Changes of the Primary and Secondary Relaxation of Sorbitol in Mixtures with Glycerol

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The dielectric relaxation experimental data on the α- and Johari–Goldstein β-relaxation dynamics of sorbitol in the neat state and in mixtures with glycerol published by Duvvuri and Richert (*J. Phys. Chem. B,* published online Apr 23, http://dx.doi.org/10.1021/jp031366b) is challenging to explain. Not only does one need a theory or model that can address both the α- and Johari–Goldstein β-relaxation dynamics in a neat glass-former, but one also a theory or model that can address them in a mixture. The coupling model fulfills these requirements. Naturally, we employ the coupling model to interpret the experimental data. Fair agreements are found between the predictions of the model and data of neat sorbitol and mixtures of sorbitol with glycerol.

1. Introduction

Mixtures of two miscible glass-formers of various compositions yield new materials that have different glass transition temperatures, mechanical properties, and equilibrium as well as glassy dynamics. The changes can be used advantageously to make materials have functions and properties to suit the purpose of some applications. On the other hand, from the basic research point of view, the changes of dynamics of a component in a binary mixture can have an impact on the interpretation of the primary and secondary relaxations of glass-formers in both the equilibrium liquid and glassy states. There are many studies of miscible mixtures of two glass-formers on the changes of the primary α-relaxation of either component.[1–5] Seldom seen is the study of 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 relaxation).[6–8] Examples include dielectric measurements of mixtures of glycol oligomer,[9] alcohol,[10] glycerol,[11] and sorbitol[12] with water. A recent dielectric study of mixtures of sorbitol with glycerol by Duvvuri and Richert[13] reported on the changes of the dynamics of both the primary and secondary relaxation of sorbitol. Such experimental investigation is interesting in the context of both blend dynamics and glass transition dynamics. For a theoretical interpretation of the dynamics in these works, one needs an approach that can address not only the change of the α-relaxation dynamics but also the concomitant changes of the Johari–Goldstein β-relaxation. As far as we know, the coupling model[14–17] is the only approach that has been extended to address the dynamics of miscible blends as well as the Johari–Goldstein (JG) β-relaxation. Naturally, we apply it to interpret the dielectric data of sorbitol/glycerol mixtures, and the results are reported in this paper.

2. Coupling Model Interpretation of α-Relaxation in Mixtures

The coupling model (CM) emphasizes the many-body nature of the α-relaxation dynamics of a neat glass-former like sorbitol (S) or glycerol (G) through the intermolecular coupling of the relaxing species with others in its environment. The many-body dynamics are heterogeneous[18–21] and give rise to the Kohl-rausch–Williams–Watts (KWW) stretch exponential correlation function.

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

Here, *A* stands for either S or G, $(1 - n_A)$ is the fractional KWW exponent, and n_A is the coupling parameter in the CM. The larger the capacity of the molecules for intermolecular coupling, the larger is the n_A value. The utility of the CM is due to the relation

$$\tau_{\alpha A} = [t_c^{-n_A}\tau_{0A}]^{1/(1-n_A)} \equiv \left(\frac{\tau_{0A}}{t_c}\right)^{n_A/(1-n_A)} \tau_{0A} \tag{2}$$

which relates the KWW relaxation time ($\tau_{\alpha A}$) to the independent relaxation time (τ_{0A}) via the KWW exponent and t_c. The latter is the crossover time from independent relaxation, $\exp(-t/\tau_{0A})$, to the heterogeneous many-body KWW relaxation and has an approximate value of 2×10^{-12} s for molecular liquids.[22]

Perhaps the first published model addressing the component dynamics of binary mixtures was by Roland and Ngai (RN).[23–28] This approach was an extension of the coupling model for neat glass-formers because it incorporated an additional but different source of heterogeneity, due both to the intrinsic mobility differences (i.e., different τ_{0A} values) of the components and to the local compositional heterogeneity from concentration fluctuations. The α-relaxation dynamics of a relaxing species (S or G) in a mixture is determined by its chemical structure as well as by the local environment, since the latter governs the intermolecular coupling and ensuing cooperativity which affects the α-relaxation. Thus, the α-relaxation of a given species in the mixture, S or G, reflects its intrinsic mobility and the varying degree of intermolecular coupling or constraints imposed on it by neighboring S and G molecules.

