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# Anomaly in dielectric relaxation dispersion of glass-forming alkoxy alcohols

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The dielectric relaxations in six primary and secondary alkoxy alcohols with varying molecular size and different separation between  $-O-$  and hydroxyl group are studied at temperatures around glass transition. The analyses of the apparent full width at half maximum of the main relaxations of the alkoxy alcohols reveal minima in the temperature dependence of the relaxation dispersions. The stretching exponents for the main relaxations of the alkoxy alcohols are also found not to follow the empirical correlations with other dynamic quantities established for generic liquids. A comparison of the relaxation dispersions in the alkoxy alcohols with those in Debye and non-Debye (generic) liquids is presented. The impacts of the  $\beta$ -relaxations on the apparent main relaxation widths are reviewed for molecular glass formers. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921941>]

## I. INTRODUCTION

The non-exponentiality is a common character of the structural relaxation in supercooled liquids, reflecting the heterogeneity in dynamics.<sup>1–5</sup> The non-exponential dynamics is usually expressed by the Kohlrausch-Williams-Watts (KWW) function in the time domain,  $\varphi = \exp[-(t/\tau_{\text{KWW}})]^{\beta_{\text{KWW}}}$ ,<sup>1</sup> where  $\beta_{\text{KWW}}$  is the non-exponential parameter (or stretching exponent), being a fraction of unity,  $1 \geq \beta_{\text{KWW}} > 0$ , and  $\tau_{\text{KWW}}$  is the relaxation time. Experimental measurements show that  $\beta_{\text{KWW}}$  of most molecular liquids generally does not exceed 0.75, and decreases or keeps constant as temperature decreases towards the glass transition temperature,  $T_g$ .<sup>6–9</sup> Yet, for some liquids, such as monoalcohols, exponential relaxation (or Debye-type,  $\beta_{\text{KWW}} = 1$ ) prevails showing the slowest relaxation time and the highest dielectric strength.<sup>10–15</sup> Accompanied by the Debye relaxation, a non-Debye relaxation is always observed, which has proven to be the “true” structural relaxation.<sup>16–19</sup> It is found that the structural relaxation is directly related to the viscous flow and calorimetric glass transition, while the Debye relaxation to the hydrogen-bonded associations.<sup>10,12,13</sup>

Our recent studies observed the Debye relaxation in the dielectric spectra of a sulfur substituted monoalcohol, 3-methylthiol-1-hexanol (3MT1H), where a  $-CH_2-$  group in the backbone of a monoalcohol is substituted by a sulfur atom. This suggests that the polarity increase imposed by the substitution of the alkyl chain by the alkylthio chain does not destroy the Debye relaxation.<sup>15</sup> Meanwhile, it is also found that the dynamic separation between the Debye and structural relaxations is greatly reduced, compared with its structurally similar monohydroxy alcohol of 2-ethyl-1-hexanol (2E1H). Oxygen and sulfur locate at the same group in the periodic table of elements, and alkoxy alcohols can be

envisioned as the substitution of a  $-CH_2-$  group by an oxygen atom in monoalcohols. Different from the sulfur substituted monoalcohols, alkoxy alcohols have been treated as generic liquids because no Debye relaxation is discernible.<sup>9</sup> Yet, the non-exponential parameters,  $\beta_{\text{KWW}}$  of such alcohols are often found to be relatively high when compared with the dielectric dispersion of other molecular glass formers with similar molecular structures.<sup>9,20,21</sup>

It is, therefore, of interest to inspect whether a Debye relaxation could be present in the dielectric spectra of alkoxy alcohols, so that the question as to whether there is continuity in dielectric spectra from monoalcohols,<sup>12</sup> sulfur substituted monoalcohols<sup>15</sup> to alkoxy alcohols can be answered. Considering the fact that the formation of the H-bonded associations in alkoxy alcohols can be modified markedly by the position of hydroxyl group, the length of molecular chain, and the relative position of  $-O-$  and  $-OH$ , an extensive study of alkoxy alcohols with varying structures would help to reveal the basic relation between the relaxation dispersions and molecular structures. In this paper, six alkoxy alcohols with varying molecular length and separation between  $-O-$  and  $-OH$  are selected to analyze the relaxation dispersions. The temperature dependence of the apparent main relaxation dispersion in the dielectric spectra of all the six alkoxy alcohols is found to share a common pattern with minima, indicative of the disturbance from other relaxation processes. The anomaly in the apparent  $\alpha$ -relaxation dispersion is explained, referring to the interference of  $\beta$ -relaxations.

## II. EXPERIMENTAL

Four glass forming alkoxy alcohols, 1-methoxy-2-propanol (1MO2P, Sigma-Aldrich 99.5%), 1-propoxy-2-propanol (1PO2P, Sigma-Aldrich 99%), 1-butoxy-2-propanol (1BO2P, TCI 95%), and 2-(2-ethylhexyloxy) ethanol (2EHOE,

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TABLE I. Molecular structures of six alkoxy alcohols, including three primary alkoxy alcohols and three secondary alkoxy alcohols.

Alkoxy alcohols	Molecular structure	References
Primary alkoxy alcohols		
3-methoxy-1-butanol (3MO1B) (C <sub>5</sub> H <sub>12</sub> O <sub>2</sub> )		21
2-isopropoxyethanol (2IPOE) (C <sub>5</sub> H <sub>12</sub> O <sub>2</sub> )		21
2-(2-ethylhexyloxy) ethanol (2EHOE) (C <sub>10</sub> H <sub>22</sub> O <sub>2</sub> )		This work
Secondary alkoxy alcohols		
1-methoxy-2-propanol (1MO2P) (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> )		This work
1-propoxy-2-propanol (1PO2P) (C <sub>6</sub> H <sub>14</sub> O <sub>2</sub> )		This work
1-butoxy-2-propanol (1BO2P) (C <sub>7</sub> H <sub>16</sub> O <sub>2</sub> )		This work

Sigma-Aldrich 97%) are measured without further purification. The data of 3-methoxy-1-butanol (3MO1B) and 2-isopropoxyethanol (2IPOE) are taken from Ref. 21. Table I presents the molecular structures of the six alkoxy alcohols. 3MO1B, 2IPOE, and 2EHOE are chosen as primary alkoxy alcohols with varying separation between –O– and –OH and different length of alkyl chains, while 1MO2P, 1PO2P, and 1BO2P are chosen as homologous series of secondary alkoxy alcohols with a fixed separation between –O– and –OH but varying molecular chain length to analyze the relaxation dispersion. To examine the dynamics of mixtures constituted by alkoxy alcohols and monoalcohols, the Debye liquid, 2-ethyl-1-hexanol (2E1H, Sigma-Aldrich 99%), is used.

