

Viscosity Measurements of Water at High Temperatures and Pressures Using Dynamic Light Scattering

Shigeru Deguchi,^{*,†} Swapan K. Ghosh,[†] Rossitza G. Alargova,^{‡,§} and Kaoru Tsujii[‡]

Extremobiosphere Research Center, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan, and Nanotechnology Research Center, Research Institute for Electronic Science, Hokkaido University, N21, W10 Kita-ku, Sapporo 001-0021, Japan

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The application of dynamic light scattering to measure viscosity of water at high temperatures and pressures is demonstrated. Viscosity was obtained from the translational diffusion coefficient of probe particles dispersed in the medium by the Einstein–Stokes relationship. Measurements were carried out with polystyrene latex, colloidal silica, and colloidal gold. Under a constant pressure of 25 MPa, good agreement was found between the measured and calculated viscosities up to 275 °C with the polystyrene latex, 200 °C with the colloidal silica, and 297 °C with the colloidal gold. It was found that failure of the measurements at high temperatures is ascribed to change in either the dispersion stability or chemical stability of the probe particles. The present results indicate that the technique could also be used for other supercritical fluids having high critical temperature and pressure, such as methanol ($T_c = 239.4$ °C, $P_c = 8.1$ MPa) and ethanol ($T_c = 243.1$ °C, $P_c = 6.4$ MPa).

Introduction

Interest has emerged in the use of supercritical fluids (SCFs) as environmentally benign solvents for extraction, in chromatography, and in chemical reactions. Supercritical carbon dioxide is by far the most extensively studied fluid because of its low critical temperature and pressure ($T_c = 31$ °C, $P_c = 7.4$ MPa). There is also a strong interest in water as a new medium for a variety of chemical reactions,^{1,2} despite experimental difficulties due to high critical temperature and pressure ($T_c = 374$ °C, $P_c = 22.1$ MPa). Precise measurements of various physicochemical properties of SCFs are, thus, becoming increasingly important for understanding chemical processes in SCFs and designing processes utilizing SCFs. Any experimental works on SCFs, however, are confronted with the development of new instruments or techniques that can deal with the fluids under pressure.

Viscosity is the most important property that determines transport phenomena in a fluid, and various methods are used to measure the viscosity of the fluids, including capillary, vibrating-wire, rotating-disk, falling-cylinder, and falling-ball-type viscometers.^{3,4} However, the application of these methods to the fluids at high pressures is hampered because of difficulty in sample containment. As an alternative and nonintrusive method, dynamic light scattering (DLS) has been applied successfully to measure the viscosity of mixtures of CO₂ and heptane under pressure.³ DLS is a technique used widely to measure the translational diffusion coefficient (D_T) of colloidal particles in dispersions. When the size of the particle is known, the viscosity of the medium can be obtained by the Stokes–

Einstein relationship. However, applying the same technique to supercritical water is not straightforward because of significantly higher temperatures and pressures.

We have developed a DLS photometer that is equipped with a high-temperature, high-pressure cell.⁵ The instrument was designed to allow DLS measurements at temperatures and pressures up to 450 °C and 50 MPa, respectively, and was used successfully to measure the translational diffusion coefficients of polystyrene latex and colloidal gold in water up to the supercritical state.^{5,6} In this paper, we evaluate DLS as a methodology to measure the viscosity of water at high temperatures and pressures up to the supercritical state. In situ optical microscopic observations have also been carried out to obtain information on the chemical stability of the probe particles, which has been found to be important for successful measurements.

Experimental Section

Materials. Particles used for the measurements included monodisperse polystyrene latex ($d_H = 214.0 \pm 0.2$ nm measured by DLS at 28.3 °C and 0.1 MPa), colloidal silica ($d_H = 137.4 \pm 1.9$ nm measured by DLS at 20.9 °C and 25.0 MPa), and colloidal gold ($d_H = 65.7 \pm 0.2$ nm measured by DLS at 24.4 °C and 25.1 MPa). They were purchased from Polysciences, Inc. (Warrington, PA), and used as received. The stock dispersions were diluted with water and used for the measurements. For in situ microscopic observations, monodisperse polystyrene latex from Seradyne ($d_H = 31.0$ μ m measured by optical microscopy) was used. The silica particles used for the in situ microscopic observations were Aerosil 200 (Nippon Aerosil Co., Ltd., Tokyo, Japan). Millipore water was used throughout the work (Millipore, Bedford, MA).

