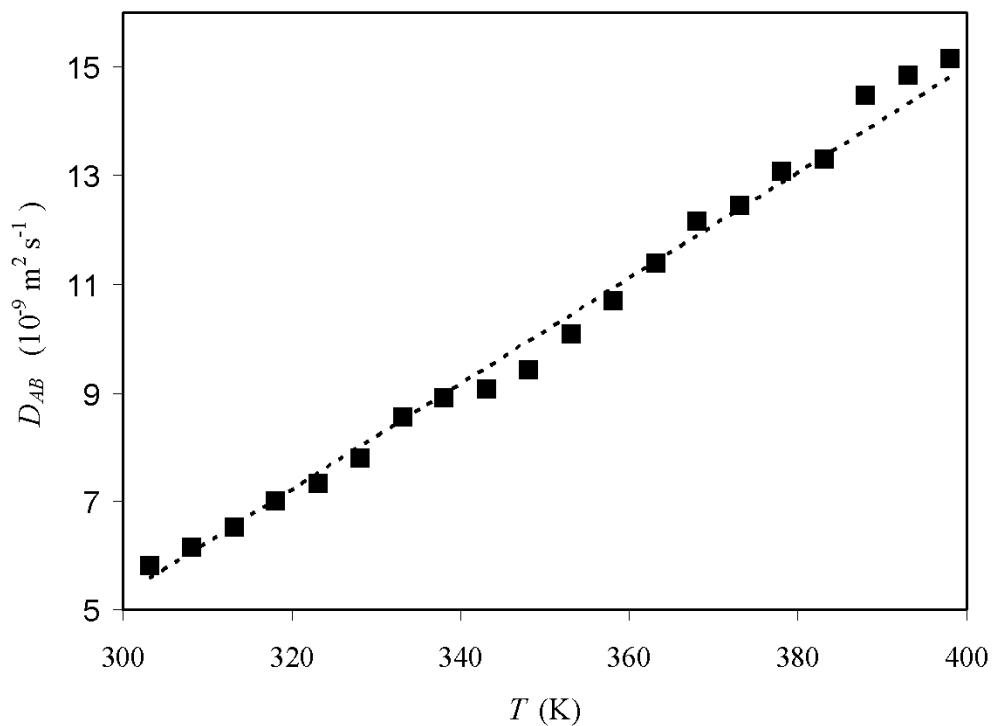


6

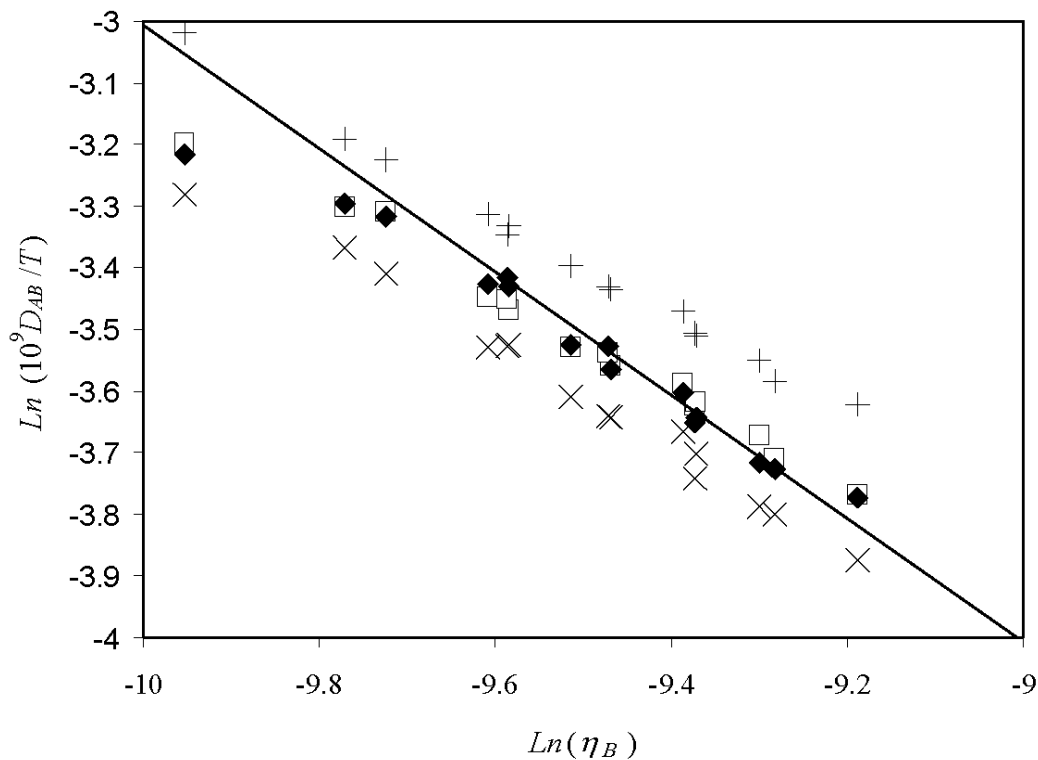
7 Fig. 2. Binary diffusivities of phenylacetylene as a function of pressure: (○) at 313.16 K, (△)
 8 at 323.16 K, (□) at 333.16 K. Solid line is the correlation with Eq.(3).



