Diffusion coefficients of metal acetylacetonates in supercritical carbon dioxide

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Abstrat

Binary diffusion coefficients, D_{12}, of metal acetylacetonates such as palladium(II) acetylacetonate and cobalt (III) acetylacetonate were measured from 308.2 to 343.2 K over the pressure range from 9.0 to 40.0 MPa at infinite dilution in supercritical carbon dioxide using the chromatographic impulse response method. The effects of pressure, temperature, density, and viscosity on D_{12} values were examined. It was observed that the D_{12} values of palladium(II) acetylacetonate and cobalt (III) acetylacetonate were larger than those of lipids with similar molecular weights, such as arachidonic acid and monoolein, respectively. Furthermore, the measured D_{12} data of each metal acetylacetonate were well correlated by the hydrodynamic equation D_{12}/T as a function of carbon dioxide viscosity.

1. Introduction

Supercritical fluid technology is a rapidly growing field due to the desirable properties as a promising alternative to the use of harmful organic solvents. As the high-pressure technology has nowadays progressed, the use of supercritical fluid is of great interest for designing green processes [1].

Organometalic complexes such as metal acetylacetonates are being extensively employed in preparation and processing of advanced functional materials as catalysts or precursors. Recently, the industrial application of combination of metal complexes and supercritical carbon dioxide is one of new research areas with significant potential [2,3]. In the accurate design and optimization of industrial processes with use of metal complexes, the estimation of mass transfer properties for the compounds becomes of particular importance. Especially, diffusion coefficients not only are necessary in engineering calculation for industrial design, but also provide basic information on the molecular interactions and structure of metal complexes in supercritical carbon dioxide. However, the binary diffusion coefficients of metal complexes, in particular, metal acetylacetonates are very scarce. As far as the authors know, only one report [4] on binary diffusion coefficients of copper(II) trifluoroacetylacetonate in supercritical carbon dioxide is available. Clearly, the diffusion data of various metal complexes in supercritical carbon dioxide are needed. Thus, the objectives of this study are to measure binary diffusion coefficients of metal acethylacetonates such as palladium(II) acethylacetonate ($Pd(acac)_2$, molecular weight = 304.6) and cobalt (III) acethylacetonate ($Co(acac)_3$, molecular weight = 356.3) in supercritical carbon dioxide by the chromatographic impulse response (CIR) method, and to correlate them with an appropriate equation.

2. Theory

The theory of the CIR technique has been described in detail previously [5,6], in here, briefly described. When a tracer is pulse injected into a fully developed laminar flow in a coated cylindrical diffusion column, the cross-sectional average concentration $C(t)$ can be described as follows:

$$C(t) = \left(\frac{m}{\pi R^2} \right) \frac{1}{(1+k)(4\pi at)^{1/2}} \exp\left\{ -\frac{(L - u_0 t/(1+k))^2}{4at} \right\} \qquad (1)$$

$$a = \frac{D_{12}}{1+k} + \frac{1 + 6k + 11k^2}{(1+k)^3} \frac{R^2 u_0^2}{48 D_{12}} \qquad (2)$$

where t is the time, m the amount of solute, R the radius of diffusion column, k the retention factor, L the distance, u_0 the average velocity of fluid, and D_{12} the infinite dilution binary diffusion coefficient of the solute. When u_0 is measured experimentally, D_{12} and k can be simultaneously determined by minimizing the root-mean-square (rms) fitting error ε, defined by Eq. (3), for the measured $C_{exp}(t)$ and calculated $C(t)$ curves. The curve fit is considered good when $\varepsilon < 1\%$, and acceptable when $\varepsilon < 2 \sim 3\%$ [6].

$$\varepsilon = \left(\frac{\int_{t_1}^{t_2} (C_{exp}(t) - C(t))^2 \, dt}{\int_{t_1}^{t_2} (C_{exp}(t))^2 \, dt} \right)^{1/2} \qquad (3)$$

where t_1 and t_2 correspond to the times at the front and latter 10% peak heights, respectively, of the measured response curve.

