Diffusion of Chelating Agents in Supercritical CO_2 and a Predictive Approach for Diffusion Coefficients

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The binary diffusion coefficients for three β-diketones (trifluoroacetylacetone, thenoyltrifluoroacetone, and 1,1,1,5,5,5-hexafluoroacetylacetone) and one metal chelate (copper(II) trifluoroacetylacetonate) were measured in supercritical carbon dioxide at infinite dilution using the Taylor−Aris dispersion technique. Measurements were made at temperatures of 308.15 K, 313.15 K, and 318.15 K. In addition, a new semiempirical predictive model for calculation of diffusion coefficients in supercritical carbon dioxide was developed on the basis of the hard-sphere theory. The predictive equation was tested against experimental diffusion coefficient data for 51 solutes in carbon dioxide involving polar, long-chain, and complex molecules. Compared with two other recommended correlations, the new equation is better with an average absolute deviation of 9.1%.

Introduction

Supercritical CO_2 has garnered wide attention for the extraction of organic compounds. Direct extraction of metal ions from solid and liquid media by supercritical CO_2 is highly inefficient due to charge neutralization requirements and weak solute−solvent interactions.[1,2] However, when metal ions are chelated with organic ligands, they may become soluble in supercritical CO_2.[3,4] This chelation may produce more environmentally sound and low-cost technologies in chemical, metallurgical, and environmental cleaning processes. The fluorinated β-diketones form soluble metal complexes in supercritical CO_2 and are effective chelating agents for the supercritical fluid extraction (SFE) of metals.[1,5] Metal β-diketonates have found use in fuel additives, metal−organic chemical vapor deposition, and trace metal analysis by chromatography.[5]

In the design and scale-up of industrial processes, transport properties are of considerable importance. The diffusion coefficients of chelating agents and relevant metal chelates are, however, very scarce. No information on diffusion of such components in CO_2 is available in the literature. Diffusion coefficients not only provide basic data for industrial design but also are useful in studying the molecular interactions and structure of chelating agents in supercritical CO_2.

Although in recent years considerable experimental data have been reported regarding the diffusion coefficients of solutes in CO_2, the work on developing a predictive theoretical approach is still very active.[6] Two main theories, hydrodynamic theory and hard-sphere theory, have usually been used as a basis in developing a predictive equation.[7] At present, no rigorous and very successful theory exists for calculating the diffusion coefficients in supercritical fluids.

The objective of this paper is twofold. First the diffusion coefficients for three β-diketones (trifluoroacetylacetone, thenoyltrifluoroacetone, and 1,1,1,5,5,5-hexafluoroacetylacetone) and one metal chelate (copper(II) trifluoroacetylacetonate) in supercritical CO_2 have been measured using the Taylor−Aris dispersion techniques. Second, a general predictive model was developed to correlate the diffusion coefficients of solutes in subcritical and supercritical CO_2. A comparison between this equation and other data was made.

Experimental Section

Chemicals. The relevant structures and properties of the solutes studied here are given in Table 1. All chemicals were obtained from Aldrich Chemicals.

Experimental Apparatus. The theoretical basis of the Taylor−Aris dispersion technique can be found in the work of Taylor,[8] Aris,[9] and Alizadeh et al.[10] The diffusion coefficients were obtained by fitting the concentration profile measured at the column exit to an analytical equation.[11] The apparatus used in this study and the data analysis techniques have been described elsewhere.[12] Zero dead volume fittings were used throughout the apparatus. A pulseless micropump was applied to supply compressed CO_2. The injection valve with helium-drive gas actuator, the diffusion column, and a UV variable-wavelength HPLC detector were used in our apparatus. The system temperature was maintained by a temperature water bath. Capillary tubing is used as the sample cell for the UV detector. This arrangement eliminates any peak broadening due to the finite volume of the flow cell of the UV detector.

Experimental Results and Discussion

To verify the reliability of the apparatus and the experimental method, the diffusion coefficients of phenanthrene in dense CO_2 were determined at 308.15 K. These results are compared with the reference data in Figure 1. The good agreement between them suggests that the experimental method and the apparatus are reliable in determination of the diffusion coefficients.

Diffusion coefficients of the four solutes in supercritical CO_2 are presented in Tables 2−5. Each data point represents an average of at least three measurements. The densities of supercritical fluid CO_2 were calculated by using

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Table 1. Solute Properties and Structure[a]

solute	abbr	R_1	R_2	molar mass	state
trifluoroacetone	TFA	CH_3	CF_3	154.09	liquid
thenoyltrifluoroacetone	TTA	thenoyl	CF_3	222.18	solid
1,1,1,5,5,5-hexafluoro-acetylacetone	HFA	CF_3	CF_3	208.06	liquid
copper(II) trifluoro-acetylacetonate	$Cu(TFA)_2$	CH_3	CF_3	369.70	solid

[a] The structure of the β-diketone is $R_1-CO-CH_2-CO-R_2$.