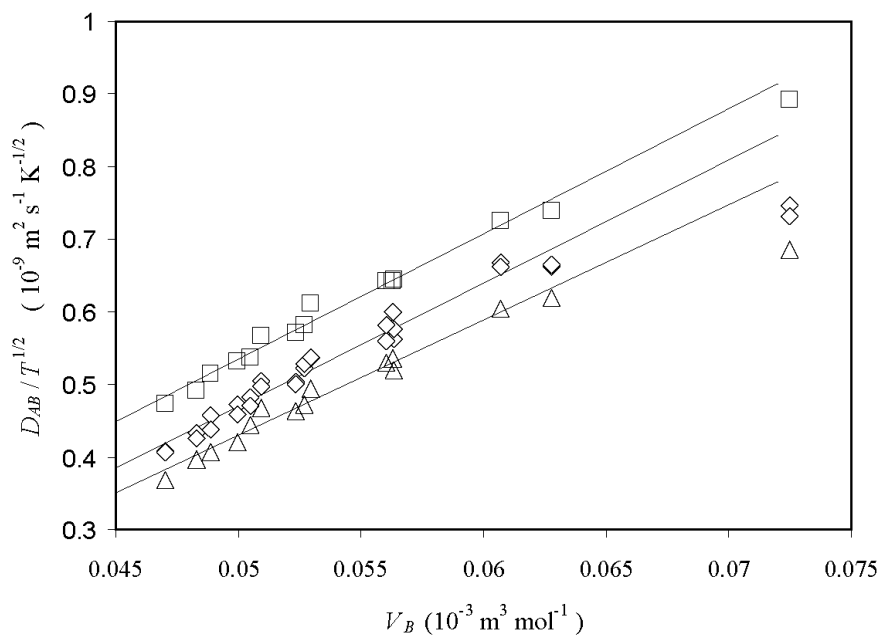
1
 2 Fig. 3. Binary diffusivities of 5-*tert*-butyl-*m*-xylene as a function of temperature: (◆) at 15.0
 3 MPa, (■) at 20.0 MPa, (▲) at 25.0 MPa, (◇) at 30.0 MPa, (○) at 35.0 MPa. Solid line is
 4 the correlation with Eq.(3).