The dielectric measurements in the frequency range between 0.01 Hz and 10 MHz are conducted in a Novocontrol broadband dielectric spectrometer (Concept 80) equipped with a liquid nitrogen cooling system. The dielectric relaxation is isothermally measured at each temperature by holding liquids between two separated brass electrodes by Teflon strips of 25  $\mu\text{m}$  thickness. The temperature is controlled by a Novocontrol Quatro controller with temperature accuracy within 0.1 K. The dielectric measurements of 1BO2P in a higher frequency range from 1 MHz to 3 GHz are conducted using the Agilent E4991A RF Impedance/Material Analyzer with two brass electrodes isolated by a Teflon ring of 100  $\mu\text{m}$  thickness.

The dielectric data are analyzed to obtain the dynamic parameters in terms of Havriliak-Negami (HN) expressions,<sup>22</sup>

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_i \frac{\Delta\varepsilon_i}{(1 + (i\omega\tau_i)^{\alpha_i})^{\gamma_i}} + \frac{\sigma_{dc}}{i\varepsilon_0\omega}, \quad (1)$$

where  $\varepsilon_\infty$  is the high-frequency dielectric constant,  $\Delta\varepsilon_i$  dielectric strength,  $\tau_i$  dielectric relaxation time,  $\alpha_i$  and  $\gamma_i$  profile shape factors of the relaxation dispersion for the  $i$ th dynamics.  $\sigma_{dc}$  is the dc conductivity. With  $\alpha = 1$ , the HN equation be-

comes Cole-Davidson (CD) equation while  $\gamma = 1$  leads to the Cole-Cole (CC) equation.

The reciprocal temperature dependence of the logarithmic relaxation time at the maximum loss of the main relaxation,  $\tau_{\max}$ , is described by the Vogel-Fulcher-Tammann equation (VFT),  $\log \tau_{\max} = A + B/(T - T_0)$ , where  $A$ ,  $B$ , and  $T_0$  are constants. The kinetic glass transition temperature  $T_{g\text{-die}}$  is defined by a temperature at which the relaxation time reaches 100 s. The kinetic fragility  $m$ -index can thus be calculated from the temperature dependence of the relaxation time,  $m = d \log_{10} \tau / d(T_g/T) |_{T=T_g}$ .<sup>2,23</sup>

The calorimetric glass transition temperatures,  $T_{g\text{-cal}}$ , and heat capacities,  $C_p$ , of the four alkoxy alcohols are determined by a Perkin-Elmer (PE) Diamond differential scanning calorimeter (DSC). The samples are initially quenched to the glass states at a cooling rate of 20 K/min, and then the calorimetric parameters are determined from the subsequent heating process at the same rate. The DSC is calibrated using indium and cyclohexane prior to the measurements.  $T_{g\text{-cal}}$  is defined as the onset temperature of heat capacity increment from the glassy to the liquid state. Based on the glass transition  $C_p$  curves, the fictive temperature,  $T_f$ , of the liquids and glasses can be calculated in terms of Moynihan's method,<sup>24,25</sup>

$$\int_{T^*}^{T_f} (C_{p\text{-liquid}} - C_{p\text{-glass}}) dT = \int_{T^*}^T (C_p - C_{p\text{-glass}}) dT. \quad (2)$$

Where  $T^*$  is an arbitrary temperature above  $T_g$ ,  $C_{p\text{-liquid}}$  and  $C_{p\text{-glass}}$  denote the heat capacity of liquid and glassy states, respectively. The normalized  $C_p$ ,  $C_{p\text{-normalized}}$ , is equivalent to the derivative of the fictive temperature  $T_f$  in terms of

$$C_{p\text{-normalized}} = (C_p - C_{p\text{-glass}}) / (C_{p\text{-liquid}} - C_{p\text{-glass}}) = dT_f / dT. \quad (3)$$

The non-exponential ( $\beta_{\text{TNMH}}$ ) and non-linear ( $x$ ) factors can be derived from  $dT_f/dT$  using the Tool-Narayanaswamy-Moynihan-Hodge (TNMH) formalism,<sup>24,26–30</sup>

$$T_f = T(t_0) + \int_{t_0}^t \{1 - \exp[-(\int_{t'}^t \frac{1}{\tau} dt'')^{\beta_{\text{KWW}}}] \} q dt', \quad (4)$$

$$\tau = \tau_0 \exp\left(\frac{xh^*}{RT} + \frac{(1-x)h^*}{RT_f}\right), \quad (5)$$

where  $h^*$  is the glass transition activation energy,  $x$  is the nonlinear parameter with  $1 \geq x > 0$ , and  $q$  is the cooling/heating rate. Prior to the application of the TNMH model,  $h^*$  is determined from the formula,  $h^* = RT_g m_{\text{cal}} \ln 10$ ,<sup>25</sup> in which  $m_{\text{cal}}$  is determined from the calorimetric measurement based on the dependence of  $T_f$  on the cooling rate.<sup>31</sup> For generic liquids,  $m_{\text{cal}}$  is proven to match well with the  $m$  value determined by the dielectric relaxation.<sup>25</sup> Consequently, calorimetric measurements can give an independent evaluation of the dynamic parameters, where the reliable  $h^*$  values for the alkoxy alcohols can be guaranteed without referring to the dielectric measurements.

### III. RESULTS AND DISCUSSION

Fig. 1 presents the dielectric loss spectra of two typical examples of a primary and a secondary alkoxy alcohol, 2-(2-ethylhexyloxy) ethanol and 1-butoxy-2-propanol, in the temperature regions around the glass transition. The fits to the main relaxation peaks of the two alkoxy alcohols are made using the one-sided Fourier transform of the KWW equation and the HN equation.<sup>32,33</sup> Apparently, the optimal KWW equation works, giving  $\beta_{\text{KWW}} = 0.75$  and  $0.84$  for 2EHOE at 177 K and 1BO2P at 162 K. However, close inspection finds that the KWW fitting curves interpolate only a few data points on the right frequency flank of the maxima. In contrast, the fitting using the HN equation might cover more data of the right flank, yielding relatively small  $\beta_{\text{KWW}}$  values, yet, the fitting could become somehow arbitrary. The two fitting models show the  $\beta$ -relaxation in the high frequency flank. However, the evaluation of the influence of the  $\beta$ -relaxation on the apparent main relaxation width appears to depend on the applied fitting models. The arrows in Fig. 1 show the possible positions of Johari-Goldstein (JG)  $\beta$ -relaxations predicted by the coupling model,<sup>34</sup>  $\tau_{\beta\text{-JG}} \approx t_c^{(1-\beta_{\text{KWW}})} \tau_{\alpha}^{\beta_{\text{KWW}}}$ , where  $t_c$  is a constant of 2 ps.

