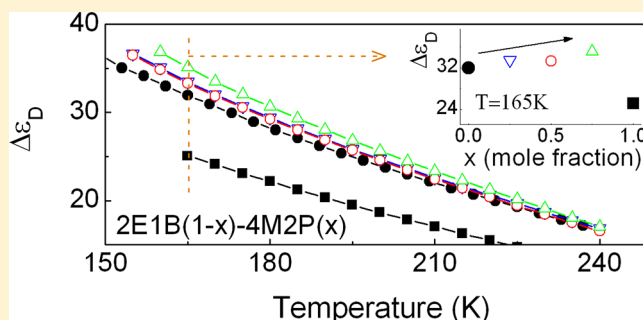


Unusual Dielectric Strength of Debye Relaxation in Monohydroxy Alcohols upon Mixing

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ABSTRACT: The dielectric strength of the Debye relaxation in the binary mixtures of two isomeric monohydroxy alcohols, 2-ethyl-1-butanol (2E1B) and 4-methyl-2-pentanol (4M2P), is studied at low temperature near glass transition. Enhanced dielectric strength is exhibited in the mixtures, remarkably different from the mixing behaviors of the structural (α -) relaxation of generic liquids. A similar result is observed when analyzing the dielectric data of the binary mixtures of 2-ethyl-1-hexanol and 2-methyl-1-butanol reported in an early study. The unusual behavior of the dielectric strength in the mixtures reveals a new feature of the Debye relaxation in monohydroxy alcohols. Yet, the calorimetric measurements of the glass transition temperature in 2E1B–4M2P mixtures show a distinct negative deviation from the ideal mixing law. The explanation of the Debye relaxation is discussed with the results.



I. INTRODUCTION

Dielectric relaxation is widely used to study liquid dynamics and glass transition in molecular glass-forming liquids with a broad frequency scan.^{1–4} For the majority of molecular liquids, the slowest relaxation dynamics with the highest dielectric relaxation strength is associated with viscous flow of liquids as well as liquid–glass transition and is taken as the structural (α -) relaxation. Structural relaxation time or viscosity dramatically increases as liquids undercool, in particular when temperature approaches the glass transition as long as crystallization can be avoided, showing a non-Arrhenius behavior in the temperature (T -) dependence.^{5,6} The non-Arrhenius dynamic character makes the structural relaxation well separated from others at low-temperature regimes, enabling the accurate determination of the relaxation dispersion.

For most glass-forming liquids, an isothermal measurement of the structural relaxation within supercooled liquid regimes generally reveals a nonexponential (time domain) or a non-Debye (frequency domain) character.^{7–9} However, there is a special category of liquids, monohydroxy alcohols, where the slowest relaxation with the highest relaxation strength in the dielectric spectra keeps Debye-typed across the whole liquid regime, although the T -dependence of the Debye relaxation time follows the non-Arrhenius behavior.^{10–15} Such liquids are named Debye liquids. A number of experimental studies argue that the Debye relaxation in monohydroxy alcohols might not be associated with the structural relaxation or viscous flow and, rather, a slightly faster relaxation which is always attached to the Debye relaxation represents the true structural relaxation.^{16–20} Although the physical origin of the Debye relaxation remains to be clarified, some unique dynamic characters have been demonstrated to understand the special dielectric behaviors in

monohydroxy alcohols.^{21,22} For instance, it is found that the high-temperature limit of the Debye relaxation frequency terminates at 10^{10} Hz, in contrast to the phonon frequency of $\sim 10^{13}$ Hz typical of the structural relaxation.¹⁸ When mixing two primary alcohols, the Debye relaxation dispersions and relaxation times are observed to follow the ideal mixing law in supercooled regimes, while the structural relaxation times of the alcohols follow nonideal mixing.²³ The Debye relaxation of monohydroxy alcohols might break down in solutions when mixed with non-Debye liquids,²⁴ while the relaxation can be still resolved in pure monohydroxy alcohols confined in a geometry of 1 nm.²⁵ Recently, high-pressure measurements show that the Debye relaxation dynamics changes with pressure much more slowly than the structural relaxation.^{26,27}

To understand the physical origin of the Debye relaxation in supercooled monohydroxy alcohols, partial/complete illustration of the dynamic characters of the special dynamics is necessary. Recent studies of the Debye relaxation dynamics in binary primary alcohols composed of 2-ethyl-1-hexanol (2E1H) and 2-methyl-1-butanol (2M1B) revealed the ideal mixing behavior of the compositional dependence of the Debye relaxation time and dispersion.²³ Yet, the mixing effect on dielectric relaxation strength of the Debye relaxation has not been available. In this paper we extend the studies to the dielectric strength of the Debye relaxation in binary mixtures of monohydroxy alcohols. In addition to the mixtures of 2E1H–2M1B, binary isomeric mixtures of primary and secondary aliphatic alcohols with the resolved Debye and α -relaxations are

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chosen. Enhanced dielectric strength of the Debye relaxation is shown upon mixing, with which a new dynamic feature of the Debye relaxation is revealed. The explanation of the new finding is expected to advance our understanding of the Debye relaxation in monohydroxy alcohols.

