

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

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Abstract

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, a lot of 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 solubilities or diffusion coefficients 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, 20, 25, 30 and 35 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 μ l 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 (12-15) 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) 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 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 its internal radius, v_0 the average velocity of the solvent and t_R 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.²⁰

2-Ethyltoluene and 3-ethyltoluene diffuse equally well within the same margin of experimental error. The diffusivities measured range from $14.52 \times 10^{-9} \text{ m}^2/\text{s}$ to $7.55 \times 10^{-9} \text{ m}^2/\text{s}$, the accuracy of the measurements decreasing as the pressure decreases.

Table 2 shows useful properties of solutes and solvent for calculating DAB 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 factor³⁵ and radius of gyration³⁶⁻³⁸ 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. 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 Fuller³⁷ 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 Groß et al.⁶⁵ Only the formulas of Scheibel, Umesi-Danner, Liu-Ruckenstein, He, He-Yu, Rah-Kwak-Eu-Lafleur and Funazukuri and coworkers 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, Lysis-Ratcliff, Kooijman, Lai-Tan and Liu-Ruckenstein tend to overestimate the experimental points.

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 – 333) K and (15.0 – 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 %.

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FIGURES

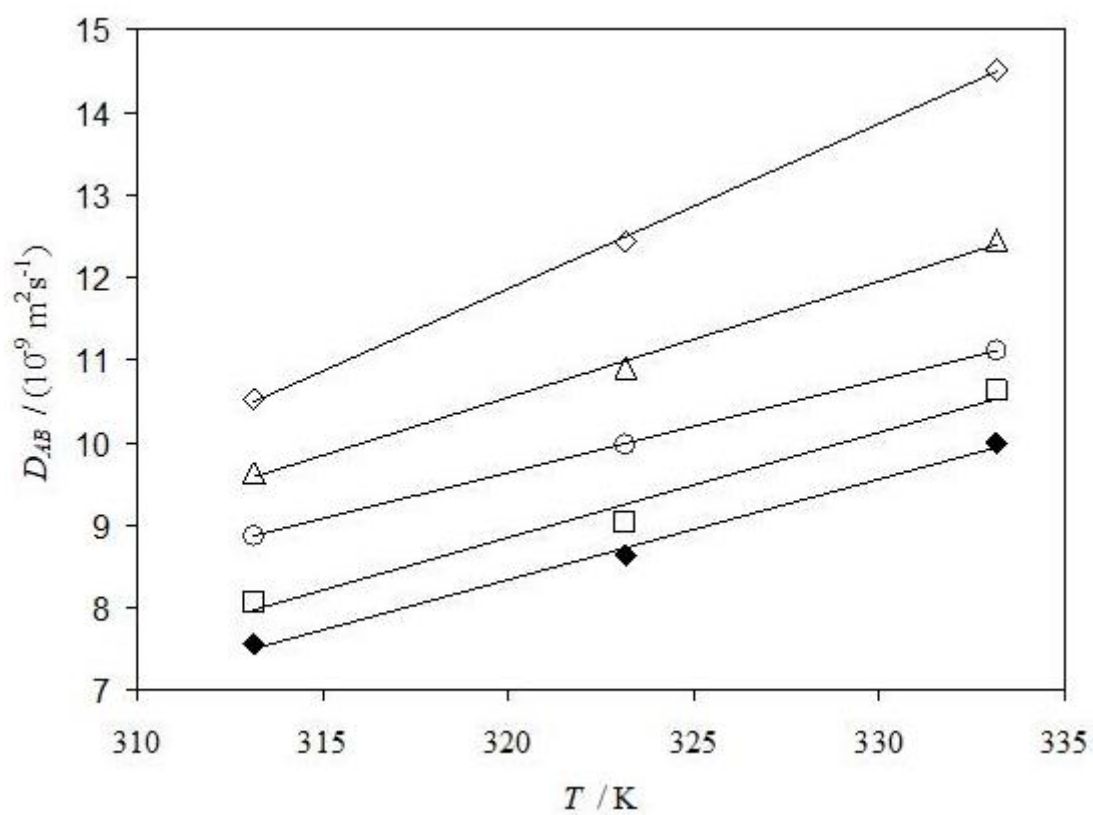


Figure 1. Binary diffusivities of 4-ethyltoluene as a function of temperature: (\diamond) at 15 MPa, (\triangle) at 20 MPa, (\circ) at 25 MPa, (\square) at 30 MPa, (\blacklozenge) at 35 MPa.

