Limiting Diffusion Coefficients of Ethyl Benzoate, Benzylacetone, and Eugenol in Carbon Dioxide at Supercritical Conditions

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The binary diffusions of ethyl benzoate, benzylacetone, and 2-methoxy-4-(2-propenyl)phenol (eugenol) at infinite dilution in supercritical carbon dioxide were measured between (15.0 and 35.0) MPa and in the temperature range of (313 to 333) K by the Taylor−Aris chromatographic method. The measured values were compared with the calculated ones using several predictive formulas. The effect of temperature, pressure, viscosity, and density is also discussed.

Introduction

Binary diffusion is a fundamental parameter in the design of mass transfer operations, together with equilibrium data. Diffusivities at infinite dilution of one solute A in a solvent B, D_{AB}, are used to calculate the binary diffusion when the concentration becomes finite. In liquid systems at atmospheric pressures, there exist many theoretical or empirical models that require limiting diffusivities with this purpose, although in supercritical carbon dioxide only a few attempts have been made to calculate diffusivities at finite concentration.[1]

Supercritical carbon dioxide has a low viscosity and a high diffusion coefficient and can be easily removed from the extraction products varying temperature or pressure and so is a good alternative to liquid–liquid or solid–liquid extraction.[2,3] The Taylor−Aris chromatographic technique is the most widely used method to measure limiting binary coefficients in CO_2.[4–6] It is based on the work of Taylor and the extension of Aris and involves the injection of a narrow pulse of solute (Dirac's delta function) into a capillary column where the solvent flows in the laminar regime. After a long residence time in the column, the dispersion "transforms" the original pulse in a Gaussian curve, the variance of which can be related with D_{AB}.

In this work, limiting binary diffusivities of ethyl benzoate, benzylacetone, and 2-methoxy-4-(2-propenyl)phenol, so-called eugenol, were measured by the Taylor−Aris technique in the ranges ($313 \le T \le 333$) K and ($15.0 \le P \le 35.0$) MPa and correlated with pressure, temperature, viscosity, and density. Predictive equations based on the Stokes–Einstein formula and on the Rough-Hard-Sphere model are also employed, and results are compared with the experimental data.

Experimental Section

The apparatus and procedures used in this study have been described elsewhere.[5,6] The equipment consists of a Hewlett-Packard G1205A supercritical fluid chromatograph (HP SFC) divided into three parts: a pump module, an oven module, and a multiple-wavelength UV detector (MWD). The capillary column (0.762 mm i.d. × 30.48 m long) is coiled inside the oven, and 0.2 μL of solute is introduced through a manual Rheodyne 7520 injector located on the oven module. The carbon dioxide flow varies between (0.14 and 0.12) $g \cdot min^{-1}$, and the retention time for all experimental conditions is (100 to 120) min. To avoid the secondary flow associated with the tube coiling, the restriction between adimensional numbers of Dean (De) and Schmidt (Sc), $De^2 \cdot Sc < 100$, is maintained.

The three solutes used were supplied by Merck (synthesis grade). Eugenol and ethyl benzoate had a minimum purity of 99 %, and benzylacetone had a minimum purity of 98 %. The wavelengths used in the MWD to monitor the solute concentration profile leaving the column were (250, 277, and 259) nm, respectively. The carbon dioxide was obtained from Air–Liquide (minimum purity of 99.998 %).

Results and Discussion

Diffusion coefficients are presented in Table 1. Each data point is the average of (7 to 10) injections, and the uncertainty is estimated as the standard deviation of all the measurements from the average. The densities of supercritical CO_2 (ρ) were calculated by the Pitzer−Schreiner equation of state,[7] and the viscosities (η) were taken from Stefan and Lucas.[8] Table 1 also shows the self-diffusion coefficients for carbon dioxide in the experimental conditions,[9] which are necessary in subsequent calculations.

A great majority of the uncertainties are within 2 %, but they tend to increase when density and pressure decrease: for example, in the case of ethyl benzoate and eugenol, standard deviations at 15 MPa range from (4 to 9) %. This may result from the experimental failure of our apparatus in the close vicinity of the critical point.

