Effects of water on the primary and secondary relaxation of xylitol and sorbitol: Implication on the origin of the Johari-Goldstein relaxation

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Dielectric spectroscopy was employed to study the effects of water on the primary α-relaxation and the secondary β-relaxation of xylitol. The measurements were made on anhydrous xylitol and mixtures of xylitol with water with three different water concentrations over a temperature range from 173 K to 293 K. The α-relaxation speeds up with increasing concentration of water in xylitol, whereas the rate of the β-relaxation is essentially unchanged. Some systematic differences in the behavior of α-relaxation for anhydrous xylitol and the mixtures were observed. Our findings confirm all the observations of Nozaki *et al.* [R. Nozaki, H. Zenitani, A. Minoguchi, and K. Kitai, J. Non-Cryst. Solids **307**, 349 (2002)] in sorbitol/water mixtures. Effects of water on both the α- and β-relaxation dynamics in xylitol and sorbitol are explained by using the coupling model.

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I. INTRODUCTION

There are many studies of miscible mixtures of two glass-formers on the changes of the primary α-relaxation of either components. Examples include miscible binary polymer blends [1–3], mixtures of polymer with a small molecule glass former [4,5] (i.e., a diluent). Seldom seen is the study the effects of mixing on both the primary α-relaxation and the secondary β-relaxation in parallel, particularly when the secondary relaxation of one of the glass formers is intermolecular in origin [i.e., a Johari-Goldstein (JG) relaxation] [6]. Such study is not only interesting in its own right but also may have implications on the interpretation of component dynamics of a blend (mixture) and the origin of the JG relaxation. Dielectric measurements of mixtures of some glass formers with water have been recently reported. The glass formers of these studies include glycol oligomer [7], alcohol [8], glycerol [9], and sorbitol [10]. Of particular interest to us is the work of Nozaki and co-workers [10]. They measured the dielectric relaxation spectra of anhydrous sorbitol and mixtures of it with various amounts of water, and characterized the dynamics of both the α-relaxation and the JG β-relaxation. For all mixtures, the measurements were made above the glass transition temperature and the broadband dielectric spectra were capable to capture both the α- and the JG β-relaxation. An increase in the concentration of the more mobile water enhances the α-relaxation rate of sorbitol and decreases significantly the glass transition temperature, T_g. This effect on the α-relaxation is unsurprising because it follows the same pattern as in other blends [1–4]. However, the sorbitol β-relaxation rates in mixtures up to 34% molar fraction of water are only increased slightly from that of anhydrous sorbitol. This difference between the α- and the JG β-relaxation is interesting and worth consideration from a theoretical point of view in the context of both blend dynamics and glass transition dynamics.

In this work, we present dielectric relaxation measurements of xylitol and its mixtures with water. Xylitol belongs to the same family of polyalcohols as sorbitol, but the molecule has one less carbon atom than sorbitol. It also has a JG β-relaxation, which is still there on addition of water, as we shall show. Our results confirm all observations of Nozaki *et al.* [10] in sorbitol/water mixtures. In particular, the α-relaxation rate increases by orders of magnitude with addition of water, while the β-relaxation rate is essentially unchanged. Thus the effects seen by Nozaki *et al.* [10] are general. A theoretical interpretation of the general result is given by using the coupling model [11–14].

II. EXPERIMENT

Xylitol was obtained from Fluka. Glass beakers containing samples of pure xylitol were placed in a humid chamber of pure water at room temperature. Each sample absorbed water during different elapsed times, and the concentration of water was determined by the weight difference before and after it was put in the chamber. The determination was confirmed by the thermobalance technique. Three mixtures were obtained. For convenience in comparing the results with sorbitol/water mixtures later on, we follow Nozaki *et al.* [10] and introduce the quantity $N_{wpx}=x/(1-x)$, where x is the molar fraction of water in the mixture [10]. Isothermal measurements of the dielectric permittivity $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ were made by using the Novo-Control Alpha dielectric spectrometer (10^{-2}–10^7 Hz) and the Agilent 4291B impedance analyzer (10^6–1.8×10^9 Hz). The sample was placed in a parallel-plate cell (diameter=20 mm, gap

