

Measurement and correlation of binary diffusion coefficients for metal complexes in high temperature supercritical carbon dioxide

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Abstract

Although a large number of data on binary diffusion coefficients for various organic compounds in supercritical fluids have been reported, the ranges of the measurement conditions are not wide because the data were measured mainly for supercritical fluid extraction. Recently, supercritical fluids have been applied to material processing, and the data at higher temperatures are required for designing reactors and estimating mass transfer rates. In the present study binary diffusion coefficients for metal complexes such as chromium acetylacetonate (III), acetylferrocene and 1,1'-diacetylferrocene in supercritical carbon dioxide were measured up to 140 °C by the chromatographic impulse response method. The measured D_{12} data more deviated from those obtained by the hydrodynamic equation, which was valid for most compounds reported in the literature. The literature data were measured at relatively lower temperatures, where scCO_2 was at the liquid like densities. The hydrodynamic equation was found to be no longer valid for D_{12} data at higher temperatures, gas-like or the transition state from liquid-like to gas-like supercritical state. The validities for some predictive correlations proposed in the literature were examined.

INTRODUCTION

While a significant quantity of diffusion data have been accumulated, together with proposals for many predictive correlations/models and estimation methods, these were measured mainly for supercritical fluid extraction (SFE), that is, at higher densities and lower temperatures of supercritical CO₂. As one of predictive correlations, a hydrodynamic equation, $D/T = \alpha\eta^\beta$, is effective for various solutes over a wider range from supercritical to liquid state [1,2], where D is the binary diffusion coefficient at infinite dilution or self-diffusion coefficient, η is the solvent viscosity, and the constants α and β are specific to solute species, irrespective of a solvent. Recently, various material processes with supercritical fluids [3,4], in particular, supercritical fluid deposition (SFD), have become focus of attention. In SFD process metal complex is carried by supercritical CO₂ close to nano-structural substrate, and then the metal is deposited by pyrolysis on substrate surfaces. To design reactors and simulate reaction kinetics diffusion coefficients of metal complexes at gas-like supercritical conditions, namely at higher temperatures and lower densities, are required [5]. However, the data in gas-like supercritical CO₂ state are scarcely available. In the present study binary diffusion coefficient of metal complexes, mainly Cr(acac)₃, were measured at higher temperatures up to 140 °C, while D_{12} for Cr(acac)₃ in scCO₂ are available from 35 to 70 °C in the literature [6,7], and the validity of the predictive correlation was discussed.

MATERIALS AND METHODS

The metal complexes studied in the present study were chromium acetyl acetonate (III), acetylferrocene and 1,1'-diacetylferrocene were employed without further purification. The chromatographic impulse response method [1,6-8] was employed to measure diffusion coefficients. The experimental apparatus was almost the same as that employed in the previous study [7] except for a GC oven as a constant temperature bath while a water bath had originally been used.

The response curve, $c_a(t)$, calculated by Eqs (1) and (2) was fit to that measured experimentally at the column exit (at $x = L$) such that the fitting error, ε , defined as Eq. (3) was minimized by choosing two parameters, binary diffusion coefficient D_{12} and retention factor k .

$$c_a(t) = \left(\frac{m}{\pi R^2} \right) \frac{1}{(1+k)\sqrt{4\pi at}} \exp \left\{ - \frac{\left(L - \frac{u_a}{1+k} t \right)^2}{4at} \right\} \quad (1)$$

and

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

Herein m is the mass of the solute injected, R is the column inner radius, L is the column length, t is the time, u_a is the average mobile phase velocity.

$$\varepsilon = \left(\frac{\int_{t_1}^{t_2} \{c_{\text{exp}}(t) - c_a(t)\}^2 dt}{\int_{t_1}^{t_2} \{c_{\text{exp}}(t)\}^2 dt} \right)^{1/2} \quad (3)$$

RESULTS AND DISCUSSION

Figure 1 shows typical response curves calculated in Eqs (1) and (2) and measured experimentally at 393.2 K, 16.0 MPa and 330 nm. As depicted, since the fitting was found to be excellent when $\varepsilon < 1\%$ [1], the response curve calculated well described that measured experimentally with the fitting error $\varepsilon = 0.389\%$. In the present study all response curves did not significantly show tailing. Figure 2 plots D_{12} vs. pressure at various temperatures. As seen for most compounds measured, diffusion coefficients D_{12} decreased with increasing pressure.