At 15.0 MPa and any temperature, ethyl benzoate diffuses faster than the other two solutes, followed by eugenol. The lowest diffusion coefficients are those of benzylacetone. When pressure increases, the ketone mobility also increases and is greater than the diffusivity of eugenol. Between (25.0 and 35.0) MPa, the data of ethyl benzoate and benzylacetone are nearly the same within the limits of experimental uncertainty.

Table 2 presents the molar mass and van der Waals parameters of the three solutes.[10] As R^{vdW} and Q^{vdW} are proportional to molecular volume and area, respectively, the ratio in the sixth column of this table is a measure of molecular sphericity, the molecules with low values of this ratio being less spherical than those with high values. Eugenol is the heaviest and the largest compound, thus explaining why at high

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Table 1. Measured D_{AB} Values and Self-Diffusion of Carbon Dioxide

P	T	ρ	η	$10^9 D_{AB}/(m^2 \cdot s^{-1})$			
MPa	K	$kg \cdot m^{-3}$	$g \cdot m^{-1} \cdot s^{-1}$	CO_2 self-diffusion	ethyl benzoate	benzylacetone	eugenol
15	313.16	781.0	0.0672	21.63	10.46 ± 0.47	8.97 ± 0.10	9.29 ± 0.46
	323.16	700.8	0.0571	26.57	12.96 ± 0.56	10.55 ± 0.18	11.45 ± 0.95
	333.16	607.1	0.0476	33.11	14.93 ± 1.33	11.50 ± 0.25	12.14 ± 0.52
20	313.16	840.8	0.0772	18.69	8.06 ± 0.15	8.05 ± 0.06	7.69 ± 0.23
	323.16	784.9	0.0688	21.97	10.12 ± 0.30	9.25 ± 0.15	9.08 ± 0.11
	333.16	724.6	0.0598	25.97	11.90 ± 0.46	10.79 ± 0.14	10.40 ± 0.16
25	313.16	880.7	0.0850	16.98	7.53 ± 0.14	7.39 ± 0.17	6.96 ± 0.14
	323.16	835.0	0.0770	19.50	8.65 ± 0.20	8.65 ± 0.07	8.03 ± 0.07
	333.16	781.2	0.0687	22.44	9.82 ± 0.31	9.59 ± 0.11	9.19 ± 0.08
30	313.16	911.2	0.0931	15.82	6.82 ± 0.07	6.95 ± 0.08	6.37 ± 0.13
	323.16	871.4	0.0851	17.91	7.82 ± 0.14	7.83 ± 0.16	7.39 ± 0.08
	333.16	830.5	0.0738	20.29	8.78 ± 0.17	8.92 ± 0.06	8.32 ± 0.09
35	313.16	936.1	0.1023	14.93	6.70 ± 0.17	6.58 ± 0.05	6.10 ± 0.06
	323.16	900.0	0.0915	16.75	7.25 ± 0.21	7.50 ± 0.19	6.91 ± 0.05
	333.16	864.0	0.0839	18.80	8.36 ± 0.36	8.29 ± 0.13	7.90 ± 0.32

Table 2. Mass and van der Waals Parameters of the Studied Substances

substance	formula	$M/(g \cdot mol^{-1})$	R^{vdW}	Q^{vdW}	(R^{vdW}/Q^{vdW}) / $(R^{vdW})^{1/3}$
ethyl benzoate	$C_9H_{10}O_2$	150.18	5.9772	4.708	0.6995661
benzylacetone	$C_{10}H_{12}O$	148.20	6.0429	4.688	0.7076894
eugenol	$C_{10}H_{12}O_2$	164.20	6.3847	4.924	0.6989438

Table 3. Properties of Employed Substances

substance	T_b/K	ω	T_c/K	P_c/MPa	$V_c/(cm^3 \cdot mol^{-1})$
ethyl benzoate[a]	485.91	0.5510	668.71	2.320	430.99
benzylacetone[b]	506.66	0.4979	722.51	3.120	500.50
eugenol[b]	526.36	0.6489	735.31	3.352	447.23
carbon dioxide[c]	216.55	0.2390	304.14	7.375	94.00

[a] From the HYSYS database. [b] Normal boiling temperatures from Lide[30] and the Merck catalog.[31] Critical properties calculated as the average of the group contribution methods of Joback[10] and Wen−Qiang.[32] The acentric factors were obtained from the formula of Lee−Kesler.[10] [c] From the Korea thermophysical properties Data Bank (KDB), whose Web site is http://infosys.korea.ac.kr/kdb/.