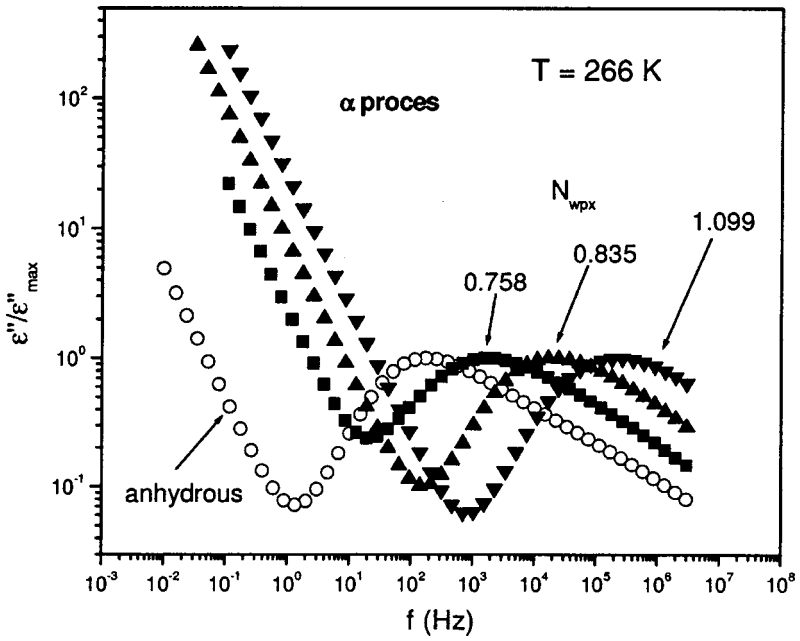

FIG. 1. Dielectric spectra of water-in-xylitol mixture at labeled concentrations N_{wpx} measured at the temperature $T=266$ K.

=0.1 mm). The temperature was controlled using a nitrogen-gas cryostat, with temperature stabilization better than 0.1 K.

III. RESULTS

The complex permittivity of neat xylitol at different temperatures both above and below $T_g(255\ \mathrm{K})$ has been obtained in previous works [15–18]. From the measurements, the dielectric dispersions of the α-relaxation and β-relaxation as well as their most probable relaxation frequencies $f_{\alpha,\max}$ and $f_{\beta,\max}$ and the corresponding relaxation times, τ_α and τ_β, were determined. Shown in Fig. 1 as an example is the dielectric loss ε'' (normalized by the maximum loss $\varepsilon''_{\max}$ of the α-relaxation) of xylitol at $T=266$ K in the anhydrous form and in three mixtures with water. The rise of $\varepsilon''(f)$ at low frequencies is due to ionic conductivity. On the addition of water, the α-relaxation loss peak shifts to higher frequencies and broadens at the same times. These trends continue with increasing water content up to $N_{wpx}=1.099$. The dc conductivity originates from ionic impurities in the sample. It is possible that additional ionic impurities are introduced into the samples during the preparation of the mixtures. This complication makes any comparison of the dc conductivity ambiguous, and therefore we do not analyze the change of the dc conductivity. The shift of the peak frequency $f_{\alpha,\max}$ on addition of water is considerable, already three decades at this temperature. Similar data were taken at other temperatures and the results of xylitol and xylitol/water mixtures are shown altogether in Fig. 2. Actually, we have plotted τ_α against 1000/T, where τ_α is $1/(2\pi f_{\alpha,\max})$. The data are fit to the Vogel–Fulcher–Tammann equation, $\log_{10}(\tau_\alpha)=A+B/(T-T_0)$, and the fits are shown as lines in Fig. 2. These fits are extrapolated to lower temperatures and the dielectric glass transition temperature T_{gx} is determined for each system by the definition $\tau_\alpha(T_{gx})=100$ s. The decrease of T_{gx} with water content is shown in Fig. 3 in a plot against $N_{wpx}=x/(1-x)$. The trend is the same as found in sorbitol/water mixtures by Nozaki *et al.* [10]. From these fits, we also obtain the steepness index [19], defined by