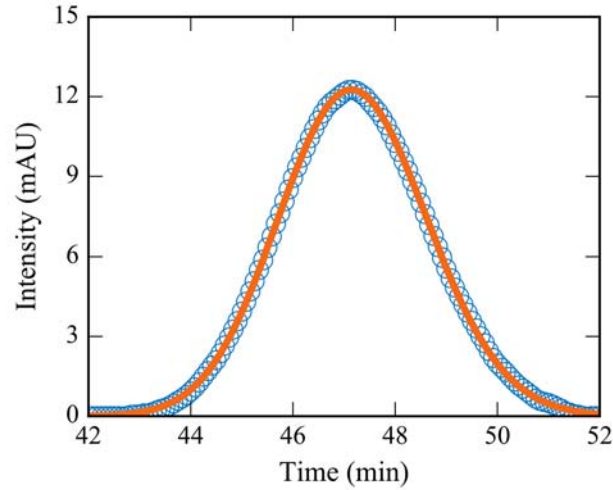


Fig. 1. Response curves measured experimentally (circle) at 393.2 K, 16.0 MPa and 330 nm and calculated (solid line) with $D_{12} = 2.87 \times 10^{-8} \text{ m}^2/\text{s}$, $k = 2.70$ and $\varepsilon = 0.389\%$.

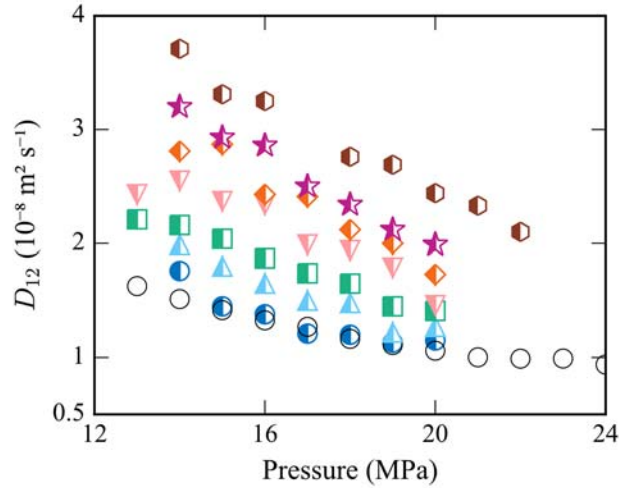


Fig. 2. Pressure dependence of D_{12} , circle; 343.2 K, triangle; 353.2 K square; 363.2 K, diamond; 373.2 K, inverted triangle; 383.2 K, star; 393.2 K, hexagon; 413.2 K, open circle: literature 343.2 K [7].

Figure 3 shows D_{12}/T vs. CO_2 viscosity in logarithmic plots for $\text{Cr}(\text{acac})_3$ in scCO_2 together with those in liquid ethanol at atmospheric pressure. Figure 3b shows an enlarged portion of Fig. 3a. Eq. (4) is the modified Stokes-Einstein equation, sometimes referred to as the hydrodynamic equation, was valid for binary diffusion coefficients in liquid and supercritical fluids as well as self-diffusion coefficients [1,2].

$$\frac{D_{12}}{T} = \alpha \eta^\beta \quad (4)$$

where D_{12} is the diffusion coefficient, T is the temperature, η is the solvent viscosity, α and β are the constants. Although Eq. (4) is valid for compounds in liquid and liquid like supercritical fluids, the data in gas-like scCO_2 deviate. The plots deviate at CO_2 viscosities lower than $40 \mu\text{Pa s}$, which correspond to CO_2 density range from 502 kg/m^3 at 353.2 K and 16.9 MPa to 467 kg/m^3 at 413.5 K and 26.5 MPa.

Figure 4 shows retention factor k vs. CO_2 density. As seen for various compounds, k values were represented by a straight line at each temperature, but the slope and intercept vary with temperature. The temperature dependence on the slope and intercept are less significant at lower temperatures.

In the presentation the D_{12} data for acetylferrocene and 1,1'-diacetylferrocene in scCO_2 will also be presented.

CONCLUSION

Infinite dilution binary diffusion coefficients D_{12} and retention factors k for chromium acetyl acetate (III), acetylferrocene, and 1,1'-diacetylferrocene were measured by the chromatographic impulse response method in scCO_2 at temperature from 313.2 to 413.2 K and

pressures up to 30 MPa. While D_{12} values were well represented by the hydrodynamic equation at CO₂ viscosities higher than 40 μPa s, as seen for various compounds in the literature, those more deviated at lower CO₂ viscosities. The data deviating could correspond to the gas-like region of scCO₂, and the former to the liquid-like region.