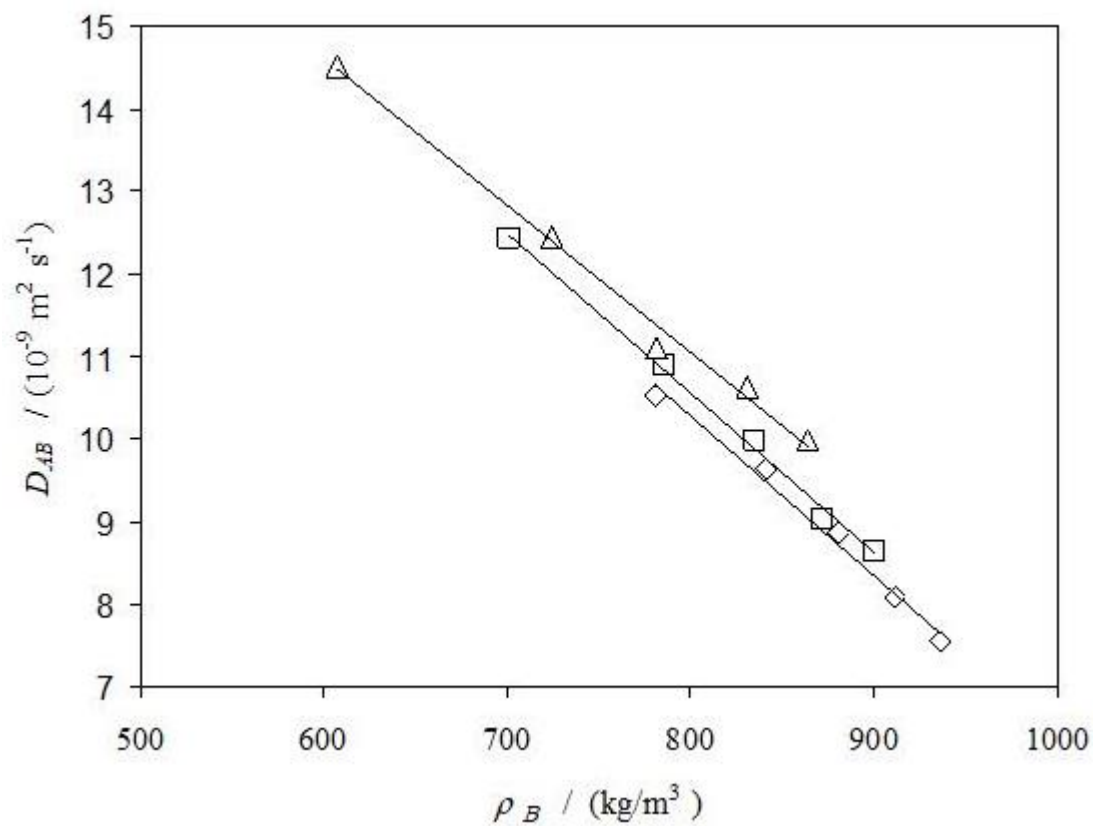


Figure 2. Binary diffusivities of 4-ethyltoluene as a function of solvent density: (\diamond) at 313.15 K, (\square) at 323.15 K, (\triangle) at 333.15 K.