$$m=\left.\frac{d\ \log\ \tau_\alpha}{d(T_{gx}/T)}\right|_{T=T_{gx}}. \tag{1}$$

Here, τ_α in seconds is given by the Vogel-Fulcher-Tammann fit to the data in Fig. 2 and T_{gx} is the dielectric glass transition temperature at which $\tau_\alpha(T_{gx})=100$ s. There is a decrease of m with increasing water content (Fig. 4), as seen previously in sorbitol/water mixtures by Nozaki *et al.* [10].

The dielectric data of the JG β-relaxation in anhydrous xylitol and its water mixtures were obtained at temperatures below T_{gx}. Representative examples of the β-loss data at $T=203$ K are shown in Fig. 5. These β-loss peaks were obtained after each spectrum was fitted by two Havriliak–Negami functions, one for the α-relaxation and the other for the β-relaxation. Although the normalized JG loss peak becomes narrower with the addition of water, the peak frequency $f_{\beta,\max}$ is only changed slightly. The same is true for other temperatures as can be seen in Fig. 2 where τ_β of neat xylitol and the mixtures are included. Again, τ_β is $1/(2\pi f_{\beta,\max})$.

IV. DISCUSSIONS

Our dielectric relaxation data of xylitol/water mixtures confirm in all respects the findings of Nozaki *et al.* [10] in sorbitol/water mixtures. The most intriguing feature of the results obtained in both studies is the contrasting effects that added water has on the α-relaxation and JG β-relaxation. While there are large decreases of τ_α, little changes occur in τ_β. To address this difference one needs a theory of mixture (blend) dynamics that can address both the α-relaxation and JG β-relaxation. Most theories of dynamics of mixtures are tailored exclusively for the α-relaxation. However, the coupling model is different [13,16]. The coupling model (CM)

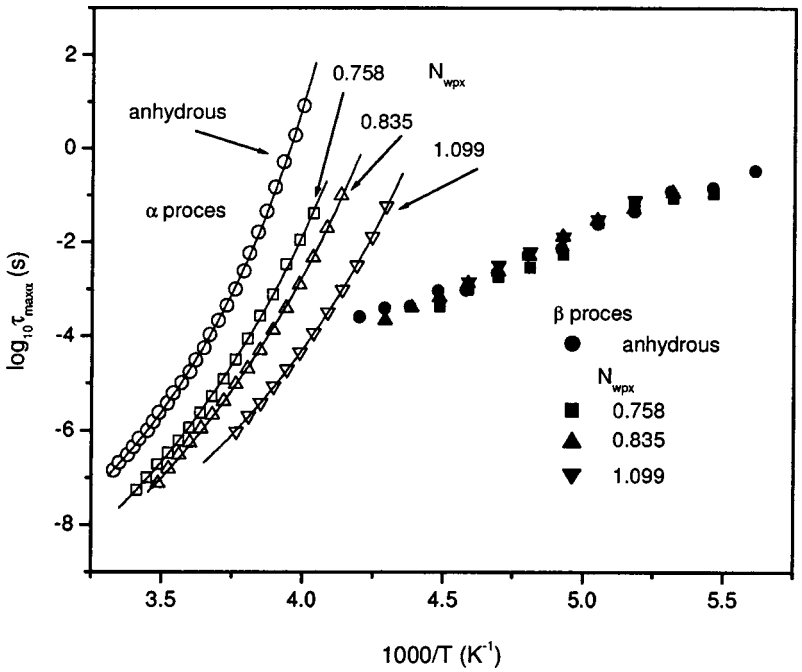

FIG. 2. Temperature dependence of the α-relaxation and the β-relaxation time obtained for anhydrous xylitiol and xylitol-water mixtures with different concentrations of water. Solid lines are fits to Vogel-Fulcher-Tammann law.

for the α-relaxation dynamics of a single glass former had been extended to treat the α-relaxation dynamics of each component of a mixture of two glass former [3,4]. Recently, the CM has also been extended to tackle the origin of the JG β-relaxation and its relation to the α-relaxation [13,14,20]. Thus, the CM is able to address both issues. It has the potential to resolve the current problem that water has drastically different effects on the α-relaxation and the JG β-relaxation, and rationalize the various features discussed in the previous section.