In order to determine the profiles of the relaxation dispersion model independently, we use the normalized width  $w$ ,  $w = W/W_D$ , where  $W$  denotes the full width at half maximum (FWHM) of  $\epsilon''$ , and  $W_D$  the Debye width, as applied in an earlier literature.<sup>35</sup> Fig. 2 shows the temperature dependence of the apparent dielectric dispersion for the main relaxations of the alkoxy alcohols. Close inspection shows that the relaxation width is dependent on the molecular structure. For example, when comparing the structures of the isomeric 3MO1B and 2IPOE where the carbon atom number of the backbone and the hydroxyl group position are fixed, as shown in Table I, one can see a decrease in  $w$  for 3MO1B. This might arise from the increased separation between the hydroxyl group and  $-\text{O}-$  group. In addition, for the three secondary alkoxy

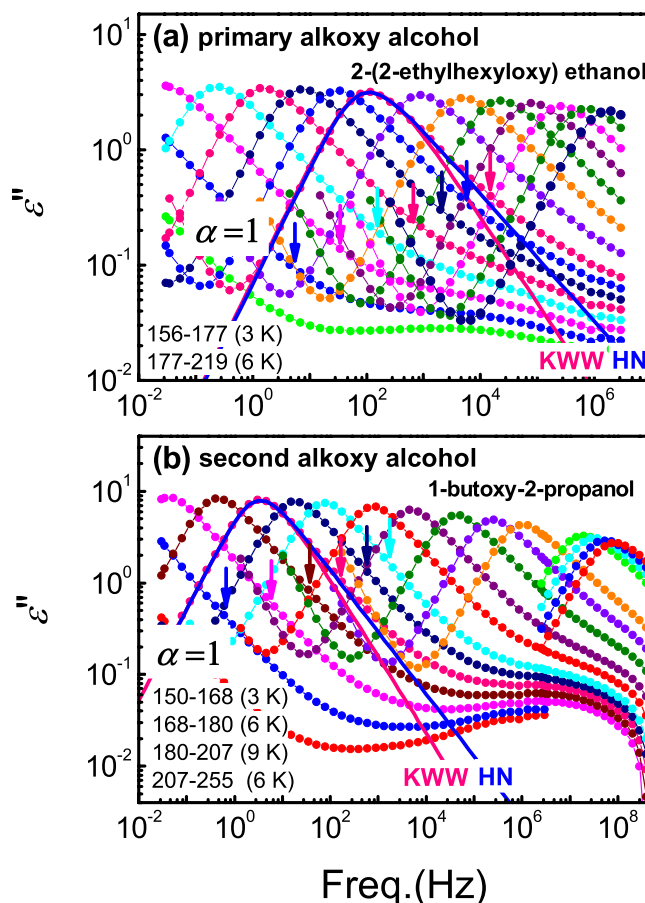


FIG. 1. Isothermal dielectric loss spectra of a primary alkoxy alcohol, 2-(2-ethylhexyloxy) ethanol (2EHOE), and a secondary alkoxy alcohol, 1-butoxy-2-propanol (1BO2P). (a) The  $\epsilon''$  dependences for 2EHOE were collected during heating from 156 to 219 K with frequency ranging from 0.01 Hz to 10 MHz. (b) The  $\epsilon''$  dependences for 1BO2P were collected at temperatures from 150 to 207 K in a lower frequency range from 0.01 Hz to 10 MHz, and from 159 to 255 K in a higher frequency range from 1 MHz to 3 GHz. The pink and blue solid lines represent the fitting curves using the KWW and HN equations to the measurement results at 177 K for 2EHOE and 162 K for 1BO2P. The vertical arrows indicate the possible frequencies of the JG  $\beta$ -relaxations predicted by the coupling model.

alcohols where the separation is fixed while the length of the alkoxy group increases in the order of 1MO2P, 1PO2P, and 1BO2P,  $w$  is observed to roughly increase. The same trend is also observed when comparing two primary alkoxy alcohols of 2IPOE and 2EHOE with different length of the alkyl groups. It is therefore inferred that the position and surrounding of the hydroxyl group in the molecular structures of alkoxy alcohols would be critical for the main relaxation profiles.

Inspection of Fig. 2 also shows minima in the temperature dependence of the apparent main relaxation dispersions for all the six alkoxy alcohols. This is quite different from the majority of generic non-Debye liquids, where the normalized width  $w$  generally either decreases or keeps constant as temperature increases.<sup>6–9,36–38</sup> The minimum behaviors suggest that the main relaxation dispersion must be affected by other relaxations immediately adjacent to it in the dielectric spectra of alkoxy alcohols. Two scenarios should be involved: the strong secondary ( $\beta$ -) relaxation at high frequency side or the Debye relaxation at low frequency side. Fig. 2 also