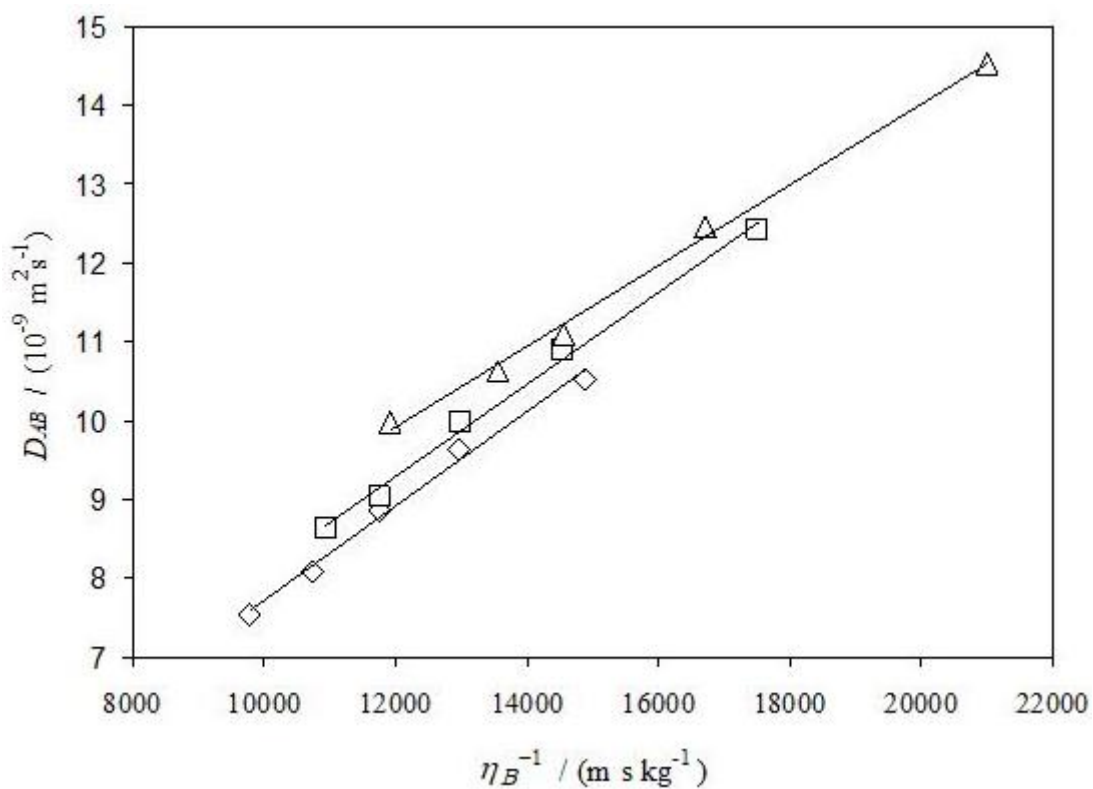


Figure 3. Binary diffusivities of 4-ethyltoluene plotted versus the inverse values of solvent viscosity: (\diamond) at 313.15 K, (\square) at 323.15 K, (\triangle) at 333.15 K.

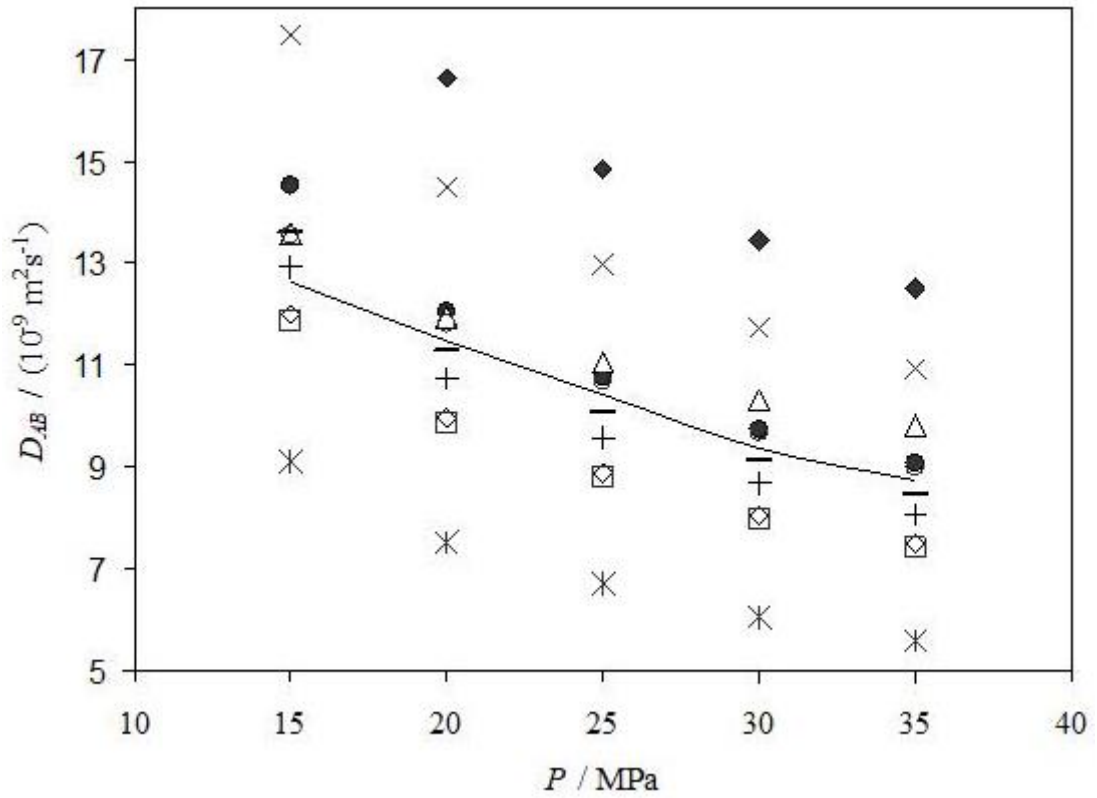


Figure 4. Binary diffusivities of 3-ethyltoluene in carbon dioxide at 323.15 K as a function of pressure. The solid line represents the experimental data and the symbols represent the values calculated with the expressions based on the SE model: (---) Scheibel, (\diamond) Wilke-Chang; (\blacklozenge) Reddy-Doraiswamy, (\bullet) Lusi-Ratcliff, (\square) Tyn-Calus, (+) Umesi-Danner, (x) Kooijman, (\triangle) Lai-Tan, (\circ) Liu-Ruckenstein, (\ast) Woerlee.