A. α-relaxation

The important parameter in the CM originating from intermolecular interaction is the coupling parameter n that characterizes the cooperative and dynamically heterogeneous dynamics of the α-relaxation. In a pure glass-former A, the coupling parameter can be identified with n_A in the stretch exponent of the Kohlrausch-Williams-Watts function that describes the time development of the α-relaxation correlation function,

$$\phi(t) = \exp[-(t/\tau_{\alpha A})^{1-n_A}], \tag{2}$$

where $\tau_{\alpha A}$ is relaxation time of neat glass former A. From the standpoint of a glass-former A molecule, on mixing with another glass-former B to form the mixture $A_{1-x}B_x$, the replacement of some of the A molecules by B molecules in its environment will change the intermolecular interactions and constraints, and hence its coupling parameter. The new environments in the mixture are not identical for all A molecules

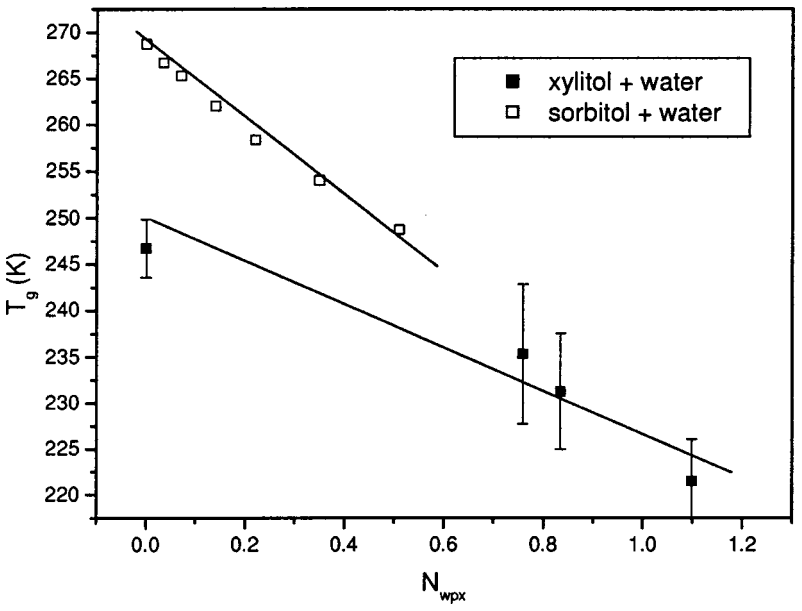

FIG. 3. T_g plotted against N_{wpx} for water-in-xylitol and water-in-sorbitol mixtures. (The data for water-in-sorbitol mixtures were taken from Ref. [10].)