From the standpoint of S, upon mixing with G to form the S_xG_{1-x} mixture, the replacement of some of the S molecules by the smaller and more mobile G molecules in its environment will reduce the intermolecular coupling and constraints, and hence, its coupling parameter is smaller than that in neat sorbitol. The fact that the G molecule has a higher intrinsic mobility than the S molecule can be inferred crudely from their difference in T_g values. However, a component with a higher T_g value

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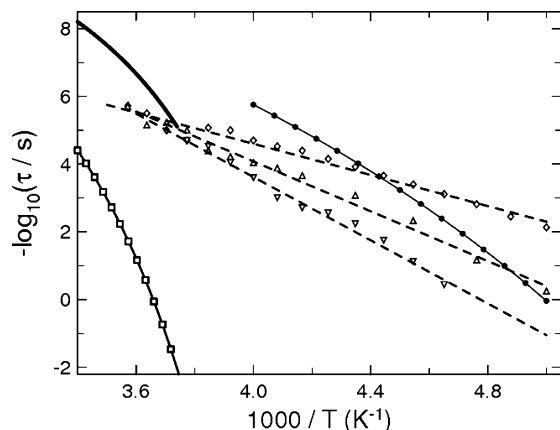*J. Phys. Chem. B, Vol. 108, No. 30, 2004* **11119**

Figure 1. Relaxation map of neat sorbitol, sorbitol in mixtures with glycerol, and neat glycerol from Duvvuri and Richert (ref 13). $\tau_{\alpha S}$ and $\tau_{\alpha G}$ as a function of temperature. The line with open squares on it is the Vogel–Fulcher–Tammann–Hesse (VFTH) fit to $\tau_{\alpha S}$ of neat sorbitol from Duvvuri and Richert (DR). The thick line above it represents τ_{0S} calculated by eq 3 with $n_S = 0.52$. The line with closed circles on it represents the VFTH fit to $\tau_{\alpha G}$. Open diamonds, open triangles, and inverted open triangles are the JG β-relaxation times of neat sorbitol and sorbitol in the S_xG_{1-x} mixtures with $x = 0.82$ and 0.67, respectively. The lines are Arrhenius fits to the data.

does not necessarily mean it has a lower intrinsic mobility and slows down the other component. This situation was found in several examples,[4,29,30] which show experimentally that the host α-relaxation time decreases instead of increases when mixing in guest molecules that have a higher T_g value in the neat state. A more reliable estimate of the intrinsic mobilities of S and G is the independent relaxation times[4,29,30] of neat sorbitol (τ_{0S}) and of neat glycerol (τ_{0G}). These independent relaxation times, τ_{0G} or τ_{0S}, can be obtained from the parameters $\tau_{\alpha A}$ and n_A of the KWW function (eq 1) used to fit the α-relaxation data of the neat materials. For example, the τ_{0S} value of neat sorbitol is given by the expression