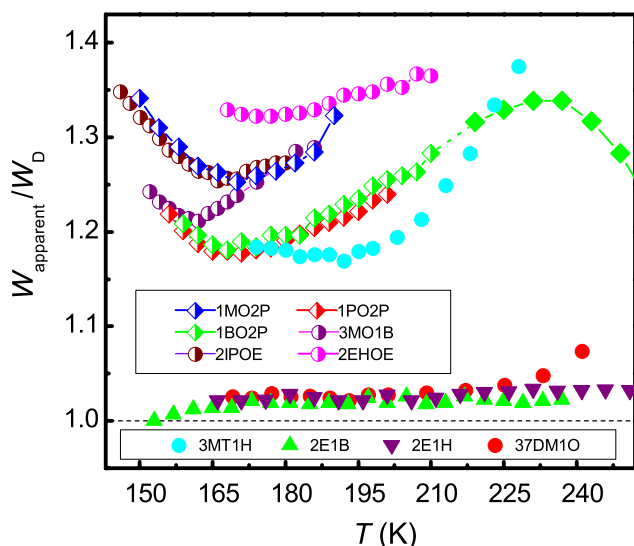


FIG. 2. Temperature dependence of the apparent normalized width,  $w = W_{\text{apparent}}/W_D$ , of the main relaxation dispersion for the six alkoxy alcohols, including three primary alkoxy alcohols 3-methoxy-1-butanol (3MO1B), 2-isopropoxyethanol (2IPOE), 2-(2-ethylhexyloxy) ethanol (2EHOE), and three secondary alkoxy alcohols, 1-methoxy-2-propanol (1MO2P), 1-propoxy-2-propanol (1PO2P), 1-butoxy-2-propanol (1BO2P).  $W$  is the full width at half maximum of  $\varepsilon''$  and  $W_D$  is the Debye relaxation width. For comparative analysis, the apparent normalized widths of Debye relaxation in four Debye liquids, 2-ethyl-1-butanol (2E1B),<sup>39</sup> 2-ethyl-1-hexanol (2E1H),<sup>40</sup> 3,7-dimethyl-1-octanol (37DM1O),<sup>40</sup> and 3-methylthio-1-hexanol (3MT1H),<sup>15</sup> are included.

shows the normalized FWHMs of the apparent main relaxations for 3-methylthiol-1-hexanol and three monoalcohols with different dynamic separations between the Debye and  $\alpha$ -relaxations.<sup>15,39,40</sup> It is interesting to see that  $w$  for alkoxy alcohols (oxygen substituted alcohols) and 3-methylthiol-1-hexanol (a sulfur substituted alcohol) has similar temperature dependences manifesting the minima behaviors. By contrast,  $w$  for the monoalcohols with the carbon number smaller than 11 are close to unity, and the slight deviation from unity should be ascribed to the interference of  $\alpha$ -relaxations.

The similarity of the minimum behaviors in the apparent main relaxation width for the alkoxy alcohols and 3-methylthiol-1-hexanol might imply the presence of Debye relaxation in the dielectric spectra of the alkoxy alcohols. There is no effective method to identify the presence of the Debye relaxation in the dielectric spectra of alkoxy alcohols. Two empirical relations have been established for the Debye relaxation based on the dielectric studies of monoalcohols.

First, studies show that  $T_g$  and  $\beta_{\text{KWW}}$  determined by the Debye relaxations in Debye liquids are generally larger than the results of calorimetric measurements.<sup>41</sup> Fig. 3 presents the glass transition heat capacity curves for 2EHOE, 1MO2P, 1PO2P, and 1BO2P with  $T_{g-\text{cal}}$  being marked. The insets of Fig. 3 show the temperature dependence of the dielectric relaxation time, from which  $T_{g-\text{die}}$  and fragility  $m$ -index are determined.  $T_{g-\text{die}}$  is seen not to be greater than  $T_{g-\text{cal}}$  for the alkoxy alcohols, which is not consistent with the empirical relation. Note that the inconsistency might not mean the absence of the Debye relaxation since when the Debye and  $\alpha$ -relaxations are in close proximity, the previously established relation will not be applicable.<sup>15</sup> The fits to the

normalized  $C_p$  curves by the TNMH equations are given in Fig. 4, yielding  $\beta_{\text{TNMH}}$  and  $x$  values of the four alkoxy alcohols. The non-exponential parameter  $\beta_{\text{KWW-die}}$  can be converted from the normalized dielectric relaxation width  $w$  based on the conversion of  $(1 - \beta) = 1.047(1 - w^{-1})$ .<sup>35</sup> Fig. 5 compares  $\beta_{\text{KWW-die}}$  and  $\beta_{\text{TNMH}}$  for the alkoxy alcohols. The data for Debye liquids<sup>15,41</sup> and generic liquids with<sup>9,32,41-46</sup> and without<sup>41</sup> resolved  $\beta$ -relaxation are also shown.  $\beta_{\text{KWW-die}}$  of the  $\alpha$ -relaxations for both Debye liquids and generic liquids is found to largely follow the master line. The three points with large deviation (up triangle) might be explained by the experimental observation of the strong  $\beta$ -relaxation in the dielectric spectra. In contrast,  $\beta_{\text{KWW-die}}$  of alkoxy alcohols are generally higher than the master line, which, again, shows the unusual of the dielectric relaxation dispersion. The values of  $T_g$ ,  $m$ , and  $\beta$  of the six alkoxy alcohols measured from the kinetic (dielectric relaxation) and calorimetric (enthalpy relaxation) measurements are listed in Table II.

Second, our studies of the dielectric relaxation of the mixtures composed of two primary monoalcohols found that the Debye relaxation time followed the ideal mixing rule.<sup>47</sup> Fig. 6 presents the dielectric relaxation measured around 181 K for the mixtures composed of a Debye-type primary monoalcohol (2E1H) and a primary alkoxy alcohol (2EHOE). The reciprocal temperature dependences of the relaxation times of the main relaxations are presented in Fig. 7 for the mixtures. The dashed line in Fig. 7 denotes the calculated relaxation time of 2EHOE in terms of the ideal mixing rule using the Debye relaxation times of 2E1H and the 79 mol. % 2E1H mixture. It appears that the calculated relaxation time of 2EHOE does not match with the experimental result. It also needs to be noted that the ideal mixing rule of the Debye relaxations might not be followed in the mixtures composed of two different types of Debye liquids.

Since the present results do not show direct signals of the Debye relaxations in the dielectric spectra of the alkoxy alcohols, the minima behavior in the temperature dependence of  $w$  for the main relaxation might also be expected to be generated by the  $\beta$ -relaxation. Fig. 8 summarizes the temperature dependence of normalized FWHMs,  $w$ , of the apparent  $\alpha$ -relaxations for generic liquids with excess wing (type A) and well-resolved  $\beta$ -relaxation (type B). Fig. 8(a) gives the normalized  $w$  for four type-A liquids represented by propylene glycol,<sup>6</sup> glycerol,<sup>36</sup> propylene carbonate,<sup>48</sup> and 2-picoline,<sup>49</sup> showing decreased  $w$  with temperature, indicative of a routine mode.<sup>8,9,38</sup> Fig. 8(b) outlines the reported temperature dependence of  $w$  in generic liquids with resolved  $\beta$ -relaxation, which can be divided into three categories. The first category shows increased  $w$  with temperature involving glass-formers such as cyclohexyl acetate,<sup>50</sup> D-sorbitol,<sup>51</sup> 4,7,10-trioxatridecane-1,13-diamine,<sup>38</sup> xylitol,<sup>38</sup> decahydroisoquinoline,<sup>38,52</sup> and toluene.<sup>49</sup> Three common features can be summarized for such glass-formers. First,  $w$  at  $T_g$  is always large ( $>1.8$ ), indicative of the wide relaxation. Second, all the glass-formers have strong  $\beta$ -relaxations, which are considered as the cause for the broadening of the apparent main relaxation dispersions. Third, fits of the HN equation to the dielectric spectra often find  $\alpha_{\text{HN}} < 1$  for the  $\alpha$ -relaxation and, for example, the  $\alpha_{\text{HN}}$  values are 0.8 and 0.73 for sorbitol and decahydroisoquinoline (DHIQ).<sup>9</sup> The second category of

