Freeze-concentrated glass transition behavior of carbohydrate solutions by quasi-elastic neutron scattering

K. Kawai[A], T. Sogabe[A], H. Nakagawa[B], T. Yamada[C]

[A]*Hiroshima Univ.*, [B]*JAEA*, [C]*CROSS*

Sugars such as glucose and sucrose are widely used as cryoprotectant for biomaterials (e.g., protein and microorganism). The sugar solutions exhibit a freeze-concentrated glass transition at a lower temperature than ice-melting temperature. The freeze-concentrated glass transition temperature (T_g') is commonly evaluated using differential scanning calorimetry (DSC). It is known that sugar solutions show two endothermic shifts suggesting two freeze-concentrated glass transitions. The shifts observed at lower temperature and higher temperature are described as T_g'$_{-1}$ and T_g'$_{-2}$, respectively. The origin of the endothermic shifts is still controversial. There are mainly two interpretations of the T_g'$_{-2}$. One is ice-melting and the other is simultaneous event of freeze-concentrated glass transition and ice-melting. However, these interpretations are originated from only DSC results. Neutron scattering, on the other hand, is a useful approach to observe the dynamics of solute and solvent directly and separately by deuterated labels. The purpose of this study was to clarify the origin of T_g'$_{-2}$ observed in glucose solution.

H-glucose/D_2O and D-glucose/H_2O samples were employed to investigate the molecular mobility of glucose (solute) and water (solvent) molecules, respectively. The water content was set to 60% (solution) and 20% (viscous solid). The solution was expected to show freeze-concentrated glass transition. The viscous solid was expected to show a glass transition without ice-melting at almost equivalent temperature to the solution according to our preliminary test.

Neutron scattering experiment was carried out using AGNES (C3-1-1). The energy resolution was 120μeV, and covered Q range was 0.20–2.7 Å^{-1} (λ = 4.22 Å, standard resolution mode). The sample was cooled to 100 K and heat-scanned up to 360 K at 0.2 K/min. Subsequently, the sample was cooled to 200 K and heated up to 240 K in a step manner. Mean squire displacement (MSD) calculated from Q-dependence of the elastic intensity, diffraction peaks height characteristic to D_2O-ice (from the first heating), and full width at half maximum (FWHM) of quasi-elastic neutron scattering (QENS) profile (from the second heating) were evaluated as the function of temperature.

Ice-melting could not be characterized by the result of QENS due to a large deviation of FWHM. The height of diffraction peaks began to decrease at T_g'$_{-2}$ (~230K), and finally the peaks disappeared above the endpoint of ice-melting observed in the DSC curve.

Temperature-dependence of MSD for H-glucose/D_2O solution and viscous solid is shown in Fig. 1. The MSD of samples increased linearly with an increase in temperature, and subsequently began to deviate from the linearity above ~230 K regardless of the presence and absence of ice-melting. This suggests that the mobility of glucose atoms changes in nature from harmonic (solid-like) motion to anharmonic (liquid-like) motion. From these results, the interpretation that the T_g'$_{-2}$ is the simultaneous event of freeze-concentrated glass transition and ice-melting was supported.

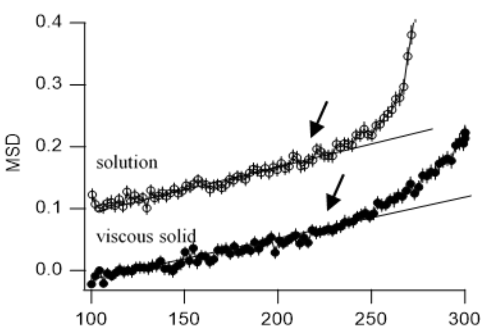

Fig.1. Temperature-dependence of MSD for H-glucose/D_2O solution and viscous solid.