Application of the Corresponding States Principle to the Diffusion in CO_2

Luis M. González, Octavio Suárez-Iglesias, Julio L. Bueno, Consuelo Pizarro, and Ignacio Medina
Dept. de Ingeniería Química y T.M.A., Universidad de Oviedo, 33071 Oviedo, Spain

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Binary diffusion coefficients at infinite dilution in supercritical carbon dioxide, D_{AB}, have been measured for the four monohalogenated benzenes (fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene) with the Taylor–Aris technique in a chromatographic apparatus as a function of temperature and pressure. The ranges covered for these two variables were 313–333 K and 15.0–35.0 MPa, respectively. As the four solutes are similar molecules, the corresponding states principle (CSP) has been tested, together with the results of several predictive equations. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 3054–3061, 2007

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Introduction

The CSP was proposed by van der Waals in 1873 and has been widely employed for the estimation of the compressibility factor of pure substances, *Z*. According to the CSP, compressibility is a universal function of reduced temperature, T_r ($= T/T_c$), and reduced pressure, P_r ($= P/P_c$), so only the critical properties T_c and P_c of each particular fluid need to be known to determine the molar volume, *V*.[1]

$$Z = \frac{PV}{RT} = f(T_r, P_r) \tag{1}$$

Nevertheless, Eq. 1 is only valid for simple fluids, and additonal variables have to be included in the universal function. The best well-known modification is that of Pitzer, who introduced the acentric factor ω, and made a linear expansion of the right term

$$Z = f(T_r, P_r, \omega) = f^{(0)}(T_r, P_r) + \omega f^{(1)}(T_r, P_r) \tag{2}$$

where $f^{(0)}$ is the function for spherical molecules and $f^{(1)}$ the deviation function. But Eq. 2 is only applicable for nonpolar or slightly polar materials. Quantic effects, polarity, and hydrogen-bonding ability require new variables, such as critical compressibilities, radii of gyration, dipolar moments, quadrupolar moments, polarizabilities, etc.[2]

To avoid the mathematical complexity of this procedure, the unknown compressibility of one substance can be determined from a linear interpolation between the compressibility of two similar fluids, in the form[3]

$$Z_B = Z_A + \frac{\omega_B - \omega_A}{\omega_C - \omega_A}(Z_C - Z_A) \tag{3}$$

here A and C are the substances for which *Z* is available, and B is the substance of interest. For all three, the compressibility factor has to be evaluated at the same reduced pressure and temperature.

For transport properties such as viscosity, thermal conductivity, and self-diffusion some expressions like Eqs. 1–3 have also been developed.[4,5] In these, *Z* is replaced by the reduced transport property, the critical value being a conveniently defined value. For example, the following emulation of Eq. 3 for selfdiffusion is due to Teja[6]:

$$D_{rB} = D_{rA} + \frac{\omega_B - \omega_A}{\omega_C - \omega_A}(D_{rC} - D_{rA}) \tag{4}$$

$$D_r = \frac{D}{D_c} \propto \frac{M^{1/2}D}{T_c^{1/2}V_c^{1/3}} \tag{5}$$

Correspondence concerning this article should be addressed to I. Medina at medina@uniovi.es.

where M is the molar mass. The proportionality constant is not important because it is common for the three substances.

In the case of binary diffusion at infinite dilution there are some problems with the definition of the reduced temperature and pressure. In principle, it could be thought these would be the solvent reduced properties T_{rB} (= T/T_{cB}), and P_{rB} (= P/P_{cB}), as assumed by Teja[6]

$$\left(\frac{D_{AB}M_A^{1/2}}{T_{cA}^{1/2}V_{cA}^{1/3}}\right) = \left(\frac{D_{1B}M_1^{1/2}}{T_{c1}^{1/2}V_{c1}^{1/3}}\right) + \frac{\omega_A - \omega_1}{\omega_2 - \omega_1}\left[\left(\frac{D_{2B}M_2^{1/2}}{T_{c2}^{1/2}V_{c2}^{1/3}}\right) - \left(\frac{D_{1B}M_1^{1/2}}{T_{c1}^{1/2}V_{c1}^{1/3}}\right)\right] \quad (6)$$

where D_{AB} is the unknown binary diffusivity of Solute A in Solvent B, and D_{1B} and D_{2B} the known diffusivities of Solutes 1 and 2 in the same solvent. Numbers are used instead of letters for clarity.

