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Small-angle X-ray scattering investigation of water droplets in mist

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Small-angle X-ray scattering measurements of water droplets in a mist were carried out using the BL15XU beamline at SPring-8. The diameter of the water droplets generated by ultrasonic atomization was found to be ≥ 50 nm and had no distribution in the range under 50 nm, as predicted. The study also showed how difficult it is to measure the small-angle scattering of low-density materials, such as liquid droplets in a mist.

1. Introduction

When a liquid is subjected to ultrasound, small liquid droplets are generated from the liquid surface. This is called 'ultrasonic atomization' and it is a very effective method of generating small liquid droplets. This method has been widely used for generating liquid droplets in mist, *e.g.* in a humidifier. It has been believed for over half a century that the size of the liquid droplets generated by ultrasonic atomization was distributed around the micrometre scale (McCubbin, 1953; Lang, 1962). However, there has been no work aimed at observing the size distribution in ranges of less than 1 µm.

In the present study, we have analyzed the size distribution of the water droplets generated by ultrasonic atomization by small-angle X-ray scattering (SAXS) measurements in order to investigate the size distribution in the nanometre range. Since the density of the mist of liquid droplets produced in the present case is only 10% of the density of air, it is a big challenge to obtain sufficient scattering intensity. *In situ* SAXS measurements of dilute free-flying particles have already succeeded in probing nanoparticle growth in a flame by doping with inorganic precursors contained in either a vapour or an aerosol (Hessler *et al.*, 2001; Beaucage *et al.*, 2004). The use of a third-generation synchrotron source and an image-intensified charge coupled device (CCD) as a two-dimensional detector facilitated the measurement time of 0.3 s for silica particles produced at a rate of 17 g h^{-1} (Beaucage *et al.*, 2004). Here we report the SAXS measurements of more familiar materials, free-flying water droplets, using a high precision powder diffractometer with a third-generation synchrotron source. We designed a liquid droplet flow cell to increase the signal-to-noise ratio.

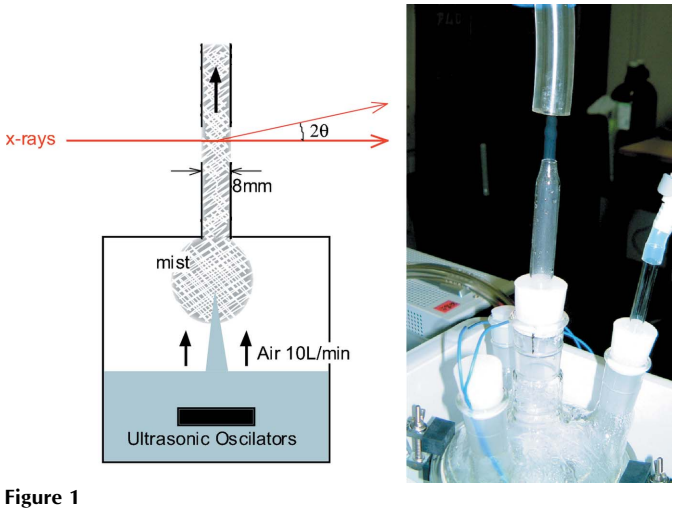

Figure 1
Liquid droplets flow cell for SAXS measurements. The ultrasonic oscillators were installed in the cell. The liquid droplets in the mist were formed and pumped out to obtain a stable stream with a diameter of 8 mm at the center of the diffractometer without any X-ray windows.

2. Experimental

SAXS measurements were carried out using the high precision powder diffractometer at the BL15XU beamline, SPring-8, Japan Synchrotron Radiation Research Institute. The energy of the incident X-ray beam was selected to be 8 keV and the minimum scattering angle 2θ was determined to be 0.15°, which is limited by the count rate of the YAP ($YAlO_3$) scintillation detector. The beam size at the sample is 0.1 mm in the scanning direction and 0.5 mm in the normal direction.