Table 4. AAD of the Predictive Equations for the Three Compounds Studied

equation	100 AAD		
	ethyl benzoate	benzyl acetone	eugenol
Lai−Tan	29.44	30.45	39.69
Liu−Ruckenstein cluster	10.10	14.08	18.31
Woerlee	17.23	21.48	12.62
Hippler−Schubert−Troe	17.42	17.81	26.41
Catchpole−King	4.75	4.66	10.71
Eaton−Akgerman	9.32	4.42	10.22
He of 1997	5.14	9.26	7.43
He of 1998	8.38	14.11	12.16
He−Yu of 1997	3.59	7.68	5.83
He−Yu of 1998	3.91	7.00	5.35
Funazukuri−Hachisu−Wakao	15.54	17.21	18.36
Funazukuri−Ishiwata−Wakao	31.59	36.12	38.78
Funazukuri−Wakao	64.59	70.55	73.46
Funazukuri−Kong−Kagei	8.57	11.27	12.03
Liu−Ruckenstein RHS	20.58	17.75	25.29
Liu−Silva−Macedo	16.92	8.52	4.72
Zhu−Lu−Zhou−Wang−Shi	16.94	14.65	21.61
Dariva−Coelho−Oliveira	5.32	8.65	2.62

pressures it is the slowest, although this is not consistent with the fact that at 15.0 MPa benzylacetone has lower diffusivities. Ethyl benzoate and benzylacetone have similar masses and volumes, which explains the similar values of D_{AB} at high pressures. The sphericity parameters of the three molecules are nearly equal, although the benzylacetone is slightly more spherical than the other two, which could indicate a shape influence at low pressures that vanishes when pressure rises.

The previous findings call into question correlative or predictive expressions in which the ratio D_{AB}/D_{AC} is constant or a function of temperature, because these two cases establish that the binary diffusivities at infinite dilution of two solutes A and C in the same solvent do not intersect each other at a given temperature.

Comparison of Experimental Results with Predictive Equations. The Stokes–Einstein-type and Rough-Hard-Sphere-type (RHS) equations were compiled and explained in other work.[11] The first class includes Lai−Tan,[12] Hipler−Schubert−Troe,[13,14] Woerlee,[15] and Liu−Ruckenstein cluster formula.[16] In the second class are Liu−Silva−Macedo,[17] Dariva−Coelho−Oliveira,[18,19] Liu−Ruckenstein RHS formula,[20] Zhu−Lu−Zhou−Wang−Shi,[21] Catchpole−King,[22] Eaton−Akgerman,[23] He of 1997,[24] He of 1998,[25] He−Yu of 1997,[26] He−Yuof 1998,[27] Funazukuri–Hachisu–Wakao,[28] Funazukuri–Ishiwata–Wakao,[29] Funazukuri−Wakao,[1] and Funazukuri−Kong−Kagei.[1] Normal boiling temperature (T_b), acentric factor (ω), and critical properties (T_c, P_c, V_c), all required for calculations, are compiled in Table 3. The average absolute deviation (AAD) of the predictive equations is shown in Table 4.

At high pressures, most of the predictive equations overestimate D_{AB}, as can be seen in Figure 1. The Woerlee equation[15]

