Dynamic light scattering studies on the diffusion of nano particles in CO_2 expanded organic liquids

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ABSTRACT

Stability and diffusion coefficients of several metal, protein and polymeric nano particles were examined using dynamic light scattering technique. Temperature was 25 or 30°C and pressure was varied from 0.1 to ca. 6.0 MPa to change the mole fraction of CO_2 in the saturated liquid phase from 0 to 0.8. Test particles were polystyrene with 300 nm in diameter, casein, a kind of protein with a broad size distribution and gold nano particles modified by hexadecanethiol. As the fluid pressure increased, diffusion coefficient of nano particles were all increased up to ca. 4 MPa. At higher pressures, the diffusion coefficients started decreasing during the observations and some structural change of the particles, such as swelling or agglomeration was suspected.

INTRODUCTION

CO_2 expanded liquid (CXL) is a mixture of CO_2 and organic solvents under the critical temperature of the mixture and in some cases it is defined as a saturated liquid phase under a gas-liquid phase co-existence condition. Thermodynamic properties of CXLs can be adjusted from liquid solvent's values to those of supercritical CO_2 (scCO_2) by tuning the fluid pressure. This adjustability may offer many advantages for applications. Several reviews on the fundamentals and applications using CXLs have been presented [1-3].

As a nano particle processing medium, CXLs are important because their properties are between those of liquids and supercritical CO_2. Anand et al. proposed to use CXLs for size selective fraction of polydispersed metal nano particles such as gold nano particles with several nano-meters in diameter by changing fluid pressure [4]. As the pressure increased, the fluid became less viscous and falling speed of nano particles to the bottom of the apparatus increased. Using a spiral tube, they succeeded in separating nano particles to several narrow size-distribution portions. This may be one of the possible applications. Another important application may be polymer processing. ScCO_2 has been used for polymerization, foaming, impregnation of CO_2 and making polymer blends, etc [5-7]. As CO_2 pressure increased, some polymers such as polystyrene (PS) was swollen, and at higher pressure their glass transition temperature reached the room temperature and structural change occurred. Under such high pressure conditions, it is possible to impregnate the precursors of other materials in the vacancy of the expanded polymers to make composites, or make polymer foams by suddenly decreasing the pressure.

Studies on the fundamental properties related to the particles such as solubility, precipitation, agglomeration, or swelling in CXLs were recently started. Anand et al. also observed the change of gold and silver nano particles dispersed in CX-hexane during CO_2

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pressurization and found that at a certain pressure point, the absorbance was diminished, indicating the precipitation of nano particles [4b]. Wu et al. examined the dissolution of polystyrene (PS) in several CXLs[8a]. Dong et al. examined diffusion of PS latex with ca. 15 nm in diameter in CO_2 expanded decahydronaphthalene [8b]. Diffusion coefficient increased with mole fraction of CO_2. However, in other studies, polymeric materials including PS were found to be swollen in supercritical CO_2 [9] and PS is also expected to be swollen in CXLs under CO_2 rich conditions.

We recently reported on the diffusion coefficient of PS latex and casein, a kind of milk protein in CO_2 expanded methanol with varying CO_2 mole fraction from 0.0 to 0.7 [10]. PS latex was swollen when the CO_2 mole fraction exceeded ca. 0.6. In the present work, the stability of several nano particles in CXLs such as methanol, ethanol and hexane is further examined.

EXPERIMENTAL
Samples

Hexane-soluble Au nano particles were prepared by the Brust synthesis as previous references [4b, 11]. 38 mL of 10 g/L $HAuCl_4 \cdot 4H_2O$ aqueous solution was mixed with 24.5 mL toluene dissolving 2.7 g tetraoctyl-ammonium bromide. After 12 hour mixing, water phase was removed by decantation and 240 μl of hexadodecanethiol was added. After 10 min. mixing, 30 ml of 0.5 g/L $NaBH_4$ aqueous solution was dropped into the solution. Then after 12 hour mixing, water phase was again removed and ethanol was added as a poor solvent. The solution was centrifuged at 14,000 rpm, 30 min. and precipitated Au nano particles were dispersed in hexane. PS latex with was purchased from Moritex Co. Ltd. The particle size was 40 and 300 nm and dispersion of the size was within ± ca. 4 %. Casein (milk protein) was purchased from Wako Co. Ltd. This sample was composed by ca. 200-300 nm sized proteins and other large sized materials such as agglomerates. We fractionated the samples before use; firstly the samples were dispersed in the solvents, stirred, ultrasonically dispersed, laid for one night or centrifuged, and corrected the upper portion of the dispersions. The fractionated samples had ca. 250-400 nm in average diameter before the addition of CO_2.

