

# Structural Relaxation Dynamics in Binary Glass-Forming Molecular Liquids with Ideal and Complex Mixing Behavior

Li-Min Wang,<sup>\*,†</sup> Yongjun Tian,<sup>†</sup> Riping Liu,<sup>†</sup> and Ranko Richert<sup>‡</sup>

State Key Lab of Metastable Materials Science and Technology, and College of Materials Science and Engineering, Yanshan University, Qinhuangdao, Hebei, 066004 China and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

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The glass transition and structural relaxation dynamics of various binary glass-forming liquids are investigated with dielectric relaxation measurements across the entire composition range. Three categories of solutions with weak, intermediate, and strong mixing effects, namely methyl-*m*-toluate in methyl *o*-toluate, methyl *m*-toluate in di-*n*-butyl phthalate, and 1,2-propandiol in 2-hexylamine, are selected to address the mixing behaviors from near-ideal to nonideal cases. The glass transition temperatures, fragility indices, and stretching exponents of the solutions are determined and their composition dependence is the focus of this study. The experimental measurements show that mixing generally generates a negative deviation of fragility *m* relative to the composition average of the results of two neat components (ideal mixing law). This excess negative fragility proves to be a universal feature of binary systems, and the increase of the nonideal mixing degree results in a more pronounced negative deviation. In contrast, the composition dependence of the stretching exponents is more complex, and a transition from the negative to positive deviation is observed for substantial nonideal character. The study assists understanding the dynamics of multicomponent glass formers.

## I. Introduction

The studies of structural relaxation dynamics in solutions are of great scientific importance in understanding the relaxation behavior of liquids and the glass transition<sup>1–3</sup> and have been explored in both high and low temperature regimes.<sup>4–6</sup> The experimental measurements on the dynamics of the mixtures of various interactions also facilitate comparisons with simulation results.<sup>7–9</sup> Mixing liquids often enhances the vitrification ability, and mixing effects on glass transitions in binary miscible solutions has been intensively studied,<sup>10–14</sup> but the effects regarding glass transition as well as glass forming ability have not been rationalized. In particular, the explanation of the glass transition temperature  $T_g$  still remains a challenge in mixtures.

The structural relaxation dynamics in solutions is governed by two aspects, the composition dependence of the liquids non-Arrhenius and nonexponential characters, which becomes increasingly important in the highly viscous regime.<sup>15–17</sup> The non-Arrhenius character is generally gauged by a fragility index *m*, which is defined as the slope in the plot of logarithmic relaxation time  $\tau$  or viscosity  $\eta$  versus reduced reciprocal temperature at  $T_g$ ,  $m = d \log \tau / d(T_g/T)|_{T=T_g}$ . The relaxation time dispersion can be characterized by  $\beta_{\text{KWW}}$  in terms of the empirical Kohlrausch–Williams–Watts (KWW) equation,  $\phi = \exp[-(t/\tau)^{\beta_{\text{KWW}}}]$ , and  $\beta_{\text{KWW}}$  is, therefore, the nonexponential (stretching or Kohlrausch) parameter,  $0 < \beta_{\text{KWW}} \leq 1$ .<sup>18–21</sup> The majority of studies regarding *m* and  $\beta$  have focused on pure (single component) liquids, while systematic scrutinies of the non-Arrhenius and nonexponential dynamics in molecular glass-forming solutions have received only some attention.<sup>22,23</sup> The dielectric relaxation measurements in xylitol–sorbitol solutions

show a slightly decrease in fragility index relative to the linear average based on the results of two neat components (ideal mixing law).<sup>24</sup> Similar results can be also derived from the measurements of quasielastic light scattering in *o*-terphenyl solutions.<sup>25,26</sup> In most cases, however, the composition dependence of fragility in binary solutions is not readily identified.<sup>27–30</sup> Recently, a theoretical work reported the calculation of the composition dependence of  $T_g$  and fragility on the basis of floppy mode densities,<sup>31</sup> but the experimental support for this approach is not straightforward.

