Study of water dynamics in aqueous glycerol solutions at cryotemperatures

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Glycerol is a typical cryoprotective substance that has been used for many years. In certain insects, for example, it is secreted into the body and binds to water molecules to stabilize the supercooled state and achieve low temperature tolerance. Elucidating the dynamic behavior of water in aqueous glycerol solutions at low temperatures is an important topic in cryobiology. DSC has shown that at a glycerol concentration of 60% (v/v), no exothermic peak associated with crystallization is observed upon cooling, indicating that water in aqueous glycerol solutions is supercooled. 50%(v/v) glycerol solution shows no crystallization peak during cooling and devitrification during heating. 40%(v/v) shows freezing of water during cooling, followed by glass transition and melting of ice during heating. It should be important to investigate the dynamics of water in the cryogenic temperature range, in particular, to understand the physical chemistry of water that supports cryoprotection and low temperature tolerance of organisms. To understand the lowtemperature behavior of aqueous glycerol solutions, Quasi-Elastic Neutron Scattering (QENS), which directly observes the dynamics of water changed by its interaction with glycerol, is considered effective. Neutron diffraction is also useful record the crystallization and melting of water. AGNES spectrometer is suitable for this study as the spatial-temporal scale to be covered.

Figure 1A shows the elastic intensity during heating over time. In 60% glycerol solution, elastic intensity decreases during heating, indicating the melting of ice. In 50% glycerol, intensity significantly increases at around 200 K, which is a sign of the devitrification. In 60% glycerol, the slightly increase of the intensity at around 200 K is observed, which would be also a sign of the devitrification. This was not observed in DSC profiles with heating rate of 5 °C /min. Figure 1B shows the incoherent

elastic intensity as a function of temperature. Over all, the intensities decrease as a function of temperature. Interestingly, in 50% glycerol, even though the diffraction peaks indicate ice formation, the incoherent elastic scattering intensity does not increase but decreases monotonically. This seemingly contradictory result is currently being investigated.

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Fig. 1. (A) Peak intensity at Q=1.6 Å⁻¹ and (B) elastic intensity during heating over time with 0.2 °C/min for glycerol solution with three different glycerol concentrations. hGly and dGly mean hydrogenated and deuterated glycerol, respectively.