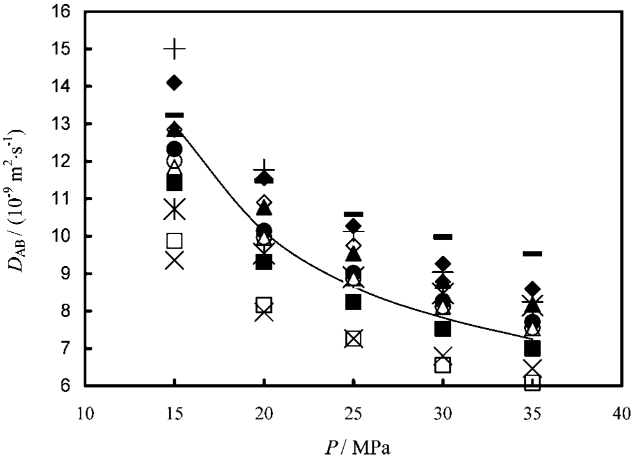

Figure 1. Binary diffusivities of ethyl benzoate in carbon dioxide at 323 K as a function of pressure. Solid line represents the experimental values and symbols the calculated ones: ◇, Liu−Ruckenstein cluster; □, Woerlee; ◆, Hippler−Schubert−Troe; ●, Catchpole−King; ⁎, Eaton−Akgerman; ○, He−Yu of 1997; △, He−Yu of 1998; ▲, Funazukuri−Kong−Kagei; −, Liu−Ruckenstein RHS; ×, Liu−Silva−Macedo; +, Zhu−Lu−Zhou−Wang−Shi; ■, Dariva−Coelho−Oliveira.

Table 5. Fitting Parameters for Equation 3

substance	$10^9\ \zeta_1$ $(\mathrm{m^2 \cdot s^{-1}})$	$10^9\ \zeta_2$ $(\mathrm{MPa \cdot m^2 \cdot s^{-1}})$	$10^9\ \zeta_3$ $(\mathrm{m^2 \cdot K^{-1} \cdot s^{-1}}\backslash)$	$10^9\ \zeta_4$ $(\mathrm{MPa \cdot m^2 \cdot K^{-1} \cdot s^{-1}})$	100 AAD
ethyl benzoate	13.35094	−1142.481	−0.03165926	3.975932	1.94
benzylacetone	−14.63044	−289.9205	0.06200457	1.131713	1.31
eugenol	−12.86578	−364.6580	0.05181050	1.454323	1.18

Table 6. Fitting Parameters for Equation 4

substance	$10^9\ \vartheta_1$ $(\mathrm{m^2 \cdot s^{-1}})$	ϑ_2 $\mathrm{MPa^{-1}}$	ϑ_3 K	ϑ_4 $(\mathrm{K \cdot MPa^{-1}})$	100 AAD
ethyl benzoate	54097.324	−0.1558104	−2594.77	41.83371	5.03
benzylacetone	1493.614	−0.0404384	−1532.611	7.761934	1.46
eugenol	1864.337	−0.03890982	−1568.878	5.400702	3.49

Table 7. Fitting Parameters for Equation 5

substance	$10^9\ \vartheta_1$ $(\mathrm{m^2 \cdot s^{-1}})$	ϑ_2 $\mathrm{MPa^{-0.75}}$	ϑ_3 K	ϑ_4 $(\mathrm{K \cdot MPa^{-0.75}})$	100 AAD
ethyl benzoate	194131.3	−0.4662358	−2938.86	125.2690	4.46
benzylacetone	2036.413	−0.1190561	−1590.866	22.7377	1.29
eugenol	2524.025	−0.1149796	−1609.171	15.79831	3.03

always predicts values lower than the real ones. The best equations are those due to Dariva−Coelho−Oliveira[18,19] and to He−Yu,[26,27] but they follow the premise that D_{AB}/D_{AC} is constant. Nevertheless, none of the equations employed reproduce the changes in the diffusion coefficients of benzylacetone and eugenol, not even qualitatively.

Temperature and Pressure Dependence of Diffusion Coefficients. Suárez et al.[33] proposed that, in the same range of pressures and temperatures as the present work, the following correlations could be employed

$$D_{AB} = a_T + b_T/P \quad \text{at constant temperature} \tag{1}$$

$$D_{AB} = a_p + b_p T \quad \text{at constant temperature} \tag{2}$$

But these two formulas could be generalized in a practical way as

$$D_{AB} = \varsigma_1 + \frac{\varsigma_2}{P} + \varsigma_3 T + \varsigma_4\left(\frac{T}{P}\right) \tag{3}$$

An Arrhenius-type formula instead of eq 2 is also proposed,[33] which is taken as a sign of resemblance between supercritical fluids and liquids. In this sense, some authors used for correlating self-diffusivities in compressed liquids[34,35] the following

$$D_{AB} = \vartheta_1 \exp\left[\vartheta_2 P + \frac{\vartheta_3 + \vartheta_4 P}{T}\right] \tag{4}$$

and Easteal[36] proposed that $\ln D = a + bP^{0.75}$ at constant temperature, so eq 4 could be modified to be

$$D_{AB} = \vartheta_1 \exp\left[\vartheta_2 P^{0.75} + \frac{\vartheta_3 + \vartheta_4 P^{0.75}}{T}\right] \tag{5}$$

Coefficients of the three expressions are presented in Tables 5 to 7. The best fitting is obtained with eq 3. Figure 2 shows that eq 5 does not capture the correct pressure dependence of binary diffusion coefficients of eugenol. The real variation with this variable is more pronounced than that proposed by Easteal for compressed liquids. Equation 4 gives almost the same values as eq 3 and is not represented for clarity.

