Binary Diffusion Coefficients of 2-Ethyltoluene, 3-Ethyltoluene, and 4-Ethyltoluene in Supercritical Carbon Dioxide[†]

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The binary diffusion coefficients of 2-ethyltoluene, 3-ethyltoluene, and 4-ethyltoluene in supercritical carbon dioxide were determined in a pressure range of (15.0 to 35.0) MPa at temperatures of (313, 323, and 333) K by means of the Taylor−Aris dispersion technique. The influence of pressure, temperature, density, and viscosity on the binary diffusion coefficients was examined, and some general trends were established. The experimental results were compared with the values estimated by several semiempirical equations based on the Stokes−Einstein formula and on the Rough−Hard−Sphere model.

Introduction

In recent years, research has been carried out in the field of supercritical fluid technology. Supercritical carbon dioxide has many desirable properties as a solvent for biomaterials, including foods. Its main advantages include the quality of the extract and its safe and environmentally friendly operating procedures. On the other hand, the capital investment cost is high due to the high-pressure equipment employed. At supercritical conditions, the fluid exists as a single phase, possessing the favorable properties of both a liquid and a gas. Its density is sufficient to afford substantial dissolution power. The diffusivity of the solutes is higher than in liquids, and the viscosity is lower. Consequently, mass transfer is enhanced. In addition, its low viscosity and the absence of surface tension in supercritical fluids increase the speed of percolation. Thus, the passage of the solvent through the interstices of the matrix is facilitated.

Knowledge of properties like solubility or diffusion coefficient in supercritical carbon dioxide is essential for evaluating the feasibility of supercritical separation processes and for establishing optimum conditions of operation. The data available on diffusivity are limited, but recent research has increased the database for binary diffusion coefficients and has made it possible to explore their influence on solute diffusivities.[1−12] Furthermore, good predictive and correlation methods for diffusion coefficients in supercritical carbon dioxide are desirable.

During the past two decades, a number of investigators have published diffusion coefficient data for various benzene derivatives in supercritical carbon dioxide. However, we were unable to find any reports on the diffusivity of the compounds 2-ethyltoluene, 3-ethyltoluene, and 4-ethyltoluene. In the present work, diffusion coefficients for these compounds are reported in the following range of temperatures, (313, 323, and 333) K, and pressures, (15.0, 20.0, 25.0, 30.0, and 35.0) MPa. The objective was to examine the differences in diffusivity values for the three isomers. Moreover, the validity of several predictive equations for binary diffusion coefficients is discussed.

Experimental Section

The experimental apparatus used was a commercial supercritical fluid chromatograph Hewlett-Packard G1205A which had been employed in previous studies.[13−15] The system consists of a pumping module, a column oven, an injection valve, a mass flow sensor, a detector, a variable restrictor, and SFC ChemStation software. The HP SFC uses an electrothermally cooled reciprocating pump to supply supercritical fluids to the system. The oven module can accommodate capillary and standard HPLC columns. The injection valve is a Rheodyne model 7520 injector of ultralow dispersion with a 0.2 μL loop. The mass flow sensor is a device located inside the pumping module. In the present work, this unit uses a multiple wavelength UV detector. 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 the mobile phase to control pressure. The SFC ChemStation consists of a PC and HP SFC software.

The temperature and the pressure were controlled within 1 K and 0.1 MPa, respectively. The system was made to run for at least 60 min at the desired temperature and pressure prior to sample injection. The solutes were introduced into the carbon dioxide stream by means of the injection valve (a Rheodyne model 7520 injector). The diffusion column consists of one stainless steel tube (0.762 mm i.d. and 30.48 m in length). The measurements were repeated at least 5 times, at intervals of (12 to 15) min to avoid any overlap of peaks, and the uncertainty is estimated as the standard deviation of all measurements from the average. A great majority of the uncertainties are within 2 %, but they tend to increase at 333 K and 15.0 MPa, in the cases of 3-ethyltoluene and 4-ethyltoluene. This may result from the experimental failure of our apparatus at low densities of supercritical carbon dioxide.

