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Infinite-Dilution Binary Diffusion Coefficients of 2-Propanone, 2-Butanone, 2-Pentanone, and 3-Pentanone in CO_2 by the Taylor Dispersion Technique from 308.15 to 328.15 K in the Pressure Range from 8 to 35 MPa

T. Funazukuri,[1,2] C. Y. Kong,[3] and S. Kagei[3]

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Infinite-dilution binary diffusion coefficients of 2-propanone, 2-butanone, 2-pentanone, and 3-pentanone in carbon dioxide were measured by the Taylor dispersion method at temperatures from 308.15 to 328.15 K and pressures from 7.60 to 34.57 MPa. The D_{12} values were obtained from the response curves by the method of fitting in the time domain. The accuracy in the fitting error was examined for each measurement. The measured D_{12} data were found to be well correlated by the Schmidt number correlation, with AAD% = 3.74% for all solutes.

KEY WORDS: binary diffusion coefficient; 2-butanone; carbon dioxide; curve fitting; 2-pentanone; 3-pentanone; 2-propanone; Schmidt number correlation; supercritical; Taylor dispersion method.

1. INTRODUCTION

Recently, many uses of supercritical fluids have been reported in various industrial fields. Since the estimation of mass transfer rates for designing reactors or simulating reactions under supercritical conditions has become increasingly important, binary diffusion coefficients of various compounds are essential, as well as other transport properties. Measurements of D_{12}

[1] Department of Applied Chemistry, Institute of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.
[2] To whom correspondence should be addressed. E-mail: funazo@apchem.chem.chuo-u.ac.jp.
[3] Department of Information and Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan..

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values are reported [1], but these are still not sufficient to design reactors. The measurements for ketones are limited, and the values are not consistent. D_{12} values are available for 2-propanone [1–6] as well as for other ketones [3, 7]. In this study measurements for 2-propanone, 2-butanone, and 2- and 3-pentanones were made by the Taylor dispersion method, and a predictive correlation for the D_{12} data is examined.

2. THEORY

In the Taylor dispersion technique [8, 9] in which a small amount of a tracer species is injected at $z=0$ into a fully developed laminar flow moving in a circular cross-sectional tubing, the response of the averaged tracer concentration C_a on the cross section at the column exit at $z=L$ can be described by Eq. (1) [1]:

$$C_a = \frac{m}{\pi R^2 (4\pi K t)^{1/2}} \exp\left[-\frac{(L-u_a t)^2}{4Kt} \right] \tag{1}$$

where

$$K = D_{12} + \frac{u_a^2 R^2}{48 D_{12}} \tag{2}$$

m is the injected amount of the tracer species, u_a is the average flow velocity, t is the time, R is the tube radius, and D_{12} is the binary diffusion coefficient. In this study the D_{12} value is obtained by the method of curve fitting in the time domain so that the root-mean-square error ε defined by Eq. (3) is minimized:

$$\varepsilon = \left(\frac{\int_{t_1}^{t_2} (C_{a,\,meas}(t) - C_{a,\,cal}(t))^2 \, dt}{\int_{t_1}^{t_2} (C_{a,\,meas}(t))^2 \, dt} \right)^{1/2} \tag{3}$$

where a fitting period between t_1 and t_2 is chosen so that the measured response curve at higher than 10% peak height is compared with the calculated curve.

3. EXPERIMENT

The experimental apparatus and the procedures are almost-identical to those employed in the previous study [1]. 2-Propanone (99.5%; Junsei Chemical Co., Ltd.), 2-butanone (99.0%; Kanto Chemical Co., Inc.), 2-pentanone (99.5%; Sigma–Aldrich), and 3-pentanone (98.0%; Wako

Pure Chemical Industries, Ltd.) were employed without further purification. Carbon dioxide with a purity higher than 99.995% (water, <40 ppm) was used. The diameter of the diffusion column, measured by an X-ray microanalyzer, is 0.817 ± 0.001 mm and the length is 35.00 m. The diffusion column, the injector (Rheodyne 7520), and a preheating column are immersed in a water bath whose temperature is controlled at the targeted temperature to within a fluctuation of ± 0.01 K. The pressure drop between the injector and the column exit is within 0.1 MPa, and the pressure fluctuation is less than 10 kPa. The tracer species is filled in a rotor (0.5 μl) of the injector in the liquid state.