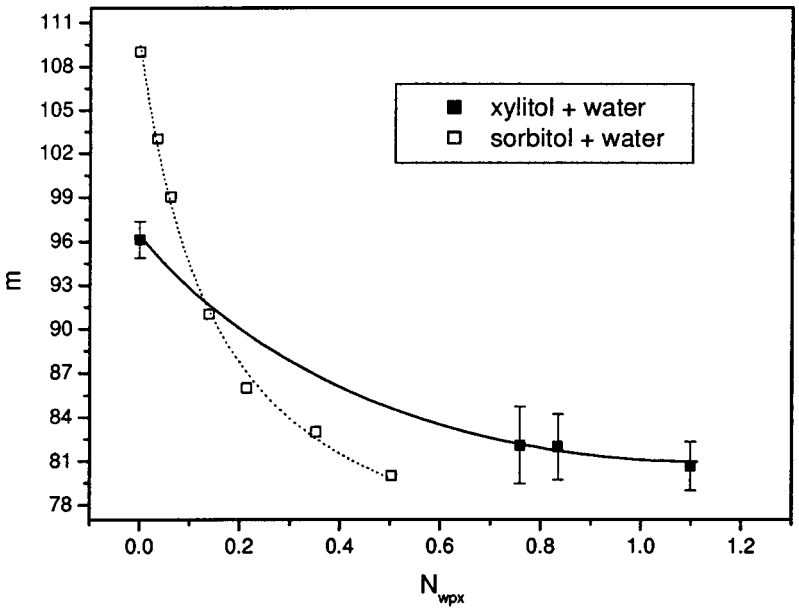

FIG. 4. Steepness index, m, plotted against N_{wpx} for water-in-xylitol and water-in-sorbitol mixtures. (The data for water-in-sorbitol mixtures were taken from Ref. [10].)

due to the inevitable fluctuations in concentration. There is a distribution of environments i of different compositions, which in turn engenders a distribution of coupling parameters $\{n_{i\mathrm{A}}\}$ for the A molecules and similarly for the B molecules in the mixture. If B molecules (e.g., water) are much more mobile than A molecules (e.g., sorbitol or xylitol), the presence of the former in the environment of an A molecule mitigate the intermolecular interaction/constraint acting on it. Hence, all $n_{i\mathrm{A}}$ in the distribution are smaller than the coupling parameter n_{A} of the neat glass-former A, i.e.,

$$n_{i\mathrm{A}} < n_{\mathrm{A}}. \tag{3}$$

The differences between n_{iA} and n_A become larger when there are more mobile B molecules in the mixture.

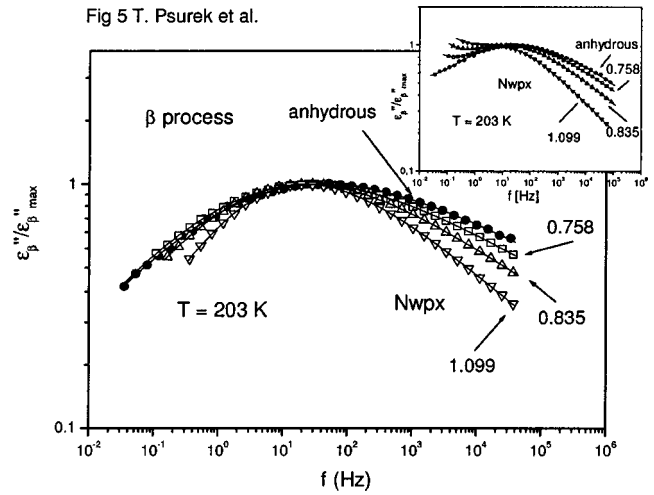

FIG. 5. The β-relaxation process in water-in-xylitol mixtures. The main plot presents β-relaxation after fitting spectra by two Havriliak–Negami functions (solid lines) and subtracting the α-relaxation part. The spectra directly from experiments are shown in the inset.

In the CM, there is a relation between the independent (or primitive) relaxation time, $\tau_{0\mathrm{A}}$, of an A molecule to the cooperative α-relaxation time, $\tau_{\alpha\mathrm{A}}$, in the neat glass-former A. The relation is

$$\tau_{\alpha\mathrm{A}} = [t_c^{-n_{\mathrm{A}}}\tau_{0\mathrm{A}}]^{1/1-n_{\mathrm{A}}} \equiv \left(\frac{\tau_{0\mathrm{A}}}{t_c}\right)^{(n_{\mathrm{A}}/1-n_{\mathrm{A}})}\tau_{0\mathrm{A}}, \tag{4}$$

where t_c is the crossover time from independent relaxation to cooperative relaxation and has the approximate value of 2×10^{-12} s for small molecule liquids [21]. We have assumed in Eq. (4) that the independent (or primitive) relaxation time, $\tau_{0\mathrm{A}}$ of an A molecule in the mixture is the same as in the pure glass-former A. In the mixture, Eqs. (2) and (4) applies to each i in the distribution. For each i the α-relaxation correlation function is given by

$$\phi_i(t) = \exp[-(t/\tau_{\alpha i\mathrm{A}})^{1-n_{i\mathrm{A}}}], \tag{5}$$