However, Teja developed Eq. 6 for diffusion in liquids. In gases at low pressures, the Chapman–Enskog formula is commonly employed[7]

$$D_{AB}^{\rho\to 0} = \frac{3}{8\rho_B(\sigma_{AB}^{IJ})^2}\sqrt{\frac{kT}{\pi m_{AB}}}\frac{1}{\Omega_{AB}^{(1,1)}} \quad (7)$$

where k is the Boltzmann constant, ρ_B is the number density of solvent (P/kT), σ_{AB} the solute–solvent mean diameter, defined as the arithmetic mean $0.5(\sigma_A + \sigma_B)$, and m_{AB} the molecular mean mass of the system, $2m_A\, m_B/(m_A + m_B)$. The superscript $\rho(0)$ indicates the low densitiy of the gas. The collision integral, $\Omega^{(1,1)}$ is a function of $T_{AB}^* = kT/\varepsilon_{AB}^{IJ}$, where $\varepsilon_{AB}^{IJ} = \sqrt{\varepsilon_A^{IJ}\varepsilon_B^{IJ}}$. Neufeld et al.[8] proposed for this

$$\Omega_{AB}^{(1,1)} = \frac{1.06036}{(T_{AB}^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635T_{AB}^*)} + \frac{1.03587}{\exp(1.52996T_{AB}^*)} + \frac{1.76474}{\exp(3.89411T_{AB}^*)} \quad (8)$$

ε^{LJ} and σ^{LJ} are the two characteristic Lennard–Jones parameters. These could be considered proportional to the critical temperature and to the cubic root of the critical volume respectively,[1] so

$$D_{AB}^{\rho\to 0} \propto \frac{T^{3/2}}{P(V_{cA}^{1/3} + V_{cB}^{1/3})^2}\sqrt{\frac{m_A + m_B}{m_A m_B}}\frac{1}{f\left(\frac{T}{\sqrt{T_{cA}T_{cB}}}\right)} \quad (9)$$

thus, the reduction criterion for temperature could be

$$T_r = T_{rAB} = \frac{T}{T_{cAB}} = \frac{T}{\sqrt{T_{cA}T_{cB}}} \quad (10)$$

but if Eq. 10 is applied, then the reduced pressure has to be defined as

$$P_r = P_{rAB} = \frac{P\left(\frac{V_{cA}^{1/3} + V_{cB}^{1/3}}{2}\right)^3}{R\sqrt{T_{cA}T_{cB}}} \quad (11)$$

however, as Eq. 11 does not reduce to P/P_{cB} when self-diffusion occurs, the critical compressibility of the mixture has to be introduced

$$P_r = \frac{P\left(\frac{V_{cA}^{1/3} + V_{cB}^{1/3}}{2}\right)^3}{Z_{cAB}R\sqrt{T_{cA}T_{cB}}} \quad (12)$$

And the critical diffusivity is

$$D_{cAB} \propto Z_{cAB}(V_{cA}^{1/3} + V_{cB}^{1/3})\frac{(T_{cA}T_{cB})^{1/4}}{m_{AB}^{1/2}} \quad (13)$$

Equations 11–13, with some modifications, are the base of the generalized charts of Bueno et al.,[9] who developed an expression equal to Eq. 2 for D_{AB}/D_{cAB} replacing ω with ω_{AB}. The acentric factor and the critical compressibilities of the mixture, ω_{AB} and Z_{AB} were taken as the arithmetic mean of the individual values. Nevertheless, the generalized charts do not cover the range $T_{rAB} < 1.0$, $D_{rAB} < 1.0$, in which the diffusivities of compressed liquids and supercritical fluids generally fall.

Excluding the works of Teja and Bueno et al., the majority of the authors who have dealt with the CSP have avoided this problem of critical conditions as they supposed that[4,10–12]

$$D_{AB} = \frac{(\rho_B D_{AB})^{\rho\to 0}}{(\rho D)_B^{\rho\to 0}}D_B = \left(\frac{2}{1 + \sigma_A^{LJ}/\sigma_B^{LJ}}\right)^2\left[\frac{1}{2}\left(1 + \frac{m_B}{m_A}\right)\right]^{1/2}\frac{\Omega_B^{(1,1)}}{\Omega_{AB}^{(1,1)}}D_B \quad (14)$$

In supercritical fluids, such as carbon dioxide, the CSP has not been analyzed in a rigorous way. The ability to calculate the diffusion coefficients of one compound from those of homologous molecules is interesting from an industrial point of view, because the values of D_{AB} are not always available for any Solute A. In the present work, the peak-broadening technique has been employed to determine the experimental diffusivities of the four monohalogenated benzenes in carbon dioxide at 313, 323, and 333 K and at five pressures between 15.0 and 35.0 MPa. Fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene are similar molecules, and their acentric factors have roughly the same value, thus the reduced diffusivity should be the same function for the four solutes. The form of this function and its predictive ability is discussed.

