Determination and correlation of infinite dilution binary diffusion coefficients for aluminum acetylacetonate in supercritical and liquid fluids

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16

17 **Abstract**

18 The infinite dilution binary diffusion coefficients D_{12} for aluminum acetylacetonate in

19 supercritical CO_2 were determined at $308.15 - 333.15$ K and at 7.80 to 40.00 MPa by the

20 chromatographic impulse response (CIR) method. And, the diffusion measurements in liquid

21 ethanol were carried out at $300.15 - 333.15$ K and at 0.10 and 30.00 MPa by the Taylor

22 dispersion method. It was found that the D_{12} values measured in supercritical CO_2 show

23 slowing down in the region of near critical point. The determined activation energies of

24 diffusion were 23.0, 13.7, 12.0, 11.3 kJ/mol at 12.00, 20.00, 25.00, 35.00 MPa in supercritical

25 CO_2 and 19.1 kJ/mol at 0.10 MPa in liquid ethanol, respectively. All determined 90 diffusion

26 data in this study can be correlated with the equation of D_{12} [m^2/s]=1.558×10^{-14} T [K] η [Pa

27 s]$^{-0.761}$ with average absolute relative deviation (AARD) of 5.6% over a wild fluid viscosity

28 range from 2.462×10^{-5} to 1.258×10^{-3} Pa s.

29

30 **Key words:** Diffusion coefficient, supercritical carbon dioxide, liquid, aluminum
31 acetylacetonate, chromatographic impulse response

32

1. Introduction

Supercritical fluids as green solvents are now being often used in chemical reaction, extraction, separation and analysis in both academia and industry thanks to unique properties like high diffusivity, low kinetic viscosity and easily adjustable solvent power. For rational design and improvement of the process with supercritical fluids, it is important to fully know basic property such as the diffusion of solutes in the supercritical system. Diffusion is a physical phenomenon commonly occurring in a variety of chemical, biological and environmental processes involving mass transfer. Therefore, the determination of diffusivities in fluids is of great significance for the estimation of mass transfer processes. A more efficient application using supercritical fluid technology often adds entrainer to the supercritical fluid. Hence the diffusion mechanisms in practical processes need to be understood not only in supercritical state but also in liquid state. Up to now, most measurements of diffusion coefficients relate only to liquid state or supercritical state. Furthermore, there is a lack of diffusion data for the same solute in both states. There are many methods [1-3] that may be used to obtain infinite dilution binary diffusion coefficients D_{12}. Among them, the Taylor dispersion method is suitable for determining the D_{12} data in liquid phase, and the chromatographic impulse response (CIR) method [4,5] can be used not only for measuring diffusion but also for measuring partial molar volumes and solubilities in supercritical fluids [6,7].

Aluminum acetylacetonate (Al(acac)$_3$) as one of aluminum source can be soluble in supercritical CO_2. Through thermal decomposition in supercritical CO_2, Al(acac)$_3$ can be used as a precursor to produce template nanoporous alumina materials [8], thin films of aluminum oxide [9,10] and many important applications [11]. Diffusion data are still inconveniently few for metal complexes [12-17] in supercritical CO_2, and it is found that no diffusion data are available for system of Al(acac)$_3$ in supercritical CO_2 or in liquid ethanol. Therefore, this

58   study was intended to measure the D_{12} values for Al(acac)$_3$ in supercritical CO_2. In addition,

59   the D_{12} data were also determined in liquid ethanol. Then, the reliability of the correlation of

60   D_{12}/T vs fluid viscosity η was examined.

61

62   **2. Theory**

63   The detail theoretical backgrounds have been given by the authors [5] for the CIR method

64   and Alizadeh et al. [18] for the Taylor dispersion method. The cross sectional average

65   concentrations $c(z,t)$ can be given by using Eq. (1) for the CIR method and Eq. (2) for the

66   Taylor dispersion method, respectively.

67
$$\begin{cases} c(z,t)=\left(\dfrac{m}{\pi R^2}\right)\left(\dfrac{u}{u_0}\right)\dfrac{1}{\sqrt{4\pi Kt}}\exp\left[-\dfrac{(z-ut)^2}{4Kt}\right] \\ \qquad K=\left[D_{12}+\dfrac{R^2}{48D_{12}}(6u^2-16u_0u+11u_0^2)\right]\left(\dfrac{u}{u_0}\right) \end{cases} \tag{1}$$

68
$$\begin{cases} c(z,t)=\left(\dfrac{m}{\pi R^2}\right)\dfrac{1}{\sqrt{4\pi Kt}}\exp\left[-\dfrac{(z-u_0t)^2}{4Kt}\right] \\ \qquad K=D_{12}+\dfrac{R^2}{48D_{12}}u_0^2 \end{cases} \tag{2}$$

69   where z is the axial distance, t is the time, m is the amount injected, R is the column radius,

70   u and u_0 are the solute and fluid velocities, respectively. The D_{12} was determined by curve

71   fit using the root mean square fitting error ε (Eq. (3)). It was found that the fit indicated

72   acceptably if $\varepsilon < 3\%$ and good if $\varepsilon < 1\%$ [5].