II. EXPERIMENTAL SECTION

The isomeric alcohols, 2-ethyl-1-butanol (2E1B, 98%) and 4-methyl-2-pentanol (4M2P, 99%), were purchased from Alfa Aesar and used without further purification. Early dielectric measurements show that 4M2P is an excellent glass-former with resolved Debye and α -relaxation.²⁸ The dielectric measurements were made in a Novocontrol broad-band dielectric spectrometer (Concept 80) equipped with a liquid nitrogen cooling system.^{29,30} The dielectric relaxation was isothermally measured at each temperature by holding liquids between two separated brass electrodes by Teflon strips of thickness 25 μm . The scanning frequency range spans from 0.01 Hz to 10 MHz. The temperature was controlled by a Novocontrol Quatro controller with temperature accuracy within 0.1 K. The dielectric data were analyzed by using the Havriliak–Negami equation together with a conductivity term³¹

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau)^\alpha]^\gamma} + \frac{\sigma_{\text{dc}}}{i\epsilon_0\omega} \quad (1)$$

where ϵ_∞ is the high-frequency dielectric constant, $\Delta\epsilon$ is the dielectric strength, τ is the dielectric relaxation time, α and γ are the profile shape factors of the relaxation dispersion, and σ_{dc} is dc conductivity. With $\gamma = 1$, the HN equation becomes the Cole–Cole (CC) equation. The calorimetric measurements of the glass transition temperatures, T_g , and heat capacity curves for the mixtures were also performed by using a Perkin–Elmer differential scanning calorimeter (DSC). The samples were quenched to glassy states at a cooling rate of 20 K/min, and the calorimetric parameters were determined from the curves measured during heating at the same rate.²⁹ The DSC was calibrated using indium and cyclohexane prior to the measurements. T_g is defined as the onset temperature of heat capacity jump from the glassy to the liquid states.

III. RESULTS

Figure 1 shows the dielectric measurement results of 2E1B and 4M2P at four selected temperatures, including the loss spectra (upper panel) and dielectric constants (lower panel). Not all the measured data are drawn here to avoid crowding. The fits of the HN equation to the slowest relaxation (dashed lines) give $\alpha = \gamma = 1$ for both of the two alcohols, indicative of the typical Debye relaxation. Compared with 4M2P, the dielectric spectra of 2E1B show a larger dynamic separation between the α - and the Debye relaxation with fully resolved α -relaxation. The dielectric strength of the Debye relaxation $\Delta\epsilon_D$ can be easily determined by fitting the real or imaginary parts. The temperature dependence of $\Delta\epsilon_D$ will be given below together with other measurements. By contrast, the accurate determination of the α -relaxation strength $\Delta\epsilon_\alpha$ is not satisfactory due to the difficulty in separating the α -relaxation from the faster relaxations. In the lower panel of Figure 1, the rough assessment of $\Delta\epsilon_\alpha$ is presented with the fits of the HN equation to the dielectric constants of the α -relaxation, as marked by solid lines. Although the option of the high-frequency dielectric constants is somewhat arbitrary, the CC

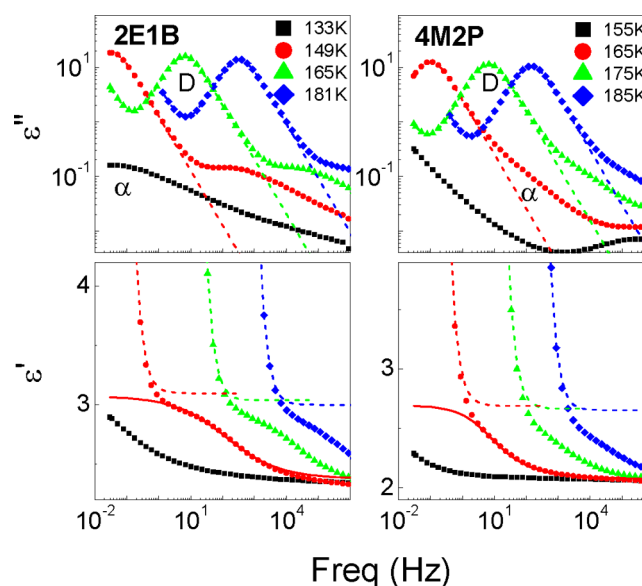


Figure 1. Dielectric spectra of 2-ethyl-1-butanol (2E1B) and 4-methyl-2-pentanol (4M2P) measured at four selected temperatures. The dashed lines show the fit of the Debye function to the slowest relaxation. The fits of the HN equation to the real parts of the structural (α -) relaxation of 2E1B (149 K) and 4M2P (165 K) are shown in the lower panels (solid lines). D and α denote the Debye and α -relaxation.