The three expressions show a decrease of diffusivity with increasing pressure at constant temperature and reveal that $(\partial D_{AB}/\partial P)_T$ is lower at high pressures. Nevertheless, the temperature dependence of $(\partial D_{AB}/\partial T)_P$ is not so clear because of the narrow range of temperatures studied in this work. In Figure 3, it can be seen that the exponential formula is almost a straight line between (313 and 333) K.

Viscosity Dependence. The viscosity dependence of binary diffusion coefficients in carbon dioxide has been widely analyzed.[37–40] It is clear in the literature that the Stokes–Einstein equation is not valid in supercritical fluids, and the empirical correlation of Hayduck−Cheng[41] for each individual binary system is used.[42]

$$D_{AB} = \theta_1 \eta_B^{\theta 2} \quad \text{at constant temperature} \tag{6}$$

The temperature dependence of θ_1 is not clear. According to Hayduck and Cheng, it is temperature independent, but other authors think that it is proportional to temperature.[43–45] The AAD of correlating experimental results with both formulas, given in Tables 8 and 9, seems to prove the last statement.

$$D_{AB} = \theta_1 T \eta_B^{\theta 2} \tag{7}$$

In Figure 4, the group D_{AB}/T is plotted against $1/\eta_B$ for the three compounds. The ethyl benzoate is the closest to the Stokes–Einstein behavior, and the benzylacetone the most distant. According to Evans et al.,[46] voluminous solutes are

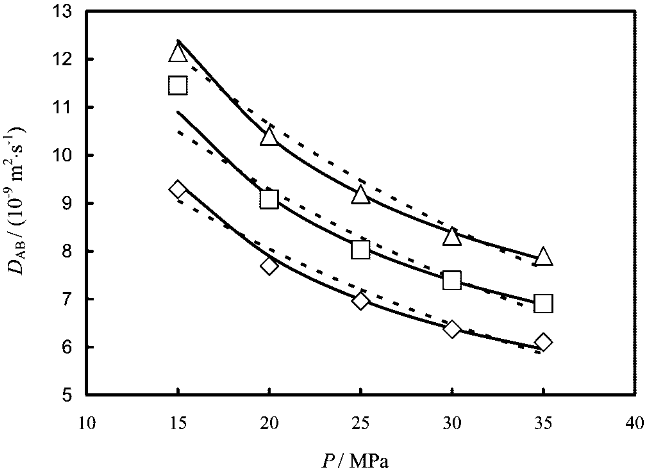

Figure 2. Binary diffusivities of eugenol as a function of pressure: ◇, 313 K; □, 323 K; △, 333 K. The solid line is the correlation with eq 3, and the broken line is the correlation with eq 5.

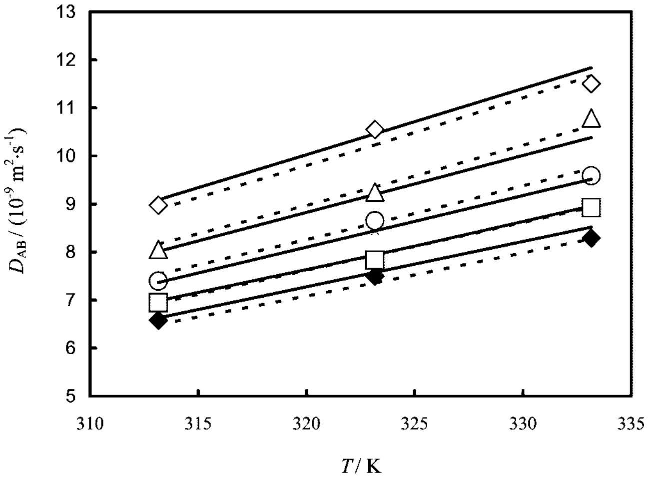

Figure 3. Binary diffusivities of benzylacetone as a function of temperature: ◇, 15.0 MPa; △, 20.0 MPa; ○, 25.0 MPa; □, 30.0 MPa; ◆, 35.0 MPa. The solid line is the correlation with eq 3, and the broken line is the correlation with eq 5.