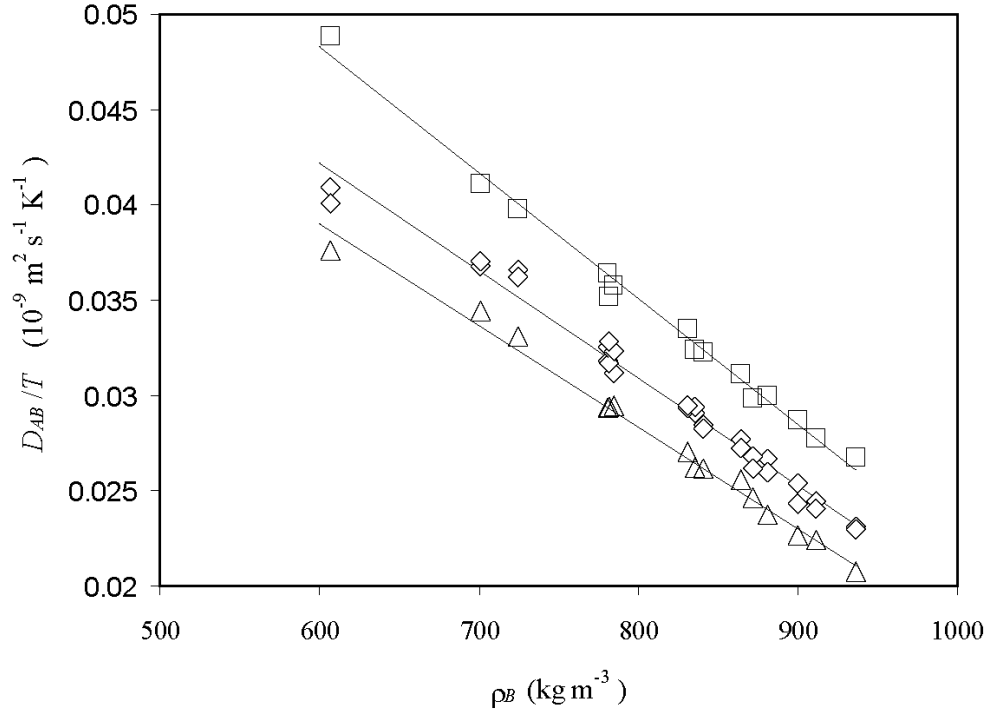
5
 6 Fig. 4. Binary diffusivities 5-*tert*-butyl-*m*-xylene as a function of temperature at 35.0 MPa
 7 (■). Broken line is the extrapolation of Eq. (3).



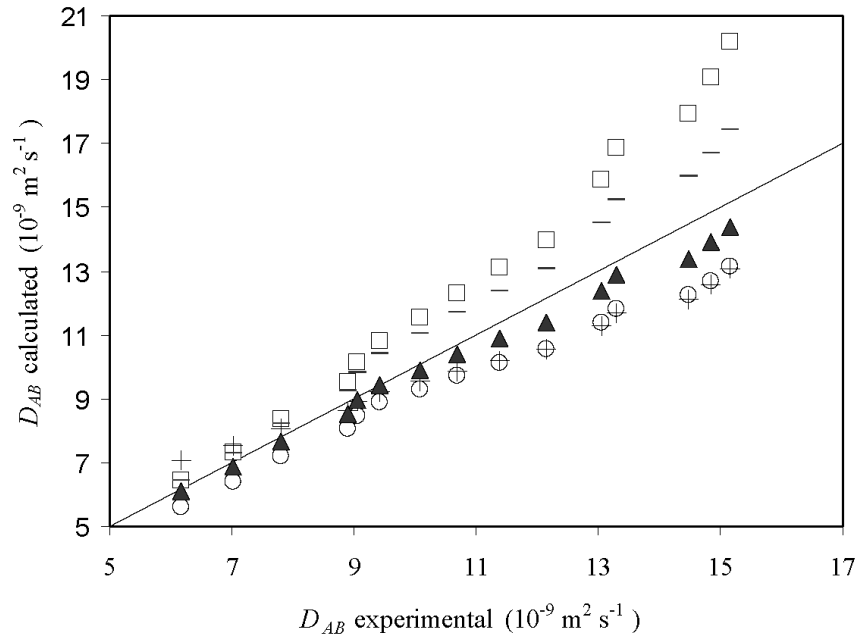
1
 2 Fig. 5. Logarithmic plot of the group D_{AB}/T vs. the viscosity of the solvent: phenylacetylene
 3 (+), 1,2-diethylbenzene (\square); 1,4-diethylbenzene (\bullet) and 5-*tert*-butyl-*m*-xylene (\times). Solid
 4 line corresponds to the slope of the Stokes-Einstein model.