function is found to apply to the dielectric spectra of 2E1B, as used in a previous study,²³ while the function does not work well for 4M2P. The fitting parameters of the α -relaxation, $\Delta\epsilon_\alpha$, $\log_{10}\tau_\alpha/\text{s}$, α_ω and γ_α are 0.69, -2.9 , 0.46, and 1 for 2E1B (149 K) and 0.62, -1.51 , 0.67, and 0.7 for 4M2P (165 K), respectively. $\Delta\epsilon_\alpha$ appears far smaller than $\Delta\epsilon_D$ for the two alcohols.

Figure 2 presents the dielectric spectra of a mixture with equimolar 2E1B and 4M2P. The fits of the HN equation to the slowest dielectric relaxation also justify the Debye relaxation. Figure 3 shows the relaxation spectra normalized by the peak value and peak position for the mixtures where each curve is selected with the dielectric loss peak located at ~ 10 Hz. Obviously, all the spectra are subject to the Debye function, suggesting that the relaxation dispersion follows the ideal mixing law. The Debye relaxation time is given in Figure 4 as a function of reciprocal temperature, and the data are found to merge into a master curve at a relaxation time of $\sim 10^{-5}$ s. The ideal mixing law of the Debye relaxation time observed in binary mixtures of primary alcohols such as 2E1H–2M1B and 1-propanol–3,7-dimethyl-1-octanol²³ is examined, and the calculated time for the equimolar case is shown in Figure 4 (dashed line) based on the data of two pure components. Whereas the ideal mixing law is followed at a bit high temperature for the mixtures of primary 2E1B and secondary 4M2P, a deviation is obvious at low temperature, remarkably differing from previous observation.

The T -dependence of the dielectric strength $\Delta\epsilon_D$ of the Debye relaxation of the mixtures is shown in Figure 5, and in the inset $\Delta\epsilon_D$ is plotted as a function of logarithmic Debye relaxation time, τ_D . Surprisingly, $\Delta\epsilon_D$ curves of the three mixtures are found to be constantly higher than those of the two pure alcohols. Figure 6 presents a quantitative comparison of $\Delta\epsilon_D$ at a fixed temperature of 170 K and a fixed Debye relaxation time of $\tau_D = 1$ s. It is striking to see not only a

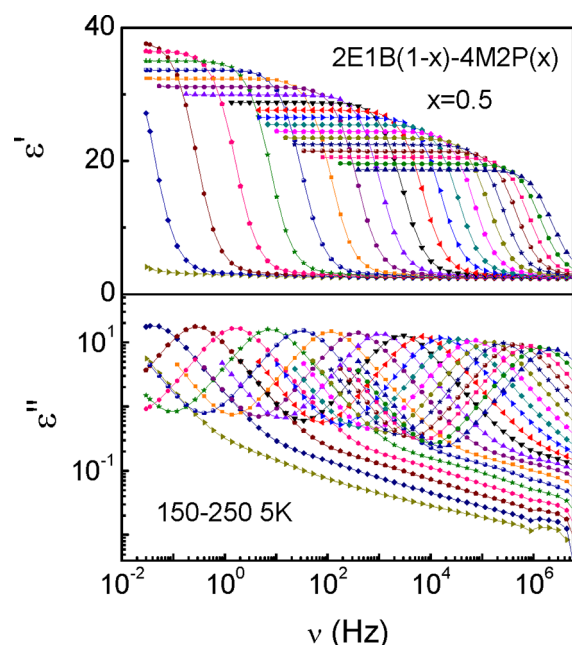


Figure 2. Dielectric real and imaginary parts of a mixture of 50 mol % 2-ethyl-1-butanol (2E1B) and 50 mol % 4-methyl-2-pentanol (4M2P) measured from 150 to 250 K with 5 K temperature interval.

