Measurements of Diffusion Coefficient for Triolein in Various Pressurized Fluids with Different Viscosities

Guoxiao Cai[a], Wataru Katsumata[a], Idzumi Okajima[a], Takeshi Sako[a], Toshitaka Funazukuri[b], Chang Yi Kong[a],*

[a] Department of Environment and Energy System, Graduate School of Science and Technology, Shizuoka University, 3-5-1 Johoku Naka-ku, Hamamatsu, 432-8561, Japan

[b] Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo, 112-8551, Japan

* To whom correspondence should be addressed.
E-mail: kong.changyi@shizuoka.ac.jp Tel : +81-53-478-1174 FAX : +81-53-478-1174

Abstract

The measurements of diffusion coefficients D_{12} of triolein were carried out at infinite dilution in various pressurized fluids such as CO_2, hexane, methanol and ethanol with different viscosities. The D_{12} values in CO_2 were measured by the chromatographic impulse response method at 303.15 to 333.15 K and at pressures up to 31.02 MPa. In addition, those in hexane, methanol and ethanol were measured by the Taylor dispersion method at 298.15 to 323.15 K and pressures of 1.00 to 12.00 MPa. The D_{12} of triolein increased from 3.059×10^{-10} m^2 s^{-1} at 298.15 K and 10.00 MPa in liquid ethanol to 6.323×10^{-9} m^2 s^{-1} at 333.15 K and 13.77 MPa in supercritical CO_2. It was found that all diffusion data of triolein measured in CO_2, hexane, methanol and ethanol in this study can be satisfactorily represented by the proposed equation ($ln D_{12} = c_0 + c_1 ln \eta + c_2 (ln \eta)^2 + c_3 ln T$) over a wide range of fluid viscosity of 41 to 1179 μPa s from supercritical state to liquid state with average absolute relative deviation of 5.3% for 154 data points.

Keywords

Diffusion coefficient, Triolein, Pressurized fluid

1. Introduction

Triolein is a triglyceride derived from glycerol and three units of the unsaturated fatty acid oleic acid. Triglyceride can be extracted from biomass such as rice bran and used to produce biodiesel fuel by the transesterification process. In recent years, environmentally-friendly pressurized fluid extraction techniques such as pressurized liquid extraction and supercritical fluid extraction [1–6] are the most widely employed in obtaining various valuable components from natural sources [7], and have emerged as efficient ways of increasing automation, shortening extraction time and reducing the amount of organic solvents [8,9].

To design, optimize, scale up and simulate a new process using pressurized fluids, the physical properties in the fluids are demanded, in particular, molecular diffusion is indispensable to accurately understand the amount of mass transferred in the system when molecular diffusion is the bottleneck of the mass transfer [10]. The knowledge of molecular diffusion is also necessary for insight into phenomena such as solute-solvent interactions. However, it is difficult to measure in the pressurized fluids. In fact, the reports on diffusion coefficients in pressurized fluids are still not sufficiently enough [11]. Furthermore, up to now, there is also a lack of diffusion data for the same compound in various fluids with a wide range of viscosity. To the best of our knowledge, there is no report on the diffusion coefficients of triolein in liquids in the literature, and only one report [12] on those of triolein in supercritical CO_2 at 313.2 K and in a narrow pressure range of 9.13 to 14.02 MPa. Furthermore, the effective correlation of diffusivity is limited. It is desirable to develop an accurate correlation for the diffusion coefficients in the wide viscosity region from liquid to supercritical states. The objective of this paper was to measure the diffusion coefficients of triolein in liquid fluids such as hexane, methanol, ethanol, and in supercritical CO_2. Furthermore, a new correlation for the diffusion data in both supercritical CO_2 and in liquid fluids, based on a hydrodynamic equation as a function of temperature and viscosity, was proposed. All the obtained diffusion coefficients of triolein in this study were well correlated by the proposed correlation in the wide viscosity region from liquid to supercritical state.