The response curves were measured with a UV–Vis multidetector (MD-1510; JASCO, Japan) obtained by scanning from 195 to 650 nm at 4-nm increments and sampling intervals of 1.6 s.

4. RESULTS AND DISCUSSION

The wavelength dependence of the D_{12} values determined from the response curve at every wavelength was examined. The D_{12} values that show no wavelength dependence were regarded as the intrinsic D_{12} values, as described elsewhere [1]. As a result, the D_{12} values for 2-propanone, 2-butanone, 2-pentanone, and 3-pentanone were obtained from the response curves measured at 275, 275, 279, and 279 nm, respectively.

Although the criterion that the effect of the secondary flow due to column coiling is as high as 1% is given by Eq. (4) [10], the dependence of the CO_2 flow velocity on the D_{12} values were examined under each measurement condition.

$$\mathrm{DeSc}^{1/2} < 8 \tag{4}$$

where De and Sc are the Dean number and the Schmidt number, respectively. The apparent D_{12} values decrease with decreasing CO_2 flow velocity, and the plateau values were regarded as the true D_{12} values. Note that Eq. (4) was satisfied at all measurement conditions.

Table I lists the D_{12} values measured for 2-propanone, 2-butanone, 2-pentanone, and 3-pentanone along with the fitting error. Note that a good fit is for $\varepsilon < 0.01$ [1], and an acceptable fit is for $\varepsilon < 0.02$. The data for 2-propanone are supplementary to those reported in the previous study with the Taylor dispersion method [1], and the present D_{12} values for 2-propanone are fully consistent with the previous data. It is observed that the difference in the D_{12} values for isomers such as 2- and 3-pentanones is not discernible, as has also been observed at 314.5 K by Dahmen et al. [3]. Figure 1 shows D_{12} values versus pressure for 2-butanone in supercritical

Table I. Measured Binary Diffusion Coefficients D_{12} for Ketones in Supercritical Carbon Dioxide at Temperatures from 308.15 to 328.15 K and Pressures from 8 to 35 MPa

Tracer	T (K)	P (MPa)	D_{12} (10^{-8} m$^2 \cdot$ s^{-1})	ε
2-Propanone	308.15	11.43	1.620	2.44×10^{-3}
		13.97	1.481	1.92×10^{-3}
		16.09	1.430	1.20×10^{-3}
		16.10	1.396	9.62×10^{-4}
		16.10	1.411	2.21×10^{-3}
		16.12	1.422	1.46×10^{-3}
		16.85	1.370	2.15×10^{-3}
		19.78	1.312	1.64×10^{-3}
		24.63	1.230	3.43×10^{-3}
		29.60	1.146	2.16×10^{-3}
		34.49	1.087	2.06×10^{-3}
	313.15	14.43	1.619	2.22×10^{-3}
		14.45	1.580	1.97×10^{-3}
		16.13	1.528	4.73×10^{-3}
		16.15	1.535	4.82×10^{-3}
		16.16	1.553	1.30×10^{-3}
		16.42	1.501	1.25×10^{-3}
		25.29	1.269	9.59×10^{-4}
	318.15	11.49	1.998	1.77×10^{-2}
		13.23	1.848	6.41×10^{-3}
		16.17	1.655	3.48×10^{-3}
		18.92	1.529	2.71×10^{-3}
		19.80	1.503	1.48×10^{-3}
		24.70	1.376	1.66×10^{-3}
		29.55	1.311	1.95×10^{-3}
		34.56	1.208	1.85×10^{-3}
	323.15	11.12	2.536	1.36×10^{-2}
		12.07	2.234	1.74×10^{-2}
		13.13	2.008	1.44×10^{-2}
		15.12	1.896	3.62×10^{-3}
		16.10	1.805	5.42×10^{-3}
		19.00	1.669	3.02×10^{-3}
		21.41	1.596	3.08×10^{-3}
		24.61	1.494	9.74×10^{-4}
		29.49	1.347	1.09×10^{-3}
		34.53	1.274	1.00×10^{-3}
	328.15	15.10	2.073	1.50×10^{-2}
		16.91	1.880	1.01×10^{-2}
		19.79	1.740	4.82×10^{-3}
		23.92	1.592	2.78×10^{-3}
		29.52	1.456	3.56×10^{-3}
		34.52	1.367	3.56×10^{-3}
2-Butanone	308.15	8.33	1.875	1.99×10^{-2}
		8.64	1.951	9.02×10^{-3}
		9.07	1.759	1.55×10^{-2}
		9.74	1.640	3.05×10^{-3}
		11.43	1.502	3.60×10^{-3}