Experimental

Measurements were carried out with a commercial Hewlett-Packard G1205A supercritical fluid chromatograph (HP SFC), the same as that used by us in previous studies.[13,14] It consists of three parts as can be seen in Figure 1: the pump module, the oven module, and the multiple-wavelength UV detector (MWD), as well as an HP Vectra PC and an HP printer. All the equipment is computer controlled by means of software called "Chemstation," which allows the processing of experimental data on a microsoft windows-based platform. The SFC pump is reciprocating, and has a pressure range from 0 to 40.0 MPa. The oven can operate between 193 and 723 K. Solutes are manually injected as liquids into the stream of carbon dioxide through a Rheodyne model 7520 injector with a 0.2-μl loop connected to a port that activates the HP SFC software. The chromatographic column is

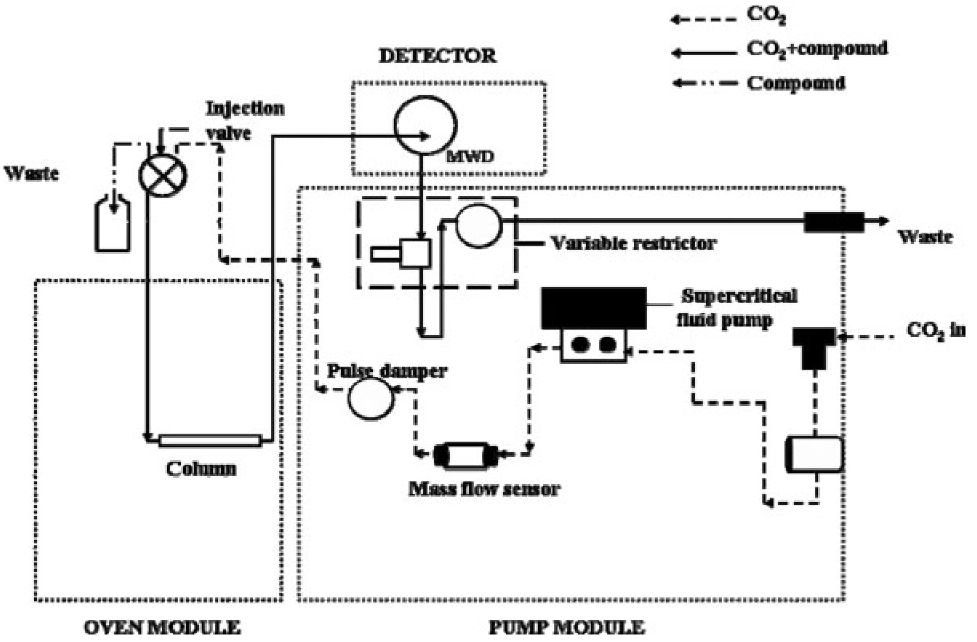

Figure 1. Experimental equipment.

a coiled stainless steel pipe of 0.762 mm i.d. × 30.48 m long, located inside the oven module. The variable restrictor is a backpressure control device located inside the pump module that consists of a pressure transducer and a nozzle.

The peak-broadening method is based on the work of Taylor,[15,16] who studied the dispersion of a pulse of solute in a solvent which flows in laminar regime through a straight pipe or chromatographic column. The pulse, which is modeled as a Dirac delta function, develops towards a Gaussian distribution, whose spatial variance s^2 is given by

$$s^2 = \frac{2D_{AB}L}{v_0} + \frac{r_0^2 v_0 L}{24D_{AB}} \tag{15}$$

where L is the length of the tube, r_0 its internal radius, and v_0 the average velocity of the solvent. Bearing in mind that in a Gaussian curve the variance can be related with the curve-width at half-height, $W_{1/2}$ (expressed in units of time), and the residence time, t_R (the time employed for the solute to cover the length L), the diffusivity can be obtained as

$$D_{AB} = \frac{v_0}{4}\left[\left(\frac{LW_{1/2}^2}{5.545t_R^2}\right) \pm \sqrt{\left(\frac{LW_{1/2}^2}{5.545t_R^2}\right)^2 - \left(\frac{r_0^2}{3}\right)}\,\right] \tag{16}$$

For liquids and supercritical fluids only the negative root of Eq. 16 is meaningful.[17] If the pipe is not straight but coiled, Eq. 16 can be applied if the following restriction is verified[18–20]

$$\left(\mathrm{Re}^2 \frac{r_0}{r_{\mathrm{coil}}}\right)\left(\frac{\eta_B}{m_B \rho_B D_{AB}}\right) < 100 \tag{17}$$

where Re is the Reynolds number, η the viscosity, and r_{coil} is the coil radius (0.13 m in our case). The HP SFC automatically measures $W_{1/2}$ and t_R.