2. Theory

The detail theoretical backgrounds have been presented by the authors [13,14] for the CIR method and by Alizadeh et al. [15] for the Taylor dispersion method. A solute pulse was injected into a fluid in laminar flow, the cross-sectional average concentration of the solute in a cylindrical diffusion column $C_{calc}(t)$ can be described by Eq. (1) for the CIR method and in Eq. (2) for the Taylor dispersion method, respectively.

$$C_{\text{calc}}(t) = \left(\frac{u}{u_0}\right)\frac{m}{\pi R^2}\frac{1}{\sqrt{4\pi E t}}\,e^{-\frac{(L-ut)^2}{4Et}}$$

$$E = \left(\frac{u}{u_0}\right)\left\{D_{12} + \left(6u^2 - 16u_0 u + 11u_0^2\right)\frac{R^2}{48}\frac{1}{D_{12}}\right\} \qquad (1)$$

$$C_{\text{calc}}(t) = \frac{m}{\pi R^2}\frac{1}{\sqrt{4\pi E t}}\,e^{-\frac{(L-u_0 t)^2}{4Et}}$$

$$E = D_{12} + u_0^2\,\frac{R^2}{48}\frac{1}{D_{12}} \qquad (2)$$

where t is the time, m is the amount injected, R is the radius of the diffusion column, E is the effective diffusivity, L is the length between injector and detector, u_0 and u are the velocities of the fluid and the solute, and D_{12} is the infinite dilution binary diffusion coefficient, respectively. The D_{12} values can be determined by the curve fitting technique with the measured $C_{\text{meas}}(t)$ and calculated $C_{\text{clac}}(t)$ concentrations. Note that the profile of $C_{\text{clac}}(t)$ shows Gaussian-like distribution. The applicability of measurements can be evaluated by Eq. (3) of the curve fitting error ε.

$$\varepsilon = \sqrt{\sum_{i=1}^{N}\left[1 - \frac{C_{\text{calc}}(t_i)}{C_{\text{meas}}(t_i)}\right]^2} \qquad (3)$$

where i is the number, t_1 and t_N correspond to the times at the frontal and latter 10% peak heights of $C_{\text{meas}}(t)$, respectively. The curve fitting is considered good when $\varepsilon < 1\ \%$, and acceptable when $\varepsilon < 3\ \%$ [14]. Note that effective mass transfer is really molecular diffusion (the random molecular motion) in combination with advection (molecules being carried along with the motion of the fluid). A widespread concentration profile in the diffusion column indicates a high effective diffusivity and a low molecular diffusion, while a sharp concentration profile means low effective diffusivity and hence high molecular diffusion.

3. Experimental

The schematic diagram of the apparatus shown in Fig. 1 (a) is for the injection of organic solution of triolein, while that shown in Fig. 1 (b) is for the injection of pressurized CO_2 solution of triolein. Both the Taylor dispersion and the CIR methods are a type of pulse response technique, and the apparatus used in the CIR method was similar to that used in the Taylor dispersion method except that a polymer coated cylindrical capillary diffusion column was used instead of an uncoated cylindrical capillary diffusion column. The apparatus is composed of a

syringe pump, a preheating column, a Heise pressure gauge, an injector, an oven, a diffusion column, an UV-vis multi-detector, a back-pressure regulator, graduated cylinder and soap bubble flow meter. The syringe pump was used at a constant flow rate to supply CO_2 or liquid fluid such as hexane, methanol and ethanol. Note that in this study the temperature and pressure were controlled accurately to ± 0.01 K and ± 0.005 MPa, respectively. Triolein was dissolved in an organic solvent such as hexane, methanol and ethanol or dissolved in pressurized CO_2 before injecting into the diffusion column through the injector. After the desired temperature, pressure and flow rate were stablished, the system was maintained under the conditions for more than 2 h prior to injection. When the system temperature, pressure and flowing system became constant, then, a single pulse of triolein was loaded through the injector into the fluid flowing for each measurement. The temporal changes in triolein concentration in terms of wavelengths were monitored with the UV-vis multi-detector. The pressurized CO_2 flow rates were determined using a soap bubble flow meter after the high pressure was reduced to atmospheric pressure.

CO$_2$ (purity of 99.95 %) was purchased from Air Gases Tokai Ltd. Japan. Triolein (CAS RN: 122-32-7, $(C_{17}H_{33}COOCH_2)_2CHOCOC_{17}H_{33}$, $C_{57}H_{104}O_6$, molecular weight of 885.43 g/mol, purity of 98.5 %), hexane (CAS RN: 110-54-3, purity of 98.5 %), methanol (CAS RN: 67-56-1, purity of 99.8 %) and ethanol (CAS RN: 64-17-5, purity of 99.5 %) and were obtained from FUJIFILM Wako Pure Chemical Co., Ltd. All chemical reagents were employed as received.
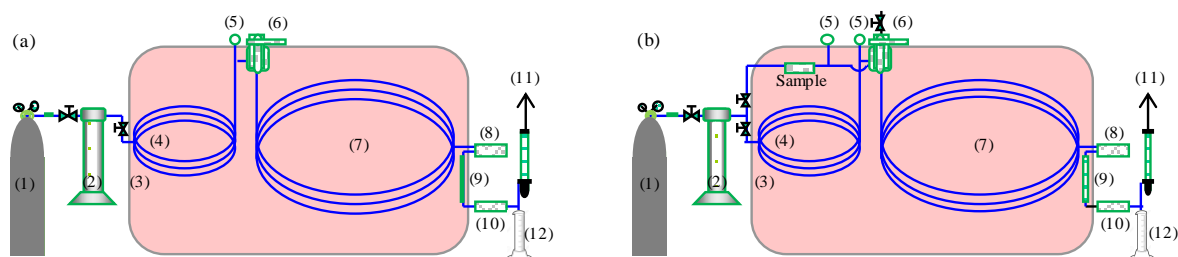