A flow cell of liquid droplets in mist (shown in Fig. 1) was fixed at the center of the diffractometer. Liquid droplets in mist were generated by ultrasonic atomization. The cell was mounted in a constant temperature bath maintained at 303 K and contained a liquid sample with a volume of 750 ml. Ultrasonic oscillators (HM2412, Honda Electronics Co., Ltd) operating at 2.4 MHz and 13 W were installed at the bottom of the system, which was 35 mm below the liquid surface level. The liquid droplets were carried by air at 10 l min^{-1} and pumped out to obtain a stable stream with a diameter of 8 mm at the center of the diffractometer.

Since a typical weight loss by ultrasonic atomization is 100 g h^{-1}, each period of the X-ray measurement was limited to a maximum of 30 min to maintain a constant atomization rate. The typical sampling time at each angle was 30 s. The background intensity, depending on the incident beam profile and scattering from air, was also measured before and after generation of the mist. A large amount of air scat-

tering was detected since the beam path of 60 cm between the sample and the detector was in air. All the measured scattering intensities were divided by the incident beam intensities I_0, which were measured using an ion chamber located before the sample.

3. Results

Fig. 2 shows the time dependence of the X-ray intensities at $2\theta = 0.8^\circ$ for pure water droplets in mist. The sampling time of each point was 1 s and the measured intensities were divided by the incident beam intensities I_0. The intensities shown at the top of the figure were measured using a flow cell with Kapton X-ray windows. When the power to the ultrasonic oscillators was on, the intensity started to decrease and became constant after 30 min, whereas when the power was off, it increased again. This is because the Kapton windows became wet when the water mist was generated and subsequently dried up again. This problem was solved by removing the Kapton X-ray windows from the cell. A significant jump was observed in the intensity, shown at the bottom in Fig. 2.

Fig. 3 shows the SAXS profile of water droplets in mist after background subtraction. The thin curves are calculated scattering intensities for spheres (Guinier & Fournet, 1955),

$$I(q, D) = N\left|\Delta\rho\,\Omega_{\rm sphere}(q, D)\right|^2, \qquad (1)$$

where

$$\Omega_{\rm sphere}(q, D) = \frac{4\pi}{q^3}\left[\sin\left(\frac{qD}{2}\right) - \frac{qD}{2}\cos\left(\frac{qD}{2}\right)\right], \qquad (2)$$

with diameters D of 10, 50 and 100 nm. N is the number of particles and $\Delta\rho$ is the difference between the electron densities of the scatterer and the matrix. The scattering intensity represented by equation (2) oscillates with a period of $q = 2\pi/D$. The modulus of the scattering vector is $q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of the incident beam, 1.55 Å. The oscillation period $\Delta 2\theta$ is estimated to be 0.1° for D = 100 nm and 0.9° for 10 nm. The amplitude of the oscillation decreases if the liquid droplets are not monodisperse. The observed data (the circles) show good agreement with Porod's law, q^{-4} (denoted by the thick solid curve), indicating the presence of smooth and sharp interfaces for spheres with diameter $D \geq 50$ nm. Using light scattering (Donnelly *et al.*, 2004) and visual analysis (McCubbin, 1953; Barreras *et al.*, 2002), it has been observed that 1–10 µm water droplets are generated by ultrasonic atomization with a frequency of around 2 MHz. In the present work, we confirm that the water droplets generated by ultrasonic atomization are not distributed in the diameter range of 1–50 nm. In contrast to the case of water droplets, we found that ethanol droplets have diameter of only 1 nm (Yano *et al.*, 2006).