3. Experimental

3.1 *Materials*

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Pd(acac)$_2$ with purity of 99% and Co(acac)$_3$ with 98% were purchased from Aldrich and Wako, respectively. They were used as received without further purification. Carbon dioxide with a purity > 99.99 vol.% was obtained from Marukyo Sanso Co., Japan.

3.2 *Apparatus and procedure*

The experimental apparatus and procedures are substantially the same as those in the previous studies [6,7]. Supercritical carbon dioxide was passed through a poly(ethylene glycol) coated capillary column (UACW-15W-1.0F, the Frontier Laboratories Ltd. Japan, polymer thickness of 1 μm, $R = 0.265$ mm, $L = 16.293$ m, and $R_{coil} = 0.155$ m) at a constant flow rate fed by a syringe pump (260D, ISCO, USA). In this study, each metal complex was dissolved in supercritical carbon dioxide prior to an injection (injector model 7520 equipped with a 0.2 μL rotor, Rheodyne, USA). The temperature of the water bath and the pressure of the system were controlled within 0.01 K and 0.005 MPa, respectively. After the desired temperature, pressure and flow rate had become stabilized, the system was held under the same condition at least more 2 hours before an injection. Response curves, as time change of the tracer concentration, in terms of absorbance were monitored with a high pressure multi-UV-Vis detector by scanning at wavelengths from 195 to 650 nm with increments of 1 nm and time interval of 1.6 s for each measurement. In this study, only a single pulse of each metal acetylacetonate dissolved in supercritical carbon dioxide was loaded for each run. The $DeSc^{1/2}$ values indicating a criterion of the secondary flow effect were mostly lower than 8, 9.9 at the maximum, where De and Sc are the Dean number and the Schmidt number, respectively. The Reynolds and the Schmidt numbers ranged from 22 to 95 and from 5 to 21 for Pd(acac)$_2$, and from 21 to 77 and from 7 to 23 for Co(acac)$_3$, respectively.

3. Results and discussion

The D_{12} data were measured for Pd(acac)$_2$ at 308.15, 313.15, 323.15, 333.15 and 343.15 K and pressures from 8.5 to 40.0 MPa, and for Co(acac)$_3$ at 313.15 and 343.15 K and 9.7 to 40.0 MPa in supercritical carbon dioxide using the CIR technique. The D_{12} and k values are presented in Table 1, together with the ε values.

Fig. 1 illustrates the effects of the wavelength from 195 to 350 nm on (a) absorbance at the maximum peak height, A_{max}, (b) $A_{max}/(u_0 \times (\text{peak area}))$, (c) k, (d) D_{12}, and (e) rms error ε for Pd(acac)$_2$ and Co(acac)$_3$ at 313.15 K and 10.0 MPa. Since D_{12} of a solute in a fluid is a physical property, it should not depend on wavelengths of the solute. However, the D_{12} values obtained were greatly influenced by wavelengths in measurements because of the experimental noise or non-linearity of the detector. In the whole wavelength range, the A_{max} values for the two metal complexes are lower than 0.01 absorbance unit, and the values of $A_{max}/(u_0 \times (\text{peak area}))$ indicating the linearity of detector were almost constant. However, at wavelengths higher than 260 nm, the values of $A_{max}/(u_0 \times (\text{peak area}))$ are slightly scattered, correspondingly the ε values show larger values, and the determined D_{12} values in the wavelength range were dependent on wavelength, especially for Pd(acac)$_2$, as shown in Fig. 1(d). This is probably caused by the noise of the detector. On the other hand, the constant k values were observed for both Pd(acac)$_2$ and Co(acac)$_3$ over the entire wavelength range. In this study, the wavelengths of 220 nm for Pd(acac)$_2$ and 225 nm for Co(acac)$_3$ were chosen to analyze response curves having moderate absorbance that resulted in a small fitting error and constant values of k and D_{12} around the wavelengths.