Table 1. Experimental Diffusivities of Monohalogenated Benzenes in Carbon Dioxide (10^{-5} cm^2 s^{-1})

T (K)	P (MPa)	ρ (kg m^{-3})	10^6 η (Pa s)	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene
313	15.0	778.92	67.2	13.17 ± 0.10	12.16 ± 0.08	12.05 ± 0.05	10.66 ± 0.16
	20.0	822.17	77.2	11.20 ± 0.13	11.02 ± 0.11	10.99 ± 0.12	9.61 ± 0.08
	25.0	852.47	85.0	10.34 ± 0.16	10.27 ± 0.09	9.99 ± 0.19	9.17 ± 0.10
	30.0	876.03	93.1	9.27 ± 0.14	9.09 ± 0.09	8.77 ± 0.05	8.25 ± 0.09
	35.0	895.40	102.3	8.97 ± 0.14	8.86 ± 0.09	8.44 ± 0.14	7.98 ± 0.13
323	15.0	678.16	57.1	15.30 ± 0.46	13.36 ± 0.10	13.03 ± 0.16	12.30 ± 0.16
	20.0	745.26	68.8	12.90 ± 0.10	12.06 ± 0.11	12.09 ± 0.17	10.60 ± 0.09
	25.0	806.30	77.0	11.47 ± 0.15	11.08 ± 0.10	10.61 ± 0.14	9.88 ± 0.07
	30.0	846.20	85.1	11.00 ± 0.25	10.36 ± 0.20	9.83 ± 0.07	9.07 ± 0.13
	35.0	878.65	91.5	10.35 ± 0.07	10.10 ± 0.04	10.06 ± 0.16	8.96 ± 0.12
333	15.0	607.37	47.6	16.97 ± 0.34	15.82 ± 0.23	15.51 ± 0.21	13.81 ± 0.27
	20.0	700.86	59.8	14.90 ± 0.18	13.77 ± 0.15	13.30 ± 0.21	11.91 ± 0.15
	25.0	761.68	68.7	13.50 ± 0.23	13.07 ± 0.16	12.74 ± 0.12	11.47 ± 0.07
	30.0	807.12	73.8	12.70 ± 0.05	11.61 ± 0.12	11.30 ± 0.10	10.29 ± 0.20
	35.0	843.51	83.9	12.21 ± 0.33	11.51 ± 0.03	11.35 ± 0.14	9.72 ± 0.14

Table 2. Properties of the Studied Substances (Most of Them Necessary for Calculations of Table 3) Taken from the Literature[1,25–27] and from the Database of the Software HYSYS

Property	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene	Carbon dioxide
T_c (K)	560	632	670	721	304
P_c (MPa)	4.55	4.52	4.52	4.52	7.38
T_b (K)	358	405	429	462	195
V_c (cm^3 mol^{-1})	269	308	324	351	94
Z_c	0.263	0.265	0.263	0.265	0.274
M (g mol^{-1})	96.10	112.56	157.01	204.01	44.01
ω	0.244	0.249	0.251	0.249	0.239
r_g (Å)	3.345	3.568	3.61	3.808	0.992
μ_p (Debyes)	1.4	1.6	1.5	1.4	0.0
V_b (cm^3 mol^{-1})	101.54	114.47	120.13	129.86	35.02
Parachor (g$^{0.25}$ cm^3 mol^{-1} s$^{-0.5}$)	215.7	244.8	257.6	279.9	49.0
R^{vdW}	3.351	3.813	3.971	4.286	1.300
Q^{vdW}	2.524	2.844	2.952	3.112	1.120
ΔH_{vb} (kJ mol^{-1})	31.37	35.41	37.75	39.50	23.08

The four halogenated benzenes were supplied by Merck (synthesis grade), and have a minimum purity of 99%. The carbon dioxide was obtained from Air Liquide with a minimum purity of 99.998%. Each injection of solute is done at intervals of 10–15 min to avoid the overlapping of peaks at the end of the column, and the total mass flow varies between 0.14 and 0.12 g min^{-1}. The Gaussian curves at the end of the column are monitored by the MWD. The wavelengths at which the solutes were measured were 255, 261, and 267 nm for fluorobenzene, 259, 266, and 273 nm for chlorobenzene and bromobenzene, and 285, 290, and 295 nm for iodobenzene.

