The Secondary Relaxation in the Dielectric Loss of Galactose-Water Mixtures[1]

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Summary

We studied the dielectric relaxation phenomena of galactose-water mixtures in the supercooled and glassy states at frequencies ranging from 0.1 Hz to 10 MHz. The dielectric loss spectra show that as the water content or temperature decreased, the relaxation time difference between the α and the secondary relaxations [1] increased and the relative relaxation strength between the α and the secondary relaxation decreased. In our previous study[2] we also found the similar results in the glucose-water mixture. Therefore, we strongly speculate that the effects of adding water or increasing temperature on the secondary relaxation are qualitatively similar to that of decreasing the rotation-translation (RT) coupling constant in the schematic mode-coupling theory [3]. Therefore, we strongly speculate that the origin of the secondary relaxation might be the RT coupling.

1. Introduction

Dielectric spectroscopy has been widely used to understand the dynamics in liquid-glass transition. The exceptionally broad frequency window accessible with this technique makes it an ideal tool to follow the decades of change in molecule dynamics. The dielectric-loss spectra of glass forming materials usually exhibit at least two relaxation processes, the α- and the β-relaxations. α-relaxation is related to a long time-scale and corresponds to the overall structural rearrangement of a system. β-relaxation is related to a short time-scale and corresponds to local dynamics[3].

The existence of an extra relaxation at frequencies between the α relaxation and the β relaxation was recognized about 35 years ago by Johari and Goldstein [4]. In particular, this excess relaxation (the secondary relaxation) has been observed in the dielectric loss spectra of complex polymer glass formers. However, it has not been found to be a common feature in rigid molecular glass formers. In the last two decades, the experimental techniques in dielectric spectroscopy have advanced enough for us to observe a variety of secondary relaxation processes in broadband dielectric spectra[5, 6, 7, 8] in addition to the α- and β-relaxations.

Sugar is a main constitution of the biological system and the systems of sugar and sugar containing materials are a matter of common interest for many researchers. Glass forming sugars have a great significance in nature; i.e., nature makes use of glasses to preserve biological tissues in the dehydrated state. A high viscosity of sugar glasses leads to a increased stability of preserved materials. Also sugars are useful material to study the glassy dynamics such as the secondary relaxation process and the aging phenomena. Since many sugars have glass transition temperatures above the room temperature, experiments on aging effects can be carried out without cryogenic equipment, facilitating rapid temperature quenches[9]. Also, sugar-water mixtures are known to reveal well pronounced secondary relaxation in dielectric loss spectra[2].

In this paper, the secondary relaxation in the monosaccharide sugar with small amounts of wa-

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ter was studied by using dielectric loss spectroscopy method. We measured the galactose-water mixtures with three different water contents at frequencies ranging from 10mHz to 10MHz. In the dielectric loss spectra, as the water content and temperature decreased the relaxation time difference between the α and the secondary relaxations increased and the relative relaxation strength between the α and the secondary relaxation decreased. This result is qualitatively similar to the effect of decreasing rotation-translation (RT) coupling strength in the schematic Mode Coupling Theory with RT coupling [3, 10].

2. Experiments

Galactose were purchased from Sigma Chemical Co. and were used without further purification. The weight percent of water in sugar-water mixtures was measured by using moisture analyzer (Sartorius MA100, Germany) with 0.1 wt% precision. The frequency dependent dielectric constants at different temperatures were carried out by using a cylindrical shape tungsten cell. Two different measurement schemes were employed depending on the frequency range under consideration. For the frequency range of 0.1 Hz to 10 kHz, the in-phase and out-of-phase currents through the capacitor were measured using a Dual Phase Lock-in Amplifier(Stanford SR 830, U.S.A.). For the frequency range of 100 Hz to 10 MHz, an Impedance Analyzer (HP 4194A, Hewlett-Packard U.S.A.) with a standard four-terminal pair configuration was used to measure the capacitance and conductance of the sample. The data obtained from the two methods were in excellent agreement where they overlapped. The temperature of the sample was controlled by using a closed-cycle He refrigerator and a temperature controller (Lakeshore 330, U.S.A.) with 0.01 K precision. The temperature of the sample was monitored by a silicon diode sensor.