$$\tau_{0S} = (t_c)^{n_S}(\tau_{\alpha S})^{1-n_S} \tag{3}$$

and a similar expression exists for the τ_{0G} value of neat glycerol. Previously, fits of the KWW function to isothermal α-relaxation dielectric data of neat sorbitol and glycerol have determined the KWW parameters $\tau_{\alpha A}$ and n_A as a function of temperature (A stands for either S or G).[16,17,31] Figure 1 shows $\tau_{\alpha S}$ and $\tau_{\alpha G}$ as a function of temperature. The line with open squares on it is the Vogel–Fulcher–Tammann–Hesse (VFTH) fit to the data of neat sorbitol from Duvvuri and Richert (DR). This together with the previously determined value $n_S = 0.52$ in the temperature range shown[16,17] enables us to calculate τ_{0S} by eq 3. Possibly, the n_S value of neat sorbitol may be <0.52 at the high temperature end, but this cannot be certain because of the overlap of the α-relaxation with the JG relaxation. The KWW exponent $(1 - n_G)$ of glycerol, over the temperature range shown in Figure 1 for $\tau_{\alpha G}$, is slightly temperature dependent, as found in an earlier work.[31] It decreases from 0.68 at $(1000/T) = 4.1$ to 0.64 at $(1000/T) = 4.9$. We have used the $(1 - n_G)$ parameters from this previous work to determine τ_{0G} by eq 3. Although we did not put τ_{0G} in Figure 1, it is shorter than $\tau_{\alpha G}$ (the line with the closed circles on it). It is thus clear by inspection of Figure 1 that $\tau_{0G} \ll \tau_{0S}$ for all temperatures, verifying that the G molecule has a higher intrinsic mobility than the S molecule. Thus, mixing sorbitol with glycerol should reduce the intermolecular coupling or constraints of the sorbitol component and speed up its α-relaxation time. Conversely, the α-relaxation of
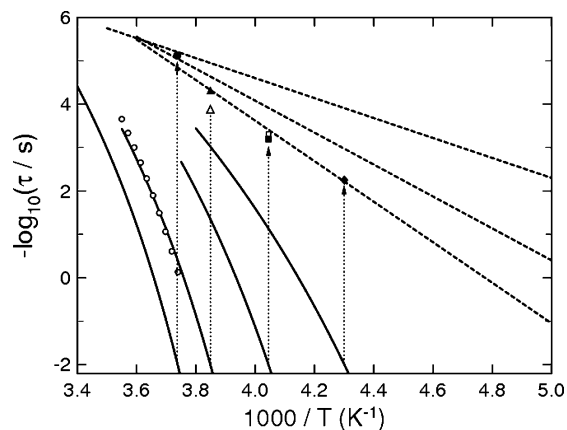

Figure 2. The thick lines are the VFTH fits to the experimentally determined α-relaxation times of neat sorbitol and sorbitol in the S_xG_{1-x} mixtures with $x = 0.82$, 0.67, and 0.54 (from left to right). The calculated $\hat{\tau}_{\alpha S}$ values for $x = 0.82$ (open circles) are in good agreement with the VFTH fit to the experimental data (the second thick line from the left) with $\hat{n}_S = 0.429$ determined for $x = 0.82$ (see text). The Arrhenius fits to the JG relaxation times (τ_{JG} values) of neat sorbitol and the S_xG_{1-x} mixtures for $x = 0.82$ and 0.67 are shown by the three dashed lines (from top to bottom). The calculated τ_{0S} values in neat sorbitol and in the mixtures at the dielectric glass transition temperature $(T_{g,x})$ are shown by the closed circle ($x = 1$), closed and open triangles ($x = 0.82$), closed and open squares ($x = 0.67$), and closed diamond ($x = 0.54$).

the glycerol component is slowed by the presence of sorbitol of a lower intrinsic mobility. Figure 2 shows the most probable α-relaxation times ($\tau_{\alpha,max}$ values) of mixtures with $x = 0.82$, 0.67, and 0.54 and of neat sorbitol. Glycerol and sorbitol have comparable dielectric strengths. Hence, only in mixtures with high x values, such as 0.82 and perhaps 0.67 from the work of DR,[13] will sorbitol molecules be responsible for the observed dielectric α-loss peak and $\tau_{\alpha,max}$ values. Certainly, glycerol molecules dominate the α-loss peak at low x values. The purpose of this work is to address in parallel the α-relaxation and the JG β-relaxation in mixtures coming from the same component, namely, sorbitol. DR reported resolved JG β-relaxation only in neat sorbitol and mixtures with $x = 0.82$, 0.67, and 0.54. Therefore, we shall confine our attention to the dielectric relaxation data of these samples from now on.

The reduction of the intermolecular coupling of sorbitol in the S_xG_{1-x} mixtures, due to the presence of the more mobile glycerol molecules in its environment, corresponds to a reduction of the coupling parameter n_S. The new environments in the mixture are not identical for all S molecules due to the inevitable composition fluctuations. There is a distribution of environments (i's) of different compositions, which in turn engenders a distribution of coupling parameters $\{n_{Si}\}$ for the S molecules and similarly for the G molecules in the mixture. All the n_{Si} values in the distribution are smaller than the coupling parameter n_S of the neat sorbitol, that is,

$$n_{Si} < n_S \tag{4}$$

The differences between n_{Si} and n_S become larger when there are more mobile G molecules in the mixture.