The carbon dioxide used in this work was supplied by Air Liquide at a purity of 99.998 %. 2-Ethyltoluene, 3-ethyltoluene, and 4-ethyltoluene were supplied by Merck (synthesis grade). The 2-ethyltoluene had a minimum purity of 99 %, whereas 3-ethyltoluene and 4-ethyltoluene had a minimum purity of 98 %. All three were used as received without further purification. The multiple wavelength UV detector monitored the solute at three wavelengths for each compound: (263, 265, and 272)

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Table 1. Experimental Values of D_{AB} for the Three Substances Studied

		ρ^a	$10^6\eta^b$	$10^9D_{AB}/(m^2\cdot s^{-1})$		
T/K	P/MPa	$(kg\cdot m^{-3})$	(Pa·S)	2-ethyltoluene	3-ethyltoluene	4-ethyltoluene
313	15.0	778.92	67.2	10.56 ± 0.11	10.57 ± 0.12	10.53 ± 0.14
	20.0	822.17	77.2	9.94 ± 0.19	9.89 ± 0.12	9.64 ± 0.09
	25.0	852.47	85.0	8.97 ± 0.08	8.96 ± 0.13	8.87 ± 0.13
	30.0	876.03	93.1	8.23 ± 0.08	8.12 ± 0.07	8.08 ± 0.14
	35.0	895.4	102.3	7.76 ± 0.06	7.71 ± 0.08	7.55 ± 0.09
323	15.0	678.16	57.1	12.63 ± 0.23	12.64 ± 0.23	12.43 ± 0.13
	20.0	745.26	68.8	11.49 ± 0.19	11.48 ± 0.11	10.90 ± 0.11
	25.0	806.3	77.0	10.42 ± 0.23	10.43 ± 0.10	9.98 ± 0.13
	30.0	846.2	85.1	9.66 ± 0.09	9.37 ± 0.12	9.04 ± 0.09
	35.0	878.65	91.5	8.82 ± 0.06	8.74 ± 0.10	8.64 ± 0.14
333	15.0	607.37	47.6	14.30 ± 0.24	14.17 ± 0.50	14.52 ± 0.69
	20.0	700.86	59.8	12.64 ± 0.24	12.45 ± 0.13	12.45 ± 0.12
	25.0	761.68	68.7	11.94 ± 0.15	12.13 ± 0.17	11.11 ± 0.11
	30.0	807.12	73.8	10.62 ± 0.16	10.73 ± 0.10	10.63 ± 0.2
	35.0	843.51	83.9	10.28 ± 0.19	10.19 ± 0.13	9.99 ± 0.21

[a] From the equation of state of Pitzer and Screiber.[20] [b] From Stephan and Lucas.[21]

nm for 2-ethyltoluene and 3-ethyltoluene; and (260, 266, and 274) nm for 4-ethyltoluene. The reliability of the experimental measurements was assessed by comparing them with the diffusivities of benzene in supercritical carbon dioxide in a previous work.[16]

Results and Discussion

The most widely used technique for determining diffusion coefficients in dense fluids is the Taylor−Aris procedure. With this method, a solute is injected into a capillary tube, and it is eluted as a Gaussian peak. The diffusion coefficient of one solute A in a solvent B, D_{AB}, is related to the peak-width at half-height, $W_{1/2}$ (expressed in units of time), through the following equation.[17−19]

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

where L is the length of the tube; r_0 is its internal radius; v_0 is the average velocity of the solvent; and t_R is the residence time (the time employed for the solute to cover the length L).

The diffusion coefficients of the three ethyltoluenes in supercritical carbon dioxide at the 15 experimental conditions mentioned above are presented in Table 1, together with the solvent densities and viscosities. The densities (ρ) were calculated by means of the equation of state of Pitzer and Schreiber,[20] and the viscosities (η) were taken from Stephan and Lucas.[21] 2-Ethyltoluene and 3-ethyltoluene diffuse equally well within the same margin of experimental error. The diffusivities measured range from $(14.52\cdot10^{-9}$ to $7.55\cdot10^{-9})$ $m^2\cdot s^{-1}$, and the accuracy of the measurements decreases as the pressure decreases.

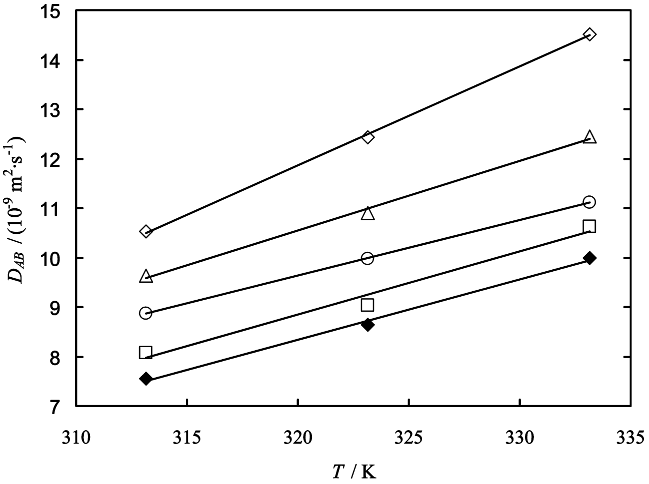

Figure 1. Binary diffusivities of 4-ethyltoluene as a function of temperature: ◇, 15 MPa; △, 20 MPa; ○, 25 MPa; □, 30 MPa; ♦, 35 MPa.