High-Temperature, High-Pressure DLS. DLS measurements were performed on a DLS-820 (Otsuka Electronics, Co., Ltd., Osaka, Japan) equipped with a high-temperature, high-

* Corresponding author. Address: Extremobiosphere Research Center, Japan Agency for Marine-Earth Science and Technology, 2-15 Natsushima-cho, Yokosuka 237-0061, Japan. Tel: +81-46-867-9679. Fax: +81-46-867-9715. E-mail: shigeru.deguchi@jamstec.go.jp.

[†] Japan Agency for Marine-Earth Science and Technology (JAMSTEC).

[‡] Hokkaido University.

[§] Present address: Vertex Pharmaceuticals Inc., 130 Waverly St., Cambridge, MA 02139.

pressure cell.⁵ The instrument allows DLS measurements at a fixed angle of 90 ° at temperatures and pressures up to 450 °C and 50 MPa. All the measurements were performed at 25.0 ± 0.2 MPa unless otherwise indicated. A detailed explanation of the high-temperature, high-pressure cell and its operation can be found elsewhere.⁵ The instrument uses homodyne configuration and measures the intensity autocorrelation function, $g^{(2)}(\tau)$, of the scattered light:⁷

$$g^{(2)}(\tau) = \frac{\langle I_S(t)I_S(t + \tau) \rangle}{\langle I_S \rangle^2} \quad (1)$$

where I_S is the intensity of the scattered light. $g^{(2)}(\tau)$ is related to the field autocorrelation function, $g^{(1)}(\tau)$, as

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2 \quad (2)$$

For a solution of spherical particles with uniform size, $g^{(1)}(\tau)$ is related to the translational diffusion coefficient of the particles, D_T , by the equation

$$g^{(1)}(\tau) = \exp(-D_T q^2 \tau) \quad (3)$$

$q = (4\pi n/\lambda_0) \sin(\theta/2)$ is the scattering vector, and n , λ_0 , and θ are the refractive index of the medium, the wavelength of the incident light, and the scattering angle, respectively. The measured diffusion coefficients are usually related to the hydrodynamic diameter d_H of the particles by using the Einstein–Stokes relation,

$$D_T = \frac{k_B T}{3\pi\eta d_H} \quad (4)$$

where k_B , T , and η are the Boltzmann constant, the temperature, and the viscosity of the medium, respectively. In this work, however, η was calculated from the measured diffusion coefficients assuming that d_H , which was measured by DLS under ambient conditions, remained unchanged throughout the measurements at high temperatures and pressures. Refractive indices of water at different temperatures were calculated according to the International Association for the Properties of Water and Steam (IAPWS) 1995 formulation by using NIST/ASME STEAM.⁸

High-Temperature, High-Pressure in situ Optical Microscopy. The chemical stability of polystyrene latex and silica particles was studied by using in situ optical microscopy. The observations were made on a Nikon TE-300 equipped with a high-temperature, high-pressure flow cell.⁹ The system allows in situ observation of a specimen in water at temperatures and pressures above the critical point of water up to 400 °C and 35 MPa with an optical resolution of 2 μm. The specimen in the cell was heated from room temperature to 400 °C under a constant pressure of 25 MPa, and changes in the course of heating were observed in situ. A detailed description of the instrument and its operation can be found elsewhere.⁹

Results and Discussion

Viscosity Measurements Using Polystyrene Latex and Colloidal Silica. The applicability of DLS as a tool to measure the viscosity of water at high temperatures and pressures was first accessed by using the polystyrene latex and the colloidal silica. Aqueous dispersions of these particles are widely used as model systems for fundamental experimental studies, because the particles of different sizes with a narrow size distribution