where $n_{i\mathrm{A}}$ is its own coupling parameter, $\tau_{\alpha i\mathrm{A}}$ its cooperative α-relaxation times, and they are related by

$$\tau_{\alpha\mathrm{A}} = [t_c^{-n_{\mathrm{A}}}\tau_{0\mathrm{A}}]^{1/1-n_{\mathrm{A}}} \equiv \left(\frac{\tau_{0\mathrm{A}}}{t_c}\right)^{(n_{i\mathrm{A}}/1-n_{i\mathrm{A}})}\tau_{0\mathrm{A}}. \tag{6}$$

The dielectric response of the mixture is the superposition of the one-sided Fourier transform of Eq. (5) each weighed by the probability of the occurrence of i in the distribution. For the most probable environment $\hat{i}$ in the distribution, let us denote its coupling parameter by $\hat{n}_{\alpha\mathrm{A}}$, the α-relaxation time by $\hat{\tau}_{\alpha\mathrm{A}}$, and the correlation function by

$$\hat{\phi}(t) = \exp[-(t/\hat{\tau}_{\alpha\mathrm{A}})^{1-\hat{n}_{\alpha\mathrm{A}}}]. \tag{7}$$

This (i.e., $i=\hat{i}$) is just a special case; $\hat{\tau}_{\alpha\mathrm{A}}$ can be calculated by Eq. (6) and it is given by the expression

$$\hat{\tau}_{\alpha A} = [t_c^{-\hat{n}_A}\tau_{0A}]^{1/1-\hat{n}_A} \equiv \left(\frac{\tau_{0A}}{t_c}\right)^{(\hat{n}_A/1-\hat{n}_A)}\tau_{0A}. \qquad (8)$$

Because $\hat{i}$ has the highest probability of occurrence, the one-sided Fourier transform of Eq. (8) is largely responsible for the maximum of the observed α-loss peak of the mixture located at $f_{\alpha,\max}=1/\tau_{\alpha,\max}$. Thus, the experimentally determined $\tau_{\alpha,\max}$ in Fig. 2 should correspond to the calculated $\hat{\tau}_{\alpha A}$, if the coupling model applies.

Since t_c is short, in the entire experimental temperature range, the ratio (τ_{0A}/t_c) is much larger than unity. It follows immediately from Eqs. (4) and (8) that τ_{0A} and $\hat{\tau}_{\alpha A}$ are much longer than τ_{0A}, and the effect of intermolecular coupling in slowing down the α-relaxation of A molecules in both the neat glass former and the mixture is clear. From Eq. (3), $\hat{n}_{\alpha A}<n_A$. It follows that the exponents, $[\hat{n}_{\alpha A}/(1-\hat{n}_{\alpha A})]$, in Eq. (8) for the mixtures is smaller than the exponent, $[n_A/(1-n_A)]$, in Eq. (4) for the neat glass-former A. This property, together with τ_{0A} being assumed to be the *same* at the same temperature for the neat glass-former A and its mixtures, leads us to the following results.

(i) $\hat{\tau}_{\alpha A}$ of a mixture is shorter than $\tau_{\alpha A}$.

(ii) The separation between $\hat{\tau}_{\alpha A}$ of a mixture and $\tau_{\alpha A}$ of the neat glass-former A, measured by the difference $\log_{10}(\tau_{\alpha A})-\log_{10}(\hat{\tau}_{\alpha A})$, increases with decreasing temperature because of the increase in τ_{0A} in Eqs. (4) and (8).

(iii) At a fixed temperature, the ratio $(\hat{\tau}_{\alpha A}/\tau_{\alpha A})$ decreases with increasing concentration of the glass-former B in the mixture because of decreasing $\hat{n}_A$.