In this work, we focus on the composition dependence of fragility indices and stretching exponents by choosing various miscible binary systems with ideal, intermediate, and complex mixing behavior. The component liquids are miscible without the formation of complexes. The dielectric measurements were applied, and the technique proves to work well to probe the mixing effect.<sup>5</sup> To obtain systematic and reliable results, an important goal is to accurately quantify fragilities for the binary systems of different mixing character. The studies are expected to provide information on the mixing effects on the dynamics of supercooled liquids. Additionally, the study of solutions is expected to shed light on the dynamics of some single component liquids, such as water or metallic melts, for which the vitrification requires the addition of a second component due to the extremely low glass forming ability.

## II. Experimental Section

Three groups of binary systems are chosen in this work, methyl-*m*-toluate (MMT 98% Alfa) in methyl *o*-toluate (MOT 99%, Alfa), methyl *m*-toluate in di-*n*-butyl phthalate (DnBP 99%, Alfa), and 1,2-propandiol (PDL 99.5%, Aldrich) in 2-ethylhexylamine (EHA 98%, Aldrich) to represent the weak, intermediate, and strong excess quantities upon mixing, respectively. MMT and MOT are isomers with similar molecular

\* To whom correspondence should be addressed. E-mail: Limin\_Wang@ysu.edu.cn.

<sup>†</sup> Yanshan University.

<sup>‡</sup> Arizona State University.

structure and polarity, and a weak intermolecular interaction is expected. MMT and DnBP are of homologous character, but different molecular size, and would generate an intermediate interaction. PDL and EHA are expected to have strong interaction due to the high negative heat of mixing between alcohols and amines.<sup>32</sup> We therefore use the three groups of solutions to mimic the ideal, near-ideal, and nonideal mixing cases. No further purification is done on the chemicals prior to the measurements.

The structural relaxation dynamics of binary glass forming solutions was studied by dielectric relaxation measurements, which proves to be reliable for characterizing the structural relaxations for simple molecular liquids.<sup>33</sup> The dielectric relaxation data are measured in two sets of apparatuses with frequency dependent impedance measurements, one being a Novocontrol broadband dielectric spectrometer (Concept 80), and the other Solartron 1260 gain-phase-analyzer equipped with a Mestec DM-1360 transimpedance amplifier and liquid nitrogen cooling system. The two dielectric systems have been described elsewhere.<sup>34,35</sup> The dielectric relaxation were isothermally measured at each temperature by holding liquid between two brass electrodes, which are separated by Teflon strips of thickness 25  $\mu\text{m}$ . The frequency range spans from 0.01 Hz to 10 MHz. The measurements start from a temperature of  $\sim 5$  K below  $T_g$  for each measurement, and temperature is controlled by a Novocontrol Quatro controller with temperature accuracy within 0.1 K. The measurements show remarkable repeatability.

The dielectric data are analyzed to obtain the dynamic parameters in terms of Havriliak–Negami (HN) equation<sup>36</sup>

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^\alpha]^\gamma} + \frac{\sigma_{dc}}{i\varepsilon_0\omega} \quad (1)$$

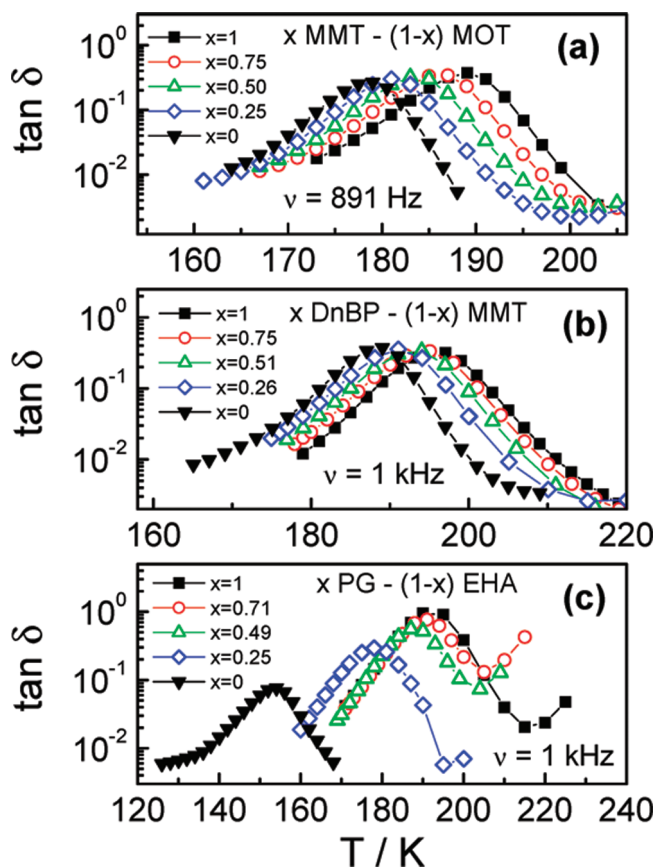
where  $\varepsilon_\infty$  is the dielectric constant in the high-frequency limit,  $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$  is the dielectric relaxation strength with  $\varepsilon_s$  being the steady state dielectric constant,  $\tau$  is the relaxation time,  $\alpha$  and  $\gamma$  are shape parameters, and  $\sigma_{dc}$  quantifies dc conductivity. The conversion of the HN exponents  $\alpha$  and  $\gamma$  to the nonexponential parameter  $\beta_{KWW}$  has been studied,<sup>37,38</sup> and in this paper,  $\beta_{KWW}$  is derived using the expression  $\beta_{KWW} = (\alpha\gamma)^{1/1.23}$ .<sup>38</sup>