The dispersion curve for all experiments was Gaussian with a linear correlation of 0.9996–0.9998 between $\ln\langle c\rangle$ and χ^2 ($\langle c\rangle$ being the crosssectional average concentration and χ the distance from the peak apex). Peaks that have an asymmetric factor greater than 1.05 have been rejected for analysis.

The estimated concentrations of halogenated benzenes under their peaks at the tubing exit are always less than 3×10^{-4} (mole fraction) or 0.05% (volume percentage), which are of the same order of magnitude of those cited in the literature for other solutes.[21,22] Therefore, the infinite dilution behavior is expected.

Results and Discussion

Table 1 presents experimental data, together with the density[23] and viscosity[24] of pure carbon dioxide. Each data point is the average of 5–10 injections, and the reproducibility of the experimental points is 2% or better except for fluorobenzene, in which it reaches 3%. As the mass and volume of the halogens increase in the order F < Cl < Br < I, the general trend in the diffusivities is not unexpected. Fluorobenzene diffuses faster than chlorobenzene and in turn bromobenzene faster than iodobenzene. Nevertheless, the coefficients of chlorobenzene and bromobenzene are very similar. Table 2 shows several properties of the four benzene derivatives, and it can be seen that the relative difference in critical volume between bromobenzene and iodobenzene is of the same order of magnitude as that between chlorobenzene and bromobenzene. In addition, the relative difference in molar mass is smaller for bromobenzene and iodobenzene than for chlorobenzene and bromobenzene, so the similarity in the mobility of these last two solutes is not easily explained.

Suarez et al.[28] proposed the following correlations for the temperature and pressure dependence of diffusivities in supercritical carbon dioxide

$$D_{\mathrm{AB}} = \alpha_{\mathrm{P}} + \beta_{\mathrm{P}} T \quad \text{at constant pressure} \tag{18}$$

$$D_{\mathrm{AB}} = \alpha_{\mathrm{T}} + \beta_{\mathrm{T}}/P \quad \text{at constant temperature} \tag{19}$$

where β_{P} and β_{T} are nonnegative values, thus at constant temperature D_{AB} decreases when pressure rises, and at constant pressure, D_{AB} increases when temperature rises. These two formulas could be generalized, in a practical way, as

$$D_{\mathrm{AB}} = c_1 + \frac{c_2}{P} + c_3 T + c_4 \left(\frac{T}{P}\right) \tag{20}$$

Equation 20 can be combined with the CSP version of Teja to obtain

Table 3. Fitting Constant of Eq. 21 for the Four Solutes and for Each Solute Individually Together with Average Absolute Deviations (%)

	Four Solutes	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene
c_1 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	−1.558958	−2.473454	−1.273768	−1.978382	−0.550771
c_2 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	−2.452214	−1.032935	−2.805793	−1.250597	−4.610415
c_3 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	1.908955	2.746122	1.630279	2.325153	0.9724228
c_4 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	3.189208	1.975771	3.419451	2.072904	5.186013
AAD (%) for fluorobenzene	2.45	0.97	7.56	2.46	3.31
AAD (%) for chlorobenzene	6.30	8.31	1.85	10.17	6.66
AAD (%) for bromobenzene	3.73	3.29	9.11	2.60	3.86
AAD (%) for iodobenzene	1.93	3.86	6.15	3.64	1.28

Table 4. Fitting Constant of Eq. 22 for the Four Solutes and for Each Solute Individually Together with Average Absolute Deviations (%)

	Four Solutes	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene
c_1 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	−0.2822238	−2.662945	−1.366094	−1.89821	−0.4828975
c_2 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	−0.5745810	−0.419015	−1.106622	−0.4659168	−1.545886
c_3 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	1.033871	4.016022	2.523517	3.318521	1.32823
c_4 (10^{-5} g$^{1/2}$ cm s^{-1} K$^{-1/2}$ mol$^{-1/6}$)	1.251545	1.063124	1.942713	1.122135	2.673441
AAD (%) for fluorobenzene	7.74	0.98	15.83	26.53	23.52
AAD (%) for chlorobenzene	4.98	21.55	1.85	11.11	11.62
AAD (%) for bromobenzene	5.28	34.64	10.77	2.60	3.61
AAD (%) for iodobenzene	3.49	46.17	16.73	5.09	1.28