Table 8. Fitting Parameters for Equation 6

substance	$10^{12}\ \theta_1$ ($\mathrm{m}^{2+\theta_2}\cdot\mathrm{s}^{\theta_2-1}\cdot\mathrm{kg}^{-\theta_2}$)	θ_2	100 AAD
ethyl benzoate	0.1700	−1.1453	3.12
benzylacetone	5.6297	−0.7715	3.37
eugenol	0.7544	−0.9792	2.78

Table 9. Fitting parameters for Equation 7

substance	$10^{15}\ \theta_1$ ($\mathrm{m}^{2+\theta_2}\cdot\mathrm{s}^{\theta_2-1}\cdot\mathrm{K}^{-1}\cdot\mathrm{kg}^{-\theta_2}$)	θ_2	100 AAD
ethyl benzoate	0.9807	−1.0798	3.13
benzylacetone	32.476	−0.7060	1.86
eugenol	4.351	−0.9137	2.48

closer to the Stokes–Einstein behavior than small molecules, which is not in accordance with the values of R^{vdW} and V_c of Tables 2 and 3, respectively.

Density Dependence. Density dependence is more complicated. Most Rough-Hard-Sphere models state that diffusivity is a complex function of viscosity and temperature and that the effect of these two variables can not be easily separated (the density is reduced with an effective diameter, which is a temperature function). Only in the equations of Catchpole−King,[22] He,[24,25] and He−Yu[26,27] can it be written as a product of two functions F and G.

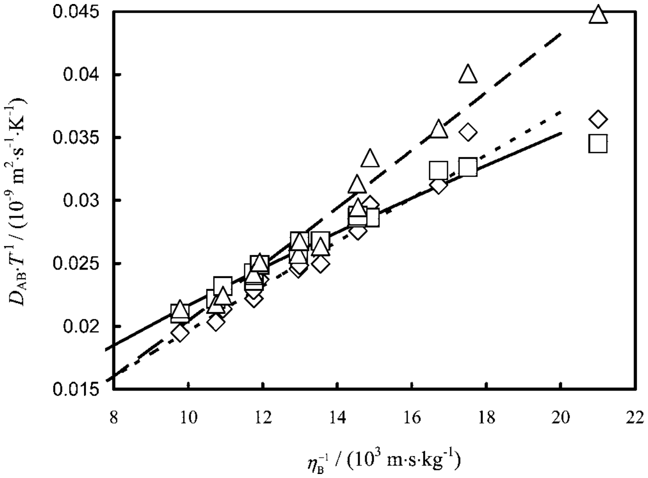

Figure 4. Influence of the viscosity of carbon dioxide on the group D_{AB}/T: - - -, ◇, ethyl benzoate; -----, △, eugenol; ——, □, benzylacetone. The lines represent the fitting to eq 7.

Table 10. Free Fitting of the Two Adjustable Parameters in Equation 9[a]

substance	$10^9\ C_1$ ($\mathrm{mol}\cdot\mathrm{m}^{-1}\cdot\mathrm{s}^{-1}\cdot\mathrm{K}^{-0.5}$)	I_D ($\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$)	100 AAD
ethyl benzoate	21841	30.48	2.16
benzylacetone	14077	19.58	2.20
eugenol	17647	27.35	1.59

[a] Data at 15.0 MPa and 333 K have been rejected because of discrepancy with the linear tendency.

Table 11. Enforced Fitting of Equation 9 with $I_D = 24.67$ $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$[a]

substance	$10^9\ C_1$ ($\mathrm{mol}\cdot\mathrm{m}^{-1}\cdot\mathrm{s}^{-1}\cdot\mathrm{K}^{-0.5}$)	100 AAD
ethyl benzoate	17304	3.68
benzylacetone	16634	2.32
eugenol	15953	1.97
carbon dioxide	38593	1.12

[a] Data at 15.0 MPa and 333 K have been rejected because of discrepancy with the linear tendency.