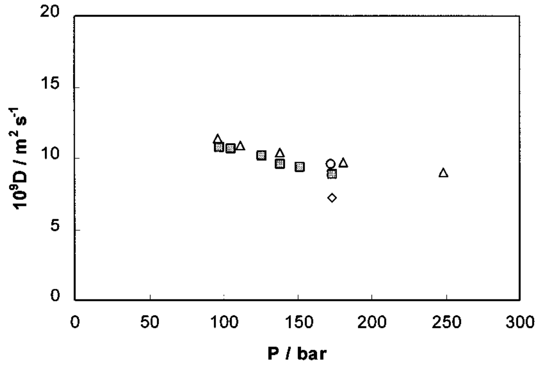

Figure 1. Diffusion coefficients for phenanthrene in supercritical CO_2 at 308.15 K: □, this work; △, Akgerman;[33] ○, Shenai;[37] ◇, Suarez.[5]

Table 2. Infinite Dilution Diffusivity for Trifluoroacetone in Supercritical CO_2

P/bar	ρ/g·cm^{-3}	$10^6\eta$/Pa·s	10^9D/m^2·s^{-1}
		$T = 308.15$ K	
107.6	0.7380	61.97	11.9 ± 0.2
126.2	0.7796	68.47	10.9 ± 0.1
153.1	0.8194	75.46	10.3 ± 0.1
183.8	0.8520	81.85	9.45 ± 0.06
215.1	0.8779	87.41	8.98 ± 0.12
		$T = 313.15$ K	
108.9	0.6801	54.17	13.5 ± 0.2
123.7	0.7290	60.75	12.4 ± 0.3
149.8	0.7806	68.71	11.6 ± 0.3
178.6	0.8184	75.33	11.0 ± 0.4
209.6	0.8489	81.25	9.45 ± 0.55
		$T = 318.15$ K	
106.9	0.5800	43.21	17.2 ± 0.3
127.6	0.6872	55.20	13.9 ± 0.2
157.9	0.7522	65.05	12.3 ± 0.1
188.2	0.8000	72.09	11.1 ± 0.2
215.8	0.8289	77.36	10.4 ± 0.1

Table 3. Infinite Dilution Diffusivity Coefficients for Thenoyltrifluoroacetone in Supercritical CO_2

P/bar	ρ/g·cm^{-3}	$10^6\eta$/Pa·s	10^9D/m^2·s^{-1}
		$T = 308.15$ K	
105.5	0.7320	61.09	9.91 ± 0.06
119.3	0.7663	66.31	8.47 ± 0.39
153.1	0.8194	75.46	7.73 ± 0.20
190.3	0.8579	83.07	6.90 ± 0.11
224.1	0.8844	88.88	6.44 ± 0.23
		$T = 313.15$ K	
106.2	0.6673	52.58	10.1 ± 0.7
122.0	0.7244	60.09	8.93 ± 0.27
155.8	0.7897	70.23	7.82 ± 0.14
189.6	0.8302	77.55	7.68 ± 0.25
215.5	0.8588	82.25	6.62 ± 0.38
		$T = 318.15$ K	
105.5	0.5672	41.98	12.4 ± 0.5
123.4	0.6727	53.37	9.93 ± 0.18
149.6	0.7421	62.88	8.74 ± 0.22
188.9	0.8008	72.23	7.82 ± 0.27
220.6	0.8138	74.55	7.12 ± 0.35

Table 4. Infinite Dilution Diffusivity for 1,1,1,5,5,5-Hexafluoroacetylacetone in Supercritical CO_2

P/bar	ρ,/g·cm^{-3}	$10^6\eta$/ Pa·s	10^9D/m^2·s^{-1}
		$T = 308.15$ K	
109.6	0.7437	62.81	9.85 ± 0.16
120.7	0.7691	66.76	9.75 ± 0.90
155.1	0.8220	75.95	8.90 ± 0.15
186.9	0.8548	82.43	7.99 ± 0.39
213.1	0.8764	87.07	7.06 ± 0.22
		$T = 313.15$ K	
104.1	0.6564	51.27	11.2 ± 0.6
116.9	0.7093	57.95	10.7 ± 0.7
153.8	0.7866	69.71	9.33 ± 0.47
187.2	0.8277	77.07	8.55 ± 0.40
211.0	0.8501	81.49	7.37 ± 0.29
		$T = 318.15$ K	
106.2	0.5672	41.98	12.8 ± 0.9
121.0	0.6633	52.23	11.8 ± 0.6
153.8	0.7499	63.93	10.6 ± 0.7
191.0	0.8032	72.65	8.72 ± 0.27
222.0	0.8346	78.46	8.62 ± 0.26

the IUPAC equation of state,[13] and the viscosity was calculated using the equation of Vescovic et al.[14]

Influence of Pressure at Constant Temperature. The influence of pressure on the diffusion coefficients for the four solutes is shown in Figure 2. It was observed that the diffusion coefficients decrease with increasing the pressure under constant temperature. This is consistent with a general trend in all previous studies. The greater influence of pressure on the diffusion coefficients at low pressure is related to a change in solvent density and viscosity, both of which change rapidly in the low-pressure range.