Table 2 shows useful properties of solutes and solvent for calculating D_{AB} through semiempirical equations. At the same solvent conditions, binary diffusivities in Hard−Sphere fluids depend only on solute mass and diameter.[22] In Lennard-Jones systems, the depth of the potential well is also taken into account.[23,24] In real substances, shape, polarity, and hydrogen bonds have importance too.[25−30] Molar volumes at critical or normal boiling point can be employed for calculating molecular diameters[31,32] and temperatures at the same points for determining depths of potential well.[33,34] The acentric factor[35] and radius of gyration[36−38] are rough measurements of molecular sphericity.

Given all of these properties, it is not easy to explain the experimental results because according to A^{vdW}, V^{vdW}, T_b, and T_c the isomers 3-ethyltoluene and 4-ethyltoluene should be those which diffuse at an equal speed, and according to the critical volumes, the diffusivities of 2-ethyltoluene and 4-ethyltoluene should be those which are the closest. If acentric factors and the radii of gyration are taken into account, none of the three solutes should exhibit the same diffusion coefficient.

The dependence of the diffusivities on temperature, density, and viscosity is illustrated in Figures 1 to 3 for 4-ethyltoluene. The trends are the same as for the other isomers. D_{AB} decreases as the pressure increases under constant temperature, as is shown in Figure 1, but this decrease is more marked at lower pressures.

Table 2. Properties of the Studied Substances

property	symbol/unit	2-ethyltoluene	3-ethyltoluene	4-ethyltoluene	CO_2
critical temperature[a]	T_c/K	651.00	637.00	640.00	304.10
critical pressure[a]	P_c/MPa	3.04	2.84	2.94	7.38
normal boiling temperature[a]	T_b/K	438.30	434.50	435.20	194.70
critical volume[a]	$10^6V_c/(m^3\cdot mol^{-1})$	460.00	490.00	470.00	93.90
volume at normal boiling point[b]	$10^6V_b/(m^3\cdot mol^{-1})$	175.960	188.005	179.981	35.020
molar mass[a]	$10^3M/(kg\cdot mol^{-1})$	120.194	120.194	120.194	44.010
acentric factor[a]	ω	0.2940	0.3600	0.3220	0.2390
radius of gyration[c]	$10^{10}r_g$/m	4.10667	4.12014	4.15043	0.92200
van der Waals volume[d]	$10^{30}V^{vdW}/m^3$	177.04	178.05	178.06	54.058
van der Waals surface[d]	$10^{20}A^{vdW}/m^2$	137.81	137.97	137.95	34.117
parachor[e]	$P/(g^{0.25}\cdot cm^3\cdot mol^{-1}\cdot s^{-0.5})$	325.1	325.1	325.1	49.0

[a] From the Korea Thermophysical Properties Data Bank (whose Web site is http://infosys.korea.ac.kr/kdb/). [b] From the Handbook of Perry and Green.[38] [c] From the HYSYS software. [d] Calculated by means of the CS Chem3D software. [e] From the textbook of Reid et al.[37]

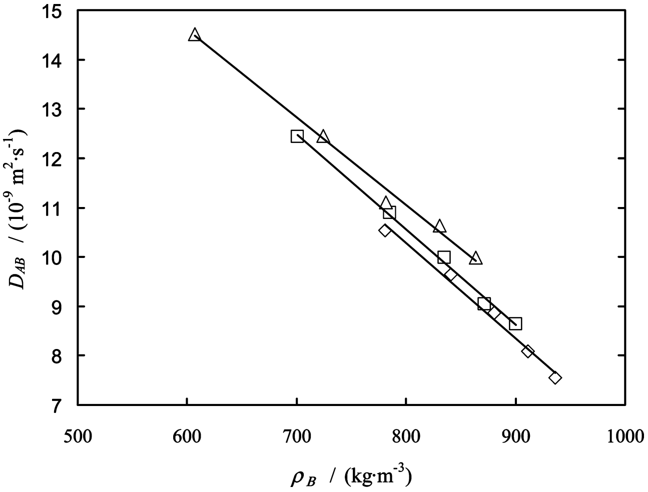

Figure 2. Binary diffusivities of 4-ethyltoluene as a function of solvent density: ◇, 313 K; □, 323 K; △, 333 K.

