

Measurement and correlation of binary diffusion coefficients of lithium acetylacetonate in supercritical carbon dioxide and in liquid ethanol



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ABSTRACT

The infinite dilution binary diffusion coefficients D_{12} of lithium acetylacetonate were measured in supercritical carbon dioxide by the chromatographic impulse response (CIR) method at 308.15–333.15 K and pressures up to 36.00 MPa. The D_{12} values were also measured in liquid ethanol at 298.15–333.15 K, and at 0.10, 10.00 and 30.00 MPa by the Taylor dispersion method. The effects of temperature, pressure and density of fluid on D_{12} values were studied. The D_{12} data increased from $1.140 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in liquid ethanol at 298.15 K and 30.00 MPa to $2.218 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ in supercritical carbon dioxide at 333.15 K and 14.00 MPa. It was observed that the D_{12} data in supercritical carbon dioxide at 15.00, 20.00 and 30.00 MPa can be well correlated as a function of temperature using an Arrhenius type equation, which provided the diffusion activation energies of 17.5, 13.4 and 11.0 kJ mol^{-1} ; that in liquid ethanol at 0.10, 10.00, 30.00 MPa gave the diffusion activation energies of 14.0, 14.2 and 13.8 kJ mol^{-1} , respectively. It was found that the proposed correlation based on hydrodynamic approach can well represent all the measured D_{12} data of lithium acetylacetonate in supercritical carbon dioxide and in liquid ethanol with the average absolute relative deviation (AARD) of 1.7% for 88 data points.

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1. Introduction

Advanced materials such as reduced graphene oxide, carbon nanotubes, fine particles and metal organic frameworks can be prepared by supercritical (sc) phases [1,2]. Expanded applications [3–5] of sc fluids as an alternative to traditional organic solvents are proving sc fluids as the green solvents. Metal acetylacetonate complexes that can be solved in sc carbon dioxide have been employed for the fabrication of catalysts, nanostructured materials, metallic covering and filling to the nano inner structure of devices by using sc carbon dioxide. Further, sc carbon dioxide can possibly be utilized instead of organic solvents for extraction of metals. In fact, sc fluid science and technology have a wide variety of applications. The combination of organometallic chemistry and sc carbon dioxide has significant potential. To simulation, design, optimisation

and scale-up of new sc process, an understanding of the fundamental properties of the sc system is needed. Estimation of mass transfer properties in the system often requires reliable information about binary diffusion coefficients in the system. Furthermore, the binary diffusion coefficients are of importance in providing information regarding the kind of interactions between different molecules of solute and solvent. On the other hand, lithium acetylacetonate (Li(acac)) is an important lithium source, which is also the smallest metal acetylacetonate complex. Now, its applicability in the sc carbon dioxide is strongly expected. Li(acac) can enhance the current efficiency of the organic light emitting devices [6]. To our knowledge, no diffusion data are available in literature for the both systems of Li(acac) in sc carbon dioxide and Li(acac) in liquid ethanol. Therefore, the objective of this work was to measure the infinite dilution binary diffusion coefficients D_{12} of Li(acac) in sc carbon dioxide by the chromatographic impulse response (CIR) method. In addition, the D_{12} data of Li(acac) in liquid ethanol were also measured by the Taylor dispersion method. Furthermore, the correlation based on hydrodynamic approach as a function of temperature and fluid viscosity was proposed for the measured diffusion data in this study.

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2. Theory

When a solute is pulse injected into a fully developed laminar flow in an uncoated capillary column in the Taylor dispersion method [7] or in a polymer coated capillary column in the CIR method [8,9], the average concentration $C(z,t)$ can be described as follows:

$$\begin{cases} C(z, t) = \left(\frac{m}{\pi R^2} \right) \frac{1}{(1+k)(4\pi Kt)^{1/2}} \exp \left\{ -\frac{(z-ut)^2}{4Kt} \right\} \\ K = \frac{D_{12}}{1+k} + \frac{1+6k+11k^2}{1+k} \frac{R^2 u^2}{48D_{12}} \\ k = \frac{u_0}{u} - 1 \end{cases} \quad (1)$$

where z is the axial distance, t is the time, m is the injected amount of the solute, R is the column radius, k is the retention factor, u_0 and u are the average velocities of fluid and solute, and D_{12} is the infinite dilution binary diffusion coefficient of the solute in the fluid. Note that the average fluid velocity u_0 is needed to obtain experimentally in the CIR method, while it is not required in the Taylor dispersion method. In the case of the Taylor dispersion method let $k=0$ in Eq. (1). In this study, the D_{12} value was determined by minimizing the root mean square fitting error ϵ , defined by Eq. (2).

$$\epsilon = \left(\frac{\int_{t_1}^{t_2} (C_{\text{meas}}(L, t) - C(L, t))^2 dt}{\int_{t_1}^{t_2} (C_{\text{meas}}(L, t))^2 dt} \right)^{1/2} \quad (2)$$

where L is the distance between injection point and detection point, t_1 and t_2 correspond to the times at the frontal and latter 10% peak heights of measured response curve $C_{\text{meas}}(L, t)$ at $z=L$, respectively. In this study the fit is considered to be excellent when $\epsilon < 1\%$, and acceptable when $\epsilon < 3\%$ [9].