### III. Results

Figure 1a–c presented the dielectric spectra in terms of  $\tan \delta = \varepsilon''/\varepsilon'$  of the three solutions, MMT–MOT, MMT–DnBP, and PG–EHA. The dielectric constants in MMT–MOT and MMT–DnBP solutions are seen to be similar. For the PG–EHA solutions, an increasing difference in  $\Delta\varepsilon$  is visible, and the dielectric constant as well as  $T_g$  changes significantly across the composition range. A single primary relaxation peak is clearly identified for each measurement in all the solutions, which facilitates the identification of structural relaxation parameters on the basis of the HN equation.

The use of eq 1 to fit to the dielectric data provides the dielectric relaxation times  $\tau$  and stretching exponents  $\beta_{KWW}$ . The temperature dependence of the relaxation time is shown in Figure 2a–c for the three solution systems.  $T_g$  is determined on the basis of a temperature at which relaxation time reaches  $\tau = 100$  s. Extrapolation of the data is implemented by fitting the Vogel–Fulcher–Tammann (VFT) equation to the experimental results,<sup>15</sup>

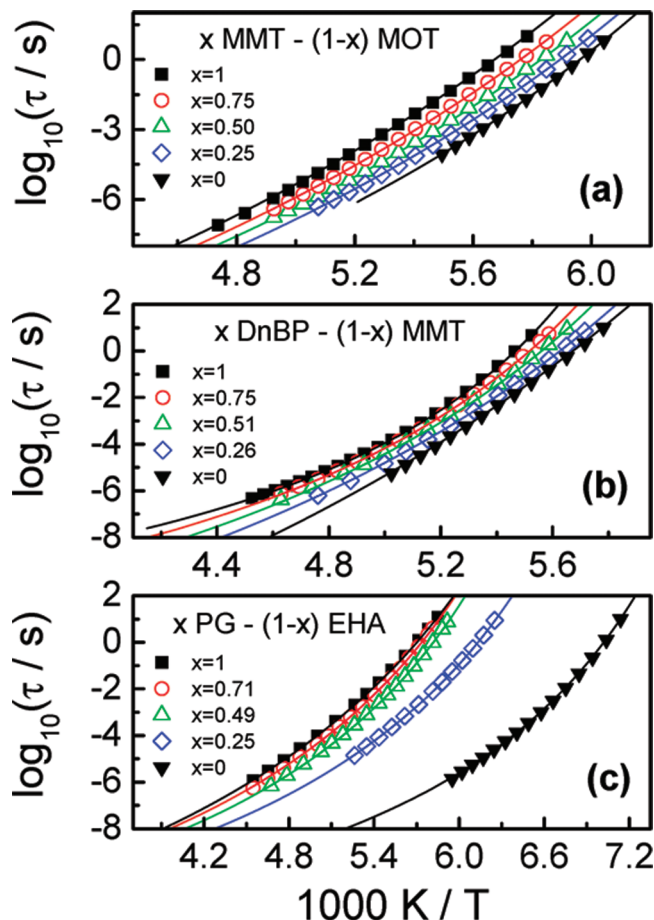
$$\tau = \tau_0 \exp[B/(T - T_0)] \quad (2)$$