DLS measurement

DLS signals of particles dispersed in CXLs were measured using a conventional DLS photometer and a high pressure DLS cell. In Fig. 1, a schematic diagram of our experimental set-up was indicated. At first, 1 mL of organic solvent dispersed with nano particles were dropped into the cell immersed in an oil bath and temperature of the cell was controlled to be a desired temperature. Then the cel was twice flushed by CO_2 gas to purge the residual air. After that, CO_2 gas was added to realize the gas-liquid coexisting condition with the desired pressure. After the addition of CO_2 gas, the cell was settled down for more than 10 min. to dissolve CO_2 gas into the liquid phase. Then DLS signals were collected 3-6 times and examined the time change of the signals. This is needed to examine the stability of the particles. After recording the signals at one condition, additional CO_2 gas was brought into the cell and the pressure was increased to measure another DLS signal at a different composition. This procedure was repeated and the DLS signals at all compositions were collected. Diffusion coefficient and DLS signals were in the following relationship,

$$g^{(2)}(\tau) = 1 + \beta \, |g^{(1)}(\tau)|^2 \quad (1)$$
$$g^{(1)}(\tau) = \exp(-q^2 D\tau) \quad (2)$$
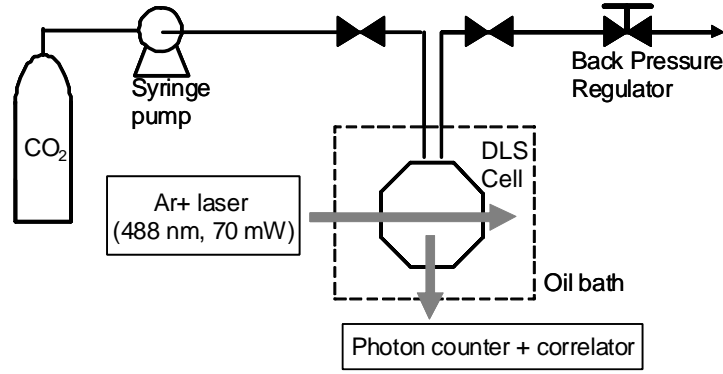$$q = (4\pi n/\lambda_0) \sin(\theta/2) \quad (3)$$

Fig. 1 Schematic diagram of DLS measurement system

Here, $g^{(2)}(\tau)$ is the time correlation function of the scattered light, β is the instrumental constant, τ is the correlation time, $g^{(1)}(\tau)$ is the first order correlation function assuming particles are sphere, D is the diffusion coefficient of the particles, q is the intensity of the scattering vector, n is the refraction index, λ_0 is the incident laser wavelength and θ is the scattering angle of the DLS measurement, which was 90° in the present study. For polydispersed particles, eq. (2) becomes a multiexponential function. The Cumulant method was employed to obtain average sizes of the particles in the fluids.

Experimental temperature was 30°C for CO_2 expanded alcohols and 25°C for CO_2 expanded hexane. Pressure was varied from 0.1 to ca. 6.0 MPa so as to change the mole fraction of CO_2 in the liquid phase from 0 to 0.8 Density and viscosity data of CO_2 expanded methanol and those of ethanol were taken from the references [12,13], respectively. Since viscosity and density data of CX-hexane were lacked, density of the CX-hexane was estimated from the Lee-Kesler equation for multi-component systems [14] using the liquid phase saturation data at 25°C (P-T-x relationship) taken from literature [15] and the viscosity of the fluid was estimated from the Chung equation for high density gases [16]. Refractive indices of all CXLs were evaluated from the Lorentz-Lorenz equation.

As a reference, the diffusion coefficients of PS in solvent mixtures at 25 °C were also examined. Refractive index and viscosity data were taken from the literature [17].