5
 6 Fig. 6. Free volume plot of the diffusion coefficients in carbon dioxide: (\diamond) both
 7 diethylbenzenes, (\triangle) 5-*tert*-butyl-*m*-xylene, (\square) phenylacetylene. The lines are the free fitting
 8 to Eq.(6).



1
 2 Fig. 7. Free volume plot of the diffusion coefficients in carbon dioxide: (\diamond) both
 3 diethylbenzenes, (\triangle) 5-*tert*-butyl-*m*-xylene, (\square) phenylacetilene. The lines are the free
 4 fitting to Eq.(7).



5
 6 Fig. 8. Comparison of experimental and calculated diffusivities of 5-*tert*-butyl-*m*-xylene in
 7 carbon dioxide. (\square) He of 1998; (-) Scheibel; (\blacktriangle) He-Yu of 1997; (\circ) Funazukuri-Kong-
 8 Kagei; (+) Funazukuri-Hachisu-Wakao. The other equations give values very close to those
 9 of He-Yu and they have been omitted for clarity.

1 **LIST OF THE TABLES**

2

3 Experimental conditions, solvent densities, solvent viscosities and measured diffusivities of the four solutes in supercritical CO₂

4

T (K)	P (MPa)	ρ_B (kg m ⁻³)	η_B (10 ⁻⁶ kg m ⁻¹ s ⁻¹)	D_{AB} (10 ⁻⁹ m ² s ⁻¹)			
				1,2-diethylbenzene	1,4-diethylbenzene	5- <i>tert</i> -butyl- <i>m</i> -xylene	phenylacetylene
313.16	15.0	781.0	67.2	9.96 ± 0.12	10.18 ± 0.18	9.19 ± 0.20	11.39 ± 0.31
313.16	20.0	840.8	77.2	8.91 ± 0.07	8.86 ± 0.10	8.19 ± 0.15	10.10 ± 0.10
313.16	25.0	880.7	85.0	8.36 ± 0.16	8.13 ± 0.14	7.43 ± 0.09	9.39 ± 0.07
313.16	30.0	911.2	93.1	7.66 ± 0.09	7.53 ± 0.09	7.01 ± 0.08	8.69 ± 0.21
313.16	35.0	936.1	102.3	7.23 ± 0.08	7.20 ± 0.09	6.51 ± 0.14	8.38 ± 0.16
323.16	15.0	700.8	57.1	11.89 ± 0.20	11.96 ± 0.18	11.13 ± 0.23	13.29 ± 0.28
323.16	20.0	784.9	68.8	10.07 ± 0.27	10.45 ± 0.21	9.52 ± 0.21	11.55 ± 0.31
323.16	25.0	835.0	77.0	9.40 ± 0.08	9.50 ± 0.11	8.48 ± 0.14	10.47 ± 0.22
323.16	30.0	871.4	85.1	8.67 ± 0.16	8.46 ± 0.18	7.97 ± 0.07	9.65 ± 0.15
323.16	35.0	900.0	91.5	8.21 ± 0.14	7.86 ± 0.19	7.32 ± 0.11	9.27 ± 0.09
333.16	15.0	607.1	47.6	13.62 ± 0.27	13.36 ± 0.27	12.52 ± 0.10	16.27 ± 0.68
333.16	20.0	724.6	59.8	12.19 ± 0.15	12.07 ± 0.14	11.02 ± 0.20	13.24 ± 0.26
333.16	25.0	781.2	68.7	10.55 ± 0.18	10.95 ± 0.26	9.79 ± 0.16	11.73 ± 0.14
333.16	30.0	830.5	73.8	9.77 ± 0.13	9.82 ± 0.06	9.01 ± 0.16	11.16 ± 0.27
333.16	35.0	864.0	83.9	9.22 ± 0.14	9.07 ± 0.15	8.53 ± 0.13	10.36 ± 0.16