73
$$\varepsilon=\left(\dfrac{\int_{t_1}^{t_2}\left(c_{\text{meas}}(L,t)-c(L,t)\right)^2 dt}{\int_{t_1}^{t_2}\left(c_{\text{meas}}(L,t)\right)^2 dt}\right)^{1/2} \tag{3}$$

74   where L is the distance between injector and detector, t_1 and t_2 are the times at the frontal and

75   latter 10% peak heights of measured curve $c_{\text{meas}}(L,t)$ at $z=L$, respectively.

76

77   **3. Experimental**

78   The measurement system basically consisted of a pump, a pressure gauge, an injector, a

3

79   diffusion column, a water bath, a thermometer, a UV-Vis multidetector and a back pressure

80   regulator. The apparatus and procedure have been described elsewhere [15-17]. The

81   measurements in this study were carried out at higher pressures, therefore, a high degree of

82   accuracy in both temperature and pressure control was desirable. The pulseless syringe pump

83   was used to supply compressed CO_2 in the CIR method, which can eliminate pressure and

84   density gradients in supercritical CO_2. Note that in this study the pressure and temperature

85   were controlled accurately to ±0.01 K and ±0.05 bar, respectively. Then, a pulse of $Al(acac)_3$

86   dissolved in hexane or ethanol was loaded through the injector. When the solute was injected,

87   the injection mode must be carefully checked. If the sample rotor was left in the flowing fluid,

88   the measured response curve with serious tailing was often gotten. But, after injected with a

89   very short time (e.g. less than 1 s), then the injection valve being immediately turned to allow

90   the fluid to flow directly to the column, it often got in a pulse like injection, the tailing may be

91   avoided and the dispersion effect of the solute was minimally-eliminated. The

92   chromatographic response curves were measured by the UV detector with 1 nm increments.

93   CO_2 with purity of 99.95% was purchased from Air Gases Tokai Ltd., Japan, aluminum

94   acetylacetonate (molecular formula: $Al(C_5H_7O_2)_3$, molecular weight: 324.3) with 99% was

95   obtained from Sigma Aldrich, ethanol with 99.5% was from Wako, hexane with 98% was

96   obtained from Tokyo Chemical Industry, and all materials used as received.

97

98   **4. Results and discussion**

99   We have examined the effects of the injected $Al(acac)_3$ concentration, the wavelength, the

100   fluid velocity and the dissolving organic solvent on D_{12} of $Al(acac)_3$ as described elsewhere

101   [17,19]. The $Al(acac)_3$ concentration of ethanol with 7.5×10^{-4} g/mL and the wavelength of

102   300 nm were used in all diffusion measurements. The fluid velocities were controlled at lower

103   than 8×10^{-3} m/s, and all measurements were made at $DeSc^{1/2} < 8$, where De is the Dean

104 number and *Sc* is the Schmidt number. In this study at least three measurements at the given

105 condition were measured, and the average diffusion datum was determined to be the D_{12} value.

106 All determined D_{12} data are presented in Table 1, together with the values of fluid density ρ

107 and viscosity η.

108

Table 1

Infinite dilution binary diffusion coefficient D_{12} data of Al(acac)$_3$ measured
in supercritical CO_2 at 308.15 to 333.15 K and in liquid ethanol at 300.15
to 333.15 K, together with the densities ρ and viscosities η of the fluids.

P (MPa)	ρ(kg/m^3)	η (10^{-6} Pa s)	D_{12} (10^{-8} m^2/s)
Measured by the CIR method in supercritical CO$_2$			
308.15 (K)			
7.80	331.50	24.62	1.163
7.95	388.81	28.15	1.096
8.00	419.09	30.17	1.072
8.05	455.61	32.54	1.028
8.10	490.76	34.95	1.004
8.20	542.80	39.26	1.004
8.30	574.13	42.12	1.045
8.40	595.70	44.21	1.045
8.50	612.12	45.87	0.992
8.80	646.10	49.52	0.964
9.00	662.13	51.36	0.926
9.50	691.50	54.92	0.882
10.00	712.81	57.68	0.840
10.50	729.76	60.00	0.802
11.00	743.95	62.03	0.788
12.00	767.07	65.51	0.754
13.00	785.70	68.50	0.718
14.00	801.41	71.15	0.709
16.00	827.17	75.81	0.667
18.00	848.04	79.88	0.620
20.00	865.72	83.56	0.607
22.00	881.15	86.97	0.593

23.00	888.20	88.59	0.573
24.00	894.88	90.16	0.571
25.00	901.23	91.69	0.564
30.00	929.11	98.86	0.518
32.00	938.84	101.54	0.515
35.00	952.29	105.42	0.505
40.00	972.26	111.57	0.480

313.15 (K)