**Figure 1.** Dielectric relaxation in terms of  $\tan \delta$  for three binary systems in their supercooled regimes, measured at a fixed frequency  $\nu \approx 1$  kHz. (a) Methyl *m*-toluate in methyl *o*-toluate, (b) MMT in di-*n*-butyl phthalate, and (c) 2-ethylhexylamine in propylene glycol. Compositions are identified by mole fractions.

where  $\tau_0$ ,  $B$  and  $T_0$  are constants and  $\tau_0$  is of the order of phonon times,  $\sim 10^{-14}$  s. The fitting results are represented by lines in the plots. The marked difference in relaxation dynamics can be seen in the three systems. The relaxation time in MMT–MOT solutions almost changes evenly upon mixing. For this system,  $\log(\tau_0/\text{s})$  is fixed at  $-22$  for the VFT fits to the data. This method has been used previously to determine fragility versus composition in binary solutions.<sup>22,30</sup> The fitting curves remain virtually parallel if the change in  $m$  is moderate. By comparison, the difference in curve shape is remarkable in MMT–DnBP solutions and increasing curvature is obvious from pure MMT toward higher DnBP content. For PG–EHA solution, the comparison is not straightforward due to the large  $T_g$  difference of the pure components. For the latter two systems, all the VFT parameters remain adjustable during fitting.

A detailed comparison of the curve profiles requires to calculate fragility index,  $m$ , which is determined with  $T_g$  values. In Figure 3 and 4, the composition dependence of  $T_g$  and  $m$  together with  $\beta_{KWW}$  are illustrated across the entire composition range. A slight negative deviation of  $T_g$  values in MMT–MOT solutions is observed relative to the ideal case, whereas in PG–EHA system, a pronounced increase in  $T_g$  is visible. It appears that no common trend in the composition dependence of  $T_g$  is accessible among the three systems. The same situation also occurs in the composition dependence of  $\beta_{KWW}$ , and a negative deviation of  $\beta_{KWW}$  is shown in MMT–DnBP solutions, while  $\beta_{KWW}$  increases in the other two solutions. Surprisingly, common to the three solution systems is that fragility indices  $m$  always display a negative deviation from the linear average



**Figure 2.** Thermal activation plots in three solution systems based on dielectric relaxation times. (a) Methyl *m*-toluate in methyl *o*-toluate, (b) MMT in di-*n*-butyl phthalate, and (c) 2-ethylhexylamine in propylene glycol. Compositions are identified by mole fractions. The lines represent VFT fits.

or ideal mixing law, which for any property  $P(x)$  as a function of mole fraction  $x$  reads

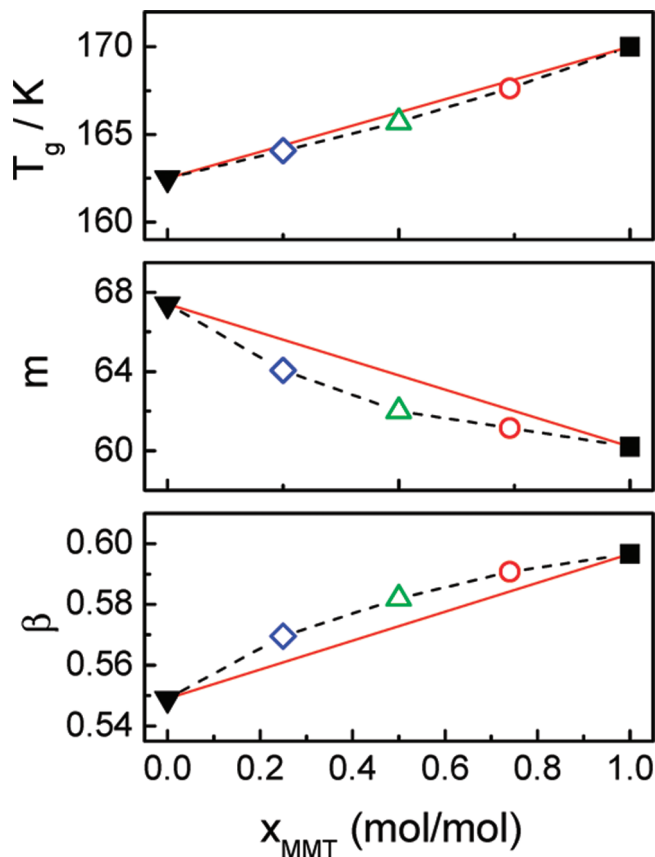
$$P(x) = xP(1) + (1 - x)P(0) \quad (3)$$

where  $P(1)$  and  $P(0)$  are the respective properties of the pure components. It needs to be noted that the error in  $T_g$ ,  $m$ , and  $\beta_{\text{KWW}}$  is negligible in regards to the present analyses.

