

Gigahertz Elastic Properties of Cryoprotective Aqueous Solutions of Ionic Liquid and Trehalose

生体凍結保護物質としてのイオン液体・糖水溶液のギガヘルツ帯弾性的性質

Haruki Takayama[†], Tomohiko Shibata, Yuto, Kuroda, Koda Shota, and Seiji Kojima
(Pure and Applied Sciences, University of Tsukuba)

高山 晴貴[†], 柴田 知彦, 黒田 雄斗, 国府田 将太, 小島 誠治 (筑波大院 数理物質科学)

1. Introduction

Ionic liquids (ILs) are substances in a liquid state around room temperature even though it is only the salts consisting of cations and anions. Recently, ILs have been used for bioscience, as the solvent for extracts and preserves proteins. [1, 2] Moreover, ILs and sucrose aqueous solution have the good stabilization for proteins [3], and such solutions are easily vitrified. Thus, these ternary solutions are expected to be cryoprotectants. In this paper, acoustic properties of ternary mixture ILs and sugar aqueous solutions were studied in order to examine the application of cryoprotective agents in cryobiology. Trehalose, known as good stabilization for protein was used as the sugar, and 1-ethyl-3-methylimidazolium Chloride ([emim]Cl) which is most popular ILs was used as ILs.

Brillouin scattering spectroscopy has been used to study the elastic properties of various liquids and glass transition processes in a high-frequency giga-hertz range and in an extremely wide temperature range. Brillouin scattering is a powerful tool to study dynamical properties of glass transitions [4-6]. We can determine the sound velocity and attenuation accurately by Brillouin scattering.

2. Experimental

[emim]Cl was purchased from Tokyo Chemical Industry. D-(+)-Trehalose of 98% purity was purchased from Fluka and no further purification was done. The refractive index was measured by the prism coupling method (Metricon, 2010/M) at 532 nm. The sound velocity was measured by Brillouin scattering [4]. The light source was a green YAG laser (532 nm, 100 mW). The Brillouin scattering spectra were measured using the Sandercock-type 3 + 3 pass tandem Fabry Perot interferometer (JRS, TFP-1) with finesse 100 at the backward scattering geometry. The sample

temperature in a heating/cooling stage (LINKAM, HTMS600) was controlled from -190 to 100 °C.

3. Results and Discussion

3.1 Refractive index

The refractive index of [emim]Cl and trehalose aqueous solutions were measured at 532 nm as shown in Fig. 1 to determine sound velocity from Brillouin frequency shift. As the [emim]Cl concentration increases, the refractive index of ternary solution increases. While on heating, the refractive index decreases.

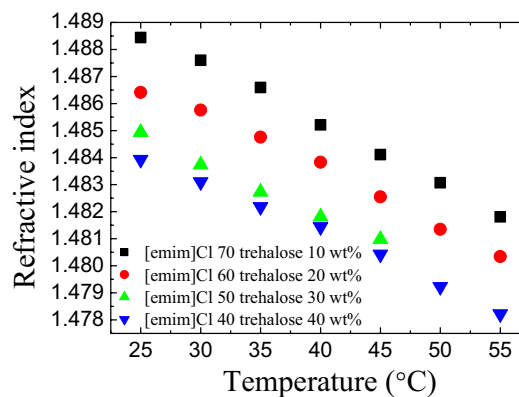


Fig. 1 Temperature dependence of refractive index at 532 nm of [emim]Cl and trehalose aqueous solutions.

3.2 Brillouin scattering

The temperature dependence of Brillouin scattering spectra of [emim]Cl 40 trehalose 40 wt % aqueous solution is shown in Fig. 2. Only longitudinal acoustic (LA) mode was observed. On heating from a glassy state at -180°C, the Brillouin shift shows marked decrease, while the FWHM shows a maximum above a few tens degrees above the room temperature.

e-mail address : s1220450@u.tsukuba.ac.jp

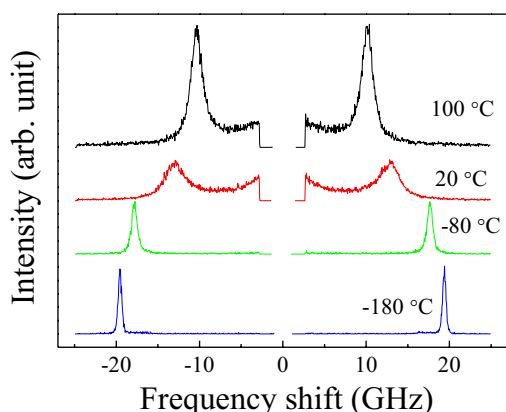


Fig. 2 Temperature dependence of Brillouin scattering spectra of [emim]Cl 40 trehalose 40 wt% aqueous solution.