Fig. 2 shows the measured and calculated response curves by the CIR model for (a) Pd(acac)$_2$ at 220 nm and (b) Co(acac)$_3$ at 225 nm in supercritical carbon dioxide at 313.15 K and 10.0 MPa. The measured curves do not show tailing, and are well represented by the calculated curves with $\varepsilon < 1\%$ for both of Pd(acac)$_2$ and Co(acac)$_3$. The obtained values of

D_{12} and ε under the condition were 1.097×10^{-8} m^2/s and 0.69% for Pd(acac)$_2$, and 0.980×10^{-8} m^2/s and 0.51% for Co(acac)$_3$, respectively.

The effects of pressure and temperature on D_{12} of Pd(acac)$_2$ are presented in Figs 3(a) and (b), respectively. The D_{12} values of Pd(acac)$_2$ were examined isothermally as a function of pressure at 308.15, 313.15, 323.15, 333.15 and 343.15 K, and isobarically as a function of temperature at 15.0, 20.0, 25.0, 30.0, 35.0 and 40.0 MPa. It was observed that the D_{12} data decreased with increasing pressure at constant temperature, and increased with increasing temperature at constant pressure. The lower pressure sensitivity of D_{12} in the range of high pressure, as shown in Fig. 3(a), is probably due to no drastical changes in fluid density and viscosity. A high temperature dependence on D_{12} at constant pressure, as indicated in Fig. 3(b), can be observed.

Figs 4 and 5 show a large density dependency on D_{12} and k for Pd(acac)$_2$ and Co(acac)$_3$ at constant temperature of 313.15 K in supercritical carbon dioxide, together with literature data of lipids such as arachidonic acid [8] having molecular weight of 304.5 and monoolein [9] having molecular weight of 356.5. The densities of carbon dioxide were obtained with the equation of Span and Wagner [10]. It was found from Figs 4(a) and (b) that the D_{12} values of Pd(acac)$_2$ having molecular weight of 304.6 are larger than those of Co(acac)$_3$ having that of 356.3, as expected. In addition, it was observed that the D_{12} values of Pd(acac)$_2$ were larger by about 28% than those of arachidonic acid [8] having similar molecular weight. On the other hand, the k values of Pd(acac)$_2$ were lower than those of arachidonic acid [8] (see Fig. 5(a)). The same tendency can be observed for Co(acac)$_3$ and monoolein [9] having similar molecular weight (Fig. 5(b)). The difference in D_{12} values for Co(acac)$_3$ and monoolein is about 18%. For each case, the D_{12} values of metal complex show larger values than those of lipid having similar molecular weight. The difference may be attributed to those in molecular shape and polarity.

As shown in Figs 5(a) and (b), the k values were correlated with carbon dioxide density ρ, as has been found for various compounds [5,6,8,9,11-17]. All k values for Pd(acac)$_2$ and Co(acac)$_3$ measured in this study were well expressed by Eq. (4).

$$\ln k = \sum_{i=0}^{3} a_i \, (\ln \rho [\mathrm{kg/m^3}])^{i} \tag{4}$$

where k is the retention factor with no dimension, a_i values are coefficients of the polynomial correlation for each complex at constant temperature, as listed in Table 2, together with the average absolute relative deviation (AARD) values.

The validity of the correlation in Eq. (5), on the basis of the hydrodynamic approach, for various compounds in supercritical carbon dioxide has been demonstrated [5,6,8,9,11-19]

$$\frac{D_{12}}{T} = \alpha \eta^{\beta} \tag{5}$$

where unites of D_{12}, T and η are $\mathrm{m^2 s^{-1}}$, K and Pa s, respectively. The values of α and β are constant, and depend on the solute and the fluid system. Fig. 6 shows the validity of Eq. (5) in plot of D_{12}/T versus carbon dioxide viscosity η for all D_{12} data of Pd(acac)$_2$ and Co(acac)$_3$ in supercritical carbon dioxide, measured in this study, together with the curve fitting errors ε. The viscosities of carbon dioxide were calculated by the method of Fenghour et al. [20]. As shown in Fig. 6(b), the errors seem to be independent of viscosity, and most ε values were smaller than 1%. This indicates that the measured response curves were well represented by the model, and the D_{12} data of Pd(acac)$_2$ and Co(acac)$_3$ measured by the CIR method in this study can be considered quite reliable. As seen in Fig. 6(a), the plots are well represented by each straight line in Eq. (5) for the D_{12} data of Pd(acac)$_2$ and Co(acac)$_3$ measured in this study. As presented in Table 3, the AARD values are 2.9% and 1.3% for 125 data points of Pd(acac)$_2$ and 38 data points of Co(acac)$_3$, respectively. In addition, since the β values are not equal to minus unity, the present D_{12} data of metal acetylacetonates in supercritical carbon dioxide do not support the Stokes-Einstein relationship.