In a mixture, eqs 1 and 2 apply to each i in the distribution. For each i, the α-relaxation correlation function of S is given by

$$\phi_{Si}(t) = \exp[-(t/\tau_{\alpha Si})^{1-n_{Si}}] \tag{5}$$

where n_{Si} is its own coupling parameter and $\tau_{\alpha Si}$ is its cooperative α-relaxation time, and they are related by the

equation

$$\tau_{\alpha Si} = [t_c^{-n_{Si}} \tau_{0S}]^{1/(1-n_{Si})} \equiv \left(\frac{\tau_{0S}}{t_c}\right)^{n_{Si}/(1-n_{Si})} \tau_{0S} \quad (6)$$

The dielectric response of S in the mixture is the superposition of the one-sided Fourier transform of the time derivative of the KWW function in eq 5, each weighed by the probability of the occurrence of i in the distribution. There is also contribution from the dielectric response of G on the high frequency side. Thus, unlike neat sorbitol, the width of the measured loss peak of sorbitol in the mixture cannot be used to deduce any of the coupling parameters n_{Si} in a straighforward manner.[23-25] Nevertheless, there is still a way to make a connection between the experimental data and the theoretical prediction. There is a most probable environment ($\hat{\imath}$) in the distribution, and for it, let us denote its coupling parameter by $\hat{n}_S$, the α-relaxation time by $\hat{\tau}_{\alpha S}$, and the correlation function by

$$\hat{\phi}_S(t) = \exp[-(t/\hat{\tau}_{\alpha S})^{1-\hat{n}_S}] \quad (7)$$

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

$$\hat{\tau}_{\alpha S} = [t_c^{-\hat{n}_S} \tau_{0S}]^{1/(1-\hat{n}_S)} \equiv \left(\frac{\tau_{0S}}{t_c}\right)^{\hat{n}_S/(1-\hat{n}_S)} \tau_{0S} \quad (8)$$

Because $\hat{\imath}$ has the highest probability of occurrence, its dielectric loss given by the imaginary part of the one-sided Fourier transform of the time derivative of the KWW function in eq 7 is largely responsible for the maximum of the observed α-loss peak of S in the mixture located at $f_{\alpha,max} \equiv 1/(2\pi\tau_{\alpha,max})$. Thus, the experimentally determined value of $\tau_{\alpha,max}$ from $f_{\alpha,max}$ shown in Figure 2 should correspond to the calculated $\hat{\tau}_{\alpha S}$ value, if the τ_{0S} value in the mixture is the same as that in neat sorbitol. Although in either the neat state or a mixture τ_{0S} is the same independent relaxation time of a sorbitol molecule, changes in the hydrogen bondings, free volume, and/or configurational entropy of the sorbitol environment in mixtures with glycerol may change τ_{0S} somewhat.