#### IV. Discussion

**a. Composition Dependence of  $T_g$ .** The composition dependence of  $T_g$  has been extensively studied in associated and nonassociated liquids, indicating positive (i.e., an increase in  $T_g$ ), zero, and negative deviation from the linear compositional averages of the component  $T_g$ 's,<sup>39–42</sup> however the interpretations have not provided a complete understanding.<sup>11,12</sup> It has been pointed out that the glass transition temperature relates to the strengths and nature of the intermolecular interactions in the liquid state,<sup>43</sup> where strong intermolecular interaction/association could account for significant excess glass transition temperatures<sup>44</sup> with the implication of large mixing enthalpies.<sup>39,45</sup>

Alternatively, entropy has been emphasized in the studies of glass transition phenomenology, and an excess  $T_g$  is explained by a decrease of entropy.<sup>46–48</sup> Among isomers of the same intermolecular interaction nature, the difference in  $T_g$  is found to be dominated by entropy.<sup>49</sup> Experimental observations show

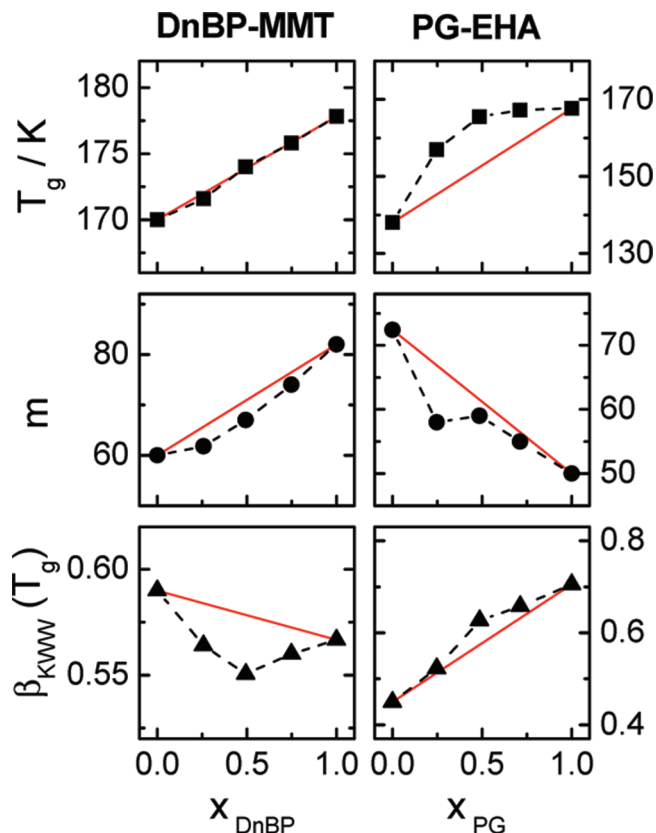


**Figure 3.** Composition dependence of glass transition  $T_g$ , fragility  $m$ , and relaxation dispersion parameter  $\beta_{\text{KWW}}$  in the solution system of methyl *m*-toluate in methyl *o*-toluate. The data are based on the dielectric relaxation measurements. The dashed lines represent ideal mixing laws.

that the pronounced positive deviation of  $T_g$  in mixtures is also generally accompanied by a negative mixing entropy,<sup>39,41,50</sup> suggesting the association of unlike components.<sup>43,45</sup> A recent molecular dynamic simulation study also found that the positive deviation of viscosity from the ideal mixing rule is associated with a negative deviation of configurational entropy.<sup>51</sup> By contrast, a negative excess  $T_g$  behavior like that shown for MMT–MOT solutions (Figure 3) has been reported only rarely.<sup>26,39,52</sup> According to Lesikar's studies, entropy-dominated mixing explains the negative deviation in  $T_g$ .<sup>39</sup> A transition from enthalpy- to entropy-dominated mixing will depend on the degree of similarity of the components with regards to structure and other properties.<sup>53</sup>