$$\frac{D_{\mathrm{AB}} M_{\mathrm{A}}^{1/2}}{T_{c\mathrm{A}}^{1/2} V_{c\mathrm{A}}^{1/3}} = c_1 + c_2 \frac{P_{c\mathrm{B}}}{P} + c_3 \frac{T}{T_{c\mathrm{B}}} + c_4 \left(\frac{P_{c\mathrm{B}} T}{P T_{c\mathrm{B}}} \right) \tag{21}$$

or with the CSP of Bueno et al., in which case

$$\frac{D_{\mathrm{AB}} \sqrt{\frac{2M_{\mathrm{A}}M_{\mathrm{B}}}{M_{\mathrm{A}}+M_{\mathrm{B}}}}}{(T_{c\mathrm{A}}T_{c\mathrm{B}})^{1/4} \left(\frac{V_{c\mathrm{A}}^{1/3}+V_{c\mathrm{B}}^{1/3}}{2} \right)} = c_1 + c_2 \frac{R\sqrt{T_{c\mathrm{A}}T_{c\mathrm{B}}}}{P \left(\frac{V_{c\mathrm{A}}^{1/3}+V_{c\mathrm{B}}^{1/3}}{2} \right)^3} + c_3 \frac{T}{\sqrt{T_{c\mathrm{A}}T_{c\mathrm{B}}}} + c_4 \frac{RT}{P \left(\frac{V_{c\mathrm{A}}^{1/3}+V_{c\mathrm{B}}^{1/3}}{2} \right)^3} \tag{22}$$

In this last expression, the compressibilities of the mixture are not taken into account as they are almost the same for the four substances. Fitting constants of Eqs. 21 and 22 applied to the four solutes at the same time are compiled in Tables 3 and 4, respectively, and as can be seen, the CSP of Teja is in general better than that of Bueno et al. When the equations are applied to one solute, and the diffusivities of the others are predicted, then the CSP of Teja is the best undoubtedly. This can also be seen in Tables 3 and 4.

Figures 2 and 3 show the results of Eqs. 21 and 22, respectively, for chlorobenzene when the 60-data points of the four solutes are employed to determine the fitting constants. It could be thought that the large deviations of the CSP of Bueno et al. were due to the fact that the data of only one solute was used caused by extrapolation, because $T_{c\mathrm{AB}}$ and $P_{c\mathrm{AB}}$ vary from solute to solute, but this is not the only cause. In Figure 2, the trend of Eq. 21 for chlorobenzene is correct, but experimental points are overestimated. In Figure 3 the predicted effect of the temperature is less than the real one, so at 313 K there is overestimation of diffusivities and at 333 K there is underestimation. This problem inherent in the CSP of Bueno et al. is common to the four halogenated benzenes.

To compare the predictive performance of Eq. 21 for D_{AB} taking the experimental values of only one solute, several predictive equations have been tested and their average absolute deviations (AAD) are listed in Table 5. The first 14 are based on the hydrodynamic model of Stokes–Einstein[4] and the following 12 are based on the Rough–Hard–Sphere model.[59–61] Equation 14 can also be considered a particular case of this last theory. Details of the input data and of calculations are given in the corresponding references. We only have to point out that

- For the formula of Nakanishi, molar volumes at 298 K were taken from Perry and Green,[25] except for carbon dioxide, calculated from V_{b} according to this author.

- The interaction parameter of the Peng–Robinson equation of state, which is necessary for the Liu–Ruckenstein expression, was taken for chlorobenzene from Wu et al.[62] For the other solutes the interaction parameters recommended by Liu and Ruckenstein were chosen.

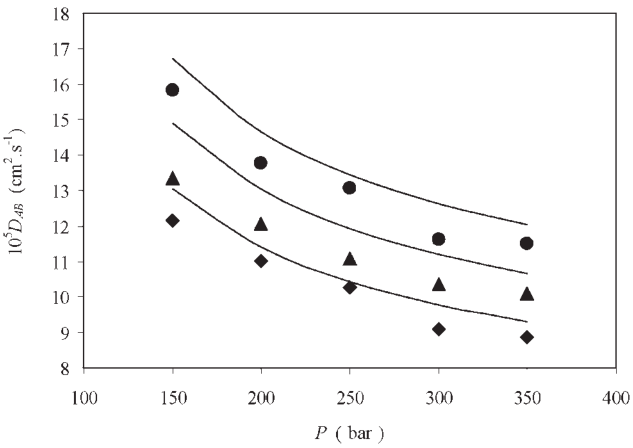

Figure 2. Experimental and correlated diffusivities of chlorobenzene with Eq. 21.