Figure 1. Schematic diagram of the apparatus for injection of triolein predissolved (a) in organic solvents and (b) in pressurized CO_2. (1) Gas cylinder or liquid tank, (2) syringe pump, (3) oven, (4) preheating column, (5) Heise pressure gauge, (6) injector, (7) diffusion column, (8) detector, (9) packed column, (10) back pressure regulator, (11) soap bubble flow meter, (12) graduated cylinder.

4. Results and discussion

In the diffusion measurements of a solute in a fluid by the Taylor dispersion method or the CIR method, the solute chromatographic solute peaks measured are important. As shown in Eqs (1) and (2), the concentration profiles in both methods of the Taylor dispersion and the CIR are
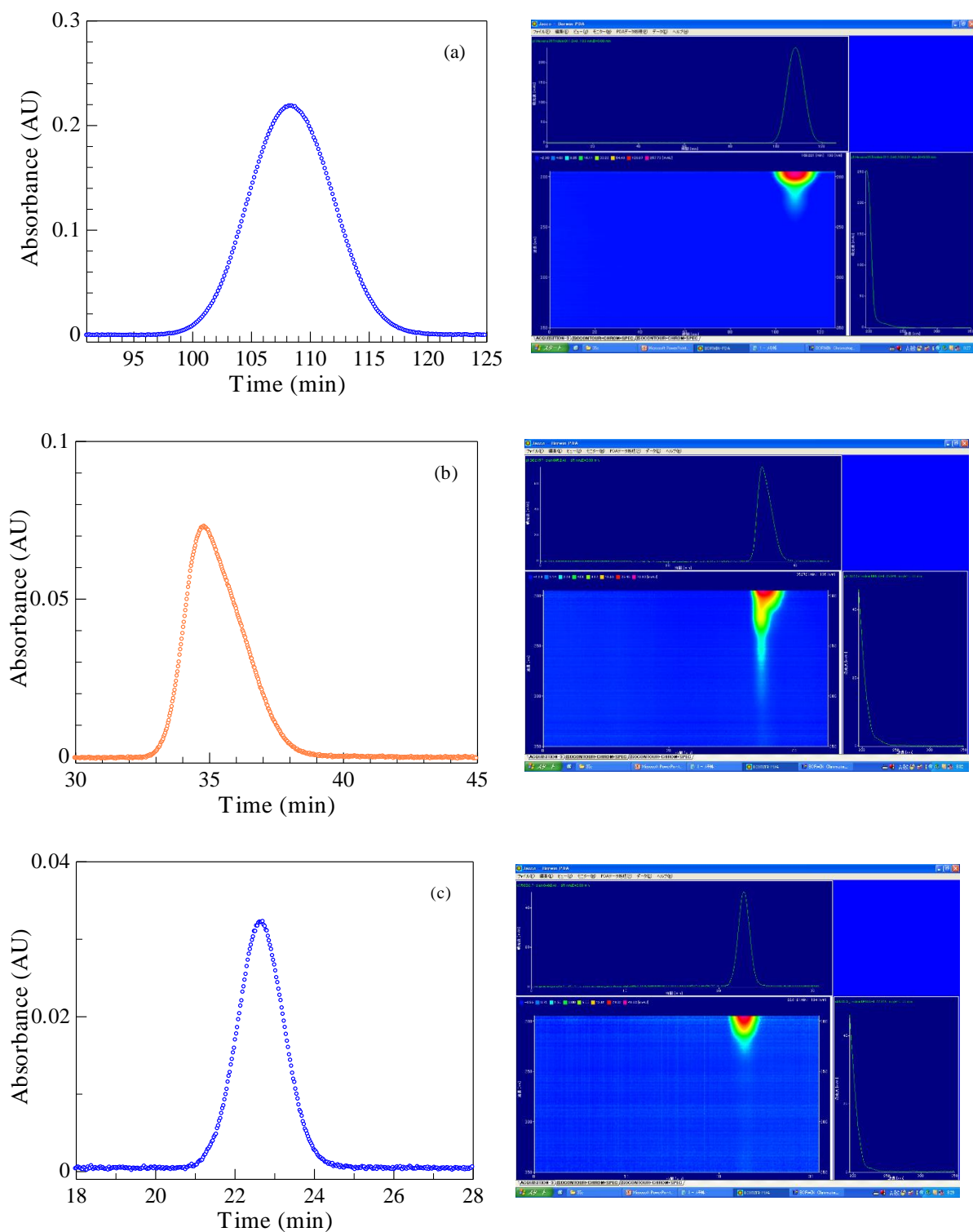
Fig. 2. Typical chromatographic peaks for triloein at 308.15 K and wavelength of 205 nm (a) in pressurized hexane measured by the Taylor dispersion method, (b) in sc carbon dioxide measured by the Taylor dispersion method and (c) in sc carbon dioxide measured by the CIR method, together with the corresponding three-dimensional images measured by the UV-Vis multi-detector.