5. Conclutions

Binary diffusion coefficients and retention factors of metal acetylacetonates at infinite dilution in supercritical carbon dioxide were measured by the chromatographic impulse response method. Measurements for palladium(II) acetylacetonate have been made at 308.15, 313.15, 323.15, 333.15, and 343.15 K over the pressure range of 8.5 to 40.0 MPa, and for cobalt (III) acetylacetonate at 313.15 and 333.15 K, and at 9.7 to 40.0 MPa. The influences of pressure, temperature, density, and viscosity on the D_{12} values were examined. In addition, it was observed that the D_{12} values of acetylacetonates were larger than those of lipids with similar molecular weights; namely, palladium(II) acetylacetonate to arachidonic acid, and cobalt (III) acetylacetonate to monoolein. The measured D_{12} data of the metal acetylacetonates in supercritical carbon dioxide were correlated by the hydrodynamic equation D_{12}/T as a function of viscosity with average absolute relative deviation of 2.9% and 1.3% for 125 data points for Pd(acac)$_2$ and 38 data points for Co(acac)$_3$, respectively. Moreover, the retention factors were also correlated with CO_2 density at each temperature.

List of symbols

AARD%   average absolute relative deviation

$C(t)$ cross-sectional average concentration given by Eq.(1)

$C_{exp}(t)$ concentration measured experimentally

D_{12} binary diffusion coefficient

De Dean number $= (2\rho u_0 R/\eta)(R/R_{coil})^{1/2}$; R_{coil}: coil radius of diffusion column;

k retention factor for solute in polymer stationary phase to supercritical fluid phase

L distance between injection point and detection point

m injected amount of solute

N	number of data points
P	pressure
R	radius of diffusion column
Sc	Schmidt number $= \eta/(\rho D_{12})$
T	temperature
t	time
u_0	average velocity of fluid
α, β	constants in Eq. (5)
ε	fitting error defined by Eq. (3)
η	viscosity
ρ	density

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Table 1. Measured D_{12} and k values for Pd(acac)$_2$ and Co(acac)$_3$ in supercritical carbon dioxide, together with fitting errors ε

Solute	T (K)	P (MPa)	D_{12} (10^{-8}m^2/s)	k	$10^2\varepsilon$
Pd(acac)$_2$	308.15	8.5	1.136	1.469	0.76
		8.5	1.130	1.466	0.84
		8.5	1.123	1.478	0.91
		9.0	1.033	1.009	0.74
		9.0	1.022	1.000	1.00
		9.5	0.977	0.795	0.96
		10.0	0.940	0.676	0.54
		10.0	0.949	0.675	0.67
		11.0	0.901	0.536	0.98
		12.0	0.858	0.452	0.54
		15.0	0.786	0.327	0.38
		15.0	0.782	0.325	0.68
		16.0	0.766	0.303	0.48
		20.0	0.707	0.232	0.69
		25.0	0.666	0.192	0.21
		25.0	0.660	0.189	0.37
		30.0	0.613	0.160	0.54
		35.0	0.578	0.145	0.74
		40.0	0.561	0.131	0.32
		40.0	0.551	0.132	0.63
	313.15	9.5	1.173	1.776	0.89
		9.5	1.190	1.773	0.83
		9.7	1.154	1.478	0.87
		9.7	1.133	1.470	0.73
		9.7	1.120	1.477	0.64
		10.0	1.089	1.184	0.25
		10.0	1.097	1.181	0.69
		11.0	0.971	0.767	0.47
		11.0	1.001	0.767	0.13
		11.0	0.995	0.769	0.10
		12.0	0.933	0.590	0.41
		13.0	0.902	0.490	0.30
		14.0	0.881	0.423	0.43
		15.0	0.847	0.374	0.49
		15.0	0.852	0.373	0.62
		15.0	0.845	0.375	0.57