● at 333 K; ▲ at 323 K; ♦ at 313 K. The symbols are the experimental values and the solid lines are the calculated values.

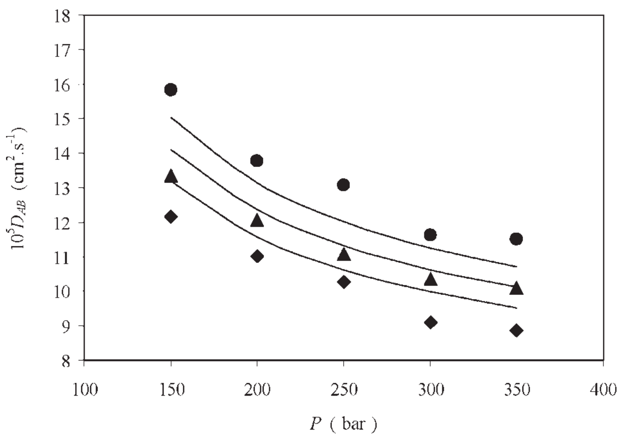

Figure 3. Experimental and correlated diffusivities of chlorobenzene with Eq. 22.

● at 333 K; ▲ at 323 K; ♦ at 313 K. The symbols are the experimental values and the solid lines are the calculated values.

Table 5. AAD(%) for Several Predictive Equations

Equation	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene
Wilke-Chang[1]	11.10	8.26	7.85	12.27
Scheibel[1]	26.68	21.73	20.54	26.22
Reddy-Doraiswamy[29]	59.43	60.43	61.53	73.55
Lusis-Ratclif[30]	23.85	21.75	21.58	28.98
Tyn-Calus[31]	12.95	13.34	13.13	8.73
Nakanishi[32]	9.18	8.87	8.34	5.48
Kooijman[33]	38.08	35.57	35.77	40.72
King-Hsue-Mao[34]	13.55	10.53	9.31	16.03
Sitaraman-Ibrahim-Kuloor[35]	4.05	4.98	5.38	19.50
Umesi-Danner[36]	6.77	7.28	6.47	5.94
Lai-Tan[37]	10.88	12.40	13.58	22.62
Liu-Ruckenstein[38]	7.74	7.43	7.83	15.40
Woerlee[39]	13.45	17.34	18.59	15.56
Hippler-Schubert-Troe[40,41]	6.32	7.39	7.52	12.80
Catchpole-King[42]	6.21	8.28	9.81	6.87
Eaton-Akgerman[43]	11.77	11.71	11.47	4.50
He (1997)[44]	5.08	7.77	18.32	20.85
He (1998)[45]	3.92	6.24	15.21	17.63
He-Yu (1997)[46]	6.03	8.84	19.50	21.98
He-Yu (1998)[47]	6.05	8.65	20.01	22.47
Funazukuri–Hachisu–Wakao[48]	10.42	10.85	8.66	13.63
Funazukuri–Kong–Kagei[49–52]	6.51	5.54	4.87	5.89
Zhu et al.[53]	9.41	8.76	8.98	11.98
Liu–Silva–Macedo[54]	8.73	12.38	16.63	13.98
Dariva–Coelho–Oliveira[55–57]	9.87	12.11	14.55	11.74
Rah-Kwak-Eu-Lafleur[58]	4.23	7.25	9.35	6.89
Eq. 14	14.96	19.39	23.45	21.68

- The Lennard–Jones molecular parameters employed in the Hippler–Schubert–Troe equation and in Eq. 14 were calculated with the empirical formulas of Chung.[1] These formulas of Chung were also employed for calculating the diameter of the excluded volume in the Woerlee equation, $b = (2/3)\pi N_{av}\sigma^3$.

- Diffusivities at low pressure in the equation of Funazukuri–Hachisu–Wakao were calculated with the formula of Fuller et al.[1] Viscosities at low pressure are from Stephan and Lucas.[24]

- The self-diffusion of carbon dioxide, which is necessary in Eq. 14 and in the equation of Rah–Kwak–Eu–Lafleur, was interpolated from Groß et al.[63]

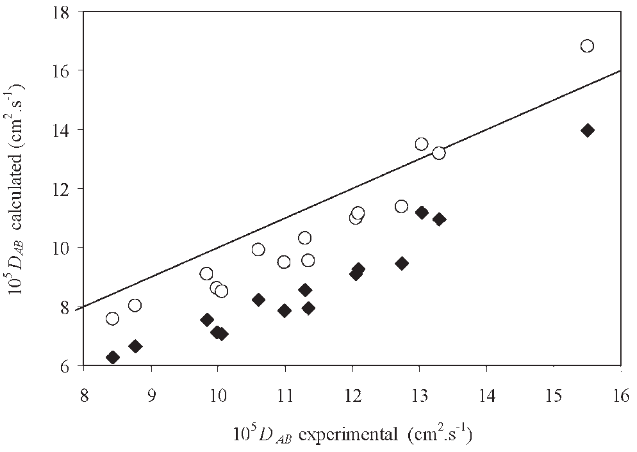

Figure 4. Calculated versus experimental diffusivities for bromobenzene.