Influence of Density (ρ) at Constant Temperature. The relationship between the diffusion coefficients and density at constant temperature is given in Figure 3. As expected, the diffusion coefficients decline with an increase of density because the path of the molecule through the solvent becomes more hindered. Figure 4 also indicates that rough linear relations exist within the density range for the four systems. It is observed that the effect of temperature at constant density is relatively small within the temperature range studied. This observation is consistent with the previous report.[15] Sassiat et al. also pointed out that the variation in diffusion coefficients is only approximately 10% over a 30 K temperature range under constant density in supercritical CO_2.[16]

Influence of Molecular Size for Different Solutes. The diffusion coefficients for the four solutes are in the following order:

$$D_{12}(\mathrm{TFA}) > D_{12}(\mathrm{HFA}) > D_{12}(\mathrm{TTA}) > D_{12}(\mathrm{Cu(TFA)_2})$$

These trends are consistent with the fact that the diffusion coefficients decrease with increasing molar mass. More specifically, the solute diffusion coefficient is dependent on its diffusional radius. The relation between the diffusion coefficient and the solute radius can be described by the Stokes–Einstein equation[17,18]

$$D_{12} = \frac{kT}{6\pi\eta r} \tag{1}$$

where k is the Boltzman constant, T is the absolute temperature, η is the fluid viscosity, and r is the solute radius. In eq 1 the correlation from the asymmetrical factor has been neglected.

Table 5. Infinite Dilution Diffusivity for Copper(II) Trifluoroacetylacetonate in Supercritical CO_2

P/bar	ρ/g·cm^{-3}	$10^6\eta$/ Pa·s	$10^9 D$/m^2·s^{-1}
		$T = 308.15$ K	
108.2	0.7399	62.25	8.77 ± 0.36
119.3	0.7663	66.31	7.49 ± 0.53
130.3	0.7869	69.70	6.81 ± 0.19
157.2	0.8244	76.40	6.07 ± 0.42
		$T = 313.15$ K	
108.9	0.6801	54.17	9.30 ± 0.11
119.3	0.7106	58.17	9.16 ± 0.17
154.4	0.7876	69.88	7.76 ± 0.15
		$T = 318.15$ K	
109.6	0.6020	45.41	11.1 ± 0.3
122.0	0.6675	52.74	9.95 ± 0.26
128.2	0.6894	55.48	9.34 ± 0.10
155.1	0.7524	64.31	8.81 ± 0.28
165.5	0.7695	66.98	8.44 ± 0.10

The Stokes–Einstein equation was originally developed to represent the diffusion of solutes in a continuum fluid, and it has also been successfully applied to the diffusion of macromolecules at infinite dilution.[19] Figure 4 is a plot of the four solutes in $kt/6\pi D$ versus η coordinates. All the plots are linear to a good approximation, though the finite nonzero intercepts imply a deviation from hydrodynamic theory. From Figure 4, it is observed that the slopes of the lines for the four solutes are different, which is in accordance with the different radii of the solutes. According to the Stokes–Einstein equation, the molecular radius of the solute can be calculated from its diffusion coefficients, and the calculated results are given in Table 6. Edward pointed out an adequate measure for molecular radius can be obtained through its van der Waals volumes (V_{vdw}) using group contribution.[20] Thus, the molecular radius can be estimated from the van der Waals volume according to $r = ((3/4\pi)V_{vdw})^{1/3}$, which is also listed in Table 6. In the calculation of the V_{vdw}, the structures of the β-diketone and β-diketonate are based on the keto–enol form of the solute molecules.[1,21] As seen in Table 6, both methods produce consistent results for the solute radii. From the analysis above, one can conclude that these fluorinated chelating agents diffuse as their single molecules in supercritical CO_2. However, for metal chelate, Cu(TFA)$_2$, this conclusion may not be applicable, due to lack of data for the Cu^{2+} group contribution value. Research has shown that association may exist for metal β-diketonates/supercritical CO_2.[5] For the chelating agent TFA and its metal chelate, Cu(TFA)$_2$, the difference in their diffusion coefficients is probably due to the change in their molecular radius. The decrease in diffusion coefficients is about 40% for the Cu(TFA)$_2$ relative to TFA.

A Predictive Approach for Diffusion Coefficients in CO_2

The rough hard-sphere theory, which extends the kinetic theory of gases to dense gases and liquids, can be used as a starting point to describe accurately the diffusion coefficients of dense fluids. According to the gas kinetic theory,[22] the mutual diffusion coefficients for a dilute gas mixture composed of hard spheres are given as follows:

$$D_{12}^{\circ} = \frac{3}{8\rho_n{\sigma_{12}}^2}\left(\frac{kT}{m_{12}\pi}\right)^{0.5} \tag{2}$$