Since $t_c \approx 2$ ps, in the entire experimental temperature range, the ratio (τ_{0S}/t_c) is much larger than unity. It follows immediately from eqs 2 and 8, respectively, that $\tau_{\alpha S}$ and $\hat{\tau}_{\alpha S}$ are much longer than τ_{0S}, and the effect of intermolecular coupling in slowing down the α-relaxation of S molecules in both the neat sorbitol and the mixture is clear. As a special case of the inequality (eq 4), we have $\hat{n}_S < n_S$. It follows that the exponent $[\hat{n}_S/(1 - \hat{n}_S)]$ in eq 8 for the mixtures is smaller than the exponent $[n_S/(1 - n_S)]$ for neat sorbitol in eq 2, after the subscript A therein has been replaced by S throughout. Upon comparing eqs 8 and 2, this property, together with the assumption that τ_{0S} is the *same* at the same temperature for the neat glass-former S and its mixtures with G, leads us to the following results. (i) The $\hat{\tau}_{\alpha S}$ value of the mixture is shorter than the $\tau_{\alpha S}$ value. (ii) The separation between the $\hat{\tau}_{\alpha S}$ value of the mixture and the $\tau_{\alpha S}$ value of the neat glass-former S, measured by the difference $\log(\tau_{\alpha S}) - \log(\hat{\tau}_{\alpha S})$, increases with decreasing temperature because of the increase in τ_{0S} in eqs 2 and 8. (iii) At a fixed temperature, the ratio $(\hat{\tau}_{\alpha S}/\tau_{\alpha S})$ decreases with increasing concentration of G in the mixture because of decreasing $\hat{n}_S$. (iv) Each $\phi_i(t)$ value in eq 5 has a narrower dispersion than the $\phi(t)$ value of the neat sorbitol (eq 2) because $n_{Si} < n_S$ (eq 3). However, the dispersion of the α-relaxation originating from sorbitol molecules in the mixture is a superposition of the $\phi_i(t)$ values in the distribution. This complication makes it impossible
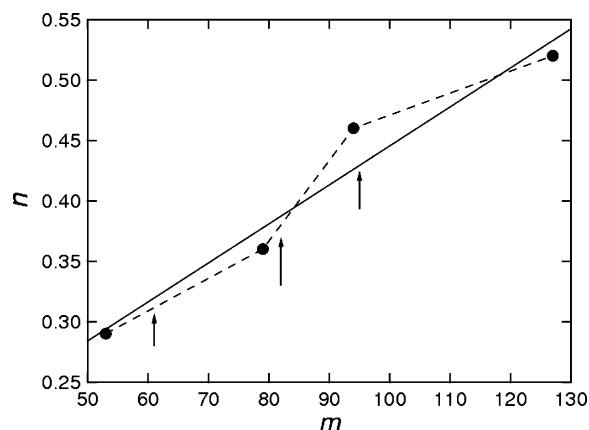

Figure 3. A plot of n against m for sorbitol, xylitol, threitol, and glycerol (in the order of decreasing m).[16,17,33] The straight line is the least-squares fit of the four data points by a linear dependence. The vertical arrows indicate experimental m values[13] of 95, 82, and 61 of the S_xG_{1-x} mixtures for $x = 0.82$, 0.67, and 0.54, respectively.

to determine the $\hat{n}_S$ value from the dielectric spectrum of the mixture, unlike the case of the n_S value of the neat sorbitol. The two factors have opposite effects on the width of the dispersion, and they cancel each other to some extent.

There is however an alternative way to determine the $\hat{n}_S$ value for the S_xG_{1-x} mixture from the steepness index or "fragility" defined by[32]

$$m = \left.\frac{d \log \hat{\tau}_{\alpha S}}{d(T_{g,x}/T)}\right|_{T=T_{g,x}} \quad (9)$$

The units of $\hat{\tau}_{\alpha S}$ in eq 9 are in seconds, and $T_{g,x}$ is the dielectric glass transition temperature at which $\hat{\tau}_{\alpha S} = 100$ s. A correlation between m and n usually exists, especially for glass-formers of the same family such as the family of polyols including sorbitol, xylitol, threitol, and glycerol,[16,17,33] as shown in Figure 3. The straight line is the least-squares fit of the four points by a linear dependence. Our KWW exponents, $(1 - \hat{n}_S) \equiv \beta_{KWW}$, for the polyols obtained in a previous work differ from the values of neat sorbitol and glycerol given by DR. The difference is due to the different fitting procedures used. In the framework of the extended coupling model,[16,17,34] the dielectric data are not the sum of a Havriliak−Negami function for the α-relaxation and a Cole−Cole function for the β-relaxation. The fit to determine the KWW exponent emphasizes the main α-loss peak. This explains why our exponent $(1 - \hat{n}_S)$ of neat sorbitol and glycerol is larger than the β_{KWW} value of DR.[13] It is reasonable to assume that the S_xG_{1-x} mixtures between two polyols obey this established correlation by the neat polyols, and hence, the $\hat{n}_S$ values can be determined from m for any S_xG_{1-x} mixture obtained by DR from their $\hat{\tau}_{\alpha S}$ values. This is shown in Figure 3, where the vertical arrows are located at $m = 95$, 82, and 61, the experimental values for $x = 0.82$, 0.67, and 0.54, respectively. The corresponding $\hat{n}_S$ values read off from the least-squares linear fit (the straight line in Figure 3) are 0.43, 0.39, and 0.32 for $x = 0.82$, 0.67, and 0.54, respectively. From the linear interpolations between the data of the neat polyols (the dashed lines in Figure 3), $\hat{n}_S$ is equal to 0.46, 0.38, and 0.31 for $x = 0.82$, 0.67, and 0.54, respectively.