♦ with Eq. 14; ○ with Eq. 14 obviating the effect of the collision integrals.

Equations of Nakanishi, Umesi–Danner, Catchpole–King, and Funazukuri–Kong–Kagei give deviations lower than 10% for the four solutes, but the best of all is the last one, in which AADs < 7%. Bearing in mind the deviations reported in the last four columns of Table 3, the CSP of Teja is as good as these equations or better, and can be applied to calculate diffusivities in supercritical carbon dioxide. Besides, there is no method of determining "a priori" which of the formulas in Table 5 is the best for a given binary system.

On the other hand, Eq. 14 systematically underestimates the diffusivities of the four compounds. Its results are presented in Figure 4 for bromobenzene, as an example. Better results are obtained if the collision integrals ratio of this formula is taken as equal to unity, as suggested by Rah et al.[58] for diffusion in liquids. In this last case, the underestimation is less severe and in three experimental conditions there is a general trend to overestimation: 323 K–15.0 MPa, 333 K–15.0 MPa, and 333 K–20.0 MPa, which coincide with the highest values of the diffusion coefficients.

Conclusions

Binary diffusivities of fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene in carbon dioxide have been measured through the peak-broadening method in a supercritical chromatograph at pressures from 15.0 to 35.0 MPa and temperatures ranging from 313 to 333 K, and the corresponding states principle of Teja (1985), developed for liquid systems has been applied to these successfully.

Experimental diffusion coefficients take values from 16.97×10^{-5} to 7.98×10^{-5} cm^2 s^{-1}, and the decreasing order fluorobenzene > chlorobenzene > bromobenzene > iodobenzene can be established. In addition, the difference between chlorobenzene and bromobenzene is much less than expected.

Notation

b = excluded volume, cm^3 mol^{-1}
c_i = fitting constants of Eqs. 20–22
D = diffusion coefficient, cm^2 s^{-1}
f () = mathematical function
k = Boltzmann constant = 1.380658 × 10^{-22} bar cm^3 K^{-1} molecule^{-1}
L = length of the Taylor–Aris tube, cm
LJ = Lennard–Jones
M = molar mass, g mol^{-1}
m = molecular mass, g molecule^{-1}
N_{av} = Avogadro number, 6.023 × 10^{23} molecules mol^{-1}
P = pressure, bar
Q^{vdW} = van der Waals surface parameter
R^{vdW} = van der Waals volume parameter
R = gas constant, 83.14 bar cm^3 K^{-1} mol^{-1}
Re = Reynolds number
r_0 = radius of the Taylor–Aris tube, cm
r_{coil} = coil radius, cm
r_g = radius of gyration, Å
s^2 = spatial variance of a Gaussian curve, cm^2
T = absolute temperature, K
t_R = retention time, s
V = molar volume, cm^3 mol^{-1}
v_0 = average velocity of a fluid in the Taylor–Aris pipe, cm s^{-1}
$W_{1/2}$ = curve-width at half-height, cm
Z = compressibility factor

Greek letters

α_P = empirical constant of Eq. 18
α_T = empirical constant of Eq. 19
β_P = empirical constant of Eq. 18
β_T = empirical constant of Eq. 19
ΔH_v = heat of vaporization, kJ mol^{-1}
η = viscosity, g. cm^{-1} · s^{-1}
μ_p = dipolar moment, Debye
ρ = number density, molecules.cm^{-3}
σ = molecular diameter, cm
$\Omega^{(1,1)}$ = collision integral for diffusion
ω = acentric factor

Superscripts

* = molecular-reduced property
(0) = refers to spherical molecules
(1) = refers to the deviation from spherical geometry
LJ = Lennard–Jones
vdW = van der Waals

Subscripts

1B, 2B = refers to the diffusion of Solutes 1 or 2 in Solvent B
A = solute
B = solvent
AB = refers to the mixture of A and B
b = normal boiling point
c = critical conditions
r = reduced property with respect to critical conditions

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