(iv) Each $\phi_i(t)$ in Eq. (5) has a narrower dispersion than $\phi(t)$ of the neat glass-former A [Eq. (2)] because $n_{iA}<n_A$ [Eq. (3)]. However, the dispersion of the α-relaxation originating from A molecules in the mixture is a superposition of the $\phi_i(t)$s in the distribution. This complication makes it impossible to determine $\hat{n}_A$ from the dielectric spectrum of the mixture, unlike n_A the neat glass-former A. The two factors have opposite effects on the width of the dispersion, and they cancel each other to some extent.

We are now ready to compare the results given above with experimental data of mixtures of xylitol and sorbitol with water. A stands for sorbitol or xylitol molecules, and B for the more mobile water molecules in the mixtures $A_{1-x}B_x$. Our present data of xylitol/water mixtures shown in Figs. 1 and 2 are in accord with the results (i)–(iv), and so are the data of sorbitol/water mixtures published by Nozaki *et al.* [10]. A more quantitative comparison is made by first using Eq. (4) to calculate τ_{0A} from the data of $\tau_{\alpha A}$ (open circles in Fig. 2) and n_A of neat xylitol. From previous work [13,14], the value $n_A=0.46$ has been determined at the lower temperatures of the neat xylitol data in Fig. 2. After τ_{0A} has been determined in Fig. 2 (*), we use Eq. (8) to calculate $\hat{\tau}_{\alpha A}$ of the mixtures, treating $\hat{n}_A$ as an adjustable parameter. The results of $\hat{\tau}_{\alpha A}$ calculated with $\hat{n}_A=0.32$(■), 0.24(▲), and 0.08(▼) and shown in Fig. 6 match the experimental data $\tau_{\max}$ of the mixtures with $N_{wpx}=0.758$(□), 0.835(△), and 1.099(▽) water. Better agreement than that shown is not expected because possible temperature variations of the coupling parameters n_A in neat xylitol and $\hat{n}_A$ in the mixtures have not been taken into account.

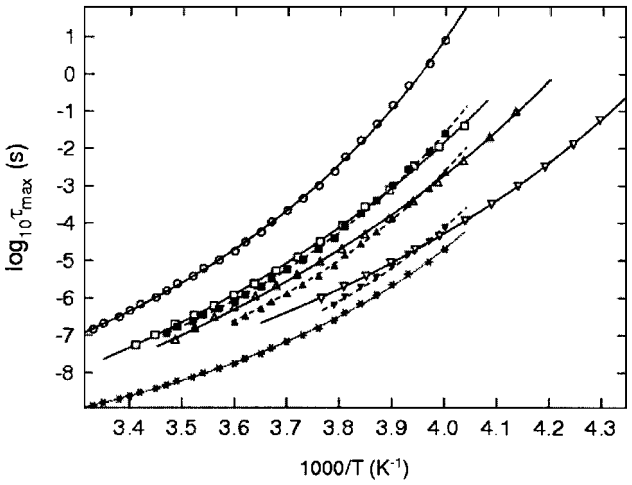

FIG. 6. The open circles are the experimentally obtained α-relaxation times $\tau_{\alpha A}$ of neat xylitol and the line through them is the Volger-Fulcher-Tammann fit. The stars are the independent relaxation times τ_{0A} of neat xylitol calculated from Eq. (4) and the dotted line is the Volger-Fulcher-Tammann fit. The α-relaxation times $\hat{\tau}_{\alpha A}$ of the mixtures are calculated by Eq. (8) with $\hat{n}_A=0.32$(■), 0.24(▲) and 0.08(▼), matching well, respectively, with the experimental data $\tau_{\max}$ of the mixtures with $N_{wpx}=0.758$(□), 0.835(△) and 1.099(▽).

We have arrived at the result that the coupling parameter $\hat{n}_A$ in the mixture $A_{1-x}B_x$ decreases with increasing water content x by fitting the calculated $\hat{\tau}_{\alpha A}(T)$ to the experimental data at temperatures above the glass transition temperature of the mixtures T_{gx}. An independent support of this conclusion can be obtained by comparing the steepness ("fragility") index defined by Eq. (1) and calculated from the Vogel–Fulcher–Tammann fits to the data shown in Fig. 2. The steepness index plotted against N_{wpx} in Fig. 4 shows a decrease with N_{wpx}, like that found by Nozaki *et al.* [10] in sorbitol/water mixtures. Thus, from the empirical fact that m decreases with a decreasing coupling parameter [19] n, we infer from Fig. 4 that $\hat{n}_A$ in the mixture $A_{1-x}B_x$ decreases with increasing water content x. The fact that the steepness index of sorbitol ($m=109$) is larger than xylitol ($m=96\pm2$) is an example of the empirical correlation [19] because $n_A=0.52$ for sorbitol while $n_A=0.46$ for xylitol.