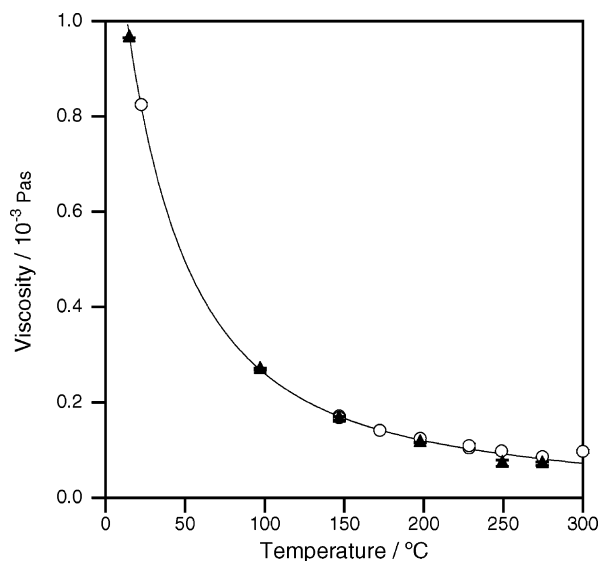


Figure 1. Viscosity of water measured by DLS using polystyrene latex ($d_H = 214.0$ nm, open circles) and colloidal silica ($d_H = 137.4$ nm, filled triangles) as the probe particle. Pressure was kept constant at 25 MPa.

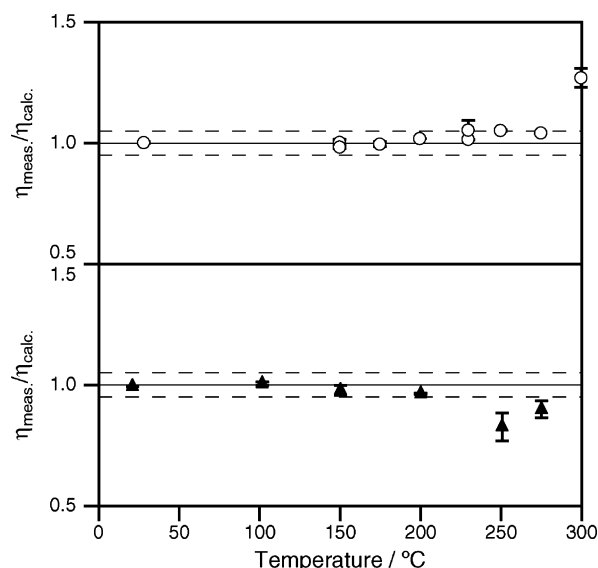


Figure 2. Relative viscosities measured by DLS using polystyrene latex ($d_H = 214.0$ nm, top panel, open circles) and colloidal silica ($d_H = 137.4$ nm, bottom panel, filled triangles) as the probe particle. The dashed lines represent ±5% error. Pressure was kept constant at 25 MPa.

are easily available. Figure 1 shows the viscosity measured by DLS using the monodisperse polystyrene latex or the colloidal silica as a probe particle. The solid curve represents the viscosity of water calculated according to the IAPWS 1995 formulation.⁸ In the case of the polystyrene latex, good agreement was found between the measured and calculated values up to 275 °C, but the measured value at 300 °C was slightly larger than the calculated value. The situation is more clearly seen if the data are plotted against temperature as relative viscosity, which is defined as the ratio between the measured viscosity and the calculated viscosity (Figure 2). The measured values agree with the calculated values within 6% error up to 275 °C, but the value measured at 300 °C was 27% larger than the calculated value.

A similar trend was observed when the colloidal silica was used as the probe particle. Good agreement was found between the measured and calculated values up to 200 °C, and the error

between the values was less than 4%. In this case, however, the measured viscosity at 251 °C was 17% smaller than the calculated value. Furthermore, strong scattering from the particles diminished at 275 °C, and a value 10% smaller than the calculated value was obtained.

The results clearly demonstrate that the viscosity of water at high temperatures and pressures can be measured by DLS, but only within a limited temperature range. The measured values did not agree with the calculated values at higher temperatures. The upper limiting temperature depended on the probe particle, and was 275 °C for the polystyrene latex and 200 °C for the colloidal silica.