Table I. *(Continued)*

Tracer	T (K)	P (MPa)	D_{12} (10^{-8} m$^2 \cdot$ s^{-1})	ε
		13.97	1.389	2.29×10^{-3}
		16.82	1.256	1.69×10^{-3}
		19.78	1.203	2.53×10^{-3}
		24.67	1.113	1.82×10^{-3}
		29.56	1.045	1.33×10^{-3}
		34.51	1.003	2.21×10^{-3}
	313.15	13.33	1.599	4.08×10^{-3}
		16.42	1.413	3.09×10^{-3}
		19.75	1.307	1.88×10^{-3}
		24.56	1.209	2.07×10^{-3}
		29.52	1.124	1.49×10^{-3}
		34.47	1.074	2.44×10^{-3}
	318.15	13.23	1.699	4.24×10^{-3}
		16.15	1.567	3.32×10^{-3}
		18.94	1.418	3.18×10^{-3}
		19.83	1.372	2.96×10^{-3}
		24.66	1.253	1.59×10^{-3}
		29.53	1.174	1.48×10^{-3}
		34.53	1.104	3.31×10^{-3}
	323.15	12.07	2.181	1.09×10^{-2}
		13.12	1.962	1.07×10^{-2}
		16.11	1.705	4.51×10^{-3}
		19.00	1.539	2.09×10^{-3}
		21.42	1.454	8.66×10^{-4}
		24.62	1.383	1.61×10^{-3}
		29.51	1.261	1.64×10^{-3}
		34.53	1.216	1.95×10^{-3}
	328.15	15.13	1.856	1.64×10^{-2}
		16.91	1.754	1.08×10^{-2}
		19.77	1.611	3.71×10^{-3}
		23.93	1.452	2.31×10^{-3}
		29.54	1.331	3.62×10^{-3}
		34.52	1.245	1.48×10^{-3}
2-Pentanone	308.15	8.88	1.563	1.77×10^{-2}
		9.36	1.645	6.56×10^{-3}
		9.86	1.471	2.13×10^{-3}
		10.76	1.405	3.08×10^{-3}
	313.15	7.60	2.541	1.76×10^{-2}
		9.32	1.952	1.69×10^{-2}
		10.08	1.708	7.14×10^{-3}
		11.45	1.551	1.39×10^{-3}
		12.54	1.470	6.02×10^{-3}
		13.80	1.404	1.32×10^{-3}
		14.80	1.367	1.02×10^{-3}
		16.42	1.281	2.22×10^{-3}
		18.68	1.220	1.26×10^{-3}
		20.54	1.168	3.90×10^{-4}
		23.02	1.119	1.26×10^{-3}