Gaussian-like type. Therefore, when the measured peaks are tailing, this means the diffusion measurements cannot be well carried out by the method. Fig. 2 shows the typical chromatographic peaks measured for triolein (a) in pressurized hexane at 308.15 K and 11.95 MPa by the Taylor dispersion method (triolein predissolved in hexane was injected into the diffusion column through injector), (b) in sc CO_2 at 308.15 K and 12.04 MPa by the Taylor dispersion method (triolein was predissolved in sc CO_2 before injection), and (c) in sc CO_2 at 308.15 K and 12.02 MPa by the CIR method (triolein was predissolved in sc CO_2 before injection), together with the corresponding three-dimensional images measured by the UV-Vis multi-detector. As shown in Fig. 2 (a), the response curve measured by the Taylor dispersion method in pressurized hexane is not tailing and the obtained curve fitting error ε is 5.9×10^{-3}. But, as shown in Fig. 2 (b), the response curve measured by the Taylor dispersion method in sc CO_2 is severe tailing and the curve fitting error ε is 8.8×10^{-2}. On the contrary, when employing the CIR method in sc CO_2, as shown in Fig. 2 (c), the response curve measured by the CIR method in sc CO_2 is not tailing and the determined curve fitting error ε is very good and about 7.6×10^{-3}. These results indicate that the D_{12} in pressurized liquid fluids can be exactly measured by the Taylor dispersion method, and the D_{12} in sc CO_2 cannot be well measured by the Taylor dispersion method, but the D_{12} in sc CO_2 can be accurately measured by the CIR method.

Fig. 3 shows the effects of absorption wavelength on (a) absorbance of the peak top of a response curve A_{max}, (b) D_{12} and ε for triolein measured by the Taylor dispersion method in hexane at 308.15 K and 11.95 MPa, and (c) A_{max}, (d) D_{12} and ε for triolein measured by the CIR method in sc CO_2 at 308.15 K and 12.02 MPa. The response curves were measured at wavelengths from 200 to 240 nm at increments of 1 nm for each run. It was found that the absorbance intensities measured in pressurized hexane and in sc CO_2 are lower than 0.3 AU and 0.05 AU for the whole wavelengths, respectively. Furthermore, the resulting D_{12} values in pressurized hexane are nearly constant at wavelengths above 198 nm and the ε values are lower than 1%. In addition, the D_{12} values in sc CO_2 are also almost constant at wavelengths below 210 nm, and the ε values are also less than 1%. In this study all D_{12} values were determined from the response curves measured at 205 nm.