Chemical Stability of Polystyrene and Silica in Water at High Temperatures and Pressures. For successful measurements of the viscosity by DLS, it is crucial that the size of the probe particle does not change during the measurements. It was reported that model colloids such as polystyrene latex or colloidal gold, which remain dispersed stably in water under ambient conditions, flocculate promptly when the dispersions are heated at a constant pressure of 25 MPa.^{5,6} The temperatures at which the flocculation starts to occur were determined to be 300 °C for the polystyrene latex and 350 °C for the colloidal gold. Although the exact reasons for the heat-induced flocculation are not known, it was suggested that the large change in the water properties such as the dielectric constant is responsible for the dispersion instability. Such instability is obviously one of the factors that determine the temperature range in which DLS can be applied to measure the viscosity.

Moreover, the chemical stability of the particles must also be considered. Under ambient conditions, it is safe to assume that the polystyrene latex or the colloidal silica are chemically inert enough, and the size of these particles does not change with time, unless rather extreme measurement conditions such as extremely high or low pH are employed. However, water at around 300 °C and 25 MPa is an incredibly harsh environment for organic compounds,² and various degradation pathways may proceed in addition to the conventional routes of chemical degradation such as hydrolysis of the sulfate groups on the surfaces of the polystyrene latex. For example, in the presence of a high amount of oxygen, even polystyrene decomposes in water at high temperatures and pressures.¹⁰

We showed that *in situ* optical microscopy is a powerful tool to investigate the colloidal dispersion under extreme conditions, and successfully studied the Brownian motion of colloids in water at high temperatures and pressures.¹¹ In this work, this technique has been used to evaluate the chemical stability of the two probe particles, polystyrene latex and colloidal silica, in water at high temperatures and pressures. Figure 3A shows a series of images showing the change in polystyrene latex in water at temperatures between 260 and 388 °C and at a constant pressure of 25 MPa. In Figure 3B, the change in the average size of the 29 latices was plotted against the temperature. No significant change in the size was seen up to 200 °C. The latices started to swell at around 250 °C, and kept on swelling up to 360 °C, above which they shrank dramatically. The average size of the polystyrene latex at 360 °C was 16% larger than the value at 200 °C.

The exact reason for the initial swelling is not clear, but it is interesting to note that the polystyrene latices are, in fact, droplets of molten polystyrene at these high temperatures, and coalescence of the droplets in contact was observed (Figure 4). The swelling with temperature could be ascribed to the thermal expansion of molten polystyrene or mixing with water of a low dielectric constant. The dramatic shrinkage above 360 °C seems

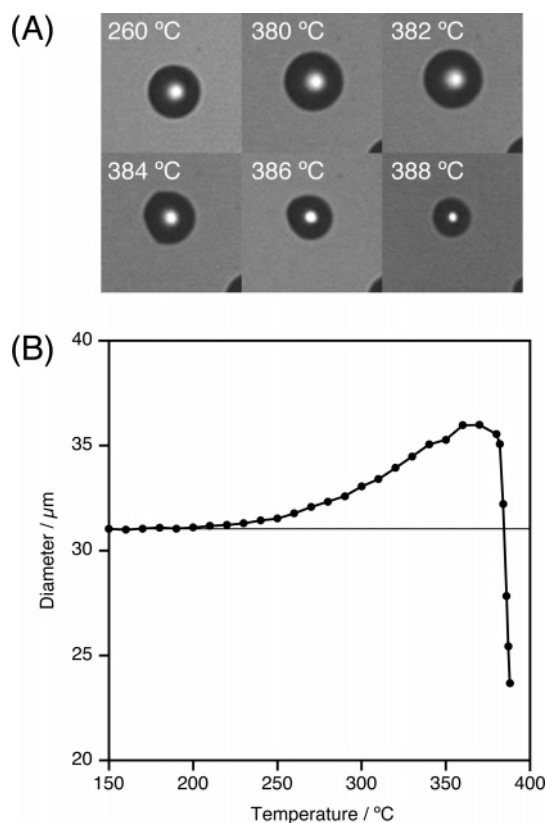


Figure 3. (A) A series of optical micrographs showing the swelling and pyrolytic decomposition of a polystyrene “droplet” in water at high temperatures and pressures up to the supercritical state. Pressure was kept constant at 25 MPa during the observation. (B) Change in size of the polystyrene “droplets” as a function of temperature. Twenty-nine particles were selected, and sizes were measured. The data shown are averages of the 29 measurements at each temperature.