Table I. *(Continued)*

Tracer	T (K)	P (MPa)	D_{12} (10^{-8} m$^2 \cdot$ s^{-1})	ε
		26.68	1.072	1.61×10^{-3}
		29.25	1.048	6.68×10^{-4}
	314.5	10.44	1.752	4.75×10^{-3}
		11.55	1.609	4.44×10^{-3}
		12.82	1.508	3.21×10^{-3}
		14.30	1.421	3.80×10^{-3}
		15.63	1.374	1.75×10^{-3}
		17.27	1.297	6.87×10^{-4}
		19.20	1.224	1.02×10^{-3}
3-Pentanone	308.15	8.65	1.731	1.45×10^{-2}
		9.08	1.676	3.55×10^{-3}
		9.74	1.522	1.07×10^{-2}
		11.43	1.368	4.53×10^{-3}
		13.97	1.271	3.34×10^{-3}
		16.84	1.161	1.75×10^{-3}
		19.77	1.129	3.23×10^{-3}
		24.65	1.033	2.64×10^{-3}
		29.58	0.965	1.52×10^{-3}
		34.51	0.921	2.05×10^{-3}
	313.15	11.47	1.537	7.29×10^{-3}
		13.34	1.466	2.56×10^{-3}
		16.42	1.307	2.11×10^{-3}
		19.74	1.187	1.72×10^{-3}
		24.57	1.115	2.05×10^{-3}
		29.51	1.042	7.60×10^{-4}
		34.48	0.980	1.28×10^{-3}
	318.15	11.49	1.801	1.39×10^{-2}
		13.24	1.601	4.90×10^{-3}
		16.15	1.455	3.89×10^{-3}
		18.91	1.307	3.02×10^{-3}
		19.83	1.283	1.32×10^{-3}
		24.69	1.165	1.96×10^{-3}
		29.53	1.105	2.87×10^{-3}
		34.57	1.036	2.67×10^{-3}
	323.15	12.07	1.969	8.29×10^{-3}
		13.12	1.802	6.95×10^{-3}
		15.14	1.581	1.73×10^{-2}
		16.11	1.571	4.04×10^{-3}
		19.00	1.437	1.94×10^{-3}
		21.42	1.353	2.26×10^{-3}
		24.60	1.267	6.41×10^{-3}
		29.52	1.163	1.34×10^{-3}
		34.53	1.100	1.70×10^{-3}
	328.15	15.10	1.762	5.56×10^{-3}
		16.90	1.675	7.60×10^{-3}
		19.76	1.496	3.70×10^{-3}
		23.94	1.369	1.14×10^{-3}
		34.49	1.101	5.87×10^{-3}