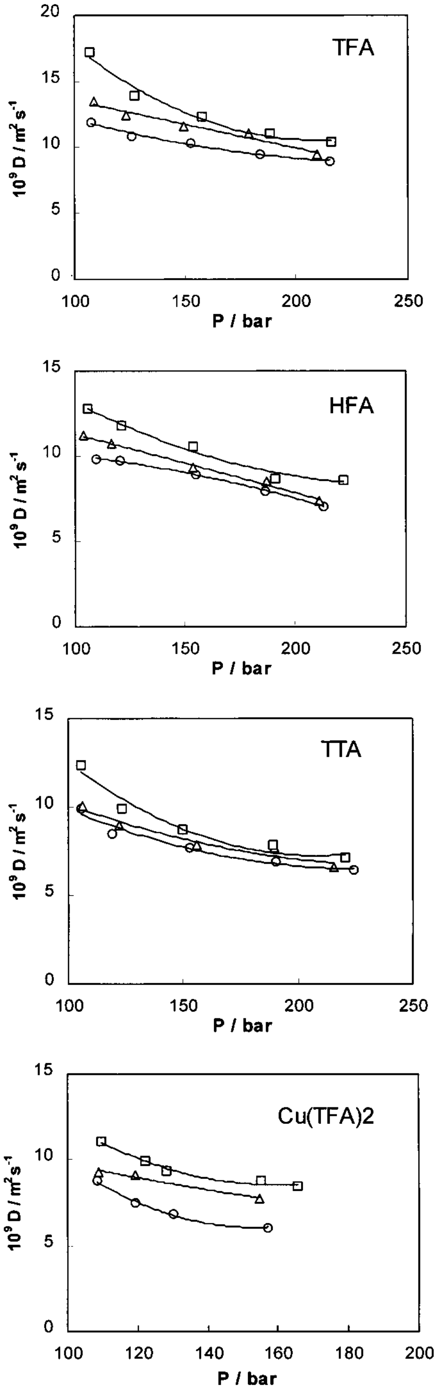

Figure 2. Diffusion coefficients of four solutes in supercritical carbon dioxide as a function of pressure: ○, 308.15 K; △, 313.15 K: □, 318.15 K.

where ρ_n is the number density of solvent 2; σ_{12} is the average diameter of the mixture and is calculated from the hard-sphere diameters of its pure components, σ_1 and σ_2, using the following relation:[22]

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \tag{3}$$

and m_{12} is calculated from the mass of its pure components, m_1 and m_2, as follows:

$$\frac{1}{m_{12}} = 0.5\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \tag{4}$$

For dense fluids, a correction is needed to represent the diffusion coefficient from the smooth hard-sphere theory

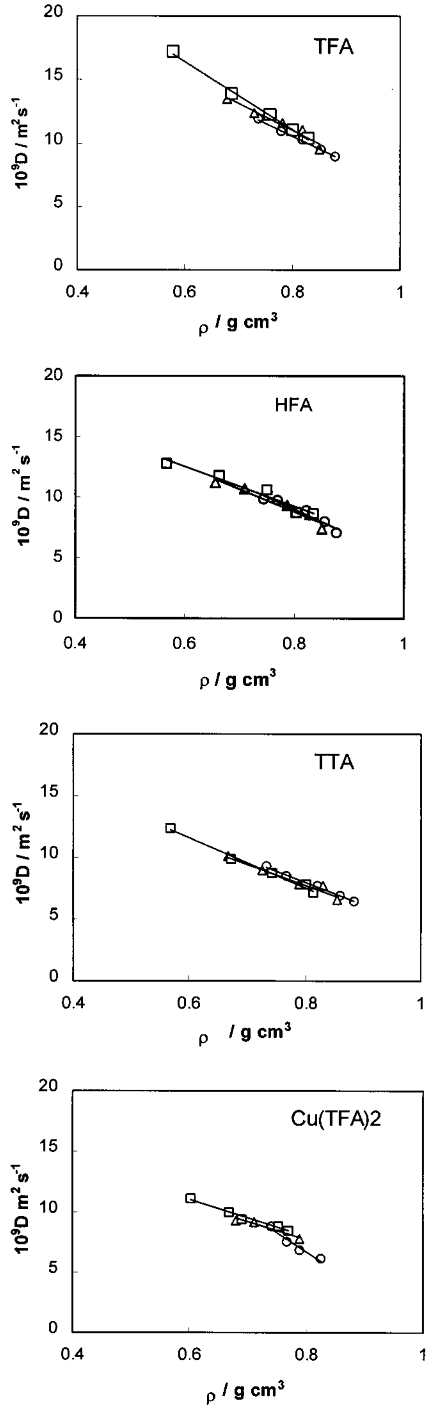

Figure 3. Diffusion coefficients of four solutes in supercritical carbon dioxide as a function of density: ○, 308.15 K; △, 313.15 K; □, 318.15 K.