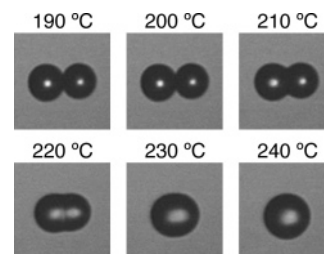


Figure 4. A series of optical micrographs showing coalescence of polystyrene “droplets” in water at high temperatures. Pressure was kept constant at 25 MPa during the observation.

to be ascribed to the pyrolytic decomposition of polystyrene. The onset of pyrolytic decomposition was evident above 300 °C by the formation of gas bubbles in the droplets (Figure 1S, Supporting Information). It seems that pyrolytic decomposition results in thermal depolymerization. The residue after heating dissolved in acetone after cooling the specimen to room temperature. Acetone is a good solvent for monomeric or oligomeric styrene, whereas it does not dissolve polystyrene. This was also evidenced by the shape of the droplet in Figure 1S (Supporting Information). The droplet after coalescence was not spherical from 300 to 380 °C, but recovered the spherical shape at higher temperatures. The change could also be ascribed to the reduction of viscosity by depolymerization.

Assuming that the size of the polystyrene latex used for the DLS measurements changes with temperature in the same manner shown in Figure 3B in terms of both the temperature dependence and the relative variation, correction was made on

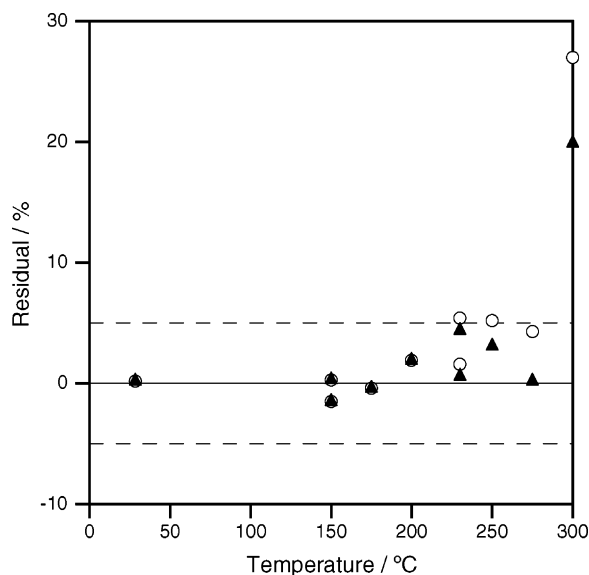


Figure 5. Improvement of measured viscosity by taking into account the swelling of polystyrene latex in water above 200 °C. Data are plotted as residual as a function of temperature. Open circles represent data obtained assuming constant size, while closed triangles represent data with the calibration incorporated. The dashed lines represent $\pm 5\%$ error.

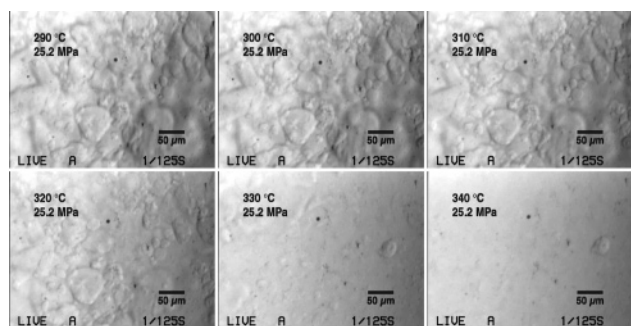


Figure 6. A series of optical micrographs showing the dissolution of silica particles in water at high temperatures. Pressure was kept constant at 25 MPa during the observation.

the measured viscosities (Figure 5). The correction indeed made the difference between the measured and calculated values smaller, but the deviation at 300 °C was still large, even after the correction. The analysis supports our previous observation that the polystyrene latex flocculates in water simply by heating to 300 °C and 25 MPa.⁵

In terms of the chemical stability in hot and compressed water, inorganic particles such as the colloidal silica are obviously more favorable. However, as is clearly seen in Figure 6, amorphous silica dissolved completely in water at around 320–330 °C. This observation leads us to the conclusion that the smaller viscosity at 251 °C and the loss of the light scattering from the sample at 275 °C reflect dissolution of the colloidal silica in water. The discrepancy between the temperature at which strong scattering diminished and the dissolution temperature observed by optical microscopy would be ascribed to the difference in the heating rate (the microscopic images were taken while heating the sample at a rate of 10–30 °C/min)⁹ and/or the size of the particles.