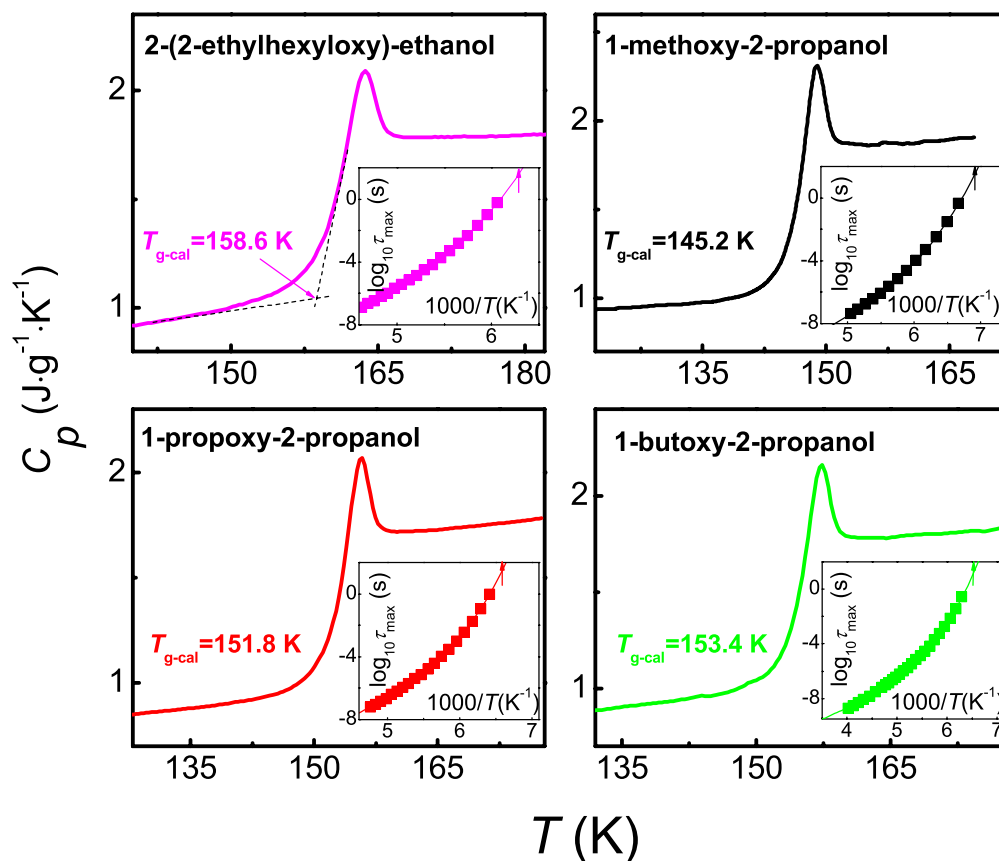


FIG. 3. Heat capacity,  $C_p$ , curves of 2-(2-ethylhexyloxy) ethanol (2EHOE), 1-methoxy-2-propanol (1MO2P), 1-propoxy-2-propanol (1PO2P), and 1-butoxy-2-propanol (1BO2P).  $T_{g\text{-cal}}$  denotes the calorimetric glass transition temperature. The insets show the activation plots of the main relaxations of four alkoxy alcohols.  $T_{g\text{-cal}}$ s are marked in the insets by vertical arrows.

glass-formers in Fig. 8(b) shows decreased or constant  $w$ , involving glass-formers such as 2-ethylhexanal,<sup>50</sup> methyl-m-toluate,<sup>42</sup> di-n-butyl phthalate,<sup>21</sup> and triacetin.<sup>53</sup> This category counts most of liquids with resolved  $\beta$ -relaxation with  $w$  of the

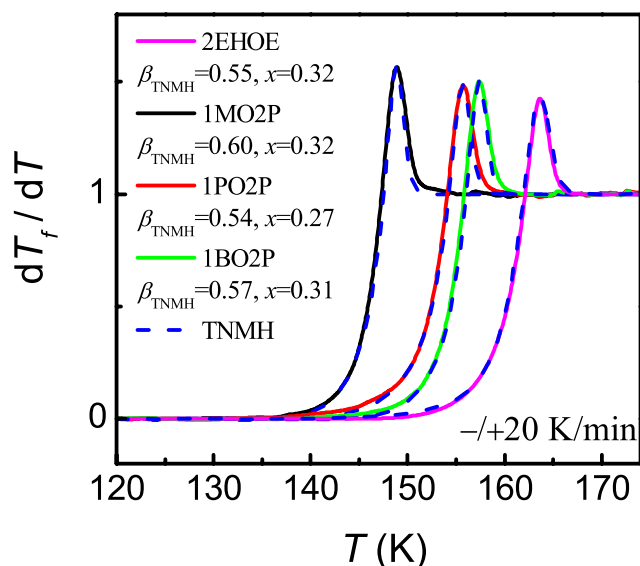


FIG. 4. Normalized heat capacity curves,  $dT_f/dT$ , of 2-(2-ethylhexyloxy) ethanol (2EHOE), 1-methoxy-2-propanol (1MO2P), 1-propoxy-2-propanol (1PO2P), and 1-butoxy-2-propanol (1BO2P). The nonlinear ( $x$ ) and stretching exponent ( $\beta_{\text{TNMH}}$ ) parameters obtained from the fitting results using the TNMH model are shown.