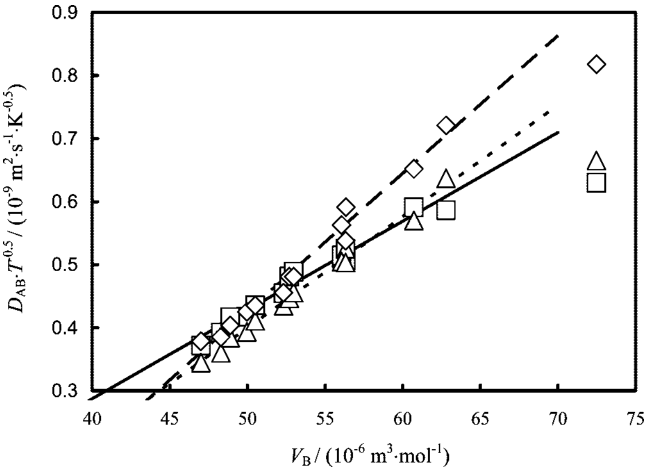

Figure 5. Free volume plot of the diffusion coefficients in carbon dioxide: - - -, ◇, ethyl benzoate; -----, △, eugenol; ——, □, benzylacetone. The lines represent the free fitting to eq 9.

$$D_{AB} = F(T)\cdot G(\rho) \qquad (8)$$

These equations are free-volume based. The free-volume theory was developed for self-diffusion by Cohen and Turnbull[47] and applied by Dymond[48,49] to molecular simulations of Alder and co-workers. The Dymond correlations are a Rough-Hard-Sphere model as well, and in the original work the effects of temperature and density were not separable. Nevertheless, Chen et al.[50] employed the following simplified formula for correlating binary diffusivities in liquids

$$D_{AB}/T^{1/2} = C_1[V_B - I_D] \qquad (9)$$

V_B is the solvent molar volume, and I_D should be a characteristic parameter of the solvent, and so solute independent. Some researchers[51−54] have applied this formula with good results, but Liu et al.[17] found that I_D varies from solute to solute in the same solvent and sometimes has negative values, which is physically meaningless. Table 10 presents the results of a free fitting of the two parameters and Table 11 the "enforced fitting" taking $I_D = 24.67\ \mathrm{cm}^3\cdot\mathrm{mol}^{-1}$. This value is obtained from the free fitting of solvent self-diffusion data to eq 9, and it can be

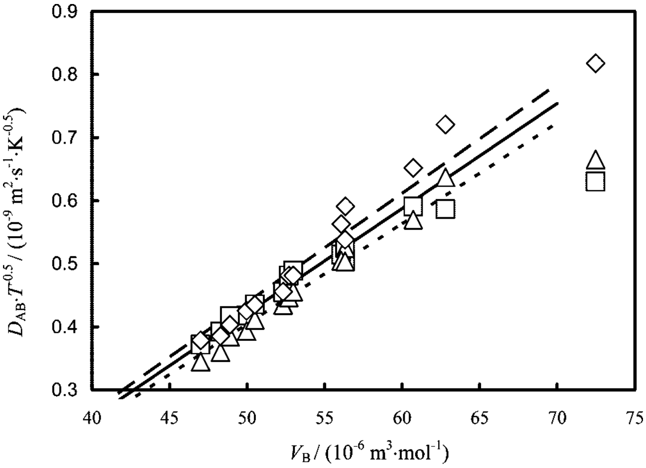

Figure 6. Free volume plot of the diffusion coefficients in carbon dioxide: - - -, ◇, ethyl benzoate; -----, △, eugenol; ——, □, benzylacetone. The lines represent the enforced fitting to eq 9.

seen that this does not greatly worsen the correlation. As $I_D = N_{av}\sigma^3/2^{1/2}$ (where N_{av} is the Avogadro number and σ is the molecular diameter of CO_2), we find $\sigma = 0.3869$ nm, a value near the 0.3941 nm obtained by Hirschfelder et al.[55] from low pressure viscosities and 0.3968 nm obtained from van der Waals volumes.[56] Figures 5 and 6 illustrate the graphical representation of the two fittings.

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