8.40	334.71	25.02	1.447
8.50	353.91	26.06	1.398
8.60	375.95	27.33	1.321
8.70	401.13	28.87	1.273
8.80	429.10	30.70	1.216
8.90	458.03	32.72	1.121
9.00	485.50	34.77	1.145
9.10	510.38	36.75	1.109
9.30	550.54	40.17	1.114
9.50	580.01	42.90	1.055
10.00	628.61	47.81	0.984
10.50	660.15	51.33	0.944
11.00	683.52	54.11	0.925
11.50	702.18	56.46	0.872
12.00	717.76	58.52	0.846
13.00	743.04	62.05	0.797
15.00	780.23	67.73	0.746
16.00	794.90	70.16	0.718
17.00	807.87	72.39	0.701
19.00	830.09	76.45	0.675
20.00	839.81	78.32	0.657
21.00	848.81	80.10	0.646
25.00	879.49	86.62	0.598
30.00	909.89	93.83	0.561
32.00	920.39	96.51	0.543
35.00	934.81	100.37	0.534
40.00	956.07	106.46	0.499

323.15 (K)

9.80	361.28	26.98	1.498
10.00	384.33	28.33	1.457
10.10	396.32	29.06	1.392
10.30	420.88	30.64	1.344
10.50	445.55	32.32	1.250
10.80	480.95	34.90	1.256
11.00	502.64	36.59	1.245
11.50	548.84	40.48	1.176
12.00	584.71	43.79	1.144
13.00	636.12	49.04	1.063
15.00	699.75	56.52	0.933
18.00	757.12	64.44	0.838
20.00	784.29	68.67	0.780
22.00	806.61	72.41	0.751
25.00	834.19	77.42	0.710
30.00	870.43	84.75	0.657
35.00	899.23	91.27	0.619

333.15 (K)

12.00	434.43	32.02	1.460
13.00	505.35	37.27	1.326
14.00	561.37	42.05	1.220
15.00	604.09	46.13	1.128
16.00	637.50	49.61	1.092
18.00	687.25	55.35	0.996
20.00	723.68	60.04	0.904
22.00	752.38	64.07	0.852
25.00	786.55	69.33	0.792
30.00	829.71	76.82	0.739
35.00	862.94	83.34	0.699

Measured by the Taylor dispersion method in liquid ethanol

300.15 (K)

0.10	783.79	1071.12	0.073
30.00	807.52	1258.39	0.063

313.15 (K)

0.10	772.56	844.89	0.106
30.00	797.97	1003.37	0.089
323.15 (K)			
0.10	763.62	711.01	0.126
333.15 (K)			
0.10	754.36	602.99	0.157

[a] Standard uncertainties are 0.02 K for $u(T)$, 0.01 MPa for $u(P)$. The combined expanded uncertainty $U_c(D_{12})$ is 4×10^{-13} m²/s at 0.95 level of confidence with $k=2$.
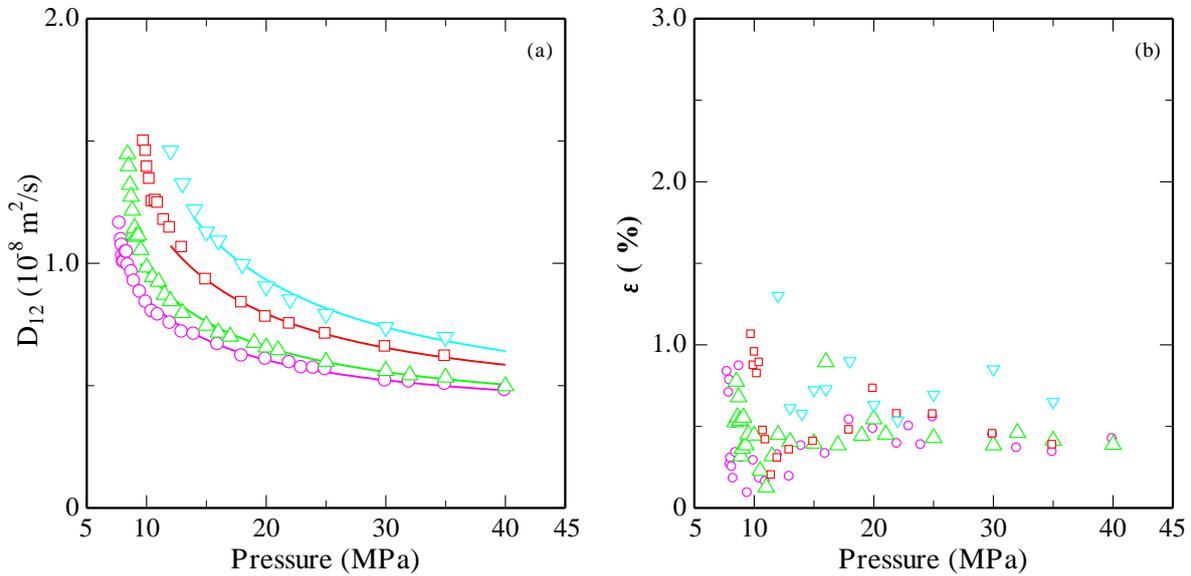
Fig. 1. Pressure dependence on the (a) D_{12} and (b) ε of Al(acac)$_3$ measured at 308.15 K (○), 313.15 K (△), 323.15 K (□) and 333.15 K (▽), and at 7.80 to 40.00 MPa in supercritical CO_2 by the CIR method, and together with the correlated line (with best AARD%) by Eq. (4).

