Relationship Between the Critical Anomaly of the Solute Diffusion Coefficient in Supercritical CO_2 and the Local and Long Range Density Augmentation Evaluated from the Kirkwood-Buff's Fluctuation Theory

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ABSTRACT

Anomal decrease observed in the dilute binary diffusion coefficients of solutes in supercritical CO_2 was revisited. Considerable causes of this decrease have been attributed to the decrease of the thermodynamic factor, the critical slowing down and/or the structural anomaly such as solvents' clustering around solutes. Effects of all these factors were evaluated in the same system. In the case of benzene in supercritical CO_2, the thermodynamic factor, the correlation length, and the Kirkwood-Buff's G factor indicated strong density and temperature depencences but O'Connell's C factor that is relating to the local solvent density augmentation around a solute did not indicate temperature dependence from 35 to 55 ℃. All factors could not explain the experimental temperature and density dependences of the diffusion coefficients observed by Taylor dispersion method.

INTRODUCTION

Supercritical fluids (SCFs) have a density between gases and liquids and many physico-chemical properties including the diffusion coefficients vary from gas kinetic dominated values to the liquid state values and sometimes they are affected by the microscopic structure such as clustering. A plenty of the diffusion coefficients in SCFs have been studied and theoretically or empirically correlated [1]. We have observed the diffusion coeffieients of several solutes in supercritical CO_2 and some solutes such as benzene [2] indicated anomalous decrease in the medium density region, which is near or below the critical density. Data of benzene were taken using Taylor dispersion method with the solute injection amount less than 0.5 μL.

Anomalous density dependence of the diffusion coefficients has been studied and attributed to the decrease of the therymodynamic factor [3]-[5], the critical slowing down that is related to the increase in the correlation length due to the density fluctuation [6-8], and the

microscopic fluid structure and their dynamics around solutes [9].

In our knowledge, there was no work that evaluated all these factors at the same time. In this paper, we will evaluate all considerable effects for the same system simultaneously. Microscopic structure of the supercritical fluids has been classified into "long-range" and "short range", or "indirect" and "direct" structures [10]. We will evaluate both direct and indirect structures by calculating Kirkwood-Buff's G factor and O'Connell's C factor, which are reflecting long-range and short-range structures, respectively. Physical meaning of C factor is not clear. It roughly relates to $g(\sigma)$ or the local solvent density increase and it is useful when the microscopic data are lacking.

Thermodynamic variables needed to calculate several factors described above were unavailable and we estimated them by Peng-Robinson equation. Such estimations may include estimation error. Thus, the main concern of this work was on the comparison of fluid condition dependences of all factors and to evaluate the considerable effect on D_{12}.

CALCULATION

Experimental diffusion coefficient data

In the following discussion, we compared the several factors which may affect the diffusion near the critical point with experimental data. Test system was our previous results, benzene in supercritical CO_2 at 35 - 55 ºC and 6 - 30 MPa [2]. Corresponding fluid densities at certain temperatures and presssures were approximately estimated from the EOS of neat CO_2 [11]. Because supercritical fluids have the densities between gases and liquids, the observed density dependence of the diffusion coefficients was not only due to the critical effects, but to the effect of the transition from gas kinetic dominated dilute region to the dense liquid region. The latter effect varies with the fluid density. We transformed the observed D_{12} in the following form for convinience of the later discussion.

$$\varsigma = kT/D_{12} \tag{1}$$

ζ is called a friction coefficient, which is linear to the fluid density in the ideal gas and linear to the viscosity if Stokes-Einstein equation is valid. As described later, this value increases if the decrease in the thermodynamic factor, the critical slowing down or the local- and/or long-range density augmentation occurs.

Thermodynamic factor

From non-equilibrium thermodynamics, the binary diffusion coefficient at a finite solute mole fraction, x_2 is expressed using a fugacity coefficient, φ_2 and an infinitely dilution diffusion coefficient, D_{12}^{∞} [12].

$$D_{12} \cong D_{12}^{\infty} B_{2,x} \tag{2a} \qquad\qquad \varsigma_{therm}/\varsigma_{back} = \left(B_{2,x}\right)^{-1} \tag{2b}$$

$$B_{2,x} = 1 + \left[\frac{\partial \ln(\varphi_2)}{\partial \ln(x_2)}\right]_{P,T} \tag{3}$$

ζ_{therm} means the friction coefficient at mole fraction of x and ζ_{back} means those at infinite dilution.   Fugacity coefficients were evaluated using Peng-Robinson equation of state [13]. Interaction parameters between benzene and CO_2 were taken from ref.[14].   Thermodynamic factors were calculated by the numerical differential of $\ln(\varphi_2)$ against $\ln(x_2)$.