5

6

7

8

1 Table 2
 2 Fitting parameters for Eq.(3)
 3

Substance	α_1 ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	α_2 ($10^{-9} \text{ MPa.m}^2 \text{ s}^{-1}$)	α_3 ($10^{-9} \text{ m}^2 \text{ K}^{-1} \text{ s}^{-1}$)	α_4 ($10^{-9} \text{ MPa. m}^2 \text{ K}^{-1} \text{ s}^{-1}$)	AAD (%)
1,2-diethylbenzene	-2.865985	-690.0343	0.02612007	2.428264	1.01
1,4-diethylbenzene	-14.26748	-440.11830	0.06074527	1.668458	1.67
Both diethylbenzenes	-8.732404	-561.4805	0.04394508	2.037240	1.32
5- <i>tert</i> -butyl- <i>m</i> -xylene	-9.333806	-509.5728	0.04409616	1.859408	0.97
phenylacetylene	10.250400	-1077.476	-0.01300569	3.684484	1.32

4
 5
 6
 7
 8
 9
 10
 11
 12
 13
 14

1 Table 3

2 Extra data of diffusion coefficients for 5-*tert*-butyl-*m*-xylene at 35.0 MPa

3

T (K)	D_{AB} ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)
308.16	6.16
318.16	7.01
328.16	7.8
338.16	8.89
343.16	9.05
348.16	9.41
353.16	10.07
358.16	10.69
363.16	11.39
368.16	12.15
373.16	12.43
378.16	13.06
383.16	13.29
388.16	14.47
393.16	14.84
398.16	15.15

4

5

1 Table 4
 2 Fitting parameters for Eq.(5)
 3

Substance	θ_1	θ_2	AAD (%)
1,2-diethylbenzene	-10.000	-0.7752	1.30
1,4-diethylbenzene	-11.245	-0.8125	2.19
Both diethylbenzenes	-11.066	-0.7938	1.80
5- <i>tert</i> -butyl- <i>m</i> -xylene	-11.344	-0.8139	1.68
phenylacetylene	-10.919	-0.7915	1.03

4
 5 Table 5
 6 Free fitting of the two adjustable parameters for Eq.(6)
 7

Substance	C_1 ($10^{-9} \text{ mol s}^{-1} \text{ K}^{-0.5} \text{ m}^{-1}$)	$(V_B)_D$ ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)	AAD (%)
1,2-diethylbenzene	16294	21.051	1.94
1,4-diethylbenzene	17637	23.519	2.14
Both diethylbenzenes	16966	22.333	2.18
5- <i>tert</i> -butyl- <i>m</i> -xylene	15867	22.941	1.86
phenylacetylene	17283	19.082	1.31
Carbon dioxide ^a	38593	24.670	1.12

8 ^a Data of CO₂ self-diffusion in the same experimental conditions, interpolated from Groß et al [28]
 9

1
2
3
4
5
6
7
8
9
10
11
12
13

Table 6
Fitting parameters of Eq.(7)

Substance	C_1 ($10^{-15} \text{ m}^5 \text{ s}^{-1} \text{ K}^{-1} \text{ kg}^{-1}$)	$(\rho_B)_D$ (kg/m^3)	AAD (%)
1,2-diethylbenzene	55.709	1355.26	1.12
1,4-diethylbenzene	57.295	1338.69	1.86
Both diethylbenzenes	56.502	1346.86	1.55
5- <i>tert</i> -butyl- <i>m</i> -xylene	53.323	1331.51	1.22
phenylacetylene	65.884	1332.65	1.17
Carbon dioxide ^a	155.94	1227.40	1.50

^a Data of CO₂ self diffusion in the same experimental conditions, interpolated from Groß et al.[28]