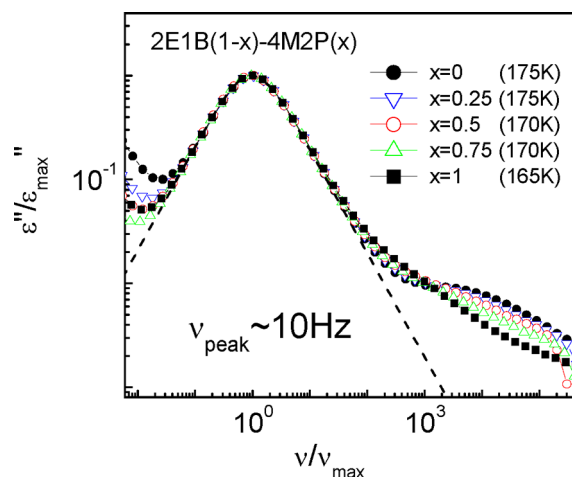


Figure 3. Dielectric loss spectra of the mixtures of 2-ethyl-1-butanol (2E1B) and 4-methyl-2-pentanol (4M2P) normalized by the peak position and peak height. The dashed line defines the Debye relaxation. x is mole fraction.

positive deviation of $\Delta\epsilon_D$ in the mixtures relative to the ideal mixing behavior, namely, the mole average of $\Delta\epsilon_D$ of the two pure liquids, but also the remarkable enhancement in $\Delta\epsilon_D$ in the composition range of 0.25–0.75 mol fraction of 4M2P. Specifically, when adding 4M2P to 2E1B, $\Delta\epsilon_D$ measured at 170 K continuously increases, and an enhancement exceeding 9% is attained at a mole fraction of 4M2P up to 0.75, albeit 4M2P has a lower $\Delta\epsilon_D$ value. Naturally, an excess in the dielectric strength of the Debye relaxation is achieved upon mixing the two alcohols.

IV. DISCUSSION

The enhanced dielectric strength in the Debye relaxation of the binary Debye liquid mixtures is unexpected. Inspection of our dielectric measurements of binary miscible mixtures composed

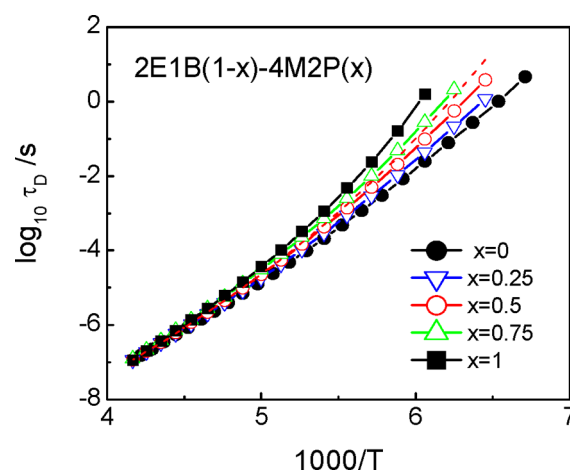


Figure 4. Dielectric relaxation time of the Debye relaxation in the mixtures of 2-ethyl-1-butanol (2E1B) and 4-methyl-2-pentanol (4M2P) as a function of reciprocal temperature. x is the mole fraction of 4M2P. The dashed line shows the calculated results from the ideal mixing law for the case of $x = 0.5$.

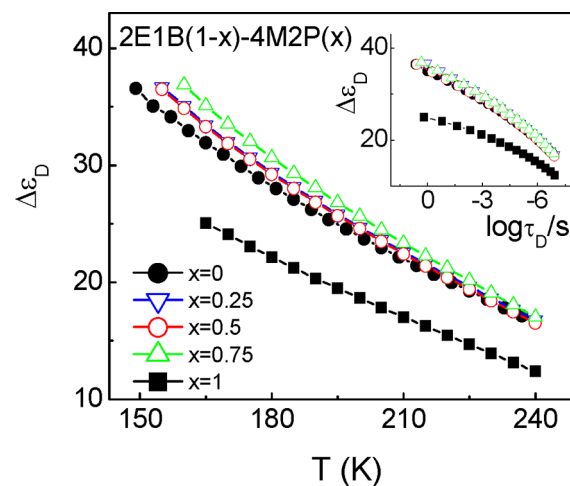


Figure 5. Temperature dependence of the dielectric strength $\Delta\epsilon_D$ of the Debye relaxation in the mixtures of 2-ethyl-1-butanol (2E1B) and 4-methyl-2-pentanol (4M2P) with various mole fractions. x is the mole fraction of 4M2P. The dependence of $\Delta\epsilon_D$ on logarithmic relaxation time is shown in the inset.

of non-Debye liquids with various mixing modes from the ideal mixing, near ideal mixing, to nonideal mixing³² indicates that a negative deviation from the ideal mixing rule is more typical when referring to the structural relaxation, although a noticeable enhancement in T_g becomes possible in some systems of nonideal mixing. A similar observation can be also seen in a number of binary mixtures of non-Debye liquids at a specific temperature.^{33–35} It needs to be noted that although the determination of $\Delta\epsilon_\alpha$ of the α -relaxation in the 2E1B–4M2P mixtures would provide an ideal comparison with the mixing behavior of the Debye relaxation, the large uncertainty in the data fitting makes the accurate determination of $\Delta\epsilon_\alpha$ extremely difficult.