Fig. 4 represents the effects of secondary flow on (a) D_{12} and (b) curve fitting error ε in pressurized hexane at 11.95 MPa measured by the Taylor dispersion method, and in sc CO_2 at 12.02 MPa measured by the CIR method. These measurements were performed at 205 nm and 308.15 K. The ε values for both measurements of the Taylor dispersion and CIR methods are almost lower than 1%, however the D_{12} values measured by the Taylor dispersion method and the CIR method are affected by the secondary flow caused by column coiling when $DeSc^{1/2} > 10$ and $DeSc^{1/2} > 20$, respectively. In this study all measurements were carried out at $DeSc^{1/2} < 10$.
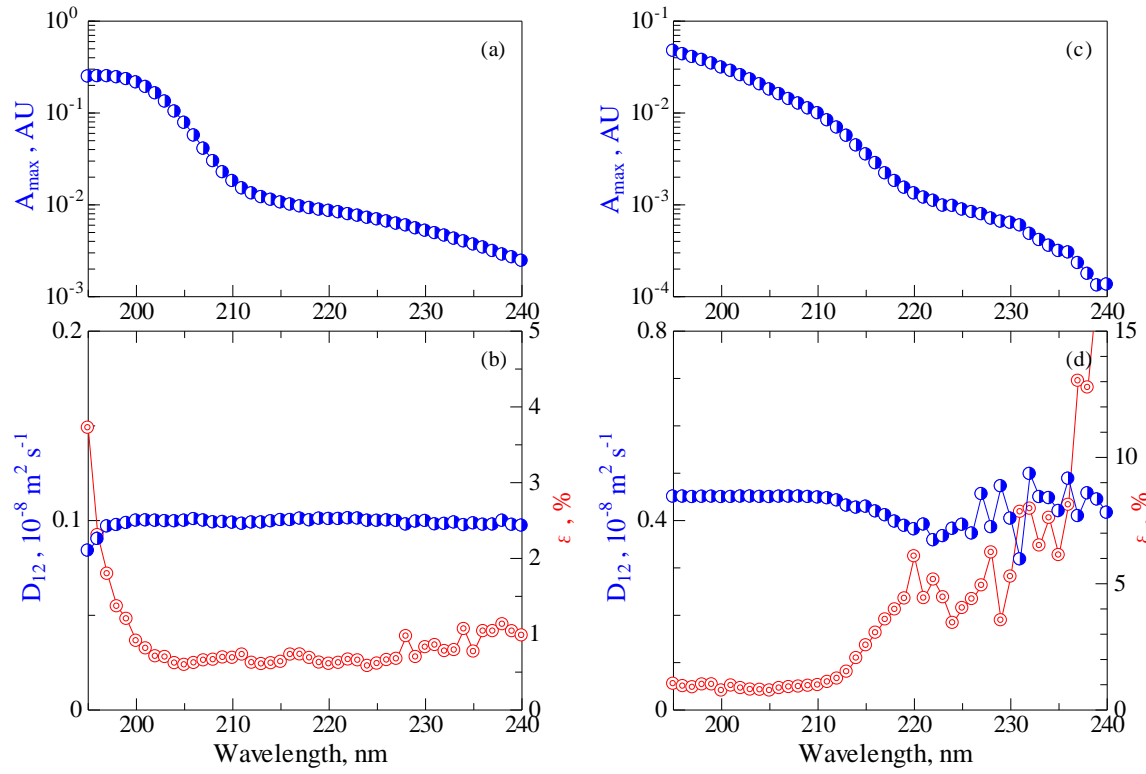
Fig. 3. Wavelength dependence on (a) absorbance of the peak top of a response curve A_{max}, (b) D_{12} and ε in pressurized hexane at 308.15 K and 11.95 MPa measured by the Taylor dispersion method, and (c) A_{max}, (d) D_{12} and ε in sc CO_2 at 308.15 K and 12.02 MPa measured by the CIR method.
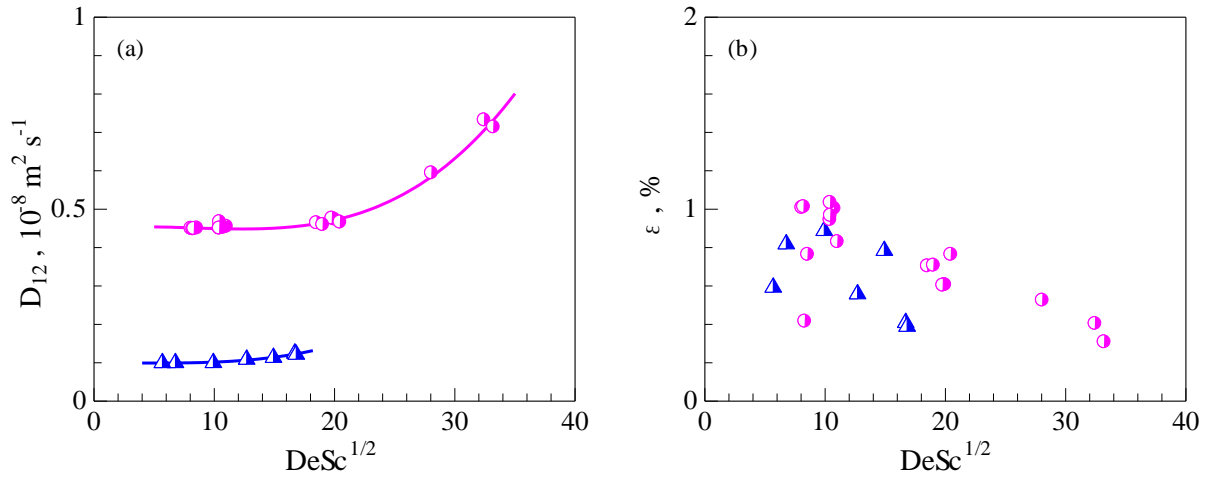

Fig. 4. Effects of the secondary flow on (a) D_{12} and (b) ε measured in pressurized hexane at 308.15 K and 11.95 MPa by the Taylor dispersion method (▲), and in sc CO_2 at 308.15 K and 12.02 MPa by the CIR method (◖).