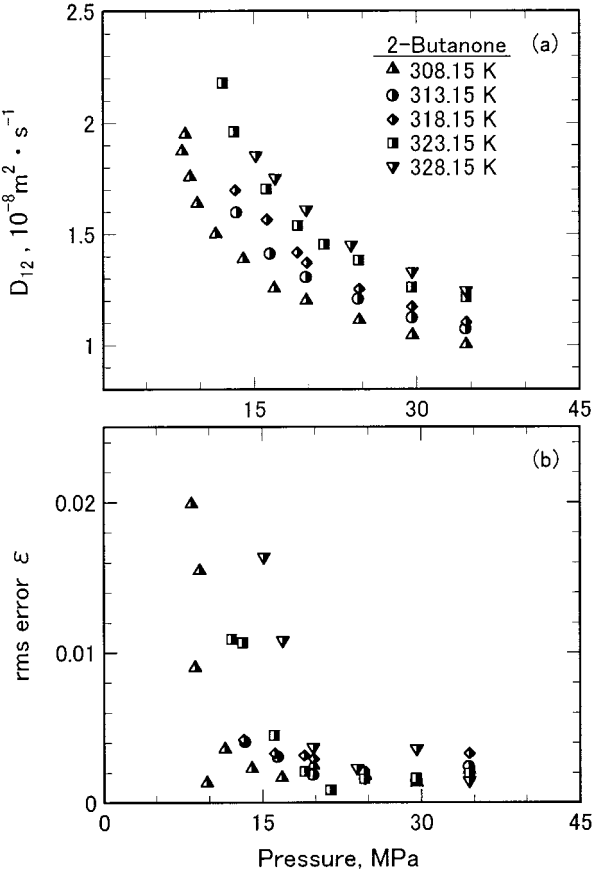

Fig. 1. Effects of pressure on (a) the D_{12} value and (b) the fitting error ε for 2-butanone at temperatures from 308.15 to 328.15 K.

CO_2 at various temperatures, together with the fitting error ε. The values decrease with increasing pressure, and the fitting error decreases drastically at pressures higher than 16 MPa. These tendencies have been observed for D_{12} values for 2-propanone in CO_2 [1].

Figure 2 shows D_{12} values versus CO_2 density (Fig. 2a) and D_{12}/T versus CO_2 viscosity (Fig. 2b) for the same data as in Fig. 1. Note that the CO_2 densities and viscosities were obtained by the equations of Pitzer and Schreiber [11] and Vesovic et al. [12], respectively. The plot of D_{12} data versus CO_2 density shows a temperature dependence. The plot at each temperature can be correlated but is not represented by a straight line. At densities lower than $750\,kg \cdot m^{-3}$, the slope seems to be different. The

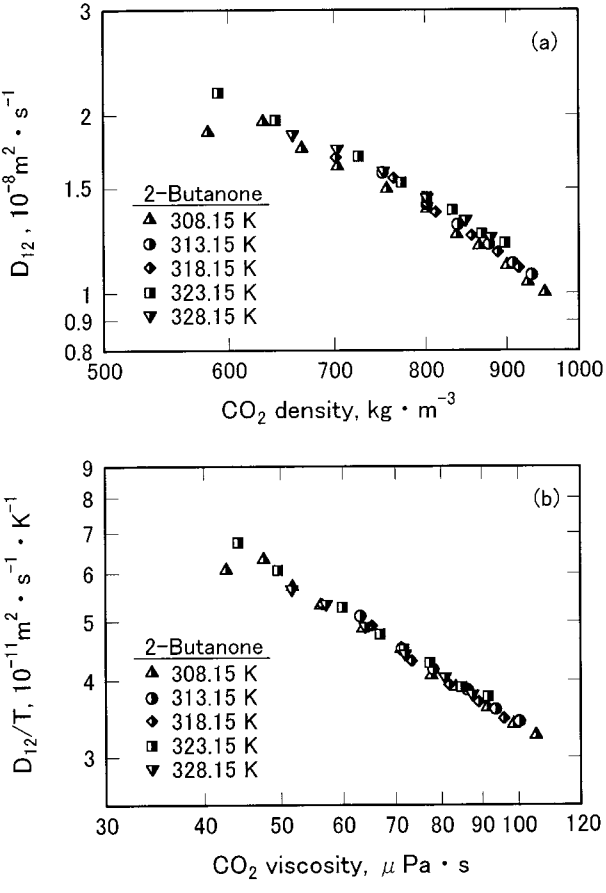

Fig. 2. (a) D_{12} vs CO_2 density and (b) D_{12}/T vs CO_2 viscosity for 2-butanone; the data are the same as in Fig. 1.

correlation with CO_2 viscosity has been reported to be valid [1]. This plot has already been shown to be valid for a specific solute, independent of the solvent [13].