There is substantial overlap of the temperature ranges where the $\tau_{\alpha S}$ and $\hat{\tau}_{\alpha S}$ values have been determined by DR for $x = 1.0$ and 0.82, respectively. We can check the reliability of the $\hat{n}_S$ value 0.43 so determined for $x = 0.82$ by calculating the $\hat{\tau}_{\alpha S}$ value using eq 8. The τ_{0S} value therein is calculated (the thick

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line in Figure 1) as a function of temperature by eq 3 from the VFTH fit to the $\tau_{\alpha S}$ values given by DR for neat sorbitol[16,17] (the line with open squares on top of it in Figure 1) and $n_S = 0.52$. One can see in Figure 2 that there is good correspondence between the calculated $\hat{\tau}_{\alpha S}$ value for $x = 0.82$ (open circles) and the experimental data shown by the VFTH fit (thick line, second from the left). Similar checks for the $\hat{n}_S$ values for $x = 0.67$ and 0.54 cannot be made because there is no overlap between the temperature range of the $\hat{\tau}_{\alpha S}$ data for these mixtures with that of the neat sorbitol (see Figure 2). However, there is another way to check for consistency, which will be demonstrated later in connection with the JG β-relaxation.

3. Coupling Model Interpretation of JG β-Relaxation in Mixtures

A recent advance of the coupling model for a neat glass-former is a description of the evolution of dynamics with increasing time.[16,17] In order of appearance, they are (1) the nearly constant loss in the short-time caged regime, (2) the local Johari−Goldstein β-relaxation with its time τ_{JG} identified with the independent relaxation time τ_0, and (3) the increasing probability of successful independent relaxations and concomitant continuous development of many-body cooperative dynamics until finally (4) the fully cooperative KWW α-dynamics take hold. The rationale for identifying τ_0 with τ_{JG} is that they are relaxation times of local and independent (noncooperative) relaxation. Experimental data on various glass-forming substances, including sorbitol,[16,17,34−37] show remarkably good correspondence between the τ_0 value calculated by eq 3 and the τ_{JG} value from experiment.

$$\tau_{JG}(T) \approx \tau_0(T) \tag{10}$$

The JG β-relaxation times of neat sorbitol and sorbitol in the S_xG_{1-x} mixtures with $x = 0.82$ and 0.67 are shown in Figure 1. We now demonstrate that eq 10 holds once again for sorbitol in the mixtures. We have already calculated τ_0 from the $\tau_{\alpha S}$ of neat sorbitol, and the results are shown in Figure 1 (thick line). Now, we take the calculated τ_0 value at the dielectric glass transition temperature $T_{g,x=1}$ of neat sorbitol at which $\tau_{\alpha S} = 100$ s. This result, shown by the closed circle in Figure 2, is close to the τ_{JG} value at the same temperature determined by DR from experiment (upper dashed line). Comparison is not made at higher temperatures because it can be inferred from high pressure experiments on sorbitol[35] that the Arrhenius temperature dependence of τ_{JG} deduced by DR does not continue to temperatures higher than $T_{g,x=1}$.

The JG relaxation times (τ_{JG} values) of the S_xG_{1-x} mixtures with higher $x = 0.82$ and 0.67 have been shown before in Figure 1. They are shown again in Figure 2 but now only as the Arrhenius fits to the actual data (the two lower dashed lines). In these two mixtures with higher x values, the experimentally determined α-relaxation time can be identified with $\hat{\tau}_{\alpha S}$. The correspondence between the observed JG relaxation time (τ_{JG}) and the τ_{0S} value in the mixture should continue to hold according to the coupling model. The prediction can be tested at the dielectric glass transition temperature $T_{g,x}$ at any one of these mixtures by calculating τ_{0S} from the $\hat{\tau}_{\alpha S}$ and $\hat{n}_S$ values of the mixture through