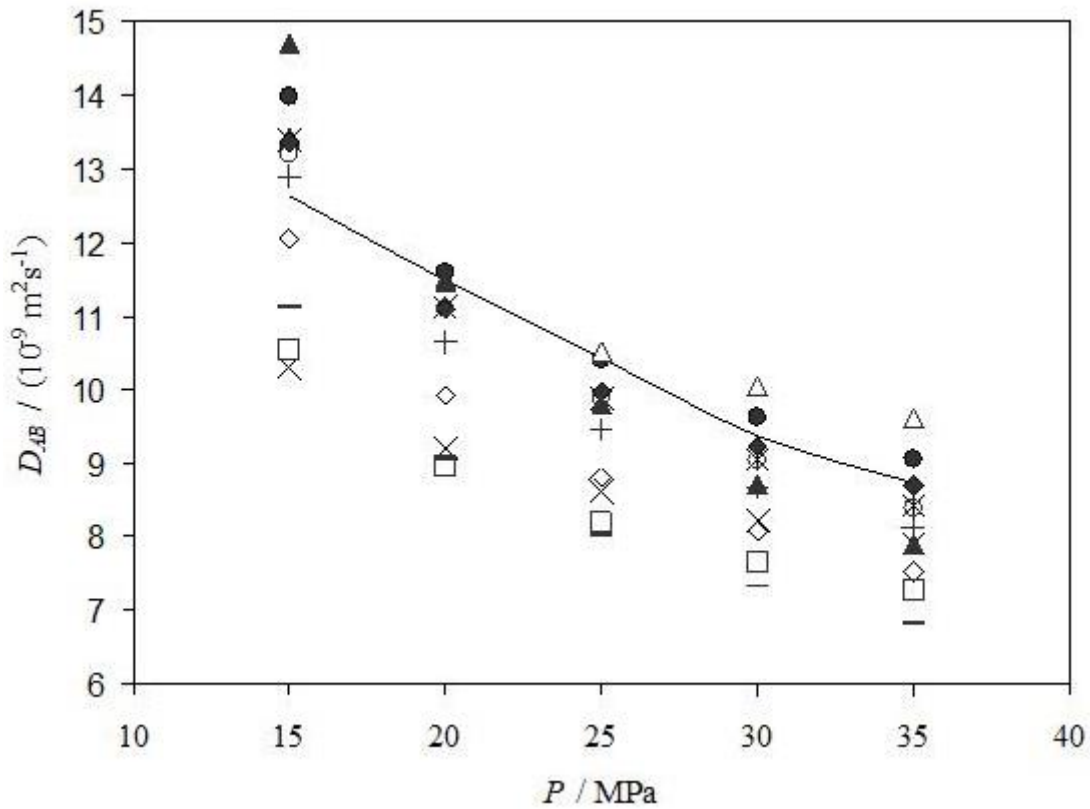


Figure 5. Binary diffusivities of 3-ethyltoluene in carbon dioxide at 323.15 K as a function of pressure. The solid line represents the experimental data and the symbols represent the values calculated with the expressions based on the RHS model: (\diamond) Catchpole-King, (\times) Eaton-Akgerman, (\blacklozenge) He of 1997, (\bullet) He of 1998, (\boxtimes) He-Yu of 1997, (\circ) He-Yu of 1998, (\triangle) Funazukuri-Hachisu-Wakao, (\square) Liu-Silva-Macedo, (\blacktriangle)Zhu-Lu-Zhou-Wang-Shi, ($-$) Dariva-Coelho-Oliveira, ($+$) Rah-Kwak-Eu-Lafleur. 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.