	15.0	0.843	0.374	0.38
	15.0	0.841	0.372	0.17
	16.0	0.828	0.338	0.28
	17.0	0.801	0.305	0.29
	17.0	0.795	0.310	0.28
	18.0	0.774	0.274	0.34
	18.0	0.777	0.286	0.17
	19.0	0.755	0.266	0.28
	20.0	0.750	0.251	0.33
	21.0	0.742	0.236	0.38
	21.0	0.726	0.238	0.46
	21.0	0.733	0.235	0.14
	22.0	0.722	0.224	0.59
	24.0	0.701	0.207	0.27
	24.0	0.691	0.204	0.61
	25.0	0.689	0.194	0.40
	30.0	0.648	0.164	0.39
	30.0	0.638	0.174	0.27
	35.0	0.610	0.149	0.37
	35.0	0.607	0.143	0.43
	40.0	0.589	0.130	0.47
	40.0	0.582	0.131	0.22
323.15	12.0	1.271	1.439	0.67
	13.0	1.150	0.908	0.40
	13.0	1.165	0.929	0.31
	15.0	1.025	0.550	0.24
	15.0	1.020	0.547	0.13
	20.0	0.881	0.294	0.75
	20.0	0.890	0.307	0.17
	25.0	0.799	0.218	0.35
	30.0	0.744	0.175	0.25
	35.0	0.704	0.149	0.22
	40.0	0.658	0.128	0.70
	40.0	0.667	0.134	0.44
333.15	14.0	1.403	1.436	0.66
	14.0	1.346	1.434	0.73
	15.0	1.272	0.986	0.47
	15.0	1.286	0.991	0.75
	15.0	1.276	0.977	0.16
	15.0	1.333	1.011	0.57
	15.0	1.293	0.976	0.54

	16.0	1.217	0.750	0.67
	17.0	1.154	0.601	0.37
	17.0	1.159	0.590	0.36
	17.5	1.127	0.535	0.81
	17.5	1.130	0.539	0.93
	17.5	1.138	0.544	0.38
	18.0	1.123	0.500	0.38
	20.0	1.038	0.380	0.48
	20.0	1.055	0.376	0.29
	20.0	1.045	0.377	0.43
	20.0	1.043	0.380	0.87
	20.0	1.048	0.381	0.26
	20.0	1.053	0.380	0.40
	20.0	1.055	0.385	0.78
	20.0	1.068	0.379	0.63
	22.0	0.991	0.308	0.95
	22.0	0.989	0.306	0.62
	22.0	0.985	0.304	0.48
	22.0	1.004	0.311	0.92
	23.0	0.964	0.280	0.11
	23.0	0.980	0.279	0.24
	24.0	0.950	0.265	0.29
	24.0	0.963	0.262	0.22
	25.0	0.927	0.237	0.78
	25.0	0.920	0.246	0.29
	30.0	0.866	0.189	0.23
	35.0	0.800	0.153	0.25
	35.0	0.806	0.157	0.52
	40.0	0.746	0.134	0.62
	40.0	0.770	0.141	0.34
343.15	17.0	1.369	0.965	0.89
	17.0	1.362	0.961	0.55
	17.0	1.354	0.954	0.40
	17.0	1.378	0.952	0.29
	20.0	1.225	0.511	0.51
	20.0	1.211	0.507	0.40
	25.0	1.050	0.282	0.38
	25.0	1.063	0.287	0.17
	25.0	1.085	0.288	0.22
	25.0	1.057	0.286	0.45
	25.0	1.065	0.286	0.23
	30.0	0.958	0.205	0.19