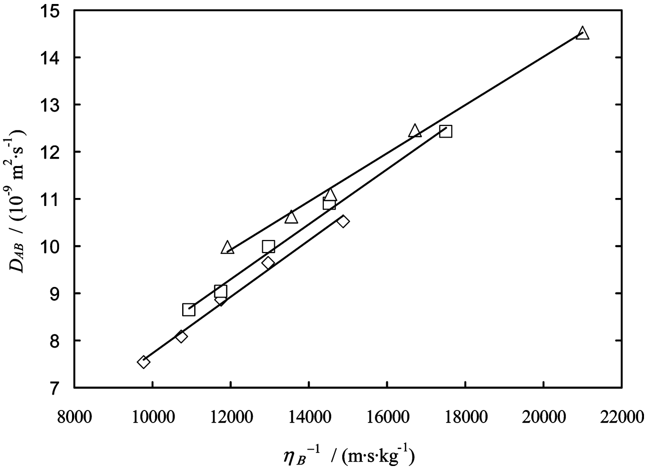

Figure 3. Binary diffusivities of 4-ethyltoluene plotted versus the inverse values of solvent viscosity: ◇, 313 K; □, 323 K; △, 333 K.

Table 3. AAD for Several Predictive Equations

	100 AAD[a]		
equation	2-ethyltoluene	3-ethyltoluene	4-ethyltoluene
Scheibel[37]	5.3	4.6	5.9
Wilke−Chang[37]	8.9	11.7	7.5
Reddy−Doraiswamy[39]	51.1	48.5	53.8
Lusis−Ratcliff[40]	10.5	7.7	12.2
Tyn−Calus[41]	13.5	12.4	10.8
Umesi−Danner[42]	6.6	6.6	4.7
Kooijman[43]	28.5	29.6	32.3
Lai−Tan[44]	10.6	9.1	12.8
Liu−Ruckenstein[45]	7.7	5.1	9.4
Woerlee[46]	30.5	32.9	29.6
Catchpole−King[47]	11.0	12.4	9.1
Eaton−Akgerman[48]	13.6	14.6	11.8
He of 1997[49]	4.4	4.5	3.8
He of 1998[50]	4.9	5.3	7.2
He−Yu of 1997[51]	5.1	5.0	3.5
He−Yu of 1998[52]	4.8	4.6	3.0
Liu−Silva−Macedo[53]	17.5	18.0	15.5
Funazukuri−Hachisu−Wakao[54]	5.8	6.7	8.4
Funazukuri−Kong−Kagei[55−58]	4.4	4.3	4.0
Dariva−Coelho−Oliveira[59−61]	17.5	19.0	15.9
Zhu−Lu−Zhou−Wang−Shi[62]	9.6	10.0	9.2
Rah−Kwak−Eu−Lafleur[63]	6.5	7.1	5.0

[a] AAD is the average absolute deviation.

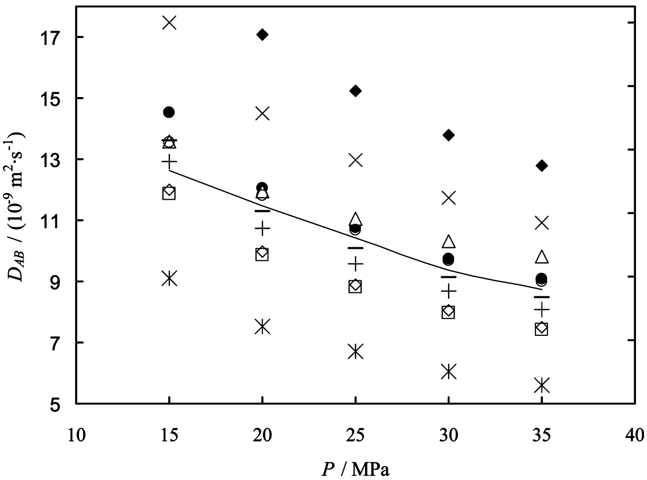

Figure 4. Binary diffusivities of 3-ethyltoluene in carbon dioxide at 323 K as a function of pressure. Solid line represents experimental data, and symbols are the calculated values with the expressions based in the SE model: −, Scheibel;[37] ◇, Wilke−Chang;[37] ♦, Reddy−Doraiswamy;[39] ●, Lusis−Ratcliff;[40] □, Tyn−Calus;[41] +, Umesi−Danner;[42] ×, Kooijman;[43] △, Lai−Tan;[44] ○, Liu−Ruckenstein;[45] *, Woerlee.[46]

Figure 1 shows the relationship between diffusivity and temperature at constant pressure: D_{AB} increases with temperature, the increase being higher at lower pressures. Figures 2 and 3 show an almost linear relationship between D_{AB} and the variables ρ and $1/\eta$, respectively, at fixed temperature. High pressures, densities, or viscosities mean that the solvent molecules are closer together, thereby impeding the movement of the solute particles. On the other hand, high temperatures indicate high kinetic energies, so that the molecules are able to diffuse faster.