In the Taylor dispersion method, solute mole fraction varies along the length direction. Rigorously, it is needed to evaluate the spatial distribution of solutes within the dispersion column at given time and calculate the cumulative effect on D_{12}.   In this work, we evaluated the mean mole fraction averaged along the z direction (flow direction) as a first approximation. In the dispersion column, mole fraction at a certain instance will be broadened in the z direction.   Mean value of the mole fraction of benzene at time t (position $z = ut$), is taken as the average within the area where $x > 1/10\, x_{max}$ (x_{max} = the maximum value of $x(z,t)$ at time t),

$$x_{mean}(z) \cong \frac{C_{solute}}{C_{co2}} = \frac{m \big/ \left(\pi R^2 4\sqrt{K\ln 10}\right)}{\rho_b(T,P)/M} \left(\frac{z}{u}\right)^{-1/2} \qquad (4)$$

$$K = D_{12} + \frac{R^2 u^2}{48 D_{12}} \qquad (5)$$

m is the amount of solute injected. M is the molecular weight of the CO_2, R is the tube inner radius, and u is the flow rate.   Averaged solute mole fraction along z-direction is

$$\bar{x} = \frac{1}{L}\int_0^L x(z)dz = \frac{2m \big/ \left(\pi R^2 4\sqrt{K\ln 10}\right)}{\rho_b(T,P)/M} \frac{1}{\sqrt{L/u}} \qquad (6)$$

L is the length of the dispersion column.   The averaged mole fraction depends on the fluid density and the diffusion coefficient of solute.   We evaluated the thermodynamic factors at given conditions using the experimental D_{12} data [2].

Correlation length

Near the critical point, diffusion coefficients is approximately expressed as follows [7],

$$D \cong kT \big/ 6\pi\eta(\xi + \sigma_{12}) \qquad (7a) \qquad\qquad \varsigma_{crit}/\varsigma_{back} \cong (\xi + \sigma_{12})/\sigma_{12} \qquad (7b)$$

ξ is the correlation length of the system, σ_{12} is the LJ diameter between CO_2 and benzene taken from a book [15] and evaluated by arithmeric average and η is the viscosity of fluids, estimated as those of CO_2 [11]. ξ was evaluated as Liu et al's method [7]. and the thermodynamic quantities and the averaged mole fractions needed in the calculation were evaluated just the same as the thermodynamic factors' calculation.

Calculation of G factor and C factor

In the dense gas theory, D_{12} is expressed as $D_{12}{}^0/g(\sigma)$ by Enskog, where $D_{12}{}^0$ is a hard sphere diffusion coefficient.   This equation can not predict the diffusion coefficient in supercritical fluids because it is based on the model of gas phase collision model and not fully includes successive collision's effects in dense fluids.   However if the radial distribution, $g(r)$ is largely increased by clustering etc., such effect may be reflected on the D_{12}.   In this

work, we did not calculate $g(\sigma)$ but used similar quantities, the Kirkwood –Buff's G factor and O'Connell's C factor because they were calculatable without simulation. The definition of these factors and the relationship with thermodynamic variables under solute infinitely dilution conditions are as follows [16].

$$G_{12}^{\infty} \equiv 4\pi \int_{0}^{\infty} \left(g_{12}^{\infty}(r) - 1\right) r^2 dr = kT\kappa_T - \overline{V}_2^{\infty} \qquad (8)$$

$$C_{12}^{\infty} = 4\pi \int_{0}^{\infty} c_{12}^{\infty}(r) r^2 dr = 1 - \overline{V}_2^{\infty} / \left(kT\kappa_T\right) \qquad (9)$$

Here, $g_{12}^{\infty}(r)$ is the radial distribution function of species 2 (solute) in species 1 (solvent) under solute infinite dilution condition and $c_{12}^{\infty}(r)$ is the direct correlation function of the same pair. ρ_1 is the number density, k is the Boltzmann constant, κ_T is the isothermal compressibility, and $\overline{V}_2^{\infty}$ is the partial molar volume of the solute. $\rho_1 G_{12}^{\infty}$ represents the long-range density augmentation [10]. $c(r)$ reflects the distribution of molecules, which were "directly" attracted by the center molecule through the intermolecular interaction. $\rho_1 C_{12}^{\infty}$ would reflect the local density augmentation. Then, change in the friction coefficient by density augmentation is approximately indicated as, $\zeta_{local} / \zeta_{back} \approx g(\sigma) \approx G_{12}^{\infty}$ or C_{12}^{∞}. $\overline{V}_2^{\infty}$ of benzene and κ_T of the solutions were estimated using Peng-Robinson equation.