Fig. 1 illustrates the pressure influence on the determined D_{12} and ε by the CIR method for Al(acac)$_3$ at 308.15, 313.15, 323.15 and 333.15 K, and pressures from 7.80 to 40.00 MPa in supercritical CO_2. Almost ε values were lower than 1% as seen in Fig. 1 (b). The greater pressure sensitivity of D_{12} at lower pressure indicates that the fluid density or viscosity is remarkable factor, because these properties change rapidly with pressure in this region. It was

123 found that an empirical correlation (Eq. (4)) can represent the 84 D_{12} data for Al(acac)$_3$

124 determined in supercritical CO_2 with the average absolute relative deviation (AARD) of 3.9%.

$$D_{12} = c_0 + c_1 \frac{1}{P} + c_2 T + c_3 \frac{T}{P} \tag{4}$$

$$\text{AARD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{D_{12,\text{meas}} - D_{12,\text{pred}}}{D_{12,\text{meas}}} \right|_i \times 100\% \tag{5}$$

127 where D_{12}, c_0, c_1, c_2, c_3, T and P are in m^2/s, m^2/s, m^2 MPa/s, m^2/(s K), m^2 MPa/(s K), K and

128 MPa, respectively, N is the number of experimental data points, and $D_{12,\text{meas}}$ and $D_{12,\text{pred}}$ are

129 the measured and predicted D_{12} data, respectively. The parameters of c_0 to c_3 determined

130 individual fittings at 308.15, 313.15, 323.15 and 333.15 K and a global fitting are presented in

131 Table 2 with the values of N and AARD. It was found [12,14,17,20] that the simple empirical

132 correlation can well represent the D_{12} data determined in this study over the higher pressure

133 region, as shown in Fig. 1 and Table 2.

134

Table 2

Correlated results using Eq. (4) for the determined D_{12} values of Al(acac)$_3$ in supercritical CO_2.

T (K)	Rang of P (MPa)	N	$c_0 \times 10^9$ (m^2/s)	$c_1 \times 10^7$ (m^2 MPa/s)	$c_2 \times 10^{11}$ (m^2/(s K))	$c_3 \times 10^9$ (m^2 MPa/(s K))	AARD (%)
308.15	Entire	29	3.458	0.535	-	-	3.0
	>8.4	22	3.563	0.497	-	-	2.0
313.15	Entire	27	3.184	0.700	-	-	5.3
	>9.5	18	3.503	0.617	-	-	1.5
323.15	Entire	17	3.095	1.002	-	-	3.5
	>12	9	3.768	0.834	-	-	1.6
333.15	Entire	11	2.593	1.333	-	-	2.6
	>14	9	3.491	1.169	-	-	1.8
Common	Entire	84	7.957	-8.476	-1.502	2.929	3.9

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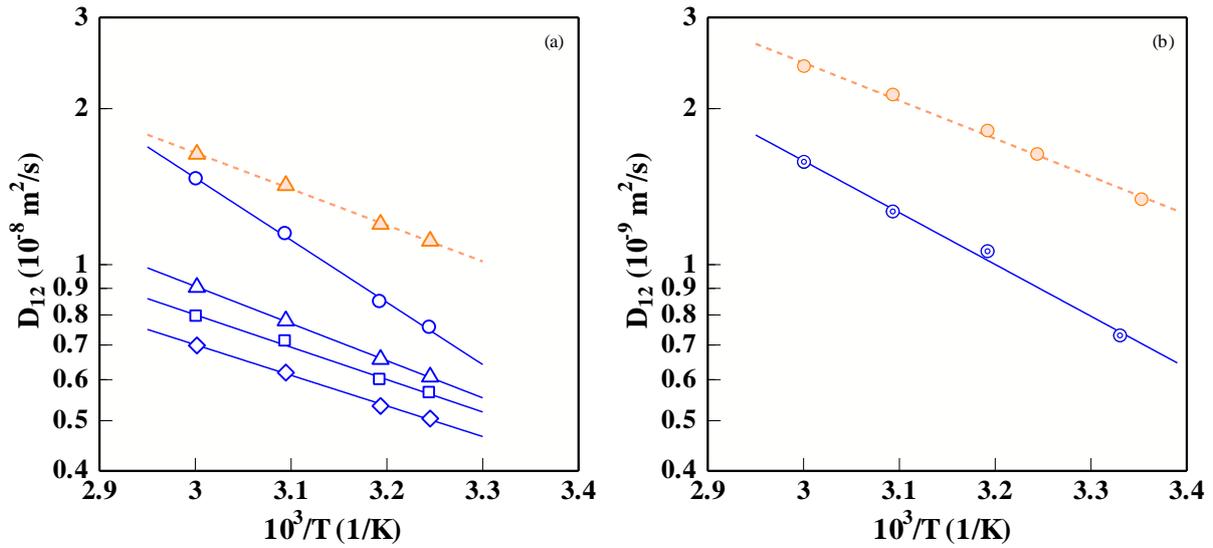
136

137 Fig. 2. Arrhenius relationship for the diffusion coefficients of Al(acac)$_3$ in (a) supercritical

138 CO$_2$ at 12.00 ($\circ$), 20.00 ($\triangle$), 25.00 ($\square$), 35.00 ($\diamond$) MPa and (b) liquid ethanol at 0.10 MPa ($\odot$),

139 together with those of Li(acac) in the literature [17] at 20.00 MPa ($\triangle$) in supercritical CO$_2$ and

140 at 0.10 MPa ($\circ$) in liquid ethanol, respectively.