Table 3 contains the average absolute deviations (AAD) of 22 predictive equations for the three isomers studied in this work. The first nine are based on the hydrodynamic model of Stokes−Einstein (SE), and the others are derived from the Rough−Hard−Sphere theory (RHS). The interaction parameters of the Peng−Robinson equation of state (which are necessary for the Liu−Ruckenstein expression) were those suggested by Ochiogrosso et al.[64] The transport properties at low pressures (required for the Funazukuri−Hachisu−Wakao expression) were calculated by means of the formula of Fuller[37] or taken from Stephan and Lucas,[21] and the self-diffusivities of the carbon dioxide (employed in the formula of Rah−Kwak−Eu−Lafleur) were interpolated from Groβ et al.[65] Only the formulas of Scheibel, Umesi−Danner, Liu−Ruckenstein, He, He−Yu, Rah−Kwak−Eu−Lafleur, and Funazukuri and co-workers give deviations lower than 10 % for all the solutes, that of Funazukuri−Kong−Kagei being the best, because in no case does the AAD exceed 4.4 %.

The predictions of the SE-type equations for the diffusivities of 3-ethyltoluene at 323 K are presented in Figure 4, and the results of the RHS-type formulas for the same solute are provided in Figure 5. They were all developed from some theoretical basis, and their results compared with a limited amount of experimental data. So if the shortcomings of SE and RHS models are not taken into account, and the starting database is not wide enough, large underestimations or overestimations can be found between predicted and real diffusivities when the equations are applied to new substances, temperatures, and pressures. For example, Wilke−Chang, Tyn−Calus, Woerlee, Catchpole−King, Eaton−Akgerman, Liu−Silva−Macedo, and Dariva−Coelho−Oliveira generally underestimate the experimental values, while Reddy−Doraiswamy, Lusis−Ratcliff, Kooijman, Lai−Tan, and Liu−Ruckenstein tend to overestimate the experimental points.

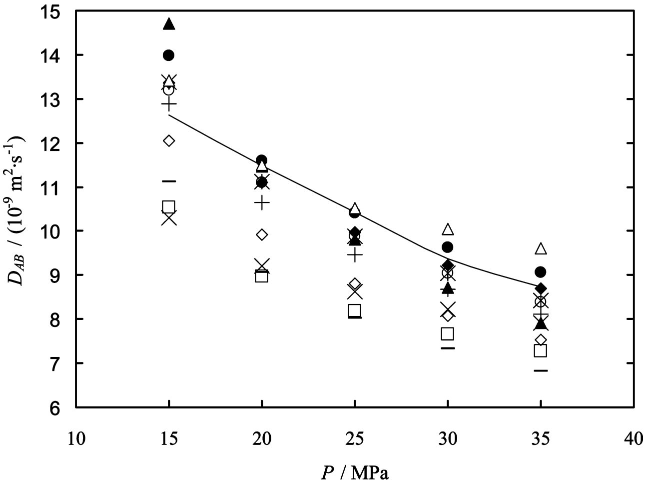

Figure 5. Binary diffusivities of 3-ethyltoluene in carbon dioxide at 323 K as a function of pressure. Solid line represents experimental data, and symbols are the calculated values with the expressions based in the RHS model: ◇, Catchpole−King;[47] ×, Eaton−Akgerman;[48] ◆, He of 1997;[49] ●, He of 1998;[50] *, He−Yu of 1997;[51] ○, He−Yu of 1998;[52] △, Funazukuri−Hachisu−Wakao;[54] □, Liu−Silva−Macedo;[53] ▲, Zhu−Lu−Zhou−Wang−Shi;[62] −,Dariva−Coelho−Oliveira;[59−61] +,Rah−Kwak−Eu−Lafleur.[63] For the sake of clarity, the results of Funazukuri−Kong−Kagei, which are very similar to those of He−Yu of 1998, are not included.

Conclusions

The binary diffusivities of 2-ethyltoluene, 3-ethyltoluene, and 4-ethyltoluene at infinite dilution in carbon dioxide were measured by the Taylor−Aris chromatographic method in the ranges of (313 to 333) K and (15.0 to 35.0) MPa (supercritical state). As was expected, an increase in pressure, density, or viscosity at constant temperature causes a decrease in diffusion, and if the temperature rises while the other three variables remain unchanged, the diffusivity increases.

Several predictive equations, such as those developed by He, He−Yu, and Funazukuri−Kong−Kagei, predict experimental points with good accuracy. Nevertheless, others like Woerlee and Reddy−Doraiswamy give errors higher than 29 %.