Fig. 5 shows the pressure dependence of D_{12} values and the curve fitting error ε of triolein (a) and (b) in pressurized hexane at 298.15 K to 323.15 K and at 1.00 MPa to 12.00 MPa, (c) and (d) in pressurized methanol at 298.15 K to 318.15 K and at 1.00 MPa to 12.00 MPa, (e) and (f) in pressurized ethanol at 298.15 K to 323.15 K and at 1.00 MPa to 10.00 MPa measured by the Taylor dispersion method. All D_{12} values in pressurized liquid fluid of hexane, methanol and ethanol decrease simply with increasing pressure and increase with increasing temperature. Note that all the curve fitting errors ε obtained in this study are almost lower than 1 %. The magnitude of D_{12} value in pressurized liquid fluid is in the order of hexane > methanol > ethanol. It was observed that the effect of pressure on the value of D_{12} in ethanol at each temperature was less than that in hexane and in methanol under the examined conditions. This is probable that the viscosity of ethanol is higher than ethanol and hexane. As shown in Figs. 5 (a), (c) and (e), The D_{12} data can be well represented by the simple empirical correlations of Eq. (4).
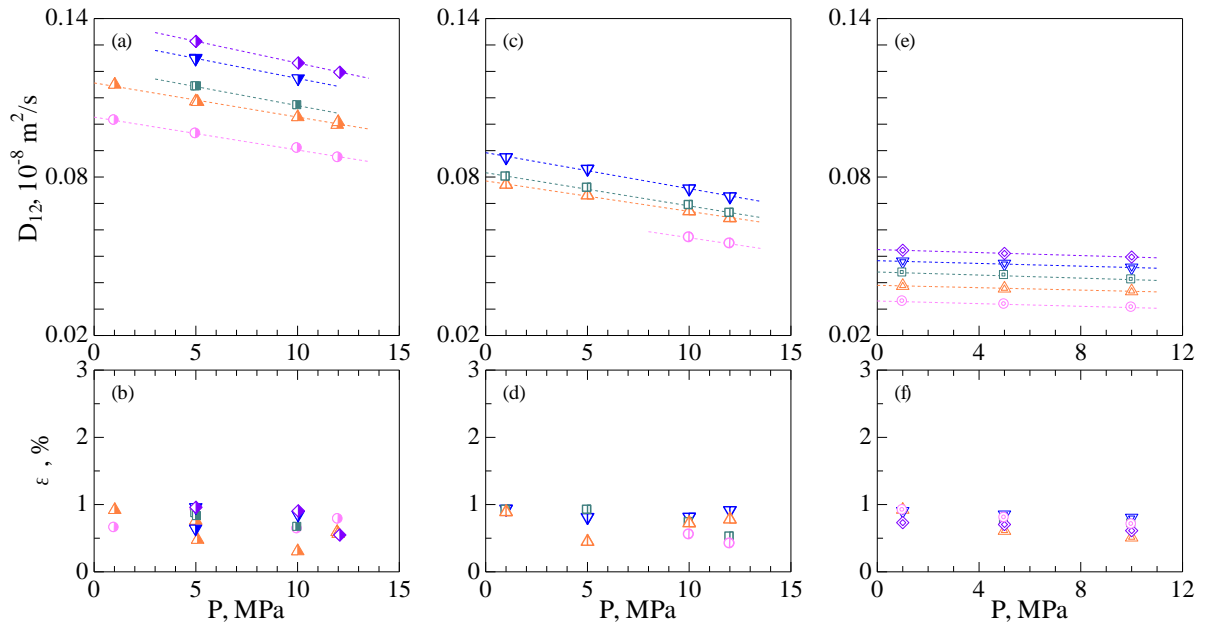
$$D_{12} = a_0 + a_1 P + a_2 T \tag{4}$$