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143 The effects of temperature on D_{12} values of Al(acac)$_3$ in supercritical CO$_2$ determined by

144 the CIR method at 308.15 to 333.15 K and at 12.00, 20.00, 25.00, 35.00 MPa, and in ethanol

145 determined by the Taylor dispersion method at 300.15 to 333.15 K and 0.10 MPa are plotted

146 in Fig. 2 along with the Li(acac) data [17] in supercritical CO$_2$ at 20.00 MPa and in ethanol at

147 0.10 MPa. A straight line was formed in all plots for each of the pressure investigated. The

148 D_{12} values can be described using the Arrhenius expression in Eq.(6), where D_0 is the

149 preexponential factor, E_a is the activation energy, T is the absolute temperature and R the

150 universal gas constant.

151 $$D_{12} = D_0 \cdot e^{-\frac{E_a}{RT}}$$ (6)

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154   In Fig. 2(a), the slope behavior at 12.00 MPa in supercritical CO_2 was distinctly separated

155 from those at 20.00, 25.00 and 35.00 MPa. The slopes of these lines, however, were different,

156 indicated different activation energies of diffusion at different pressures. At 20.00 MPa, the

157 slopes in the plots for $Al(acac)_3$ and $Li(acac)$ in supercritical CO_2 appeared to be no

158 significant differences, however, there were considerable differences between the D_{12} values.

159 Similar behavior can be seen in liquid ethanol as shown in Fig. 2 (b). From the slopes of the

160 lines in Figs 2 (a) and (b), the activation energies of diffusion for $Al(acac)_3$ in supercritical

161 CO_2 and in liquid ethanol were determined. The achieved E_a values of $Al(acac)_3$ were listed in

162 Table 3 as well as $Li(acac)$ [17]. The results showed that the activation energies of the

163 diffusion for $Al(acac)_3$ were 13.7 and 19.1 kJ/mol at 20.00 MPa in supercritical CO_2 and at

164 0.10 MPa in liquid ethanol, respectively. These values were slightly higher than those for

165 $Li(acac)$ under the same conditions [17]. And the determined activation energy values for

166 $Al(acac)_3$ in supercritical CO_2 were higher at lower pressures, indicating that diffusion

167 behavior tended to be more temperature sensitive at lower pressures than it was at higher

168 pressures.

169

170

Table 3.

The values of the activation energy E_a for diffusion in supercritical CO_2 and in liquid
ethanol.

Fluid	Solute	E_a (kJ/mol)				
		0.10 (MPa)	12.00 (MPa)	20.00 (MPa)	25.00 (MPa)	35.00 (MPa)
Supercritical CO_2	$Al(acac)_3$		23.0	13.7	12.0	11.3
	$Li(acac)$			13.4[a]		
Liquid ethanol	$Al(acac)_3$	19.1				
	$Li(acac)$	14.0[a]				

[a]Reported E_a value of $Li(acac)$ in the literature [17].

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Fig. 3. Relationship between the D_{12} data at 313.2 K and 11.0 MPa in supercritical CO_2 and molecular weight M of Al(acac)$_3$ ($\odot$, M=324.3 g/mol), together with the other metallic complexes such as Li(acac) ($\triangle$, M=106.1 g/mol) [17], ferrocene ($\triangledown$, M=186.0 g/mol) [15], 1,1'-dimethylferrocene ($\square$, M=214.1 g/mol) [15], Pd(acac)$_2$ ($\blacktriangledown$, M=304.6 g/mol) [14], Co(acac)$_3$ ($\bullet$, M=356.3 g/mol) [14], Pt(acac)$_2$ ($\blacktriangle$, M=393.3 g/mol) [16], and the organic compounds of nonmetallic elements ($\circ$, M=32.0 – 1137.9 g/mol) [21].

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Fig. 3 plots the D_{12} values measured in this study and reported in literature [14-17, 21] at 313.15 K and 11.00 MPa in supercritical CO_2 against the solute molecular weights M for various compounds. Overall, a strong dependence of the D_{12} on the solute molecular weight was found for molecules diffusing within supercritical CO_2. The D_{12} data of Al(acac)$_3$ (M=324.3 g/mol) measured in this study and literature for other metallic complexes such as Li(acac) (M=106.1 g/mol) [17], ferrocene (M=186.0 g/mol) [15], 1,1'-dimethylferrocene (M=214.1 g/mol) [15], Pd(acac)$_2$ (M=304.6 g/mol) [14], Co(acac)$_3$ (M=356.3 g/mol) [14], Pt(acac)$_2$ (M=393.3 g/mol) [16] in supercritical CO_2 seemed to be inversely proportional to

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189   their molecular weights at constant temperature and pressure with a slope of about −0.5.