RESULTS AND DISCUSSION
Compare among several factors

Figs. 1(a)-(d) are the calculation results. All factors were plotted as the ratio ζ / ζ_{back}, which is larger than unity if anomal decrease occurs. Thermodynamic factors, correlation length related frictions, and G_{12} had a peak at around 300-500 kg m^{-3} and indicated obvious temperature dependence. The shapes of these curves were slightly different. Thus, if the measurement of the diffusion coefficients was precise, it may be possible to distinguish all effects by observing both the temperature and density dependences.

Peak value of $(B_{2,x})^{-1}$ reached 1.3 and D_{12} was predicted to depress up to ca. 20 % at 35 ºC. Averaged benzene mole fraction at that condition was ca. 0.003. In the previous studies, the thermodynamic factors were estimated at fixed mole fractions [3]-[5]. Then, we also evaluate them at the fixed mole fraction of benzene, $x = 0.005$ at 35 and 40 ºC. Results were indicated in Fig. 1(a) as the curves with marks. Obviously the curves of fixed x and of fixed injection amount were different and precise estimation of x would be important to evaluate the decrease of diffusion coefficient for the experiments using Taylor dispersion.

Effect of correlation length was much significant. ζ / ζ_{back}, reached ca. 5 at 35 ºC and D_{12} was predicted to decrease ca. 80 % at that condition. Maximum correlation length was ca. 20 Å. This value was almost the same as the correlation length of CO_2 at the same temperature ($T_r = 1.013$) [17] and the evaluation of the correlation length seemed to be correct. However as indicated in later, the actual diffusion coefficients did not decrease such largely. In the original Lee and Ruckenstein's study, this effect was improved by introducing the
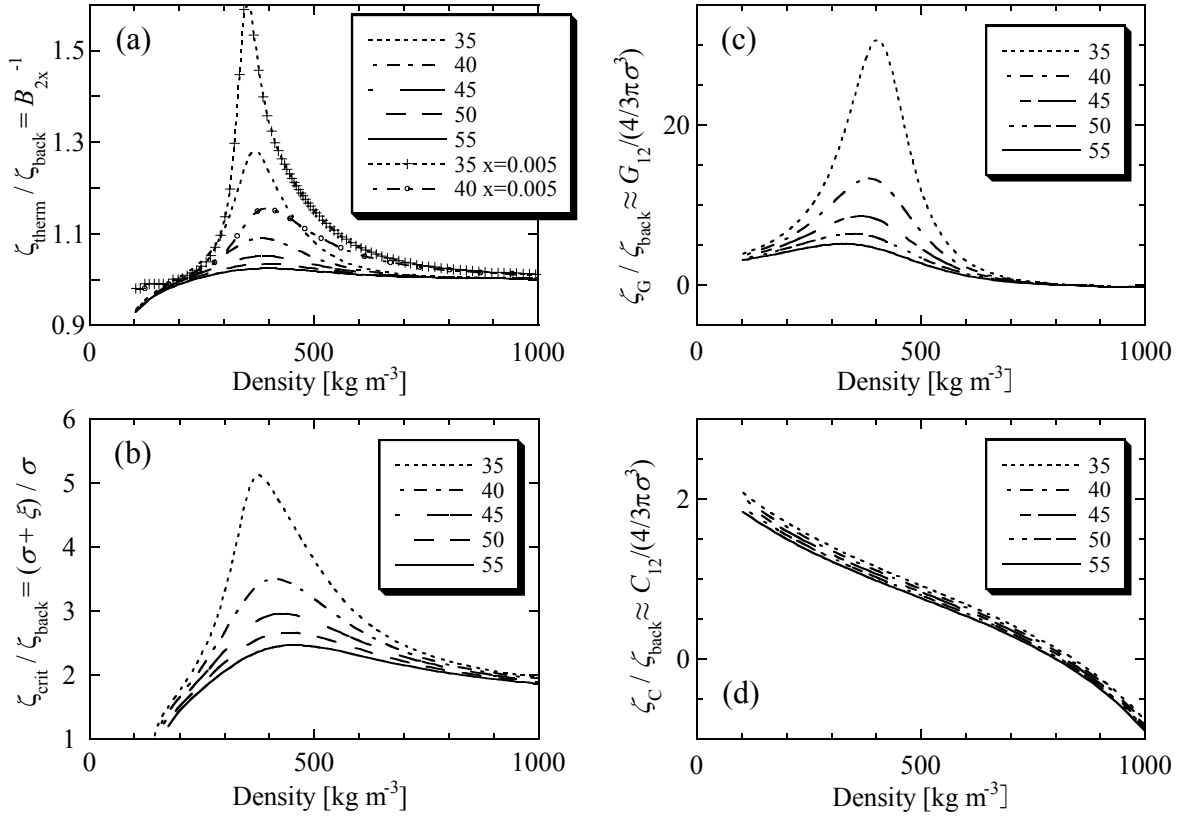
Fig. 1 Calculated factors for benzene – CO_2 system, plotted against the fluid density (a) B_{12}^{-1}, (b) $(\xi+\sigma_{12})/\sigma_{12}$, (c) $G_{12}/(4/3\pi\sigma_{12}^3)$, (d) $C_{12}/(4/3\pi\sigma_{12}^3)$.   Numbers in figures indicate temperature in unit of ºC.
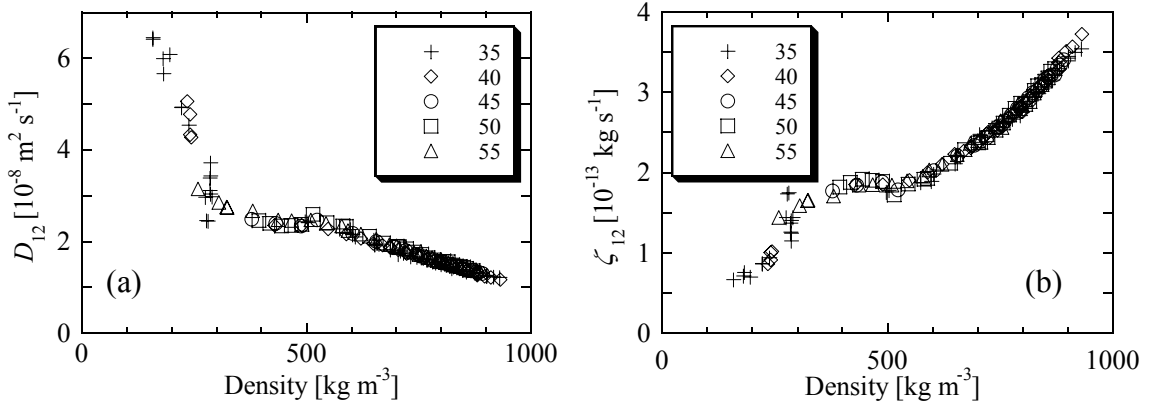