Fig. 5. Pressure dependence on (a) D_{12} and (b) ε in pressurized hexane measured at 298.15 K (◐), 308.15 K (▲), 313.15 K (■), 318.15 K (▼), 323.15 K (◆), and at 1.00 to 12.00 MPa, (c) D_{12} and (d) ε in pressurized methanol measured at 298.15 K (◑), 308.15 K (△), 313.15 K (⬒), 318.15 K (▽), and at 1.00 to 12.00 MPa, (e) D_{12} and (f) ε in pressurized ethanol measured at 298.15 K (◎), 308.15 K (△), 313.15 K (⬚), 318.15 K (▽), 323.15 K (◇), and at 1.00 to 10.00 MPa, and together with the correlated line by Eq. (4).
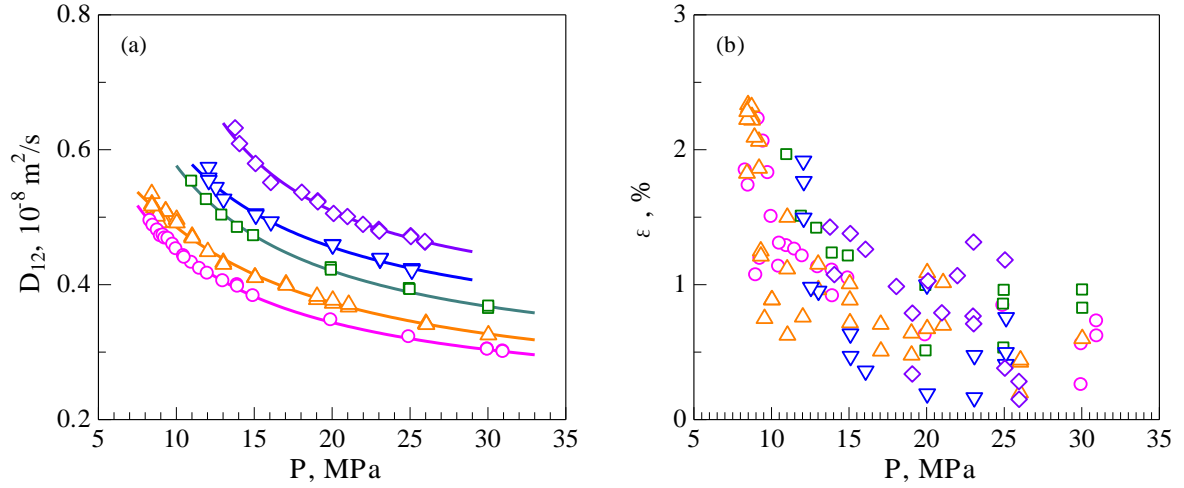
Fig. 6. Pressure dependence on the (a) D_{12} and (b) ε measured in CO_2 at 298.15 K ($\circ$), 308.15 K ($\triangle$), 318.15 K ($\square$), 323.15 K ($\triangledown$) and 333.15 K ($\diamond$), and at 8.36 to 31.02 MPa by the CIR method, and together with the correlated line by Eq. (5).

Fig. 6 shows the pressure dependence of (a) D_{12} values and (b) the curve fitting error ε of triolein in CO_2 measured by the CIR method at 298.15, 308.15, 318.15, 323.15, 333.15 K and at 8.36 to 31.02 MPa. The large changes in D_{12} values were seen up to 20 MPa, and the changes linearly decreased above 20 MPa. Note that all curve fitting error ε obtained in this study were lower than 3%. The D_{12} data can be well represented by the simple empirical correlations of Eq. (5) with an AARD of 1.2% for 106 data points.

$$D_{12} = b_0 + b_1 \frac{1}{P} + b_2 T + b_3 \frac{T}{P} + b_4 \frac{1}{P^2} + b_5 \frac{T}{P^2} \tag{5}$$

$$\text{AARD} = \frac{1}{N} \sum_{i=1}^{N} \left| 1 - \frac{D_{12,\text{calc}}}{D_{12,\text{meas}}} \right|_i \times 100\% \tag{6}$$

where diffusion coefficient D_{12}, pressure P and temperature T are in m^2/s, MPa and K, b_0 to b_5 are constants, N is the number of experimental data points, and $D_{12,\text{calc}}$ and $D_{12,\text{meas}}$ are the calculated and measured D_{12} data, respectively.