3. Results & Discussion

Figures 1(a)-1(c) show the frequency dependent dielectric loss spectra of galactose-water mixtures above the glass transition temperature with different water contents. In these figures, we can clearly observe the α- and the secondary relaxations. As the temperature decreased, both the α- and the secondary relaxation progressively shifted to lower frequencies. However, the α-relaxation moved faster than the secondary

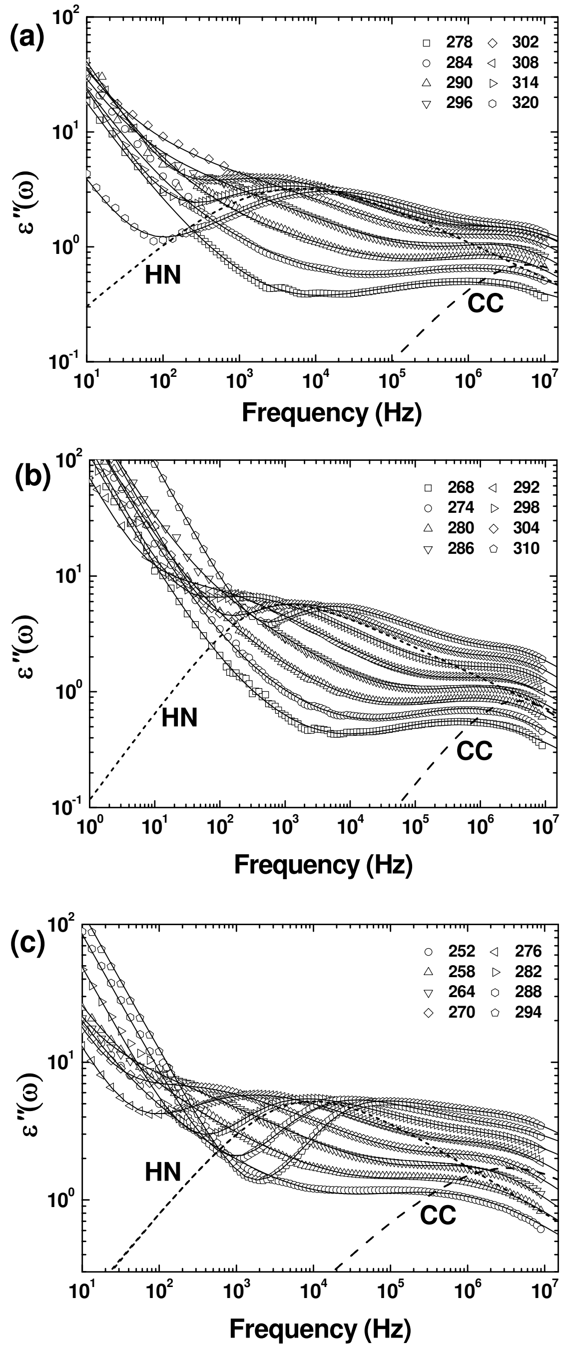

Fig.1 Frequency dependent dielectric loss spectra in galactose-water mixture at different temperatures with water contents of (a) 3 wt.%, (b) 5 wt.%, and (c) 10 wt.%. The temperature range used in experiments covered the supercooled and the glassy states of the sample. The solid line is the fitted results with superposition of power law, HN and CC equations. The short dashed line and dashed lines is the fitted results of the the Havriliak-Negami and the Cole-Cole equations at 314K, 304K and 282K for 3 wt.%, 5 wt.%, and 10 wt.%, respectively.

relaxation, therefore two relaxations were clearly separated near the glass transition temperatures. The observed dielectric loss spectra of galactose water mixture were almost the same to those of glucose water mixture[2] because the chemical structures of glucose and galactose are very similar[11].

We fitted our data to the superposition of the power law function for DC part, the Havriliak-Negami(HN) [12] function for the α-relaxation and the Cole-Cole(CC) [13] function for the secondary relaxation. The fitting function used is as follows.

$$\varepsilon^*(\omega) = \omega^{\alpha} + \frac{\Delta\varepsilon_{\alpha}}{[1+(i\omega\tau_{\alpha})^{a_{\alpha}}]^{b_{\alpha}}} + \frac{\Delta\varepsilon_{2nd}}{1+(i\omega\tau_{2nd})^{a_{2nd}}} \quad (1)$$

where, $\Delta\varepsilon_{\alpha}$ and $\Delta\varepsilon_{2nd}$ are the relaxation strengths, τ_{α} and τ_{2nd} are the relaxation times, and are the parameters of distribution broadness of a_{α} and b_{α}, respectively, and b_{2nd} is a parameter reflecting the skewness of the relaxation spectra. At high temperatures, the peak of α relaxation was broaden and ambiguous due to the overlap with secondary relaxation. Therefore we analyzed the data together with dc part so that we could obtain the clear peak position of the α relaxation. As can be seen in Figs. 1 (a)-(c), good fits to the experimental data were achieved in this way for all galactose-water mixtures.