RESULTS AND DISCUSSION
Averaged diffusion coefficients and size distributions from DLS measurements

In Fig. 2a, the diffusion coefficient of PS in CX-methanol and ethanol are plotted against the mole fraction of CO_2, x_{CO2}. Initial particle diameter of PS in methanol was roughly ca. 400 nm. This is ca. 1.3 times larger than the original size and it is suspected that PS was swollen in alcohols before the CO_2 addition. As the fluid pressure increased and x_{CO2} increased, the diffusion coefficients increased with x_{CO2} up to x_{CO2} = 0.6 (P =5.83 MPa for CX-methanol, 5.68 MPa for CX-ethanol). More than x_{CO2} > 0.7 (P =6.15 MPa for CX-methanol, 6.05 MPa for CX-ethanol), the diffusion coefficients started decreasing and they kept decreasing with time. In Fig. 2b, the corresponding particle diameters estimated from the observed diffusion coefficients with assuming the Stokes-Einstein relationship were plotted. As in Fig. 2a, up to x_{CO2}=0.6, the particle diameter gradually increased with x_{CO2} but it reached constant values within an hour. However above x_{CO2} > 0.7, particle diameter did not reach a constant value and it finally exceeded our experimental observation limit (d <

3000 nm). This result suggests that some structural change in PS, like glass transition from glass to rubbish state occurred under such high pressure conditions as observed in $scCO_2$ [5].

In Fig. 3a and 3b, the diffusion coefficients and corresponding particle diameters of casein (milk protein) in CX-methanol and ethanol are indicated. Average particle diameters of casein did not vary with time up to x_{CO2}=0.6 in CX-methanol and ethanol. Above that mole fraction or pressure, the diffusion coefficients started dropping suddenly. Particle size kept increasing and the intensity of DLS signals diminished. This indicates the precipitation or agglomeration of proteins, which may be caused by the transformation of the protein and the change in the polarity of the fluids.

Figs 4a and 4b are the diffusion coefficients and corresponding particle diameters of Au nano particles in CO_2 expanded hexane. Up to x_{CO2}=0.455 MPa (P=3.2 MPa), the diffusion coefficients of Au nano particles seemed to be stable and did not vary with time. However, above 3.7 MPa (x_{CO2}=0.536), the diffusion coefficient started decreasing and the particle size rapidly increased within several tens of minutes. This result suggests that the particle aggregation or precipitation was accelerated at above 3.7 MPa, which agreed with the results of the previous study [4b].

As a reference, the diffusion coefficients and corresponding particle diameters of PS latex with ca. 40 nm in diameter in water-methanol mixture were plotted in Fig. 5a and 5b, respectively. As clearly seen, particle diameter did not vary and diffusion of these particles obeys the SE equations in the liquid mixtures.
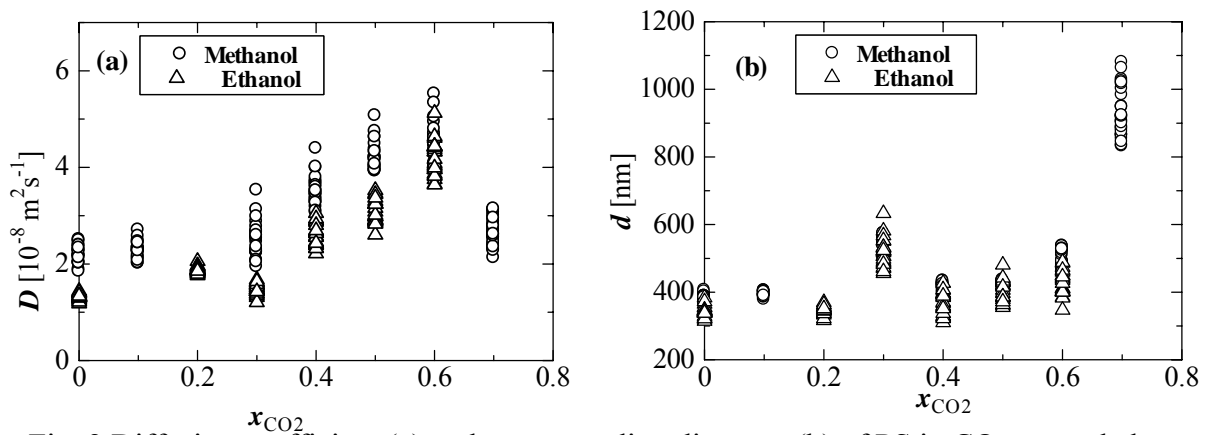