$$D_{12}{}^{\mathrm{SHS}} = D^{\circ}_{12}P(\rho^*) \tag{5}$$

where $P(\rho^*)$ represents the effect of correlated molecular motions at high density on the diffusion coefficients. $P(\rho^*)$ cannot be obtained analytically. $P(\rho^*)$ has two extreme conditions: $P(\rho^*) = 1$ occurs when hard-sphere molecules can transfer freely at the low-density extreme; $P(\rho^*) = 0$ occurs when the molecule cannot transfer at all in the metastable fluid range at the high-density extreme. The effect is usually studied by molecular dynamics and is expressed as a function of reduced density ρ^* ($=\rho_n\sigma_2{}^3$). Speedy[23] used the results of computer simulations on hard-sphere fluids by Alder et al.[24] to study the density dependence of diffusion coefficients for smooth hard-sphere fluids, and obtained

$$P(\rho^*) = \left(1 - \frac{\rho^*}{1.09}\right)[1 + (\rho^*)^2(0.4 - 0.83(\rho^*)^2)] \tag{6}$$

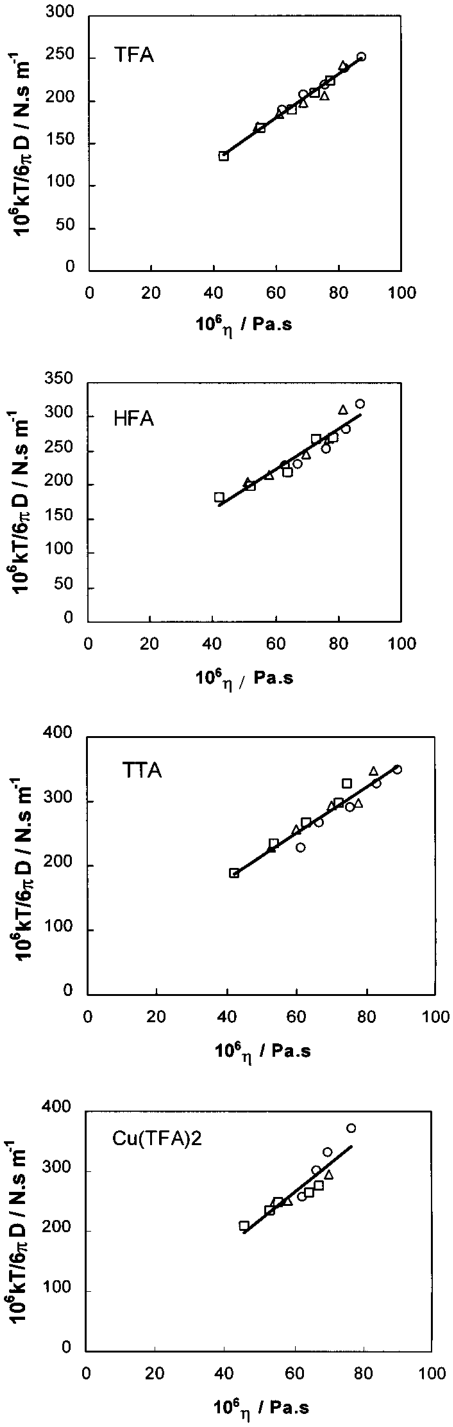

Figure 4. Relationship between diffusion coefficients and viscosity based on the Stokes–Einstein equation: ○, 308.15 K; △, 313.15 K; □, 318.15 K.

Sandro et al.[25] studied the effect of the density correction (eq 6) on the estimation of diffusion coefficients in liquids and liquid mixtures. An average absolute deviation (AAD %) of 10.2% was obtained for 13 binary systems. Dariva et al.[26] used the same approach for correlating and predicting the self-diffusion coefficients and mutual diffusion coef-

Table 6. Estimated Molecular Radius for the Solutes

solute	$10^{10}r^a$/m	$10^{10}r^b$/m
TFA	3.03	2.56
HFA	3.14	2.97
TTA	3.34	3.55
Cu(TFA)$_2$	3.76^c	4.68

[a] Obtained using atomic group contribution. [b] Obtained from the Stokes−Einstein equation. [c] Only for ligands.

ficients in subcritical and supercritical fluids. However, the average AAD % was as high as 18%.

Recently, Salim and Trebble[27] used the hard-sphere theory with eq 6 to correlate the binary diffusion coefficients at infinite dilution for n-alkane systems. In their work, the effect of $P(\rho^*)$ was replaced by that of $P(\rho^*)^n$, where n is considered to represent the effect of long-chain molecules. A variable ×a6 is also introduced to account for the coupling between translational and rotational momentum exchange between unlike molecules, molecular shape, and molecular multiple collisions. From the model of Salim and Trebble[27] the diffusion coefficient is expressed as

$$D_{12} = D_{12}^{\circ} P(\rho^*)^n \times \mathrm{a6} \tag{7}$$

According to Sandro et al.,[25] the hard-sphere diameter is a function of temperature and density. The average diameter σ_{12} is replaced by the effective diameter d_{12}, which is dependent on temperature and density. Following this approach, d_{12} is calculated by

$$d_{12} = \sigma_{12} 2^{1/6}\left\{1 + \left[\frac{(T^* + a_2 T^{*2} + a_3 T^{*4})}{a_1(1 + a_4\rho^* + a_5\rho^{*2} + a_6\rho^{*3})}\right]^{1/2}\right\}^{-1/6} \tag{8}$$

where $T^* = T/(\epsilon_{12}/k)$ is the reduced temperature and ϵ_{12} is the Lennard-Jones energy parameter for the mixture.[28] The constants in eq 8 are $a_1 = 1.5001$, $a_2 = -0.033\,67$, $a_3 = 0.000\,393\,5$, $a_4 = -0.098\,35$, $a_5 = 0.004\,937$, and $a_6 = -0.1415$.[28]