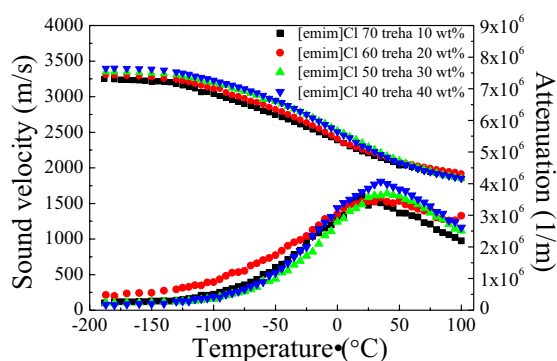


Fig. 3 Temperature dependence of sound velocity and attenuation of the LA mode in trehalose aqueous solutions.

Figure 4 shows the temperature dependences of sound velocity and attenuation of the LA mode, which were determined using the observed values of refractive index described in Sec. 3.1. On heating, sound velocity decreases and the slope of sound velocity increases above the glass transition temperature T_g . While, attenuation factor shows a peak above T_g and then decreases for further heating. Such behaviors indicate a typical structural relaxation as a precursor dynamic process of a liquid-glass transition of structural glass.

Fig. 3 shows the comparison of sound velocity and attenuation with the solution including lysozyme. By adding lysozyme only 100 mg/ml to [emim]Cl 50 trehalose 30 wt% solution, the attenuation of acoustic wave increases.

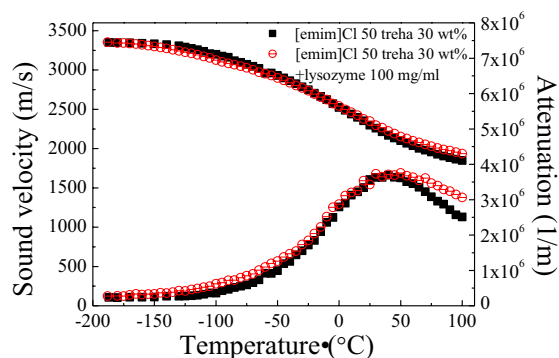


Fig. 4 Temperature dependence of sound velocity and attenuation of the LA mode in [emim]Cl and trehalose aqueous solutions and solution added lysozyme.

4. Conclusion

The bioprotective effect of [emim]Cl and trehalose aqueous solutions has been studied by micro-Brillouin scattering excited at 532 nm. Temperature and composition dependences of refractive index of ternary aqueous solutions have been determined at 532 nm accurately to determine the sound velocity and attenuation. The acoustic anomaly of ternary aqueous solutions shows the typical structural relaxation in the supercooled liquid state, and undergoes a liquid-glass transition at low temperatures. Our results verify that the glass transition behavior of ternary aqueous solutions is similar to typical cryoprotectants such as aminopropanol. [7]

References

1. Z. Du, Y. L. Yu, and J. H. Wang: Chem. Euro. J., **13**, (2007) 2130.
2. W. T. Heller, H. M. O'Neill, Q. Zhang, and G. A. Baker: J. Phys. Chem. B, **114**, (2010) 13866.
3. N. Byrne, L. M. Wang, J. P. Belieres, and C. A. Angell: Chem. Commun., **26**, (2007) 2714.
4. S. Kojima: Jpn. J. Appl. Phys. **49** (2010) 07HA01.
5. Y. Ike, E. Hashimoto, Y. Aoki, H. Kanazawa, and S. Kojima: J. Mol. Struct. **924–926** (2009) 157.
6. Y. Seshimo, Y. Ike, and S. Kojima: Jpn. J. Appl. Phys. **47** (2008) 3836.
7. Y. Ike and S. Kojima: J. Mol. Struct. **744–747** (2005) 521.