B. Johari-Goldstein β-relaxation

We have seen in the previous subsection that the large reductions, in $\hat{\tau}_{\alpha A}(T)$ of xylitol or sorbitol in the mixtures with water are mainly due to the mitigation of intermolecular coupling or the decrease of the coupling parameter from n_A of the neat glass-former A to a smaller value $\hat{n}_A$ of the mixture with water. The α-relaxation is intermolecularly coupled, while the independent relaxation of the CM is not. Thus, mixing with water has no effect on the independent relaxation time τ_{0A}, at least as far as intermolecular coupling is concerned. In fact, we found that no change in the independent relaxation time τ_{0A} is needed to obtain the fits to the

data in Fig. 6. However, we do not exclude a small change in τ_{0A} due to a change in packing, hydrogen bonding, or potential when water is introduced.

A recent application of the CM is the identification of τ_{0A} with the Johari-Goldstein β-relaxation time, τ_{JG}. The rationale for identifying τ_{0A} with τ_{JG} has been extensively discussed before. Experimental data on various glass-forming substances, including sorbitol and xylitol [16,17,22], show remarkably good correspondence between τ_{0A} calculated by Eq. (4) and τ_{JG} from experiment. Hence, from the insensitivity of τ_{0A} to the water content and the relation $\tau_{0A} \approx \tau_{JG}$, we conclude that τ_{JG} of sorbitol or xylitol is insensitive to mixing with water. The experimental data of τ_{JG} in the xylitol/water mixtures shown in Fig. 2 and the sorbitol/water mixtures of Nozaki *et al.* [10] are in accord with this conclusion. We reiterate the possibility of some change of τ_{JG} due to changes in packing, hydrogen bonding, or potential when water is introduced but the change is much smaller than that of the α-relaxation time because the latter depends sensitively on intermolecular coupling, which definitely has been reduced.

Minoguchi and Nozaki [23] measured complex permittivity of sorbitol during isothermal crystallization. The crystallites are immobile and their presence in the vicinity of sorbitol molecules in the amorphous region enhance the intermolecular constraints acting on the latter and increase their coupling parameters $\{n_{iA}\}$ above that of neat sorbitol, n_A. The effect is in opposite direction to the addition of water, which decreases $\{n_{iA}\}$ to below n_A. It follows from Eqs. (4) and (6) that the increase of $\{n_{iA}\}$ above n_A has the consequence of making the α-relaxation times, $\{\tau_{\alpha iA}\}$, much longer. On the other hand, this effect is absent for the independent relaxation time τ_{0A}. Hence, as sorbitol crystallizes, the increase in τ_{0A} is much smaller than in $\{\tau_{\alpha iA}\}$. From the relation $\tau_0 \approx \tau_{JG}$, we conclude that the JG relaxation time τ_{JG} changes little compared with $\tau_{\alpha A}$ as sorbitol crystallizes. This difference was found in the experimental work of Minoguchi and Nozaki [23].

V. CONCLUSION

From the dielectric response of anhydrous xylitol and xylitol-water mixtures of different concentrations, we found that the α- and the β-relaxations change in different ways with the amount of water added to xylitol. While the α-relaxation speeds up immensely with an increasing concentration of water, the relaxation rate of JG β-process is practically unchanged. The relaxation pattern observed for water-in-xylitol mixtures is in harmony with recent findings obtained in sorbitol-water mixtures by Nozaki and coworkers [10]. The experimental findings on both the α- and the β-relaxations can be rationalized by the predictions of the coupling model.

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