main relaxation at  $T_g$  generally smaller than 1.8. In addition, Fig. 8(b) also exhibits one more type of glass-formers, which usually show maxima in the temperature dependence of  $w$ , as pointed out by Dyre's group using the minimum slopes in the log-log plot of loss spectra of the  $\alpha$ -relaxation.<sup>54</sup> This category includes liquids such as dicyclohexyl-2-methylsuccinate,<sup>38,54</sup> dipropylene-dimethylglycol-dimethylether,<sup>38,54</sup> phenolphthalein-dimethylether,<sup>38,54</sup> and 4 *tert*-butyl pyridine (4-TBP).<sup>55</sup>

Interestingly, different from the hitherto reported scenarios of the temperature dependence of the apparent main relaxation width (Fig. 8), the alkoxy alcohols exhibit a distinctive mode with the minimum  $w$ , as plotted in Fig. 2. To our knowledge, similar behavior is only observed in sucrose benzoate among generic liquids, as denoted by the royal stars in Fig. 8(b).<sup>38</sup> If the  $\beta$ -relaxations are considered to be responsible for the minimum behavior for the apparent main relaxation dispersions, it is reasonably imagined that the broadening degree depends definitely on the  $\beta$ -relaxation strength and the separation between the  $\alpha$ - and  $\beta$ -relaxations. For glass formers where the disturbance of  $\beta$ -relaxation on apparent main relaxation dispersion is negligible, the intrinsic decrease in relaxation width ( $w$ ) is expected, and an eventual Debye relaxation ( $w = w_D$  or  $\beta_{\text{KWW}} = 1$ ) is reached.<sup>9</sup> If no other relaxation than  $\alpha$ - and  $\beta$ -relaxations is involved in the measured temperature regimes for the alkoxy alcohols, the minimum behaviors of  $w$  of the apparent main relaxation

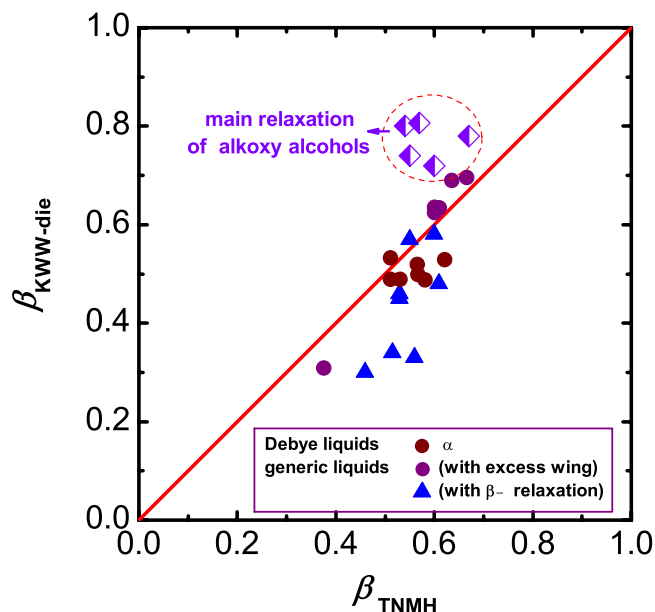


FIG. 5. Correlation between the non-exponential parameters obtained from dielectric ( $\beta_{\text{KWW-die}}$ ) and enthalpy ( $\beta_{\text{TNMH}}$ ) measurements for the alkoxy alcohols except 2IPOE. The master line represents  $\beta_{\text{TNMH}} = \beta_{\text{KWW-die}}$ . Some Debye liquids and generic liquids are also presented. The data for generic liquids with resolved  $\beta$ -relaxations are shown by blue triangle, including decahydroisoquinoline,<sup>41</sup> 2-ethylhexylamine,<sup>41</sup> di-n-butyl phthalate,<sup>41</sup> methyl-m-toluate (MMT),<sup>42</sup> xylitol,<sup>9,43</sup> glucose,<sup>44,45</sup> fructose,<sup>44,45</sup> and D-arabinose.<sup>32,46</sup>

dispersions should be a consequence of the balance between the intrinsic decrease in  $w$  of  $\alpha$ -relaxations and broadening effect generated by  $\beta$ -relaxations. It is seen in Fig. 1 that at low temperatures the resolved  $\beta$ -relaxations of the alkoxy alcohols are quite weak. For simplicity, when fitting the dielectric spectra using the combination of CD (for  $\alpha$ -relaxations) + CC (for  $\beta$ -relaxations) modes, the fast change in both  $\beta$ -relaxation strength (increase) and  $\beta$ -relaxation width (reduction) is yielded as the temperature exceeds  $T_g$ . It needs to be pointed out that the resolved  $\beta$ -relaxations do not coincide

TABLE II. Glass transition parameters determined by calorimetric and dielectric measurements for six alkoxy alcohols. The calorimetric values of  $T_{g\text{-cal}}$  are determined with cooling/heating rates of  $\pm 20$  K/min while the kinetic  $T_{g\text{-die}}$  is obtained based on the relaxation time at the maximum dielectric loss for the main relaxation,  $\tau_{\text{max}}$ , reaching 100 s.  $m$  denotes the fragility parameter.  $\beta_{\text{KWW-die}}$  is the stretching parameter converted from the relaxation dispersion width in the dielectric loss spectra, and  $\beta_{\text{TNMH}}$  is determined in terms of the TNMH model.

	$T_g$ (K)		$m$		$\beta(T_g)$	
	$T_{g\text{-die}}$	$T_{g\text{-cal}}$	$m_{\text{die}}$	$m_{\text{cal}}$	$\beta_{\text{KWW-die}}$	$\beta_{\text{TNMH}}$
3MO1B	145.3 <sup>a</sup>	146.9 <sup>a</sup>	62 <sup>a</sup>	...	0.78 <sup>b</sup>	0.67 <sup>a</sup>
2IPOE	141 <sup>c</sup>	...	69 <sup>c</sup>	...	0.71 <sup>b</sup>	...
2EHOE	157.9	158.6	58	73	0.74	0.55
1MO2P	143.6	145.2	63	73	0.72	0.60
1PO2P	150.6	151.8	67	75	0.80	0.54
1BO2P	151.9	153.4	68	78	0.81	0.57

<sup>a</sup>The data are taken from Ref. 41.

<sup>b</sup>Note that the values are a bit larger than the reported value in Ref. 9 determined from Havriliak-Negami equation.

<sup>c</sup>The data are taken from Ref. 9.