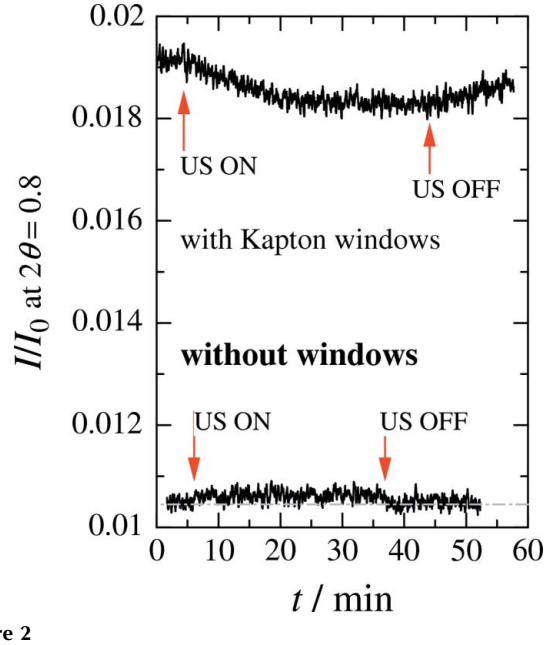

Figure 2
Time dependence of the X-ray intensities at $2\theta = 0.8^\circ$ for pure water droplets in mist using a flow cell with (above) and without (below) Kapton windows. When the power to the ultrasonic oscillators (US) was on, a significant jump was observed when using the flow cell without Kapton windows (below).

4. Discussion

The diameter of a liquid droplet produced by ultrasonic atomization is known to be determined by a relationship based on the macroscopic properties of the liquid, $D = \alpha(\sigma/\rho F^2)^{1/3}$, where σ is the surface tension, ρ is the liquid density, F is the ultrasound frequency and α is a constant (Lang, 1962). Using this relationship, the diameter D at an ultrasound frequency of 2.4 MHz is determined to be about 2 µm both for water and ethanol. This relationship seems to be appropriate for water. For ethanol, however, the observed diameter (Yano *et al.*, 2006) deviates significantly from this expected value, suggesting that it is influenced not just by the macroscopic properties. We believe the intermolecular structure of the bulk liquid also affects the droplet size.

In the present study, we have observed SAXS from liquid droplets in a mist. To measure the scattering intensities from the materials with a very low density, the background scattering needs to be reduced. This was partially solved by removing the Kapton X-ray windows. However, the scattering intensity of the mist is still 2% that of the background.

In future studies, we aim to obtain better signal-to-noise ratios by: (1) developing a vacuum X-ray path to reduce background scattering from air, and (2) using a two-dimensional detector to improve counting statistics.

5. Summary

We have carried out SAXS measurements of water droplets in mist generated by ultrasonic atomization. The water mist was found to

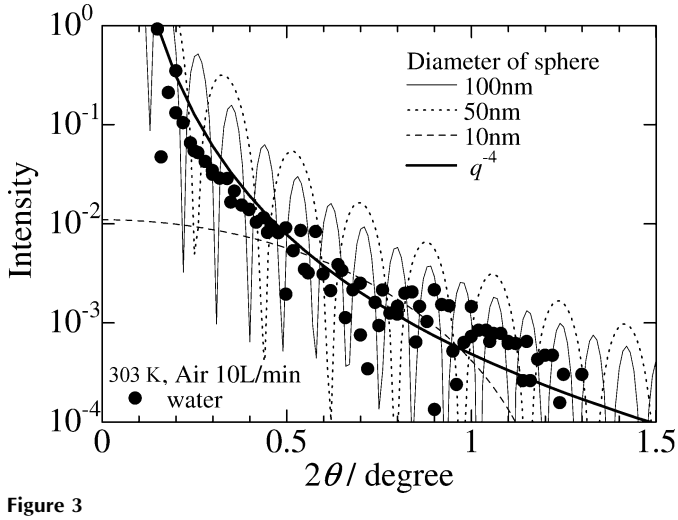

Figure 3
SAXS intensity profile after background subtraction for the water mist (the circles). The thin curves are the calculated intensities for spheres with diameters of 10, 50 and 100 nm. The profiles with diameters above 50 nm have the same envelope defined as q^{-4} denoted by the thick solid curve.

have polydisperse spherical droplets with diameters $D \geq 50$ nm, which agrees with previous works. To define the droplet diameter distribution more exactly, we need to obtain data with higher signal-to-noise ratios by developing a vacuum X-ray path and using a two-dimensional detector.

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