Viscosity Measurements Using Colloidal Gold. The microscopic observations revealed that chemical stability in water at high temperatures and pressures is an important criterion for the choice of the appropriate probe particle for successful measurements of the viscosity by DLS. We have performed the DLS measurements using different probe particles that seem to

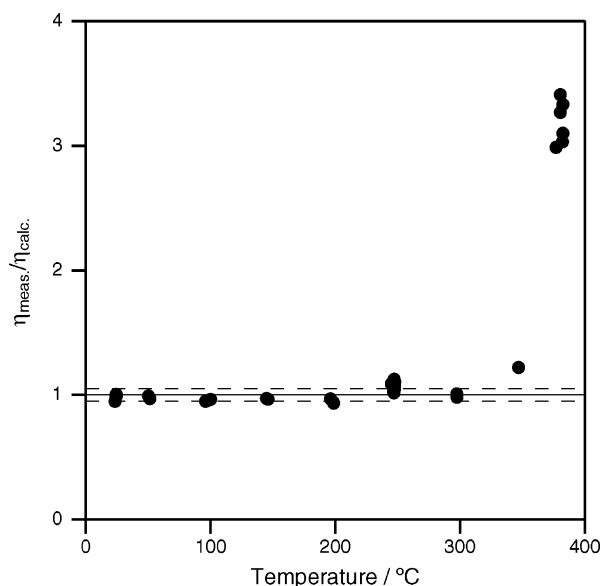


Figure 7. Relative viscosities of water measured by DLS using colloidal gold ($d_H = 65.7$ nm) as the probe particle. The dashed lines represent $\pm 5\%$ error. Measurements were done at 25 MPa, except at 380 °C, where measurements were done at 30 or 35 MPa to avoid strong scattering from the density fluctuation of water. The data used to calculate viscosity were taken from ref 6.

fulfill the requirement. These included colloidal gold, C₆₀ nanoparticles,¹² clay particles, diamond powder, and titanium dioxide. Among these, the colloidal gold was found to be the best probe particle (Figure 7) in terms of the temperature range in which good agreement was found between the measured and calculated viscosities. Good agreement between the measured and the calculated values was found up to 297 °C.

Even in this case, the value obtained at 347 °C was 22% larger than the calculated value. The measurements at even higher temperatures were hampered by strong scattering from the water due to critical density fluctuation, as the experimental conditions were close enough to the critical point of water.⁶ This effect was circumvented by performing the measurements at higher pressures (30 or 35 MPa). The measurements gave values 30% larger than the calculated value. The results demonstrate that DLS can be applied to viscosity measurements of water up to 297 °C when colloidal gold is used as the probe particle.

Conclusion

In summary, we demonstrate that DLS can be used to measure the viscosity of water at high temperatures and pressures. Using colloidal gold as the probe, the viscosity of water was measured successfully up to 297 °C and at constant pressure of 25 MPa. It was found that the applicability of the technique is limited by the colloidal stability and the chemical stability of the probe particles used. Our results indicate that the technique could also be used for other SCFs having high critical temperature and pressure, such as methanol ($T_c = 239.4$ °C, $P_c = 8.1$ MPa) and ethanol ($T_c = 243.1$ °C, $P_c = 6.4$ MPa).

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Supporting Information Available: Photograph showing coalescence, swelling, and pyrolytic decomposition of the polystyrene “droplets” in water at high temperatures and pressures, a movie showing the behaviors of polystyrene latex in water at high temperatures and pressures up to the supercritical state, and a movie showing the dissolution of silica particles in water at high temperatures and pressures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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