Figures 3 and 4 show the Schmidt number correlation [1, 14] for 2-butanone, 2-pentanone, and 3-pentanone, and that for 2-propanone, respectively, together with literature data [1–7], which were all measured by the Taylor dispersion method. The measured D_{12} values for all solutes were found to be well represented by this correlation, excluding low pressures and correspondingly low v_0/v values, where v_0 is the hard-sphere closest-packed volume for CO_2, which can be obtained from the correlation [15]. The average absolute deviations AAD% of each solute from the

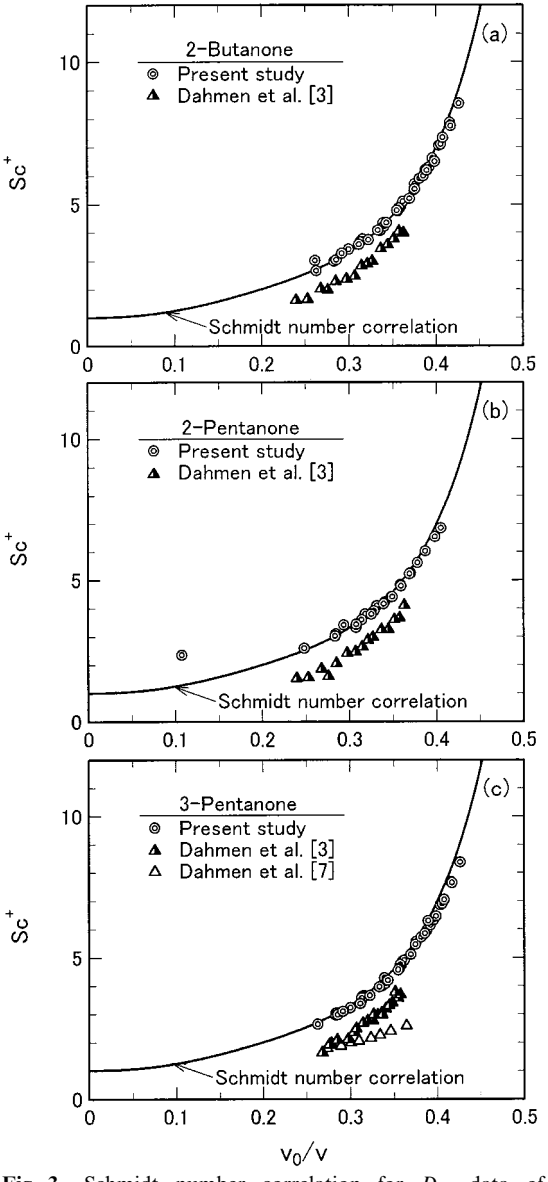

Fig. 3. Schmidt number correlation for D_{12} data of (a) 2-butanone, (b) 2-pentanone, and (c) 3-pentanone, measured in this study and reported in the literature.