$$\tau_{0S} = (t_c)^{\hat{n}_S}(\hat{\tau}_{\alpha S})^{1-\hat{n}_S} \tag{11}$$

which is the equivalent of eq 8. For all mixtures considered in this work, $T_{g,x}$ is defined as the temperature at which experimentally determined α-relaxation time of the sorbitol

component is equal to 10^2 s. The calculated τ_{0S} values at $T_{g,x=0.82}$ for $x = 0.82$ with $\hat{n}_S = 0.46$ and 0.43, the two possible values deduced from Figure 3, are shown in Figure 2 by the closed and open triangles, respectively. Similarly, for $x = 0.67$, the calculated τ_{0S} values at $T_{g,x=0.67}$ with $\hat{n}_S = 0.38$ and 0.39 are shown in Figure 2 by the closed and open squares, respectively. For $x = 0.54$, the calculated τ_{0S} value at $T_{g,x}$ with $\hat{n}_S = 0.31$ is represented by the closed diamond. Comparisons made with the actual τ_{JG} data of DR near $T_{g,x}$ instead of the Arrhenius lines in Figure 2 show overall that they are in good agreement with the calculated τ_{0S} values at $T_{g,x}$.

4. Activation Enthalpy of JG β-Relaxation in Neat Sorbitol and Mixtures

The fictive temperature of Tool[38] was introduced to characterize the structure of a glass-former. When the structure of the liquid state is in equilibrium, the fictive temperature is the same as the temperature. The α-relaxation time (τ_α) follows the temperature dependence

$$\tau_\alpha(T) = A \exp[B/(T - T_0)] \tag{12}$$

where A, B, and T_0 are the parameters of the VFTH equation. Upon cooling the liquid, τ_α becomes so long that its structure falls out of equilibrium at some temperature, and the fictive temperature departs from T. At temperatures sufficiently below the calorimetric or dielectric T_g value, the structure is frozen and the fictive temperature assumes a constant value of T_f, which is dependent on the cooling rate and thermal history. In this glassy state, the temperature dependence of τ_α is Arrhenius. Hodge[39] showed that τ_α depends on T and T_f according to the following expression

$$\tau_\alpha(T, T_f) = A \exp\{B/[T(1 - T_0/T_f)]\} \tag{13}$$

where A, B, and T_0 are the constants in eq 12. At equilibrium, $T_f = T$ and eq 13 becomes identical to eq 12. In the isostructural glassy state, τ_α has the Arrhenius temperature dependence

$$\tau_\alpha(T, T_f) \equiv A \exp[E_\alpha(T_f)/RT] \tag{14}$$

with the activation enthalpy ($E_\alpha(T_f)$) given by[40]

$$E_\alpha(T_f) = RB/(1 - T_0/T_f) \tag{15}$$

where R is the gas constant. From this and the relationship between τ_0 and τ_α (eq 2), the independent relaxation time of the isostructural glassy state also has Arrhenius temperature dependence

$$\tau_0(T, T_f) = A_0 \exp[E_0(T_f)/RT] \tag{16}$$

with activation enthalpy

$$E_0(T_f) = (1 - n)E_\alpha(T_f) \tag{17}$$

where n is the coupling parameter. The correspondence (eq 10) between the Johari−Goldstein β-relaxation time (τ_β) and τ_0 should continue to hold at temperatures below T_g. For glass in the isostructural state, τ_β invariably has Arrhenius temperature dependence with the activation enthalpy ($E_\beta(T_f)$). The correspondence between τ_β and τ_0 (eq 10) implies that

$$E_0(T_f) \approx E_\beta(T_f) \tag{18}$$

Hence, from the VFTH equation for the τ_α value of the equilibrium liquid (eq 12), we can calculate $E_\beta(T_f)$ by following the