		30.0	0.961	0.205	0.31
		30.0	0.970	0.204	0.35
		35.0	0.895	0.166	0.64
		35.0	0.891	0.166	0.17
		35.0	0.898	0.165	0.13
		40.0	0.846	0.141	0.36
Co(acac)$_3$	313.15	9.7	1.037	1.048	0.38
		9.7	0.998	1.091	0.67
		10.0	0.980	0.859	0.51
		10.0	0.966	0.856	0.89
		11.0	0.877	0.531	0.39
		11.0	0.888	0.545	0.84
		11.0	0.874	0.552	0.98
		11.0	0.870	0.546	0.54
		13.0	0.770	0.351	0.90
		13.0	0.764	0.349	0.97
		13.0	0.786	0.334	1.13
		13.0	0.785	0.340	0.99
		18.0	0.686	0.195	0.89
		20.0	0.654	0.177	0.24
		20.0	0.658	0.176	0.47
		25.0	0.604	0.139	0.69
		25.0	0.582	0.139	0.55
		25.0	0.587	0.142	0.52
		30.0	0.571	0.114	0.23
		30.0	0.552	0.131	0.56
		30.0	0.567	0.119	0.10
		40.0	0.501	0.098	0.79
		40.0	0.511	0.106	0.79
	333.15	15.0	1.058	0.662	0.47
		18.0	0.944	0.326	0.40
		20.0	0.866	0.250	0.82
		20.0	0.877	0.243	0.92
		25.0	0.761	0.172	0.81
		25.0	0.765	0.152	0.36
		25.0	0.785	0.162	0.36
		25.0	0.777	0.166	0.63
		30.0	0.690	0.128	0.94
		30.0	0.689	0.128	0.71
		30.0	0.703	0.126	0.84
		30.0	0.689	0.129	0.70

30.0	0.700	0.131	0.59
40.0	0.615	0.101	0.41
40.0	0.632	0.094	0.58

Table 2.   Determined a_i values in Eq. (4)

Solute	T (K)	a_0	a_1	a_2	a_3	$AARD(\%)$[a]	N[b]
Pd(acac)$_2$	308.15	-1689.0865	772.4500	-116.9558	5.8608	0.6	20
	313.15	-1358.1553	626.7435	-95.5976	4.8182	0.9	38
	323.15	-342.4442	169.4373	-27.0101	1.3908	1.3	12
	333.15	-1439.8514	673.2468	-104.1175	5.3243	1.2	37
	343.15	-1604.5016	751.1043	-116.4198	5.9730	0.6	18
Co(acac)$_3$	313.15	-2887.3212	1327.1167	-202.5106	10.2565	2.2	23
	333.15	-1222.8282	583.1404	-91.8158	4.7726	2.5	15

[a] $$AARD = \frac{100}{N} \sum_{i=1}^{N} \left| 1 - \frac{D_{12,\,corr}}{D_{12,\,exp}} \right| (\%)$$

[b] Number of data points

Table 3.   Determined α and β values in Eq. (5)

Solute	α	β	$AARD$ (%)	N
Pd(acac)$_2$	1.031×10^{-14}	-0.822	2.9	125
Co(acac)$_3$	8.999×10^{-15}	-0.819	1.3	38

Figure captions

Fig. 1. Effects of wavelength on (a) absorbance at the maximum peak height, A_{max}, (b) $A_{max}/(u_0 \times (\text{peak area}))$, (c) k, (d) D_{12}, and (e) rms error ε for Pd(acac)$_2$ (–△–) and Co(acac)$_3$ (–○–) in supercritical carbon dioxide at 313.15 K and 10.0 MPa.

Fig. 2. Comparison of experimental data (○) and calculated response curves (—) for (a) Pd(acac)$_2$ at 220 nm and (b) Co(acac)$_3$ at 225 nm. The data are the same as in Fig. 1.

Fig. 3. D_{12} of Pd(acac)$_2$ in supercritical carbon dioxide as a function of (a) pressure at constant temperatures of 308.15 K (○), 313.15 K (△), 323.15 K (□), 333.15 K (▽) and 343.15 K(◇), and (b) temperature at constant pressures of 15.0 MPa (◇), 20.0 MPa (▽), 25.0 MPa (□), 30.0 MPa (△), 35.0 MPa (○) and 40.0 MPa (☆).