190   Similar behavior has been observed in the literature [21] for organic compounds of

191   nonmetallic elements. In addition, most of the D_{12} values of organic compounds of

192   nonmetallic elements (M=32.0 − 1137.9 g/mol) in the literature [21] were lower than those of

193   metallic complexes (M=106.1 − 393.3 g/mol) at the same molecular weights. This result

194   suggested that the apparent radiuses of metallic complexes appeared to be smaller than those

195   of organic compounds of nonmetallic elements in supercritical CO_2. Furthermore, it was also

196   observed that the D_{12} value of Pt(acac)$_2$ (D_{12}=9.350×10^{-9} m^2/s) [16] with M of 393.3 g/mol

197   had slightly larger value to Al(acac)$_3$ (D_{12}=9.250×10^{-9} m^2/s) with M of 324.3 g/mol at 313.15

198   K and 11.00 MPa in supercritical CO_2. It may be considered that the apparent molecular size

199   of Pt(acac)$_2$ with two acac ligands in supercritical CO_2 exhibited lower value than that of

200   Al(acac)$_3$ with three, and in this case the D_{12} value depended not on solute molecular weight.

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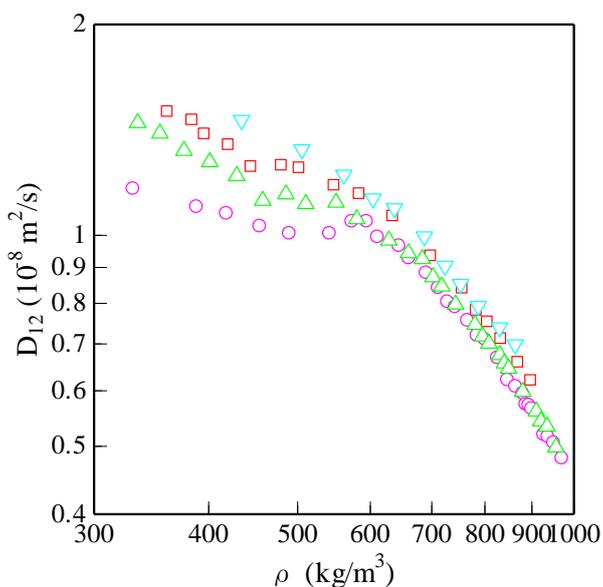
204   Fig. 4. Density dependence of D_{12} of Al(acac)$_3$ in supercritical CO_2 at 308.15 K (○), 313.15

205   K (△), 323.15 K (□) and 333.15 K (▽) masured by the CIR method in this study.

206   Fig. 4 shows the D_{12} vs CO_2 density ρ for Al(acac)$_3$ in supercritical CO_2. The plots

207   pointed significant temperature dependence over the region of lower density, but those in the

208   higher density region slightly do. In addition, in the CO_2 density region higher than about 580

209   kg/m^3, the D_{12} values can be linearly correlated with the density at each temperature, but the

210   D_{12} values expressed slowing down in the region of lower density. This slowing down

211   behavior was found clearly as the critical point of CO_2 (31.1 °C, 7.38 MPa) was approached.

212   The behavior of diffusion in the critical region is important to understanding transport

213   phenomena in supercritical fluids. So far, many compounds such as acetone [22], alkane [22],

214   benzene [22, 23], 15-crown-5 [21], dimethylnaphthalene isomers [24], ferrocene [15],

215   myristoleic acid methyl ester [25], naphthalene [24], phenylbutazone [20] and vitamin K$_3$ [26]

216   have been observed the similar slowing down. But, Yang et al [27] reported that the D_{12} data

217   of benzoic acid, biphenyl, 1,4-dichlorobenzene, phenanthrene and phenol in supercritical CO_2

218   diminished sharply near the critical point. According to Clifford and Coleby [28], the

219   diffusion coefficients for a solute in a supercritical fluid did not show any significant

220   anomalous behavior in the critical region, if the solute concentration was sufficiently low.

221   The measured D_{12} data of Al(acac)$_3$ at 308.15, 313.15, 323.15 and 333.15 K in

222   supercritical CO_2 and at 300.15, 313.15, 323.15 and 333.15 K in liquid ethanol as a function

223   of T/η is shown in Fig. 5 with the solid line representing Eq. (7).

224    $$D_{12} = \frac{R}{6\pi r} \frac{T}{\eta} \tag{7}$$

225   where R is the universal gas constant, r is the radius of the diffusing solute and η is fluid

226   viscosity. In this study the diffusion data measured in supercritical CO_2 (with higher T/η

227   values) indicated one order of magnitude larger value than those determined in liquid ethanol

228   (with lower T/η values). The plot in liquid state showed a linear relationship with the slope of

229   1, obviously the well-known Stokes-Einstein equation held good under the liquid condition,

230 but it did not hold well under the conditions including the supercritical state. This indicated

231 that the apparent molecular diameter of the Al(acac)$_3$ was leaded to decrease with increasing

232 viscosity. As a result, the Stokes-Einstein equation was inadequate to describe the diffusion in

233 supercritical system.