TABLE 1: Experimental and Calculated Parameters of the α-Relaxation and the JG β-Relaxation of Neat Sorbitol and Sorbitol in a Binary Mixture with Glycerol, with a Sorbitol Mole Fraction of $x = 0.82^a$

x	A (s)	B (K)	T_0 (K)	n or $\hat{n}_S$	T_f (K)	$E_\alpha(T_f)$ kJ/mol	$E_0(T_f) = (1-n)E_\alpha(T_f)$ (kJ/mol)	E_β exptl (kJ/mol)
1.0	10^{-15}	1722.6	223.5	0.52	262.8 (10^4 s)	95.73	45.9	44.0
					260.9 (10^5 s)	99.88	47.9	44.0
					259.1 (10^6 s)	104.2	50.0	44.0
0.82	10^{-15}	1821.7	213.3	0.43	255.0 (10^4 s)	92.63	52.8	70.4
					252.9 (10^5 s)	96.79	55.2	70.4
					251.0 (10^6 s)	100.78	57.5	70.4

^{a} The experimental parameters are taken from ref 13.

steps in the order of eqs 15, 17, and 18 once the T_f value of the isostructural glassy state is known. The ideal way to determine T_f is to calculate it by the method of Hodge, by following the thermal history leading to the glassy state. This was carried out in ref 40 for the neat glass-former dipropyleneglycol dibenzonate. However, the thermal history in the work of DR was not specified, and only estimates of T_f are obtained from the temperature at which the τ_α value of the equilibrium liquid given by the VFTH equation (eq 12) attains a long time, say 10^4, 10^5, or 10^6 s. These are representative τ_α values at which the liquid is expected to fall out of equilibrium times when cooled at some typical rates in the laboratory. With such T_f values, the prediction of eq 18 is tested for neat sorbitol and the $x = 0.82$ mixture. The results are shown in Table 1 together with the parameters taken from DR and used in the calculations. There is approximate agreement between the experimental value of the activation enthalpy (E_β) of neat sorbitol given by DR and the $E_0(T_f)$ value calculated by eq 17, as the product $(1 - n)E_\alpha(T_f)$ for any of the three T_f values was obtained by assuming that, at T_f, $\tau_\alpha(T_f) = 10^4$, 10^5, or 10^6 s. Good agreement between the experimental E_β and the calculated $E_0(T_f)$ values has been found before in another neat glass-former, dipropyleneglycol dibenzonate.[40] However, for the $x = 0.82$ mixture, the experimental E_β value is 20−30% larger than the calculated $E_0(T_f)$ value. The discrepancy may be due to the contribution from the α-relaxation of glycerol molecules in the mixture. As can be seen in the relaxation map of Figure 1, the τ_α value of neat glycerol is tending to pervade the JG β-relaxation of the mixtures (dashed lines). The α-relaxation times of the glycerol molecules in the mixture are longer than those of neat glycerol, and hence, it is possible that the glycerol α-relaxation contribution has distorted the JG β-relaxation coming from the sorbitol molecules already in the $x = 0.82$ mixture at low temperatures. In fact, if the fitting of the JG β-relaxation time of $x = 0.82$ to the Arrhenius temperature dependence were restricted to the range $T = 220−255$ K (i.e., neglecting the last two low temperature points in Figure 1, which show marked deviation from the Arrhenius behavior likely due to contribution from the relaxation of the glycerol component), a value of 57.8 ± 2 kJ/mol instead of 70.4 kJ/mol by DR for the experimental activation enthalpy is obtained, in good agreement with our prediction (see Table 1). The distortion is more severe in mixtures with $x = 0.67$ and 0.54 and may explain the large increase of the apparent experimental E_β value of these mixtures. Due to the expected distortion, it serves no purpose for us to calculate the $E_0(T_f)$ value and compare it with the experimental E_β values of these other mixtures.

5. Conclusion

The experimental data on the changes of the α- and Johari−Goldstein β-relaxations of sorbitol when mixing with glycerol are challenging to explain because the explanation requires a theory or model that addresses both the α- and β-relaxations in a neat glass-former as well as in a miscible mixture of two glass-formers (components). As far as we know, the coupling model is the only approach that has been developed to the extent that it can address both the α- and Johari−Goldstein β-relaxations of a neat glass-former, and of any one of the two components in the binary mixture. The predictions from this approach are demonstrated for neat sorbitol and its mixtures with glycerol at higher concentrations of sorbitol.

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