Substituting σ_{12} with d_{12}, eq 7 is reduced to

$$D_{12} \times 10^9 = \beta_{12}\frac{3}{8{d_{12}}^2\rho}\left(\frac{RT}{\pi M_{12}}\right)^{0.5}[1 - (\rho^*)^2(0.4 - 0.83(\rho^*)^2)]^n \tag{9}$$

where $M_{12} = 2M_1M_2/(M_1 + M_2)$ and M_1 and M_2 are the molar weights of component 1 and component 2, respectively. β_{12} is a parameter dependent on the system of interest.

To calculate the diffusion coefficient using eq 8, it is necessary to know the energy parameter ϵ and hard-sphere diameter σ for every component. These values are determined from the semiempirical relations given by[29]

$$\sigma_i = \sigma_{\mathrm{r}i}\left(\frac{6V_{\mathrm{c}i}}{\pi N_{\mathrm{a}}}\right)^{1/3} \quad (i = 1, 2) \tag{10}$$

$$\epsilon_{ii}/k = 0.77T_{\mathrm{c}}i \quad (i = 1, 2) \tag{11}$$

$$\sigma_{\mathrm{r}i} = 0.552803 - 0.0026776Tr_i \tag{12}$$

where $Tr_i = T/T_{\mathrm{c}i}$ and N_{a} is Avogadro's constant.

Table 7. Critical Properties and Molecular Weights for Components Studied

system	T_c/K	V_c/cm^3·mol^{-1}	M/g·mol^{-1}
tetrahydrofuran	540.1	224.0	72.11
diisopropyl ether	500.3	386.0	102.2
p-xylene	616.8	379.0	106.2
hexachlorobenzene	847.7	557.5	284.8
m-xylene	617.1	376.0	106.2
o-xylene	630.3	369.0	106.2
chloroform	536.4	238.9	119.4
diethyl ether	466.2	280.0	74.12
phenol	694.2	229.0	94.11
benzoic acid	752.0	341.0	122.1
acetone	508.1	209.0	58.08
2-butanone	536.8	267.0	72.11
ethyl acetate	523.2	286.0	86.11
mesitylene	664.5	480.0	120.2
isopropyl benzene	631.1	428.0	120.2
n-propylbenzene	638.2	440.0	120.2
ethylbenzene	617.2	374.0	106.2
toluene	591.8	316.0	92.14
naphthalene	748.4	413.0	128.2
caffeine	855.6	485.0	194.2
butyric acid ethyl ester	579.0	400.0	116.2
3-pentanone	561.1	301.0	86.13
bromobenzene	670.0	324.0	157.0
chlorobenzene	632.4	308.0	112.6
cyclopentanone	634.6	268.0	84.12
iodobenzene	721.0	351.0	204.0
caprylic acid ethyl ester	655.7	621.5	172.3
behenic acid ethyl ester	987.8	1405.5	368.7
capric acid ethyl ester	699.3	733.5	200.0
docosahexaenoic acid ethyl ester	867.1	1285.0	356.5
docosahexanenoic acid methyl ester	852.4	1229.0	342.5
myristic acid ethyl ester	788.4	957.5	256.4
palmitic acid ethyl ester	835.0	1069.5	284.48
stearic acid ethyl ester	883.4	1181.5	312.5
pentane	469.7	304.0	72.15
hexane	507.5	370.0	86.18
heptane	540.3	432.0	100.2
octane	568.8	492.0	114.2
nonane	594.6	548.0	128.3
decane	617.7	603.0	142.3
undecane	638.8	660.0	156.3
dodecane	658.2	713.0	170.3
tetradecane	694.0	830.0	198.4
benzene	562.2	259.0	78.11
phenanthrene	873.0	554.0	178.2
eicosapentanoic acid methyl ester	823.4	1137.5	356.5
dichloromethane	510.0	245.5	84.93
1-octene	566.7	464.0	112.2
TFA	538.8	400.5	148.0
HFA	475.8	413.5	208.1
TTA	521.2	481.0	222.2
CO$_2$	304.2	94.00	44.01

The following mixing rule is adopted to calculate the energy parameter ϵ_{12}

$$\epsilon_{12}/k = \frac{\sqrt{{\sigma_1}^3(\epsilon_{11}/k){\sigma_2}^3(\epsilon_{22}/k)}}{{\sigma_{12}}^3} \tag{13}$$

Equation 9 was used to correlate the diffusion coefficients of solutes in CO$_2$. In this study, the diffusion coefficients for 51 solutes in supercritical and subcritical CO$_2$ have been fitted. For most systems studied here, the densities of CO$_2$ were provided by the same references as those used for the diffusion coefficient data. If density is not available in the references, it can be calculated by the CO$_2$ equation of state.[13] From the calculated results, it is found that the model correlates the diffusion coefficients well. The calculation analysis shows that the parameter n can be related to fluid density in order to improve the correlation accuracy.