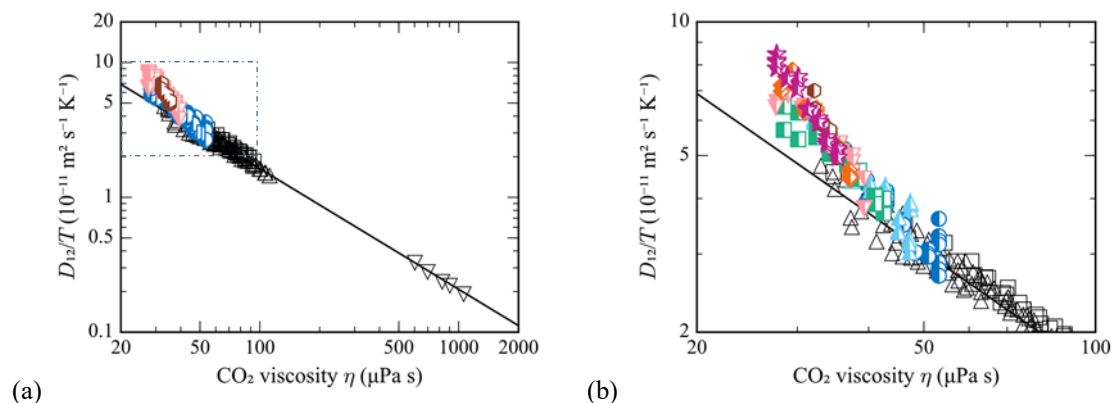


Fig. 3. D_{12} estimation by the hydrodynamic equation, circle; 343.15 K, triangle; 353.15 K square; 363.15 K, diamond; 373.15 K, inverted triangle; 383.15 K, star; 393.15 K, hexagon; 413.15 K, open triangle; literature at 308.15–343.15 K [7], open square; literature at 308.15–333.15 K [6]. Fig. 3(b) shows an enlarged portion of Fig. 3(a).

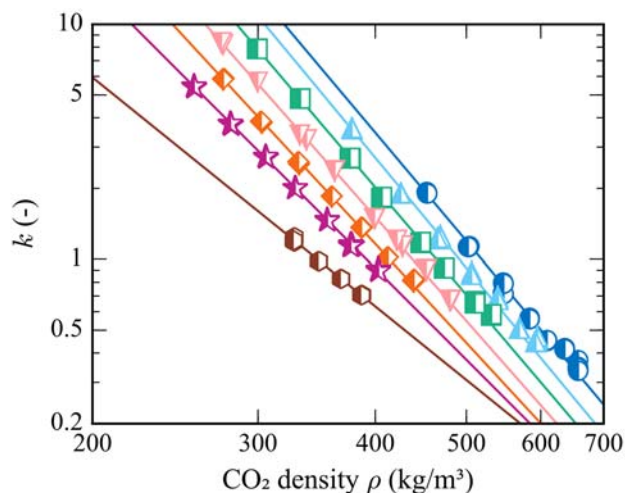


Fig. 4. CO₂ density dependence of k , circle; 343.2 K, triangle; 353.2 K square; 363.2 K, diamond; 373.2 K, inverted triangle; 383.2 K, star; 393.2 K, hexagon; 413.2 K.

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REFERENCES

- [1] FUNAZUKURI T., KONG C. Y., KAGEI S., "Impulse response technique to measure binary diffusion coefficients under supercritical fluids," *J. Chromatogr. A*, Vol. 1037, 2004, p. 411.
- [2] FUNAZUKURI T., KONG C. Y., KAGEI S., "Predictive correlation of binary diffusion and self-diffusion coefficients under supercritical and liquid conditions," *J. Supercrit. Fluids*, Vol. 46, 2008, p. 280.
- [3] SUI R., CHARPENTIER P., "Synthesis of metal oxide nanostructures by direct sol-gel chemistry in supercritical fluids," *Chem. Rev.*, Vol. 112, 2012, p. 3057.
- [4] TKALEC G., PANTIĆ M., NOVAK Z., KNEZ Ž., "Supercritical impregnation of drugs and supercritical fluid deposition of metals into aerogels," *J. Mater. Sci.*, Vol. 50, 2015, p.1.
- [5] FUNAZUKURI T., "Concerning the determination and predictive correlation of diffusion coefficients in supercritical fluids and mixtures," *J. Supercrit. Fluids*, Vol. 134, 2018, p.28.
- [6] CORDEIRO J., MAGALHÃES A. L., VALENTE A. A., SILVA C. M., "Experimental and theoretical analysis of the diffusion behavior of chromium (III) acetylacetonate in supercritical CO₂," *J. Supercrit. Fluids*, Vol. 118, 2016, p. 153.
- [7] KONG C. Y., WATANABE K., FUNAZUKURI T., "Measurement and correlation of the diffusion coefficients of chromium (III) acetylacetonate at infinite dilution in supercritical carbon dioxide and in liquid ethanol," *J. Chem. Thermody.*, Vol. 105, 2017, p. 86.
- [8] FUNAZUKURI T., KONG C. Y., MUROOKA N., KAGEI S., "Measurements of binary diffusion coefficients and partition ratios for acetone, phenol, alpha-tocopherol, and beta-carotene in supercritical carbon dioxide with a poly(ethylene glycol)-coated capillary column," *Ind. Eng. Chem. Res.*, Vol. 39, 2000, p. 4462.