1
2
3
4

Table 7
Properties of the studied substances

Property	1,2-diethylbenzene	1,4-diethylbenzene	5- <i>tert</i> -butyl- <i>m</i> -xylene	phenylacetylene	carbon dioxide
A^{vdW} (10^{-20} m ² molecule ⁻¹)	199.54	198.87	237.17	142.95	54.06
V^{vdW} (10^{-30} m ³ molecule ⁻¹)	155.20	155.11	187.41	110.70	34.12
Parachor ($\text{g}^{0.25}\text{cm}^3\text{mol}^{-1}\text{s}^{-0.5}$)	365.1	365.1	440.0	279.2	49.0
V_b (10^{-6} m ³ mol ⁻¹)	187.00	184.19	229.11	127.20	35.02
T_c (K)	669.6	657.9	684.85	655.41	304.10
P_c (MPa)	29.90	28.00	23.90	44.00	7.38
T_b (K)	457.00	456.94	480.16	418.41	194.70
V_c (10^{-6} m ³ mol ⁻¹)	487.50	480.50	591.75	337.50	93.90
M (10^{-3} kg mol ⁻¹)	134.22	134.22	162.28	102.14	44.01
ω	0.3540	0.4040	0.3803	0.2390	0.2390

5
6
7
8
9
10
11
12
13

1 Table 8

2 AAD (%) for predicting experimental data of Table 1

Equation	1,2- diethylbenzene	1,4-diethyl benzene	5- <i>tert</i> -butyl- <i>m</i> -xylene	phenylacetylene
Scheibel [30]	9.38	10.74	5.93	22.95
Wilke-Chang [30]	4.87	4.13	7.40	7.80
Reddy-Doraiswamy [34]	60.91	62.25	64.15	61.70
Luis-Ratcliff [35]	16.79	17.99	16.28	23.87
Tyn-Calus [36]	11.30	11.46	10.53	13.59
Kooijman [37]	32.26	32.34	30.25	37.32
Lai-Tan [38]	18.26	19.20	22.24	16.05
Liu-Ruckenstein [39] ^a	13.27	12.94	14.88	10.34
Woerlee [40]	27.58	26.51	30.69	18.03
Catchpole-King [41]	6.56	6.11	6.38	4.31
Eaton-Akgerman [42]	7.95	7.75	6.99	8.79
He of 1997 [43]	3.57	4.04	3.26	4.60
He of 1998 [44]	7.78	8.15	7.01	9.18
He-Yu of 1997 [45]	3.22	3.02	2.55	3.86
He-Yu of 1998 [46]	2.88	2.52	2.14	3.38
Liu-Silva-Macedo [27]	13.42	14.08	15.04	8.64
Funazukuri-Hachisu-Wakao [46]	7.28	7.64	5.06	13.64

Funazukuri-Kong-Kagei [14-17, 48]	3.27	2.84	5.09	6.70
Dariva-Coelho-Oliveira [49-51]	13.82	13.35	13.87	7.15
Zhu-Lu-Zhou-Wang-Shi [52]	10.00	9.32	10.65	8.84
Rah-Kwak-Eu-Lafleur [53] ^b	4.21	3.94	4.71	3.59

1 ^a For the three alkylbenzenes, the values of the interaction parameters of the Peng-Robinson equation of state were those suggested by Occhiogrosso et al. [54]. For
2 phenylacetylene, these values were those recommended by Liu and Ruckenstein.

3 ^b Self-diffusivities of carbon dioxide, required for the formula of Rah-Kwak-Eu-Lafleur were interpolated from Groß et al [28]
4
5

6 Table 9

7 AAD (%) of the best equations of Table 8 for the nineteen points of 5-*tert*-butyl-*m*-xylene at 35.0 MPa ranging from 308.16 to 398.16 K
8

Equation	AAD
Scheibel	9.17
Wilke-Chang	4.12
He of 1997	2.73
He of 1998	16.31
He-Yu of 1997	2.54
He-Yu of 1998	3.50
Funazukuri-Hachisu-Wakao	9.27
Funazukuri-Kong-Kagei	10.30
Rah-Kwak-Eu-Lafleur	7.54

9