Literature Cited

(1) Pizarro, C.; Suárez-Iglesias, O.; Medina, I.; Bueno, J. L. Diffusion coefficients of n-butylbenzene, n-pentylbenzene, 1-phenylhexane, 1-phenyloctane, and 1-phenyldodecane is supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **2008**, *47*, 6783–6789.
(2) Suárez-Iglesias, O.; Medina, I.; Pizarro, C.; Bueno, J. L. Limiting diffusion coefficients of ethylbenzoate, benzylacetone, and eugenol in carbon dioxide at supercritical conditions. *J. Chem. Eng. Data* **2008**, *53*, 779–784.
(3) Raspo, I.; Nicolas, C.; Neau, E.; Meradji, S. Diffusion coefficients of solids in supercritical carbon dioxide: modeling of near critical behaviour. *Fluid Phase Equilib.* **2008**, *263*, 214–222.
(4) Pizarro, C.; Suárez-Iglesias, O.; Medina, I.; Bueno, J. L. Molecular diffusion coefficients of phenylmethanol, 1-phenylethanol, 2-phenylethanol, 2-phenyl-1-propanol, and 3-phenyl-1-propanol in supercritical carbon dioxide. *J. Supercrit. Fluids* **2008**, *43*, 469–476.
(5) González, L. M.; Suárez-Iglesias, O.; Bueno, J. L.; Pizarro, C.; Medina, I. Application of the corresponding status principle to the diffusion in CO_2. *AIChE J.* **2007**, *53*, 3054–3061.
(6) Suárez-Iglesias, O.; Medina, I.; Pizarro, C.; Bueno, J. L. Diffusion coefficients of 2-fluoroanisole, 2-bromoanisole, allylbenzene and 1,3-divynylbenzene at infinite dilution in supercritical carbon dioxide. *Fluid Phase Equilib.* **2007**, *260*, 279–286.
(7) Pizarro, C.; Suárez-Iglesias, O.; Medina, I.; Bueno, J. L. 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. *J. Chromatogr. A* **2007**, *1167*, 202–209.
(8) Kong, C. Y.; Takahashi, N.; Funazukuri, T.; Kagei, S. Measurements of binary diffusion coefficients and retention factors for dibenzo-24-crown-8 and 15-crown-5 in supercritical carbon dioxide by chromatographic impulse response technique. *Fluid Phase Equilib.* **2007**, *257*, 223–227.
(9) González, L. M.; Suárez-Iglesias, O.; Bueno, J. L.; Pizarro, C.; Medina, I. Limiting binary diffusivities of aniline, styrene, and mesitylene in supercritical carbon dioxide. *J. Chem. Eng. Data* **2007**, *52*, 1286–1290.
(10) Funazukuri, T.; Kong, C. Y.; Kagei, S. Simultaneous determination of binary diffusion coefficients from multiple response curves by chromatographic measurements. *J. Chromatogr. A* **2007**, *1150*, 105–111.
(11) Suárez-Iglesias, O.; Medina, I.; Pizarro, C.; Bueno, J. L. Diffusion of benzyl acetate, 3-phenylethyl acetate, and dibenzyl ether in mixtures of carbon dioxide and ethanol. *Ind. Eng. Chem. Res.* **2007**, *46*, 3810–3819.
(12) Yisong, H.; Yiwen, Y.; Pingdong, W. Binary diffusion coefficients of arachidonic acid ethyl esthers, cis-5,8,11,14,17-eicosapentaenoic acid ethyl esthers, and cis-4,7,10,13,16,19-docosahexanenoic acid ethyl esthers in supercritical carbon dioxide. *J. Chem. Eng. Data* **2007**, *52*, 555–559.
(13) Medina, I.; Bueno, J. L. Solubilities of zopiclone and nimodipine in supercritical carbon dioxide. *J. Chem. Eng. Data* **2001**, *46*, 1211–1214.
(14) González, L. M.; Bueno, J. L.; Medina, I. Determination of binary diffusion coefficients of anisole, 2,4-dimethylphenol, and nitrobenzene in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 3711–3716.
(15) González, L. M.; Bueno, J. L.; Medina, I. Measurement of diffusion coefficients for 2-nitroanisole, 1,2-dichlorobenzene and tert-butylbenzene in carbon dioxide containing modifiers. *J. Supercrit. Fluids* **2002**, *24*, 219–229.
(16) Bueno, J. L.; Suárez, J. J.; Dizy, J.; Medina, I. Infinite dilution diffusion coefficients: benzene derivatives as solutes in supercritical carbon dioxide. *J. Chem. Eng. Data* **1993**, *38*, 344–349.
(17) Aris, R. Dispersion of a solute by diffusion, convection, and exchange between phases. *Proc. R. Soc. A (London)* **1959**, *252*, 538–550.
(18) Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. The theory of the Taylor dispersion technique for liquid diffusivity measurements. *Int. J. Thermophys.* **1980**, *1*, 243–284.
(19) Liong, K. K.; Wells, P. A.; Foster, N. R. Diffusion in supercritical fluids. *J. Supercrit. Fluids* **1991**, *4*, 91–108.
(20) Pitzer, K. S.; Schreiber, D. R. Improving equation-of-state accuracy in the critical region; equations for carbon dioxide and neopentane as examples. *Fluid Phase Equilib.* **1988**, *41*, 1–17.
(21) Stephan, K.; Lucas, K. *Viscosity of dense fluids*; Plenum.Press: New York, 1979.
(22) Alder, B. J.; Alley, W. E.; Dymond, J. H. Molecular dynamics XIV. Mass and size dependence of the binary diffusion coefficient. *J. Chem. Phys.* **1974**, *53*, 3813–3826.
(23) Yamaguchi, T.; Kimura, Y.; Hirota, N. Molecular dynamics simulation of solute diffusion in Lennard Jones fluids. *Mol. Phys.* **1998**, *94*, 527–537.
(24) Ould-Kaddour, F.; Levesque, D. Molecular dynamics investigation of tracer diffusion in a simple liquid: text of the Stokes-Einstein law. *Phys. Rev. E.* **2000**, 011205/1–011205/9.
(25) Easteal, A. J.; Woolf, L. A. Solute-solvent interaction effects on tracer diffusion coefficients. *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 1287–1295.
(26) Chan, T. C. Diffusion of pseudospherical molecules: an investigation on the effects of dipole moment. *J. Chem. Phys.* **1983**, *79*, 3591–3593.
(27) Chan, T. C. Diffusion of aromatic compounds: an investigation on the effects of molecular shape, mass, and dipole moment. *J. Chem. Phys.* **1984**, *80*, 5862–5864.
(28) Chan, T. C.; Chan, M. L. Diffusion of pseudo-planar molecules: an experimental evaluation of the molecular effects on diffusion. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2371–2374.
(29) Chan, M. L.; Chan, T. C. Diffusion of pseudoplanar solutes: an investigation on the effects of hydrogen bonding. *J. Phys. Chem.* **1995**, *99*, 5765–5768.
(30) Chan, T. C.; Ma, N. L.; Chen, N. The effects of molecular association on mutual diffusion in acetone. *J. Chem. Phys.* **1997**, *107*, 1890–1895.
(31) Chen, N. H.; Othmer, D. F. New generalized equation for gas diffusion coefficients. *J. Chem. Eng. Data* **1962**, *7*, 37–41.
(32) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular theory of gases and liquids*; John Wiley & Sons: New York, 1964.
(33) Halm, R. L.; Stiel, L. I. A fourth parameter for the vapor pressure and entropy of vaporization of polar fluids. *AIChE J.* **1967**, *13*, 351–355.
(34) Bauer, H. Correspondence principle for transport properties of dense fluids. *Ind. Eng. Chem. Fundam.* **1974**, *13*, 286–287.