Table 8. Systems Studied and Data Sources

system	T_r	P_r	ρ_r	ND	ref
tetrahydrofuran	1.029−1.095	1.098−2.196	0.481−1.707	15	34
diisopropyl ether	1.029−1.095	1.098−2.196	0.481−1.707	15	34
p-xylene	1.029−1.062	2.032−3.386	1.669−1.702	6	35
hexachlorobenzene	1.012−1.078	1.310−3.351	0.855−1.924	14	33
m-xylene	1.029	2.167	1.699−1.702	2	35
o-xylene	1.029	2.167	1.699−1.702	2	35
chloroform	1.029	2.167	1.702	1	35
diethyl ether	1.029−1.095	1.098−2.196	0.419−1.700	16	34
phenol	1.012−1.078	1.392−1.959	0.703−1.719	16	36
benzoic acid	0.982−1.079	0.962−3.733	1.148−1.960	13	37, 38
acetone	0.997−1.029	1.558−3.590	1.090−1.881	10	35, 39, 16
2-butanone	1.029	2.167	1.702	1	35
ethyl acetate	1.012−1.078	1.295−1.937	1.384−1.723	11	35, 36
mesitylene	0.997−1.095	1.761−4.741	1.091−1.881	8	35, 16
isopropylbenzene	1.029−1.095	2.031−4.741	1.084−2.001	20	35, 16, 40
n-propylbenzene	1.029−1.095	2.031−4.741	1.298−2.001	16	35, 40
ethylbenzene	1.029−1.095	1.017−4.741	1.298−2.001	16	35, 40
toluene	1.006−1.095	1.306−3.590	0.726−2.001	36	35, 36, 40, 41
naphthalene	0.997−1.095	1.088−1.942	0.855−1.881	51	35, 33, 16, 42
caffeine	1.012−1.078	1.309−2.851	0.913−1.723	18	36
butyric acid ethyl ester	1.013−1.046	1.355−2.032	1.282−1.817	16	15
3-pentanone	1.033	2.032−3.386	1.282−1.817	8	43
bromobenzene	1.029−1.062	2.032−3.386	1.498−1.998	6	6
chlorobenzene	1.029−1.062	1.355−2.438	1.498−1.998	6	6
cyclopentanone	1.032	2.032−3.386	1.669−1.945	8	43
iodobenzene	1.029−1.062	1.309−2.851	1.498−1.998	6	6
caprylic acid ethyl ester	1.019−1.046	1.309−2.851	1.282−1.817	16	15
behenic acid ethyl ester	1.019−1.046	1.309−2.851	1.282−1.817	17	18
capric acid ethyl ester	1.019−1.046	1.309−2.851	1.282−1.817	16	15
docosahexaenoic acid ethyl ester	1.019−1.046	1.309−2.851	1.282−1.817	18	18
docosahexanenoic acid methyl ester	1.019−1.046	1.309−2.851	1.282−1.817	18	18
myristic acid ethyl ester	1.019−1.046	1.309−2.851	1.282−1.817	16	15
palmitic acid ethyl ester	1.019−1.046	1.309−2.851	1.282−1.817	17	15
stearic acid ethyl ester	1.019−1.046		1.282−1.817	17	18
pentane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
hexane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
heptane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
octane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
nonane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
decane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
undecane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
dodecane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
tetradecane	0.983−1.013	1.219−1.422	1.819−1.561	5	39
benzene	0.997−1.095	1.422−4.741	1.090−1.924	39	16, 40, 41, 44, 45
phenanthrene	0.997−1.095	1.307−3.733	1.090−1.924	24	33, 16
eicosapentanoic acid methyl ester	1.019−1.046	1.039−2.851	1.282−1.817	19	18, 46
dichloromethane	1.029	2.167	1.702	1	35
1-octene	1.029	2.167	1.702	1	35
TFA	1.013−1.046	1.448−2.923	1.239−1.877	15	this work
HFA	1.013−1.046	1.448−2.923	1.239−1.877	15	this work
TTA	1.013−1.046	1.448−2.923	1.239−1.877	15	this work

Further, it can be represented by

$$n = 1.0 \quad \text{for} \quad \rho_r \geq 1.11 \tag{14}$$

$$n = 1.0 + 5.241(1.11 - \rho_r) \quad \text{for} \quad \rho_r < 1.11 \tag{15}$$

where $\rho_r = V_{c2}/V$ is the reduced fluid density. Correlation results show that the parameter β_{12} is independent of temperature and density.