Fig. 2 Diffusion coefficient (a) and corresponding diameter (b) of PS in CO_2 expanded methanol and ethanol. Experimental temperature was 30 °C.
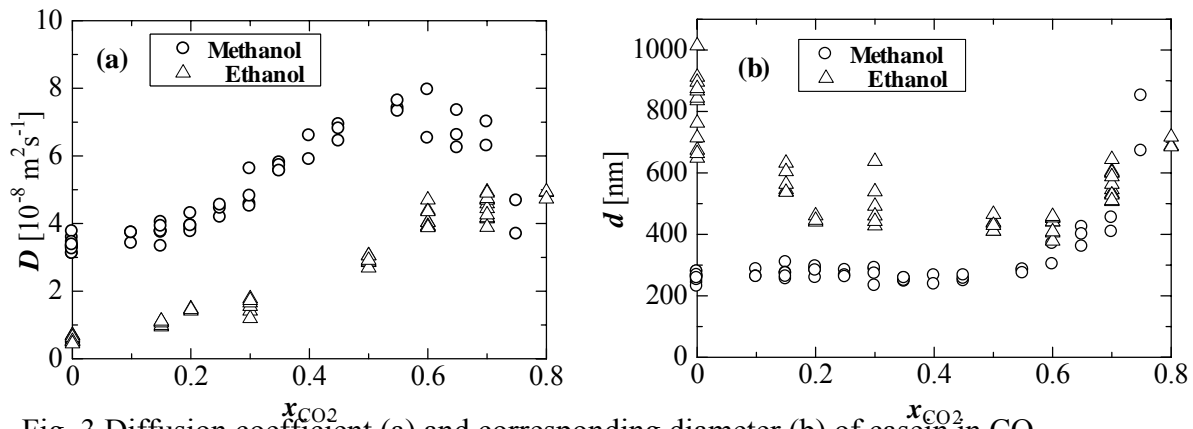

Fig. 3 Diffusion coefficient (a) and corresponding diameter (b) of casein in CO_2 expanded methanol and ethanol. Experimental temperature was 30 °C.
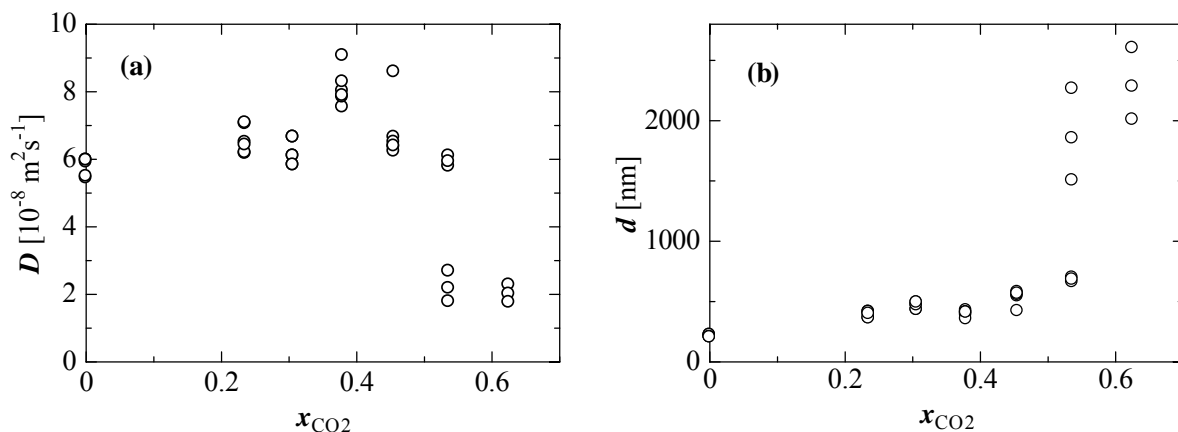
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Fig. 4 Diffusion coefficient (a) and corresponding diameter (b) of Au nano particles in CO_2 expanded hexane. Experimental temperature was 25 °C.
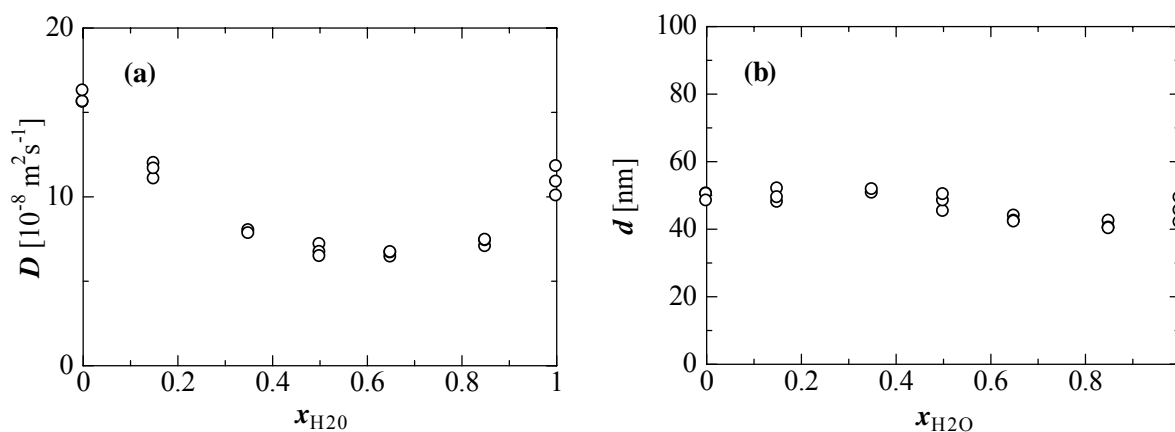