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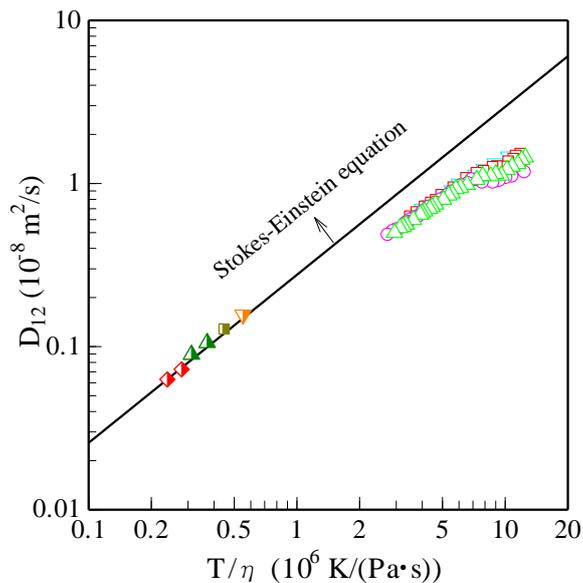
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236   Fig. 5. Plot of D_{12} vs. T/η for all the D_{12} values measured by the CIR method at 308.15 K

237 (○), 313.15 K (△), 323.15 K (□) and 333.15 K (▽) in suprcritical CO$_2$, and measrued by the

238 Taylor dispersion method at 300.15 K (◆), 313.15 K (▲), 323.15 K (◼) and 333.15 K(▼) in

239 liquid ethanol. The solid line was obtained from the Eq. (7).

240

241

242   On the hydrodynamic approach for predicting D_{12} in fluids, we have demonstrated

243 [2,4,5,13-17,20,21,23,25] the validity of the correlation among the properties of D_{12}, T and η,

244 as shown in Eq. (8). Fig. 6 indicates D_{12}/T vs η for all the D_{12} data of Al(acac)$_3$ measured in

245 this study, together with deviations between the $D_{12, \text{meas}}$ and the $D_{12, \text{pred}}$ values by Eq. (8).

246    $$\frac{D_{12}}{T} = \alpha \eta^{\beta} \qquad (8)$$

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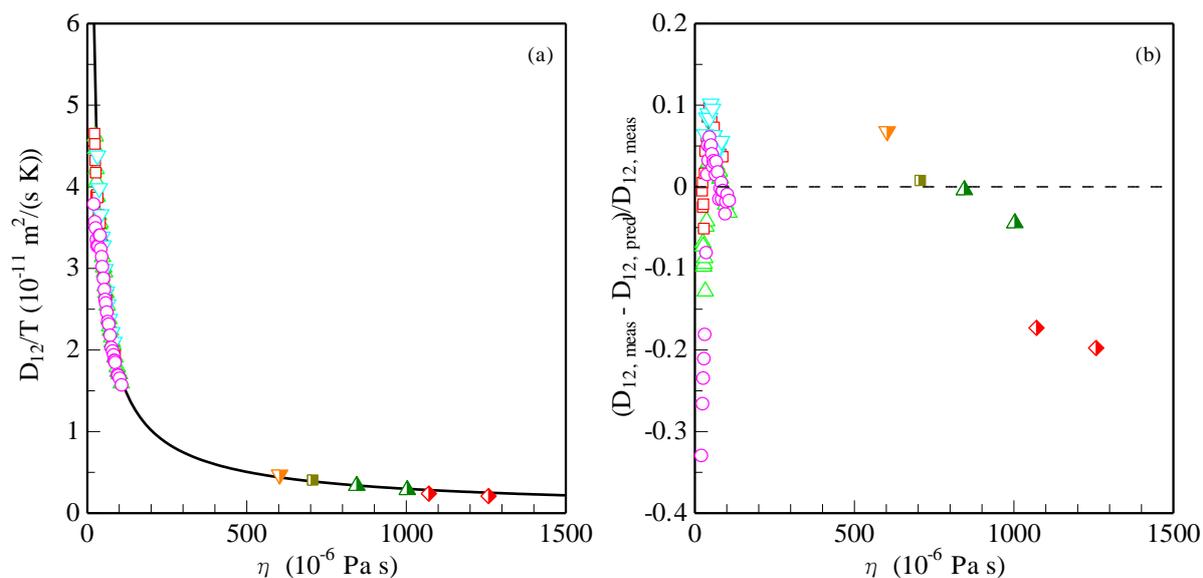
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Fig. 6. Plots of (a) D_{12}/T and (b) $(D_{12, \text{meas}} - D_{12, \text{pred}})/D_{12, \text{meas}}$ vs. η for all the D_{12} values measured by the CIR method at 308.15, 313.15, 323.15 and 333.15 K in suprcritical CO_2, and measrued by the Taylor dispersion method at 300.15, 313.15, 323.15 and 333.15 K in liquid ethanol. The solid line in (a) was obtained with the parameters of $\alpha=1.558\times10^{-14}$ and $\beta=-0.761$ using the Eq. (8). The key is the same as in Fig. 5.