**b. Mixing Effect on Fragility.** To arrive at a definitive conclusion regarding the composition dependence of fragility, data of binary glass forming solutions studied previously were collected, and the available relevant data were analyzed. In Figure 5 we show the relative change of fragility  $m$  with composition in five systems, including the relative changes in  $T_g$ . The data of glycerol–sorbitol and 2-ethyl-1-hexanol in EHA are taken from previous publications.<sup>22,54</sup> Figure 5 highlights the fact that the mixing of miscible liquids indeed invariably generates a negative effect on fragility. The same behavior is also observed in experimental measurements of other binary molecular solutions such as mixtures with *o*-terphenyl,<sup>24–26</sup> even in inorganic systems.<sup>55,56</sup> It appears that this behavior differs qualitatively from the composition dependence of  $T_g$ , where both positive and negative deviations have been observed. We conclude that mixing miscible binary liquids leads invariably to the decrease of fragility relative to the linear average, eq 3,



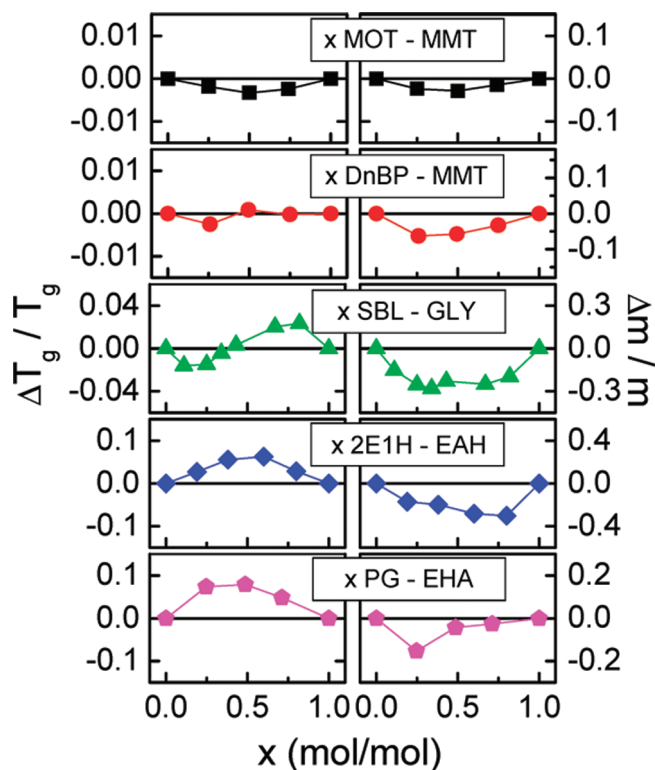


**Figure 4.** Composition dependence of glass transition  $T_g$ , fragility  $m$ , and relaxation dispersion parameter  $\beta_{KWW}$  in the two binary solution systems, methyl *m*-toluate in di-*n*-butyl phthalate and 2-ethylhexylamine in propylene glycol. The data are based on the dielectric relaxation measurements. The dashed lines represent ideal mixing laws.

of the properties of neat components. According to this conclusion, it is further inferred that the solutions with more than two components would probably produce stronger liquids within an Angell plot classification. This is indeed supported by the studies of bulk metallic glasses, where the fragility indices are found to decrease with an increasing number of metallic elements.<sup>57</sup> This also implies a kinetically driven increase of the glass forming ability in multicomponent alloys, because stronger liquids retain higher viscosities and slower diffusivities in much of their supercooled liquid regimes upon cooling.

Let us consider the following two scenarios, ideal and more complex mixing behavior. For the former case, a linear composition dependence of  $T_g$  is expected,<sup>39,58</sup> and the linear dependence of fragility is also observed experimentally.<sup>59</sup> The latter cases usually display a cusp in the composition dependence of  $T_g$ , which has been related to the formation of complexes.<sup>45</sup> However, an analysis of the composition dependence of fragility is usually not available for such systems. On the other hand, studies of glass forming molten salts (ionic liquids) may prove useful for assessing the fragility in cases of complex mixing behavior.<sup>60</sup> The same results might not be expected for the dynamics of binary polymeric blends, due to their complexity of the structural relaxation.