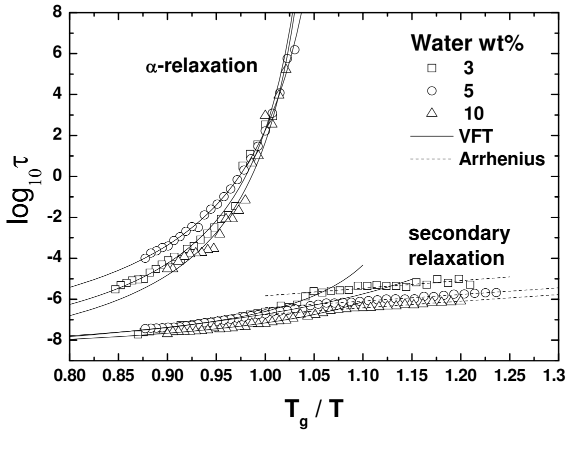

Fig.2 Temperature dependent α- and the secondary relaxation times of galactose-water mixture with different water contents. The relaxation times were determined from the fit as shown in Fig. 1. The reciprocal temperature was re-scaled by T_g. We determined glass transition temperatures of mixtures from the DSC experiments. T_g = 288 K, 272 K, and 254 K for 3, 5, and 10 wt.% water content mixtures.

Figure 2 shows the temperature dependent relaxation times for both the α and the secondary processes with different water contents. The relaxation times are plotted logarithmically against the reciprocal temperature scaled by T_g. Normally, the structural relaxation of glass forming materials followed the non-Arrhenius temperature dependence. We tried to fit the temperature dependent relaxation times of α- process with the Vogel-Fulcher-Tamman [14] law. All water concentrations exhibit the VFT temperature dependence when $0.8 < T_g/\mathrm{T} < 1$. In the case of the secondary process, the type of temperature dependent relaxation time changed from the Arrhenius law to the VFT law as the temperature increased and deviated near the glass transition temperature. The overall temperature dependence of relaxation processes of galactose-water mixture was very similar to that of glucose-water mixture[2]. There are slight difference in the deviation point of the secondary relaxation. In the case of the glucose-water mixtures, the deviation point moved to higher temperatures with increasing water contents. However, in the case of galactose-water mixture, the deviation temperatures were almost the same $T_g/\mathrm{T} \simeq 1$.

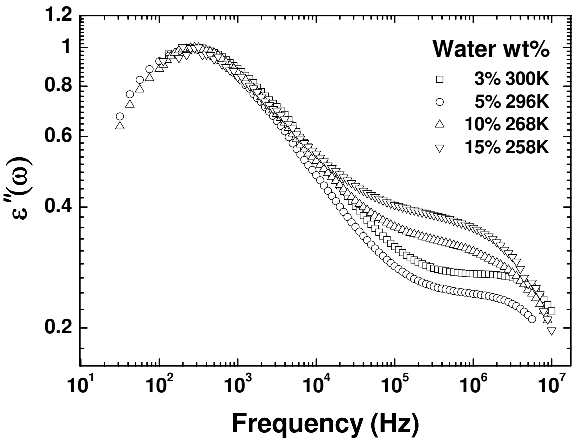

Fig.3 The effect of water on secondary relaxation process. Selected spectra have the same α-peak positions. The temperatures of selected spectra are 300K, 296K, 268K, and 258K for 3, 5, 10, and 15 wt% water contents, respectively.

The effect of water on the secondary relaxation in the galactose-water mixtures can be seen in Fig. 3. Fig. 3 shows a group of data which have the same α-peak position with different water contents and at different temperatures. The data was re-scaled with the α-peak amplitude in order to compare the relative characteristics of the secondary relaxation to the α-relaxation. The α-relaxations of all galactose-water mixtures have similar spectra at the same peak position. However, it is clear that there exists a large variation of the relative position and strength of the secondary relaxations. As can be seen in Fig. 3, the secondary relaxation of 3 wt% galactose-water mixture is well separated from the α-relaxation, and the peak width seems to be small. By contrast, the secondary relaxation of 15 wt% galactose-water mixture is not well separated from the α-relaxation, and the peak width seems to be large. We observed as the water content increased that the secondary relaxation time increased in Fig. 3. These findings are consistent with the results in Fig. 1. Therefore, it seems that the effect of adding water on the secondary relaxation is the same as increasing the temperature. This result is qualitatively similar to the effect of decreasing rotation-translation (RT) coupling strength in the schematic mode coupling theory with RT coupling [3, 10].

4. Conclusion

In this study, the dielectric relaxations in the galactose-water mixture with different water contents were studied in order to investigate the properties of the secondary relaxation process in the supercooled and glassy states. We found that as the water content or temperature decreased the relaxation time difference between the α and the secondary relaxations increased and the relative relaxation strength between the α and the secondary relaxation decreased. The effect of adding water or increasing temperature on the secondary relaxation process was qualitatively similar to the effect of decreasing RT coupling constant in the schematic MCT with RT coupling[3]. In our previous study[2] we also found the same effect of adding water or increasing temperature on the secondary relaxation in glucose-water mixture. Therefore, we strongly suggest that this RT coupling might be the origin of the secondary relaxation. The secondary relaxation appears differently depends only on the RT coupling constant.

Acknowledgments

This work was supported by a Korea Research Foundation Grants 2006-005-J02802 and 2006-005-J02803.

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