where α and β are constants. As has been seen for many compounds, the D_{12}/T values decrease simply with increasing fluid viscosities. It was found that the values of D_{12}/T for all D_{12} data of Al(acac)$_3$ measured in this study were also well correlated with the η values of fluids, which viscosities were varied over a wide range of values from 2.462×10^{-5} to 1.258×10^{-3} Pa s. And most of the deviation values of $(D_{12, \text{meas}} - D_{12, \text{pred}})/D_{12, \text{meas}}$ were less than ±0.2 as seen in Fig. 6 (b). The proposed correlation of D_{12} [m^2/s]$=1.558\times10^{-14}$ T [K] η [Pa s]$^{-0.761}$ can represent the measured 90 D_{12} data in this work with 5.6% AARD values for the two studied systems of Al(acac)$_3$ in supercritical CO_2 and Al(acac)$_3$ in liquid ethanol.

16

5. Conclusions

266

267   The infinite dilution binary diffusion coefficients D_{12} for aluminum acetylacetonate were

268 determined by the CIR method in supercritical CO_2 at 308.15, 313.15, 323.15 and 333.15 K

269 and 7.80 to 40.00 MPa. Furthermore, the D_{12} data in liquid ethanol at 300.15, 313.15, 323.15

270 and 333.15 K and at 0.10 and 30.00 MPa were obtained by the Taylor dispersion method. It

271 was found that the D_{12} values measured in supercritical CO_2 show slowing down in the near

272 critical region. The determined activation energies of diffusion were 23.0, 13.7, 12.0, 11.3

273 kJ/mol at 12.00, 20.00, 25.00, 35.00 MPa in the temperature range of 308.15 − 333.15 K in

274 supercritical CO_2 and 19.1 kJ/mol at 0.10 MPa in the temperature range of 300.15 − 333.15 K

275 in liquid ethanol, respectively. All D_{12} data for aluminum acetylacetonate determined in

276 supercritical CO_2 and in liquid ethanol were correlated with the equation of D_{12}

277 $[m^2/s]=1.558 \times 10^{-14}$ T [K] η [Pa s]$^{-0.761}$ over a wild fluid viscosity range from 2.462×10^{-5} to

278 1.258×10^{-3} Pa s and the average absolute relative deviation of the correlation for 90 data

279 points is 5.6%.

280

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322

Figure Captions

Fig. 1. Pressure dependence on the (a) D_{12} and (b) ε of Al(acac)$_3$ measured at 308.15 K (○), 313.15 K (△), 323.15 K (□) and 333.15 K (▽), and at 7.80 to 40.00 MPa in supercritical CO_2 by the CIR method, and together with the correlated line (with best AARD%) by Eq. (4).

Fig. 2. Arrhenius relationship for the diffusion coefficients of Al(acac)$_3$ in (a) supercritical CO_2 at 12.00 (○), 20.00 (△), 25.00 (□), 35.00 (◇) MPa and (b) liquid ethanol at 0.10 MPa (⊚), together with those of Li(acac) in the literature [17] at 20.00 MPa (△) in supercritical CO_2 and at 0.10 MPa (○) in liquid ethanol, respectively.

Fig. 3. Relationship between the D_{12} data at 313.2 K and 11.0 MPa in supercritical CO_2 and molecular weight M of Al(acac)$_3$ (⊚ , M=324.3 g/mol), together with the other metallic complexes such as Li(acac) (▲ , M=106.1 g/mol) [17], ferrocene (▽ , M=186.0 g/mol) [15], 1,1'-dimethylferrocene (□ , M=214.1 g/mol) [15], Pd(acac)$_2$ (▼ , M=304.6 g/mol) [14], Co(acac)$_3$ (◓ , M=356.3 g/mol) [14], Pt(acac)$_2$ (▲ , M=393.3 g/mol) [16], and the organic compounds of nonmetallic elements (○ , M=32.0 – 1137.9 g/mol) [21].

Fig. 4. Density dependence of D_{12} of Al(acac)$_3$ in supercritical CO_2 at 308.15, 313.15, 323.15 and 333.15 K masured by the CIR method in this study. The key is the same as in Fig. 1.

Fig. 5. Plot of D_{12} vs. T/η for all the D_{12} values measured by the CIR method at 308.15 K (○), 313.15 K (△), 323.15 K (□) and 333.15 K (▽) in suprcritical CO_2, and measrued by the Taylor dispersion method at 300.15 K (◆), 313.15 K (▲), 323.15 K (■) and 333.15 K(▼) in liquid ethanol. The solid line was obtained from the Eq. (7).

Fig. 6. Plots of (a) D_{12}/T and (b) $(D_{12, meas} - D_{12, pred})/D_{12, meas}$ vs. η for all the D_{12} values measured by the CIR method at 308.15, 313.15, 323.15 and 333.15 K in suprcritical CO_2, and measrued by the Taylor dispersion method at 300.15, 313.15, 323.15 and 333.15 K in liquid ethanol. The solid line in (a) was obtained with the parameters of α=1.558×10^{-14} and β=–0.761 using the Eq. (8). The key is the same as in Fig. 5.

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353   Graphical abstract

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