(35) Bosse, M. A.; Reich, R. Correlation for the third virial coefficient using Tc, Pc, bipolar polarizability and mean radius of gyration as parameters. *Chem. Eng. Commun.* **1988**, *66*, 83–99.

(36) Tarakad, R. R.; Danner, R. P. An improved corresponding states method for polar fluids: correlation of second virial coefficients. *AIChE J.* **1977**, *23*, 685–695.

(37) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(38) Perry, R. H.; Green, D. W. *Chemical Engineer's Handbook (Spanish edition)*, 7th ed.; McGraw-Hill: Madrid, 2001.

(39) Reddy, K. A.; Doraiswamy, L. K. Estimating liquid diffusivity. *Ind. Eng. Chem. Fundam.* **1967**, *6*, 77–79.

(40) Lusis, M. A.; Ratcliff, G. A. Diffusion in binary liquid mixtures at infinite dilution. *Can. J. Chem. Eng.* **1968**, *46*, 385–387.

(41) Tyn, M. T.; Calus, W. F. Diffusion coefficients in dilute binary liquid systems. *J. Chem. Eng. Data* **1975**, *20*, 106–109.

(42) Umesi, N. O.; Danner, R. P. Predicting diffusion coefficients in non polar solvents. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 662–665.

(43) Kooijman, H. A. A modification of the Stokes-Einstein equation for diffusivities in dilute binary mixtures. *Ind. Eng. Chem. Res.* **2002**, *41*, 3326–3328.

(44) Lai, C.-C.; Tan, C.-S. Measurement of molecular diffusion coefficients in supercritical carbon dioxide using a coated capillary column. *Ind. Eng. Chem. Res.* **1995**, *34*, 674–680.

(45) Liu, H.; Ruckenstein, E. Predicting the diffusion coefficients in supercritical fluids. *Ind. Eng. Chem. Res.* **1997**, *36*, 888–895; Correction in 1997, 37, 3524.