To make the model above more practical, the parameter β_{12} must be related to the properties of the systems studied, that is, the properties of the solutes. We developed the following expression to evaluate the parameter β_{12}.

$$\beta_{12} = B_0 + B_{01}k_1 + B_{02}{k_1}^2 + B_{03}{k_1}^3 + B_1M_1 + B_{20}k_2 + B_{21}{k_2}^2 + B_3T_{c1} \tag{16}$$

where $k_1 = V_{c1}/M_1$ and $k_2 = \ln(V_{c1})$, V_c is in $\text{cm}^3\cdot\text{mol}^{-1}$, T_c is in K, and M is in $\text{g}\cdot\text{mol}^{-1}$. The constants in eq 16 are $B_0 = 17.8303$, $B_{01} = 1.2581$, $B_{02} = -1.6111$, $B_{03} = 0.2770$, $B_1 = -0.020\,29$, $B_{20} = -6.1725$, $B_{21} = 0.7837$, and $B_3 = 9.4574 \times 10^{-4}$. β_{12} is calculated from the critical volume, the critical temperature, and the molecular weight of the solutes. The required critical properties are given in Table 7. Most critical property data are from Reid et al.[30] For solutes with no available critical properties, these were estimated using a group contribution method.[30]

Predictive Results and Discussion

The above predictive model has been used to estimate the diffusion coefficients of the solutes in dense CO_2. Table 8 shows the systems examined, the temperature and density range, and the source of data. The predicted results are given in Table 9. For comparison, the predictive results based on the equation of He[31] and the Eaton and Akgerman model[32] are also shown in Table 9. For 51 systems (600 data) the average relative deviation (AAD %) is about 9.1%. Considering that there is a relatively large experimental uncertainty in diffusion coefficient measurements, the agreement between the predictive and experimental data is good. In comparison with the other two predictive

Table 9. Predictive Results for Diffusion Coefficients in CO_2

solute	AAD %		
	this work	ref 31	ref 33
tetrahydrofuran	14	9.0	
diisopropyl ether	5.7	8.8	
p-xylene	7.6	5.0	13
hexachlorobenzene	16	26	11
m-xylene	11	5.5	11
o-xylene	10	4.5	12
chloroform	1.5	20	
diethyl ether	7.7	6.5	
phenol	12	3.2	
benzoic acid	10	11	13
acetone	15	4.0	5.3
2-butanone	11	3.0	
ethyl acetate	11	8.0	
mesitylene	12	6.1	5.7
isopropylbenzene	6.5	4.7	8.4
n-propylbenzene	8.2	6.8	10
ethylbenzene	11	5.0	8.9
toluene	13	6.1	6.5
naphthalene	12	11	12
caffeine	15	5.0	18
butyric acid ethyl ester	7.3	3.5	11
3-pentanone	4.8	6.0	
bromobenzene	5.1	19	
chlorobenzene	11	8.0	
cyclopentanone	3.2	9.0	
iodobenzene	10	27	
caprylic acid ethyl ester	4.0	2.2	10
behenic acid ethyl ester	2.9	2.4	20
capric acid ethyl ester	6.2	3.0	11
docosahexaenoic acid ethyl ester	5.6	2.0	16
docosahexanenoic acid methyl ester	4.0	2.3	16
myristic acid ethyl ester	9.1	2.9	12
palmitic acid ethyl ester	12	2.4	14
stearic acid ethyl ester	11	3.0	15
pentane	5.0	5.3	
hexane	5.6	13	
heptane	3.8	18	
octane	3.8	22	
nonane	4.1	25	
decane	5.3	27	
undecane	7.6	28	
dodecane	7.9	29	
tetradecane	6.3	24	
benzene	15	7.0	6.0
phenanthrene	11	12	15
eicosapentanoic acid methyl ester	8	4.8	16
dichloromethane	21	12	
1-octene	27	17	
TFA	11	9.1	
HFA	6.8	3.6	
TTA	9.8	11	
average	9.1	11	

methods, our result is equivalent to the method of He[31] and better than the Akgerman[33] methods. However, in He's method the predictive AAD % for *n*-alkanes is somewhat higher, especially for long-chain molecules.[31] Our method shows somewhat better predictive accuracy for all the solutes in dense CO_2. Therefore, this new model possesses wide applicability in the prediction of diffusion coefficients in CO_2.

Conclusions

The diffusion coefficients for the three β-diketones, trifluoroacetylacetone, thenoyltrifluoroacetone, and 1,1,1,-5,5,5-hexafluoroacetylacetone, and one metal β-diketonate, copper(II) trifluoroacetylacetonate, were measured at 308.15 K, 313.15 K, and 318.15 K for pressures ranging from 105.5 bar to 225 bar. The experimental diffusion coefficients ranged from 6.07×10^{-9} to 17.2×10^{-9} m²/s. The influence of temperature and pressure on the diffusion coefficients was found to be largely dependent on the density change of CO_2. The effect of the molecular size on the diffusion coefficients was investigated.

On the basis of the hard-sphere theory, a semiempirical model was developed for the diffusion coefficients at infinite dilution in dense CO_2. A better predictive result for the diffusion coefficients was obtained by this equation with the AAD % being 9.1% for 51 systems.

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