Liquid fragility is associated with thermodynamic properties,<sup>61</sup> and scales with the ratio of excess vibrational to configurational entropies.<sup>20,21</sup> If this link between dynamic and thermodynamic fragility applies to binary systems, the decrease in fragility index upon mixing miscible liquids means that mixing enhances the fraction of configurational degrees of freedom in the excess entropy of a liquid relative to the crystal. Further identification



**Figure 5.** The relative change of glass transition temperature ( $\Delta T_g / T_g$ ) and fragility ( $\Delta m / m$ ) with the composition in various binary glass forming liquids.  $\Delta$  refers to the difference between the actual value and the ideal mixing law. (a) Methyl *m*-toluate in methyl *o*-toluate; (b) MMT in di-*n*-butyl phthalate; (c) glycerol in sorbitol from ref 22; (d) 2-ethylhexanol in 2-ethylhexylamine from ref 54; (e) 2-ethylhexylamine in propylene glycol. Common to the systems is the negative excess fragility.

of the contribution of mixing to the configurational entropy would offer better insight into the dynamics in solutions.

Finally we address the composition dependence of the stretching exponent  $\beta_{KWW}$ . Intuitively, a broadening of the relaxation time dispersion is expected upon mixing on the basis of concentration fluctuations. For most liquid mixtures, spectral broadening (a decrease in  $\beta_{KWW}$ ) is experimentally observed. The studies of the solutions of intermediate departure from ideal mixing, such as glycerol–propylene glycol<sup>23,41</sup> and glycerol–sorbitol,<sup>22</sup> show a slightly negative effect regarding  $\beta_{KWW}$  (broadening). The same case can also be seen in MMT–DnBP systems. By contrast, an increase of  $\beta_{KWW}$  as shown in MMT–MOT (Figure 3) and PG–EHA (Figure 4) solutions is more unusual. Whereas the narrowing of the relaxation dispersion width in the PG–EHA systems is due to the strong interactions (similar behavior was reported in diol–amine solutions at high temperature<sup>62</sup>), the same reasoning for the narrowing behavior in MMT–MOT will not apply. The composition dependence of  $T_g$  in *o*-terphenyl/bis-cresol cyclohexane-dimethylether exhibits a negative effect,<sup>26</sup> indicating an entropy-dominant mixing similar to MMT–MOT. And a positive behavior (an increase in  $\beta_{KWW}$ ) is implied,<sup>26</sup> albeit with some uncertainty. As a consequence, the unique nonexponential dynamic character in the isomeric mixtures might not be a surprise. It seems that the relaxation time dispersion is not always subject to broadening when mixing two miscible liquids, and the results of concentration fluctuations can be compensated by other effects. It needs to be emphasized that for the entropy-dominant mixing, the change in  $\beta_{KWW}$  is small. By contrast, in the PG–EHA solutions, a change up to 10% in  $\beta_{KWW}$  is

observed. It is thus expected that for the enthalpy-controlled mixing effects, a transition from the negative to positive excess  $\beta_{\text{KWW}}$  might occur with increased nonideality regarding mixing.

## V. Concluding Remarks

The glass transitions and structural relaxation dynamics have been investigated in binary solutions that span the range from ideal mixing to complex mixing behavior, that is, from vanishing to significant excess quantities. The present study focuses on the composition dependence of fragility  $m$  and stretching exponent  $\beta_{\text{KWW}}$  in miscible binary systems. Remarkably, the fragility indices of the solutions are found to exhibit a negative deviation from ideality as a common signature of nonideal mixtures. This differs qualitatively from the composition dependence of the glass transition temperature  $T_g$  and the stretching exponent  $\beta_{\text{KWW}}$ , which are subject to both positive and negative deviations. The reduction of fragility index upon mixing becomes more pronounced as the degree of nonideal mixing increases. Thermodynamic studies of the glass transition in solutions, particularly those of configurational and excess vibrational entropy, are expected to yield important clues for rationalizing the composition dependence of the dynamics. Whether the correlations between dynamics and thermodynamic variables that have been established for single-component liquids apply equally to mixtures remains to be clarified by systematic investigations. To our knowledge, only few studies have emphasized these aspects.<sup>63,64</sup> Binary eutectic molecular alloys might be good candidates for exploring the thermodynamics of mixing, and we will focus on these in future studies.

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