TABLES

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

T / K	P / MPa	ρ^a	$10^6 \eta$	$D_{AB} / (10^{-9} \text{ m}^2 \text{ s}^{-1})$		
		$(\text{kg} \cdot \text{m}^{-3})$	$(\text{Pa} \cdot \text{s})$	2-ethyltoluene	3-ethyltoluene	4-ethyltoluene
313	15	778.92	67.2	10.56 ± 0.11	10.57 ± 0.12	10.53 ± 0.14
	20	822.17	77.2	9.94 ± 0.19	9.89 ± 0.12	9.64 ± 0.09
	25	852.47	85.0	8.97 ± 0.08	8.96 ± 0.13	8.87 ± 0.13
	30	876.03	93.1	8.23 ± 0.08	8.12 ± 0.07	8.08 ± 0.14
	35	895.4	102.3	7.76 ± 0.06	7.71 ± 0.08	7.55 ± 0.09
323	15	678.16	57.1	12.63 ± 0.23	12.64 ± 0.23	12.43 ± 0.13
	20	745.26	68.8	11.49 ± 0.19	11.48 ± 0.11	10.90 ± 0.11
	25	806.3	77.0	10.42 ± 0.23	10.43 ± 0.10	9.98 ± 0.13
	30	846.2	85.1	9.66 ± 0.09	9.37 ± 0.12	9.04 ± 0.09
	35	878.65	91.5	8.82 ± 0.06	8.74 ± 0.10	8.64 ± 0.14
333	15	607.37	47.6	14.30 ± 0.24	14.17 ± 0.50	14.52 ± 0.69
	20	700.86	59.8	12.64 ± 0.24	12.45 ± 0.13	12.45 ± 0.12
	25	761.68	68.7	11.94 ± 0.15	12.13 ± 0.17	11.11 ± 0.11
	30	807.12	73.8	10.62 ± 0.16	10.73 ± 0.10	10.63 ± 0.2
	35	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

Table 2. Properties of the Substances Studied

property	symbol/ unities	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	$10^6 V_c / (\text{m}^3 \text{mol}^{-1})$	460.00	490.00	470.00	93.90
volume at normal boiling point ^b	$10^6 V_b / (\text{m}^3 \text{mol}^{-1})$	175.960	188.005	179.981	35.020
molar mass ^a	$10^3 M / (\text{kg mol}^{-1})$	120.194	120.194	120.194	44.010
acentric factor ^a	ω	0.2940	0.3600	0.3220	0.2390
radius of gyration ^c	$10^{10} r_g / \text{m}$	4.10667	4.12014	4.15043	0.92200
van der Waals volume ^d	$10^{30} V^{vdW} / \text{m}^3$	177.04	178.05	178.06	54.058
van der Waals surface ^d	$10^{20} A^{vdW} / \text{m}^2$	137.81	137.97	137.95	34.117
parachor ^e	$P / (\text{g}^{0.25} \text{cm}^3 \text{mol}^{-1} \text{s}^{-0.5})$	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

Table 3. AAD for Several Predictive Equations

equation	100 AAD ^a		
	2-ethyltoluene	3-ethyltoluene	4-ethyltoluene
Scheibel ³⁷	5.30	4.63	5.91
Wilke-Chang ³⁷	8.91	11.65	7.45
Reddy-Doraiswamy ³⁹	51.13	48.52	53.81
Lusis-Ratcliff ⁴⁰	10.54	7.72	12.18
Tyn-Calus ⁴¹	13.52	12.42	10.82
Umesi-Danner ⁴²	6.59	6.55	4.69
Kooijman ⁴³	28.46	29.61	32.33
Lai-Tan ⁴⁴	10.59	9.14	12.77
Liu-Ruckenstein ⁴⁵	7.73	5.05	9.35
Woerlee ⁴⁶	30.51	32.91	29.63
Catchpole-King ⁴⁷	11.02	12.39	9.08
Eaton-Akgerman ⁴⁸	13.55	14.55	11.79
He of 1997 ⁴⁹	4.42	4.54	3.79
He of 1998 ⁵⁰	4.88	5.29	7.16
He-Yu of 1997 ⁵¹	5.13	4.99	3.45
He-Yu of 1998 ⁵²	4.78	4.63	3.04
Liu-Silva-Macedo ⁵³	17.54	17.99	15.54
Funazukuri-Hachisu-Wakao ⁵⁴	5.83	6.69	8.43
Funazukuri-Kong-Kagei ⁵⁵⁻⁵⁸	4.39	4.27	4.04
Dariva-Coelho-Oliveira ⁵⁹⁻⁶¹	17.48	19.04	15.86
Zhu-Lu-Zhou-Wang-Shi ⁶²	9.60	10.03	9.15
Rah-Kwak-Eu-Lafleur ⁶³	6.49	7.05	4.95

^a AAD is the average absolute deviation.