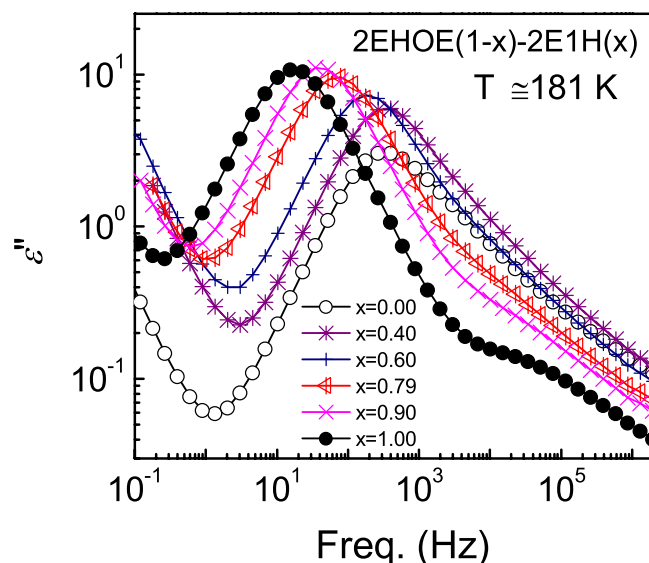


FIG. 6. Isothermal dielectric loss spectra recorded around 181 K for 2EHOE, 2E1H, and their mixtures at various compositions.  $x$  represents the mole fraction of 2E1H.

with the JG  $\beta$ -relaxations predicted by coupling model (Fig. 1). If the JG  $\beta$ -relaxations are considered for the broadening of the main relaxation of the alkoxy alcohols, the case would become more complicated.

The dielectric spectra of 1BO2P in the higher frequency ranging from 1 MHz to 3 GHz are also presented in Fig. 1(b), and not all of the measurements are shown to avoid crowding. The corresponding temperature dependence of the normalized FWHMs is plotted in Fig. 2 with green solid diamonds.  $w$  is seen to initially increase with temperature till  $\sim 237$  K, following the temperature dependence determined by the low frequency measurements, subsequently to decrease. The maximum behavior is similar to the observation in Dyre's group,<sup>54</sup> showing the critical temperature where the strongest

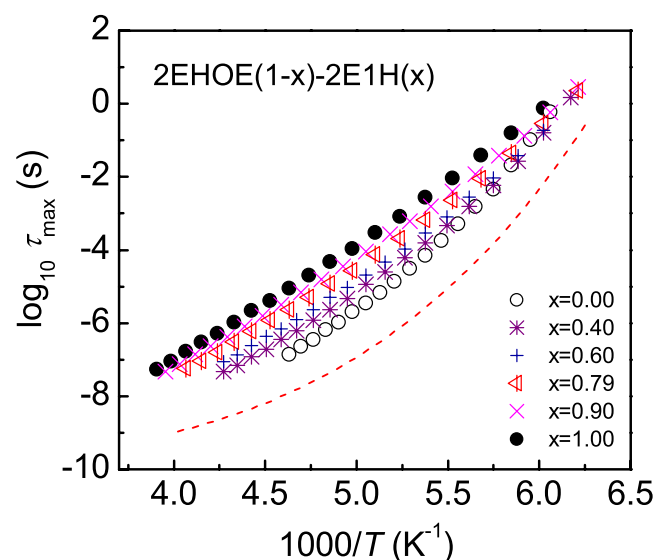


FIG. 7. Activation plots of the Debye relaxation (for  $x > 0.50$ ) and main relaxation (for  $x < 0.50$ ) for 2EHOE, 2E1H, and their mixtures at various compositions. The dashed line represents the predicted Debye relaxation time of 2EHOE from the mixtures of  $x = 0.79$  based on the ideal mixing rule.  $x$  represents the mole fraction of 2E1H.

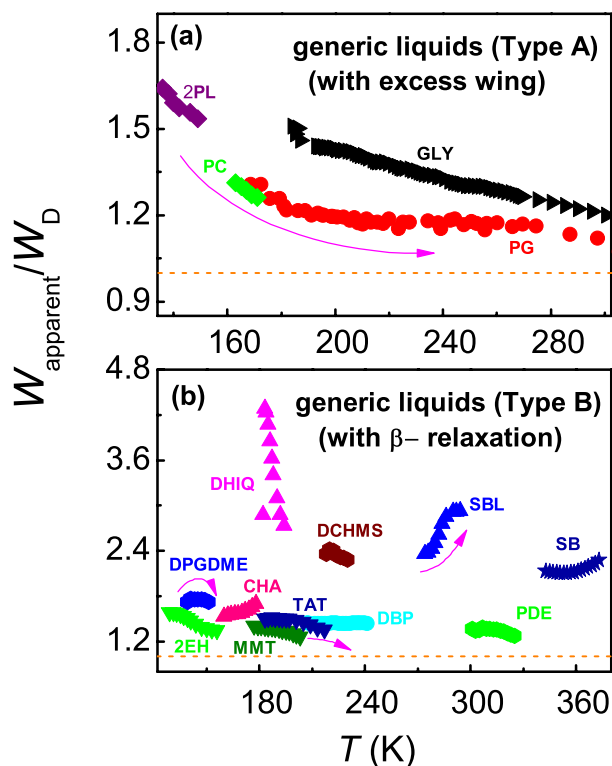


FIG. 8. Temperature dependence of the apparent  $w$  values of the main dielectric relaxations for generic liquids (type A) with excess wing (a), and generic liquids (type B) with resolved  $\beta$ -relaxation (b). The generic liquids (type A) include propylene glycol (PG),<sup>6</sup> glycerol (GLY),<sup>36</sup> propylene carbonate (PC),<sup>48</sup> and 2-picoline (2PL).<sup>49</sup> The generic liquids (type B) include 2-ethylhexanal (2EH),<sup>50</sup> D-sorbitol (SBL),<sup>51</sup> cyclohexyl acetate (CHA),<sup>50</sup> methyl-m-toluate (MMT),<sup>42</sup> triacetin (TAT),<sup>53</sup> di-n-butyl phthalate (DBP),<sup>21</sup> decahydroisoquinoline (DHIQ),<sup>52</sup> dipropylene-dimethylglycol-dimethylether (DPGDME),<sup>38,54</sup> dicyclohexyl-2-methyl-succinate (DCHMS),<sup>38,54</sup> phenolphthalein-dimethylether (PDE),<sup>38,54</sup> and sucrose benzoate (SB).<sup>38,54</sup>

interference of the  $\beta$ -relaxation on the apparent  $\alpha$ -relaxation width. It is noted that at 237 K, the relaxation time of 1BO2P arrives at  $\sim 1$  ns, and the maximum broadening at the temperature therefore suggests that the  $\beta$ -relaxation still has a marked effect on the apparent  $\alpha$ -relaxation dispersion.