Fig. 5 Diffusion coefficient (a) and corresponding diameter (b) of PS latex in water-methanol mixtures. Experimental temperature was 25 °C.

Factors affecting to the size change

As described above, there was no particle which was stable in CXLs in the wide composition range from $x_{CO2} = 0$ to 0.8. The particles were suspected to make aggregates or be swollen in CO_2 rich phases. In the case of PS, no obvious difference was observed between in CX-methanol and CX-ethanol. The mole fraction and the pressure, at which the particle rapidly started expansion were almost the same in both solutions. At these pressures (ca. 6 MPa), the glass transition temperatures of PS in $scCO_2$ were at around 310-320 K [5]. The present experimental temperature was 303 K and that is slightly lower than the glass transition temperature in $scCO_2$. Thus, CXLs may be a good solvent for polymers to expand.

In the case of casein, the diameters roughly kept constant up to $x_{CO2}=0.6$. Here, we evaluated these diameters using the Stokes-Einstein relationship. Our result indicates that if the casein's molecular shape actually did not vary in CXLs with the mole fraction, it can be said that the diffusion of the particle obeyed the Stokes-Einstein low and any solvent effects on the diffusion process did not occur up to $x_{CO2}=0.6$. However, the conclusion could not be determined unless particle diameters were detected by another method, simultaneously with the DLS measurements.

The results on the Au nano particles agreed with the Robert et al.'s study [4b]. DLS measurement may be effective for monitoring the particle diameter in real time and evaluating the precipitation rate.

From the measurement of particle diffusion in the water-methanol mixture, though the microscopic structure of the mixture was known to be largely non-uniform [17], the particle diameter of 40 nm PS latex did not varied. This result may be an evidence of the validity of using Stokes-Einstein equation. However, in CXLs, structural non-uniformity may become very large, at least at around the consolute point of the mixture. Therefore, further search of stable particles or the methods to measure the particle diameters in CXLs simultaneous with DLS measurements were needed in the future works.

CONCLUSIONS
・Aggregation or swelling behavior of PS, casein, and Au nano particles in CX-methanol, ethanol, and hexane were examined. There was no particle which was stable under wide composition range from x_{CO2}=0 to 0.8.
・Swelling behavior of PS latex in CO_2 expanded alcohols were similar to that in $scCO_2$. However, glass transition was suspected at $P = 6$ MPa and 30°C ($x_{CO2} = 0.7$). This transition temperature is a slightly lower than in $scCO_2$ at the same pressure.
・Aggregation of Au nano particles in CO_2 expanded hexane at 25°C was confirmed by the DLS measurements.

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