Fig. 4. Effects of carbon dioxide density ρ on D_{12} at 313.15 K in supercritical carbon dioxide for (a) Pd(acac)$_2$ (▲) in the present study and arachidonic acid (△) in the literature [8], and for (b) Co(acac)$_3$ (●) in the present study and monoolein (○) in the literature [9].

Fig. 5. Effects of carbon dioxide density ρ on k at 313.15 K in supercritical carbon dioxide for (a) Pd(acac)$_2$ (▲) in the present study and arachidonic acid (△) in the literature [8], and for (b) Co(acac)$_3$ (●) in the present study and monoolein (○) in the literature [9].

Fig. 6. Plots of (a) D_{12}/T and (b) ε vs. carbon dioxide viscosity η for all D_{12} data measured of Pd(acac)$_2$ at 308.15 K (△), 313.15 K (○), 323.15 K (▽), 333.15 K (□), 343.15 K (◇), and for Co(acac)$_3$ at 313.15 K (●) and 343.15 K (■) in this study.
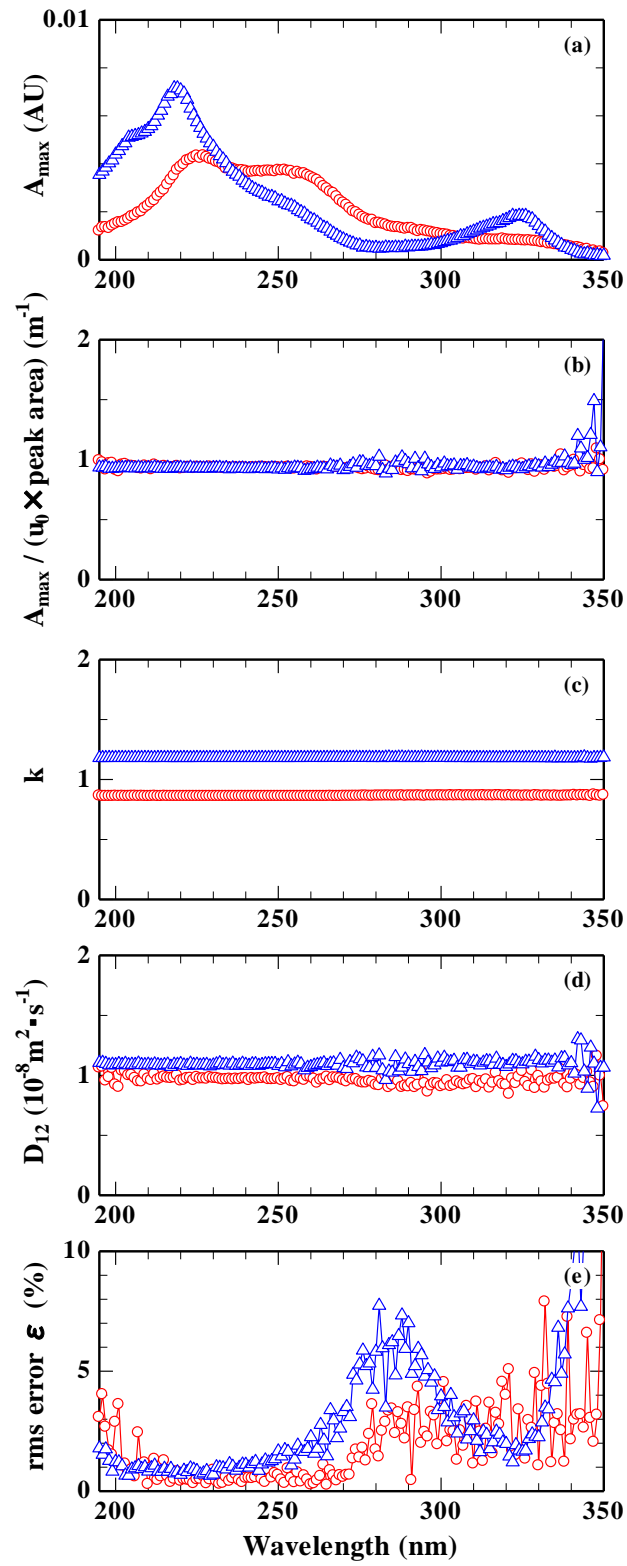
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6