Fig. 2 Diffusion coefficients D_{12} (a) and friction coefficient ζ_{12} (b) of benzene in sc CO_2 [2]

factor of f and we could not presently judge whether it is correct or not. C_{12} did not indicate clear peaks or obvious temperature dependences.   This result is not contradicting to the image of the local density augmentation because the local density is linear to $\rho_1 C_{12}$.   This value also did not match the observed decrease of D_{12}.

Compare with experimental data

Figs. 2(a) and (b) are the plots of D_{12} of benzene in scCO$_2$ taken from our previous

work [2] and the friction coefficient ζ_{12} evaluated from eq. (1). Anomal decrease of D_{12} was observed at around 300-500 kg m^{-3} and temperature dependence was weak. Friction coefficients increased with the fluid density. Apart from the anomaly increasing region, they were almost linear to the fluid density.

When we compare the experiments with calculations, all considerable factors could not explain the temperature and density dependences of experimental data. Some of the discrepancy may be attributed to the limitation of using Taylor dispersion method near the critical point, due to the buoyancy or turbulency or other factors which did not accounted into the solution of Taylor dispersion method. However, some descrepancy should be attributed to using the Peng-Robinson equation, which is less reliable near critical region. It is needed to observe both density and temperature dependences of D_{12} of solutes, of which thermodynamic data were reported, using several different methods for further discussion.

CONCLUSION
・All factors considered here could not explain the overall fluid condition dependences of the benzene diffusion coefficients in scCO$_2$.
・All factors depended on the fluid condition differently and if the D_{12} is precisely measured, it may be possible to distinguish what dominates the diffusion process in scfs.

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