(46) Woerlee, G. F. Expression for the viscosity and diffusivity product applicable for supercritical fluids. *Ind. Eng. Chem. Res.* **2001**, *40*, 465–469.

(47) Catchpole, O. J.; King, M. B. Measurement and correlation of binary diffusion coefficients in near critical fluids. *Ind. Eng. Chem. Res.* **1994**, *33*, 1828–1837; Correction in 1997, 36, 4013.

(48) Eaton, A. P.; Akgerman, A. Infinite-dilution diffusion coefficients in supercritical Fluids. *Ind. Eng. Chem. Res.* **1997**, *36*, 923–931.

(49) He, C.-H. Prediction of binary diffusion coefficients of solutes in supercritical solvents. *AIChE J.* **1997**, *43*, 2944–2947.

(50) He, C.-H. Infinite-dilution diffusion coefficients in supercritical and high-temperature liquid solvents. *Fluid Phase Equilib.* **1998**, *147*, 309–317.

(51) He, C.-H.; Yu, Y.-S. Estimation of infinite-dilution diffusion coefficients in supercritical fluids. *Ind. Eng. Chem. Res.* **1997**, *36*, 4430–4433.

(52) He, C.-H.; Yu, Y.-S. New equation for infinite-dilution diffusion coefficients in supercritical and high-temperature liquid solvents. *Ind. Eng. Chem. Res.* **1998**, *37*, 3793–3798.

(53) Liu, H.; Silva, C. M.; Macedo, E. A. New equations for tracer diffusion coefficients of solutes in supercritical and liquid solvents based on the Lennard-Jones fluid model. *Ind. Eng. Chem. Res.* **1997**, *36*, 246–252; Correction in **1998**, 37, 308.

(54) Funazukuri, T.; Hachisu, S.; Wakao, N. Measurement of binary diffusion coefficients of C16-C24 unsaturated fatty acid methyl esters in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **1991**, *30*, 1323–1329.

(55) Higashi, H.; Iwai, Y.; Arai, Y. Solubilities and diffusion coefficients of high boiling compounds in supercritical carbon dioxide. *Chem. Eng. Sci.* **2001**, *56*, 3027–3044.

(56) Higashi, H.; Iwai, Y.; Takahashi, Y.; Uchida, H.; Arai, Y. Diffusion coefficients of naphthalene and dimethylnaphthalene in supercritical carbon dioxide. *Fluid Phase Equilib.* **1998**, *144*, 269–278.

(57) Funazukuri, T.; Kong, C. Y.; Kagei, S. Effects of molecular weight and degree of unsaturation on binary diffusion coefficients for lipids in supercritical carbon dioxide. *Fluid Phase Equilib.* **2004**, *219*, 67–73.

(58) Funazukuri, T.; Kong, C. Y.; Kikuchi, T.; Kagei, S. Measurements of binary diffusion coefficient and partition ratio at infinite dilution for linoleic acid and arachidonic acid in supercritical carbon dioxide. *J. Chem. Eng. Data* **2003**, *48*, 684–688.

(59) Dariva, C.; Coelho, L. A. F.; Oliveira, J. V. Predicting diffusivities in dense fluid mixtures. *Braz. J. Chem. Eng.* **1999**, *16*, 213–227.

(60) Dariva, C.; Coelho, L. A. F.; Oliveira, J. V. A kinetic approach for predicting diffusivities in dense fluid mixtures. *Fluid Phase Equilib.* **1999**, *158−160*, 1045–1054.

(61) Coelho, L. A. F.; Marchut, A.; De Oliveira, J. V.; Balbuena, P. B. Theoretical studies of energetics and diffusion of aromatic compounds in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **2000**, *39*, 227–235.

(62) Zhu, Y.; Lu, X.; Zhou, J.; Wang, Y.; Shi, J. Prediction of diffusion coefficients for gas, liquid and supercritical fluid: application to pure real fluids and infinite dilute binary solutions based on the simulation of Lennard-Jones fluid. *Fluid Phase Equilib.* **2002**, *194−197*, 1141–1159.

(63) Rah, K.; Kwak, S.; Eu, B. C.; Lafleur, M. Relation of tracer diffusion coefficient and solvent self-diffusion coefficient. *J. Phys. Chem. A* **2002**, *106*, 11841–11845.

(64) Occhiogrosso, R. N.; Igel, J. T.; McHugh, M. A. Phase behavior of carbon dioxide-aromatic hydrocarbon mixtures. *Fluid Phase Equilib.* **1986**, *26*, 165–179.

(65) Groβ, T.; Buchhauser, J.; Lüdemann, H.-D. Self-diffusion in fluid carbon dioxide at high pressures. *J. Chem. Phys.* **1998**, *109*, 4518–4522.

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