Another dynamic feature of the alkoxy alcohols is the narrow dielectric relaxation dispersion. The low  $w \sim 1.15$ -1.4 or the high  $\beta_{\text{KWW}}$  of the alkoxy alcohols also reminds one of some dynamically strong H-bond liquids such as propylene glycol and glycerol. For the latter liquids, the disturbance of the  $\beta$ -relaxation is quite weak within the whole temperature region, as exhibited in Fig. 8(a). This appears to be quite different from the case for the alkoxy alcohols. Additionally, earlier studies show that  $\beta_{\text{KWW}}$  of the  $\alpha$ -relaxations for most generic glass forming liquids is correlated with kinetic fragility (Böhmer's correlation).<sup>7</sup> Fig. 9 re-plots Böhmer's correlation using the dielectric and calorimetric  $\beta_{\text{KWW}}$  of the alkoxy alcohols. Similar to Fig. 8,  $\beta_{\text{KWW-die}}$  shows a pronounced deviation, whereas  $\beta_{\text{TNMH}}$  works. Some Debye liquids<sup>15,41</sup> and generic liquids with<sup>7,9,21,32,41-46,52,56-71</sup> and without<sup>41</sup> well-resolved  $\beta$ -relaxation are also shown in Fig. 9. The data are seen to generally fall in the area defined by Böhmer's correlation, indicating for most glass formers with well-resolved  $\beta$ -relaxation that the presence of the  $\beta$ -relaxations

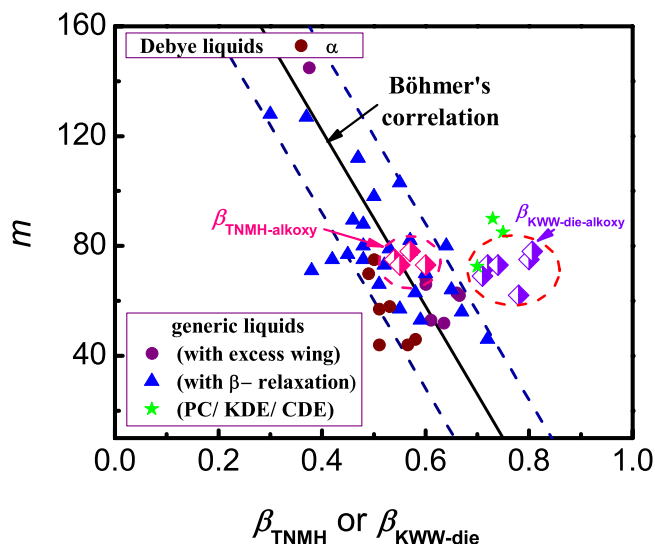


FIG. 9. Böhmer's correlation between kinetic fragility  $m$  and stretching exponent  $\beta_{\text{TNMH}}$  or  $\beta_{\text{KWW-die}}$ . The black solid line and blue dashed lines represent the original Böhmer's correlation with the uncertainty. Some Debye liquids and generic liquids are also shown. Generic liquids with resolved  $\beta$ -relaxations include those mentioned in Fig. 5 and sucrose benzoate,<sup>7</sup> D-sorbitol,<sup>56</sup>  $m$ -toluidine,<sup>9</sup> toluene,<sup>9</sup>  $o$ -terphenyl,<sup>57</sup> butyronitrile,<sup>58</sup> squalane,<sup>52</sup> 3-dimethylamino-1-propanol,<sup>9</sup> threitol,<sup>59,60</sup> diethyl phthalate,<sup>61,62</sup> di-iso-butyl phthalate,<sup>21,63</sup> 3-fluoroaniline,<sup>9,64</sup> tri-propylene glycol,<sup>9,65</sup> bis-5-hydroxypentylphthalate,<sup>9,66</sup> 4-methylheptane,<sup>67</sup> 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane,<sup>9,68</sup> 2-methyl-tetrahydrofuran,<sup>69</sup> dioctyl phthalate,<sup>66,70</sup> and salol.<sup>44,71</sup> Three generic liquids with high  $\beta_{\text{KWW-die}}$ , including propylene carbonate (PC),<sup>73</sup> phenolphthalein-dimethylether (PDE),<sup>73</sup> and KDE,<sup>73</sup> are shown as green stars.

does not lead to large deviation of  $\beta_{\text{KWW-die}}$  of the  $\alpha$ -relaxations from the correlation. Again, the unusual behavior of  $\beta_{\text{KWW-die}}$  for the alkoxy alcohols can be seen from Fig. 9. Note that some glass forming liquids,<sup>34</sup> such as propylene carbonate (PC),<sup>72</sup> phenylphthalate dimethylether (PDE),<sup>73,74</sup> and cresolphthalate dimethylether (KDE),<sup>75</sup> also show higher  $\beta_{\text{KWW}}$  obtained from dielectric relaxation than those from other techniques such as light scattering and mechanical shear modulus even for the dielectric modulus  $M^*(\omega)$  transformed from dielectric susceptibility,  $\epsilon^*(\omega)$ , and markedly deviate from Böhmer's correlation, as shown in Fig. 9. Apparently, the three liquids share the same feature as the alkoxy alcohols in Fig. 9, however, the relaxation width of the three liquids continuously decreases or keeps constant with temperature, like typical generic liquids.

#### IV. CONCLUSIONS

The dielectric relaxations of six glass-forming alkoxy alcohols are studied at temperatures around the glass transition. No direct evidence is exhibited for the Debye relaxation in the dielectric spectra of alkoxy alcohols, and no continuity in the dielectric spectra is revealed from monoalcohols, sulfur substituted monoalcohols, to alkoxy alcohols. However, a distinctive dynamic feature is identified in the alkoxy alcohols, showing the minimum width in the temperature dependence of the apparent main relaxation dispersions. The stretching exponents of the alkoxy alcohols determined by the dielectric relaxations are also found not to follow the empirical correlations with other dynamics quantities established for



generic liquids. When the  $\beta$ -relaxations are considered for the minimum behaviors, a direct conclusion is attained that the  $\beta$ -relaxations do not disappear at high temperatures where the  $\alpha$ -relaxation dynamics is quite fast with the relaxation time being around nano-second.

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