3. Experimental

The experimental apparatuses and the procedures for the CIR and the Taylor dispersion methods are substantially the same as those reported in our previous studies [10,11]. The temperature and pressure of the system were measured by a pressure indicator (PM digital, HEISE, USA) and a thermometer (APT-100, ANRITSU, Japan), respectively. The stabilities of the temperature and pressure of the system were controlled to within ± 0.01 K and ± 0.005 MPa, respectively. A pulse (1.0 μL) of Li(acac) dissolved in ethanol was loaded through an injector (Model 7520, 1.0 μL rotor, Rheodyne, USA) into the diffusion column. All measurements were carried out under the conditions of $DeSc^{1/2} < 8$, the flow velocities of the fluids were lower than $8 \times 10^{-3} \text{ m s}^{-1}$, and the Reynolds and the Schmidt numbers were from 40 to 113 and from 5 to 12 in the CIR

method and from 3 to 7 and from 333 to 1174 in the Taylor dispersion method, respectively. Note that the densities of carbon dioxide were obtained with the equations of Pitzer and Schreiber [12] and Span and Wanger [13], and the viscosities of carbon dioxide were calculated by the method of Fenghour et al. [14]. And the densities and viscosities of ethanol were based on the literature [15,16].

Carbon dioxide (99.95%) was obtained from Air Gases Tokai Ltd., Japan, lithium acetylacetonate (molecular formula: $\text{C}_5\text{H}_7\text{LiO}_2$, molecular weight: 106.05) with purity 97% was obtained from Sigma-Aldrich and ethanol with 99.5% was purchased from Wako, and used as received. In this study at least three measurements were carried out for a given temperature and pressure, and the average diffusion value of the measurements was considered to be the D_{12} value at the given condition.

4. Results and discussion

Fig. 1 indicates the typical chromatographic response peaks measured (solid line) and calculated (dash line) of Li(acac) in sc carbon dioxide at 270 nm, 313.15 K and at three pressures of (a) 11.00, (b) 15.00 and (c) 20.00 MPa by the CIR method. The concentration of Li(acac) dissolved in ethanol with $4 \times 10^{-3} \text{ g mL}^{-1}$ was used. Excellent agreements were found between the experimentally measured and theoretically calculated peaks for the three cases. Note that in this study all the experimental peaks were used just as obtained.

The injected solution volume of Li(acac) in ethanol was 1.0 μL for each measurement in this study, generally with the injection time less than 1 s, to ensure that the measurement was at dilute concentration. To make clear the effect of the injected quantity of Li(acac) on D_{12} values, the measurements were carried out at several different injected Li(acac) concentrations of ethanol. Fig. 2 shows the effects of the injected Li(acac) concentrations on D_{12} and ϵ values measured by the CIR method in the sc carbon dioxide at 313.15 K and at three pressures (11.00, 15.00, 20.00 MPa). Seven difference solutions of Li(acac) in ethanol over the wide range of the concentrations (5×10^{-4} , 1×10^{-3} , 2×10^{-3} , 3×10^{-3} , 4×10^{-3} , 5×10^{-3} and $6 \times 10^{-3} \text{ g mL}^{-1}$) were used. Correspondingly the injected amounts of Li(acac) were 4.71×10^{-3} , 9.43×10^{-3} , 1.89×10^{-2} , 2.83×10^{-2} , 3.77×10^{-2} , 4.71×10^{-2} and $5.66 \times 10^{-2} \mu\text{mol}$, respectively. As shown in Fig. 2(a), the D_{12} values were almost constant for the different injected concentrations at each fixed pressure, and all the obtained ϵ values were lower than 2%. This indicates that there is no effect of the injected amounts of Li(acac) on the measured D_{12} values. The ϵ values increased with decreasing pressure. This might be from the decreasing the density of carbon dioxide, corresponding to lower solvent power of the system. Furthermore, the ϵ values gave the lowest values at $4 \times 10^{-3} \text{ g mL}^{-1}$ for all the examined pressures of 11.00, 15.00 and

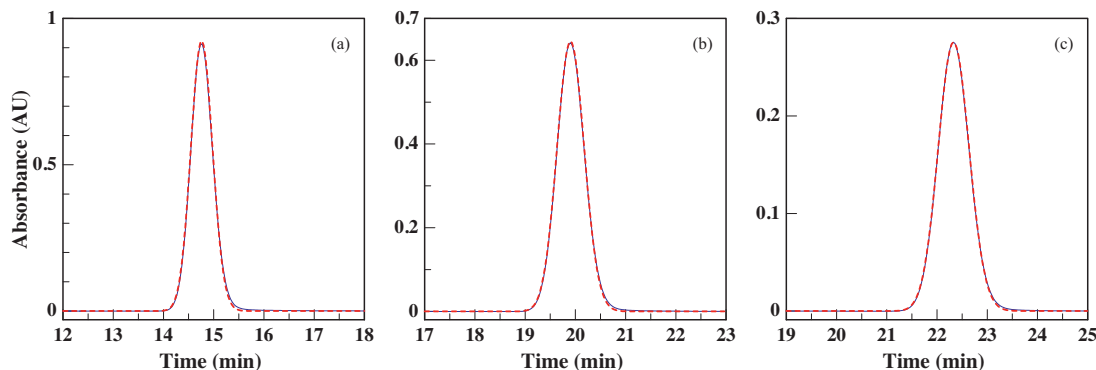


Fig. 1. Typical chromatographic peaks measured (solid line) and calculated (dash line) by the CIR method for Li(acac) in sc carbon dioxide at 313.15 K, and (a) 11.00 MPa, (b) 15.00 MPa and (c) 20.00 MPa.

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