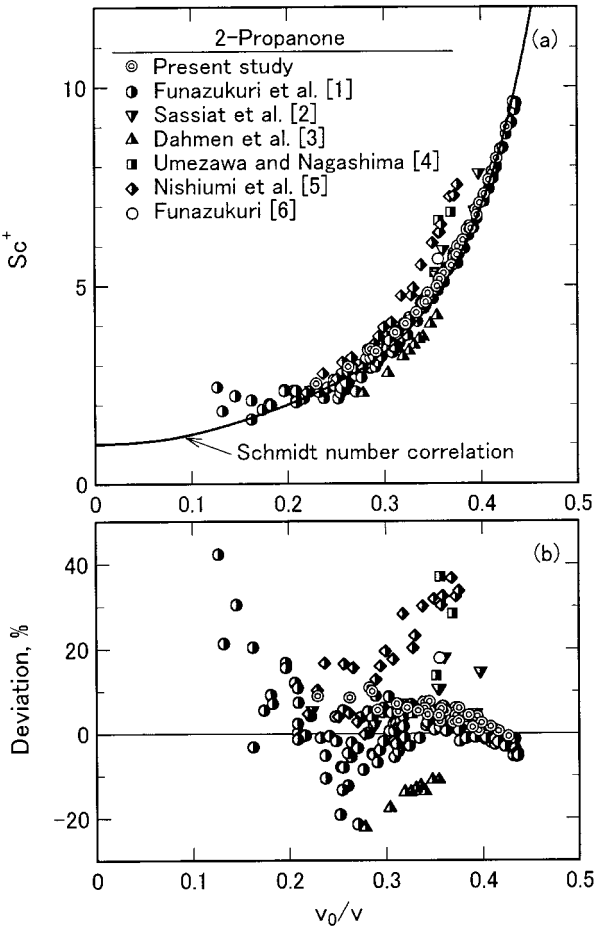

Fig. 4. Schmidt number correlation for 2-propanone in CO_2 for (a) D_{12} data measured here and (b) deviations of the D_{12} data in the present study and the literature.

correlation are listed in Table II. It is found that AAD% values for all solutes are less than 5.0%, and the correlation represents the D_{12} data well. Note that the overall AAD% for all solutes is 3.74% for 143 data points. The plotted values of Dahmen et al. [3] for all solutes are lower than the correlation or literature data by 10 to 30%, and correspondingly the D_{12} values are higher. The D_{12} values for 2-pentanone and 3-pentanone are found to be almost-identical, and the difference in the isomers is not discernible. For 2-propanone the data reported previously by the authors are consistent with those in the present study. The data of Nishiumi et al. [5]

Table II. Uncertainty of the D_{12} Values Calculated from the Schmidt Number Correlation for Ketones in CO_2

Solute	AAD %[a]			No. of data points		Maximum deviation (%)	
	Total	$\varepsilon < 0.01$	$\varepsilon > 0.01$	$\varepsilon < 0.01$	$\varepsilon > 0.01$	$\varepsilon < 0.01$	$\varepsilon > 0.01$
2-Propanone	4.94	4.35	8.48	36	6	7.60	10.85
	5.00[b]	3.90[b]	9.51[b]	131[b]	32[b]	21.42[b]	42.35[b]
2-Butanone	2.24	2.01	3.48	32	6	6.09	11.14
2-Pentanone	4.36	2.35	18.41	21	3	7.03	45.45
3-Pentanone	3.53	3.84	0.84	35	4	8.06	1.80

[a] $\text{AAD}\% = (100/N) \sum |1 - D_{12,\text{crrl}}/D_{12,\text{exp}}|$; $D_{12,\text{crrl}}$ is obtained from the Schmidt number correlation.

[b] Includes D_{12} data of Funazukuri et al. [1].

are higher. While their injected tracer amounts range from 0.7 to 13.1 μl, the data for 0.7 μl are plotted. Some data of Sassiat et al. [2] and of Umezawa and Nagashima [4] are almost consistent with those in this study.

In the previous study [1], the D_{12} data for 2-propanone at 308.2 K and pressures less than 8.3 MPa, and at 313.2 K and pressures less than 9.1 MPa showed significant deviations from the correlation, and the deviation increased with decreasing pressure. A similar tendency was observed for all solutes in the present study. The D_{12} values deviated from the correlation with a large fitting error, and this results mainly from the distortion of the response curve. Deviations of the calculated values from experimental values become larger as the pressure decreases. We will discuss this behavior in future work.

5. CONCLUSIONS

Infinite-dilution binary diffusion coefficients of 2-propanone, 2-butanone, 2-pentanone, and 3-pentanone in carbon dioxide were measured by the Taylor dispersion method. The measured data were well correlated with the Schmidt number correlation.

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NOMENCLATURE

AAD%	Average absolute deviation
C_a	Average concentration on cross sectional area
D_{12}	Binary diffusion coefficient
De	Dean number
L	Column length
m	Injected amount of tracer
P	Pressure
R	Tube radius
Sc	Schmidt number
Sc^+	Ratio of the Schmidt number at high pressure to that at atmospheric pressure
T	Temperature
t	Time
u_a	Average velocity
v	CO_2 molar volume
v_0	CO_2 hard-sphere closest-packed volume
z	Axial distance
ε	Error defined by Eq. (3)

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