Figure 7 indicates (a) D_{12}/T and deviation of $(D_{12,\text{meas}} - D_{12,\text{calc}})/D_{12,\text{meas}}$ over fluid viscosity, together with the literature data measured by the CIR method at 313.21 K and at 9.13 to 14.02 MPa in sc CO_2 [12]. It was found that the values of D_{12}/T measured in this study and reported in literature [12] are well correlated with the fluid viscosities in a wide range of horizontal axes from the supercritical to the liquid state. The deviations are almost within ±0.15. In this study, a new correlation was proposed, as Eq. (7):

$$lnD_{12} = c_0 + c_1 \, ln \, \eta + c_2(ln \, \eta)^2 + c_3 \, ln \, T \qquad (7)$$

where D_{12} is the diffusion coefficient in m^2/s, T is the temperature in K, η is the viscosity in Pa s, and c_0 to c_3 are constants, respectively. The D_{12} values measured in this study can be represented by the proposed correlation of Eq. (7) over a wide fluid viscosity range of 41 to 1179 μPa s from supercritical state to liquid state, with AARD = 5.3% for 154 data points. The correlation proposed in this study can well express the literature data [12] with AARD = 1.8% for 10 data points.
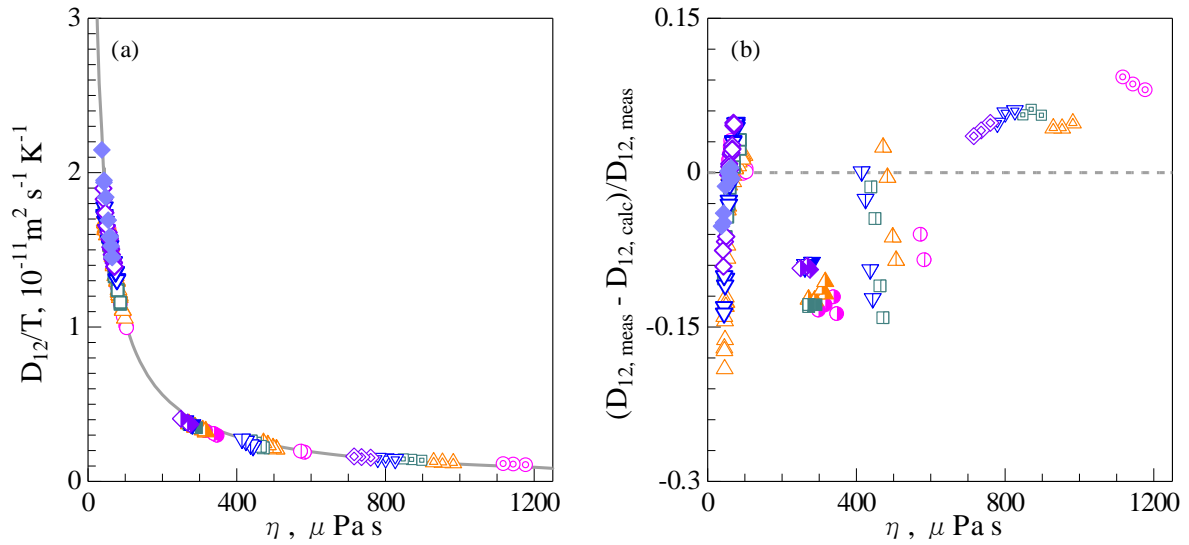

Fig. 7. Plots of (a) D_{12}/T and (b) $(D_{12, meas} - D_{12, calc})/D_{12, meas}$ vs. fluid viscosity η for all the D_{12} values measured in this study. Together with the literature D_{12} values (◆) measured by the CIR method at 313.21 K and at 9.13 to 14.02 MPa in sc CO_2 [12]. The solid line in (a) was obtained from the Eq. (7) and the key is the same as in Fig. 5 and Fig.6.

5. Conclusions

The diffusion measurements of triolein were carried out at infinite dilution in various pressurized fluids such as CO_2, hexane, methanol and ethanol with different viscosities. The D_{12} values in CO_2 were measured by the chromatographic impulse response method at 303.15 to 333.15 K and at pressures up to 31.02 MPa. In addition, those in hexane, methanol and ethanol were measured by the Taylor dispersion method at 298.15 to 323.15 K and pressures of 1.00 to 12.00 MPa. The D_{12} of triolein increased from 3.059×10^{-10} m^2 s^{-1} at 298.15 K and 10.00 MPa in liquid ethanol to 6.323×10^{-9} m^2 s^{-1} at 333.15 K and 13.77 MPa in supercritical CO_2. It was found that all D_{12} data of triolein measured in CO_2, hexane, methanol and ethanol

in this study can be satisfactorily represented by the proposed equation ($lnD_{12} = c_0 + c_1 \ln\eta + c_2 (\ln\eta)^2 + c_3 \ln T$) over a wide range of fluid viscosity of 41 to 1179 µPa s from supercritical state to liquid state with AARD of 5.3% for 154 data points.

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