The unusual phenomenon of the enhancement in dielectric strength upon mixing Debye liquids has not been reported before, and, naturally, more data needs to be investigated to determine if similar observation can be reproduced in other binary Debye liquids. We reanalyze the dielectric results of

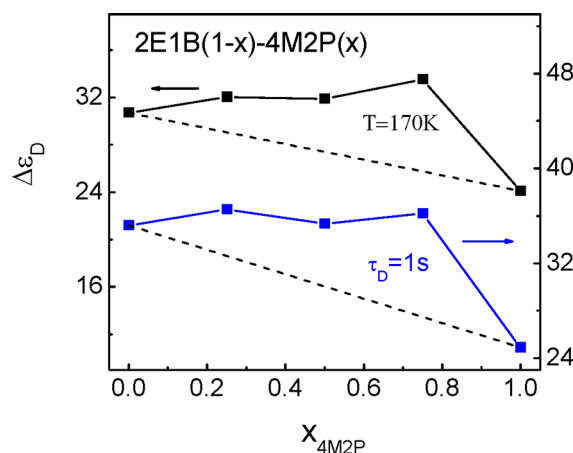


Figure 6. Compositional dependence of the dielectric strength $\Delta\epsilon_D$ of the Debye relaxation at a temperature and a relaxation time for the mixtures of 2-ethyl-1-butanol (2E1B) and 4-methyl-2-pentanol (4M2P). The dashed line shows the ideal mixing behavior. x is the mole fraction of 4M2P.

binary mixtures of 2-ethyl-1-hexanol (2E1H) and 2-methyl-1-butanol (2M1B) reported from Richert's group,²³ and the dependences of $\Delta\epsilon_D$ on temperature (left panel) and Debye relaxation time (right panel) are shown in Figure 7. There

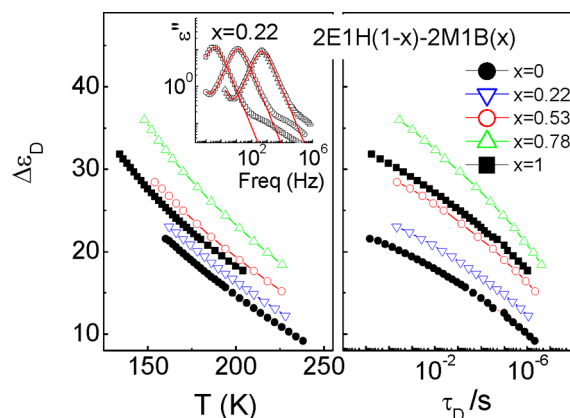


Figure 7. Dielectric strength $\Delta\epsilon_D$ of the Debye relaxation in the mixtures of 2-ethyl-1-hexanol (2E1H) and 2-methyl-1-butanol (2M1B) as functions of temperature (left panel) and Debye relaxation time τ_D (right panel). x is the mole fraction of 2M1B. The dielectric loss spectra of a mixture with $x = 0.22$ are shown in the inset at three temperatures of 162, 174, and 190 K. The data are obtained from the dielectric measurements involved in ref 23. The dashed lines denote the fit of the Debye function with conductivity to the data.

typical dielectric loss spectra of the mixture with 22 mol % 2M1B are given in the inset at temperatures of 162, 174, and 190 K. Similarly, when comparing the $\Delta\epsilon_D$ data of the mixtures measured at a fixed temperature of 170 K or a fixed Debye relaxation time of 1 s, a remarkable enhancement of up to 20% in $\Delta\epsilon_D$ is detected in Figure 8 relative to that of 2M1B when mixed with ~20 mol % of 2E1H, which, notwithstanding, has lower $\Delta\epsilon_D$ than 2M1B. Obviously, the experimental results measured from the two sets of mixtures of 2E1B–4M2P and 2E1H–2M1B exhibit a common behavior that mixing two Debye liquids is capable of giving rise to an enhancement in the dielectric strength associated with the Debye relaxation. Therefore, a new and unusual behavior is revealed for the

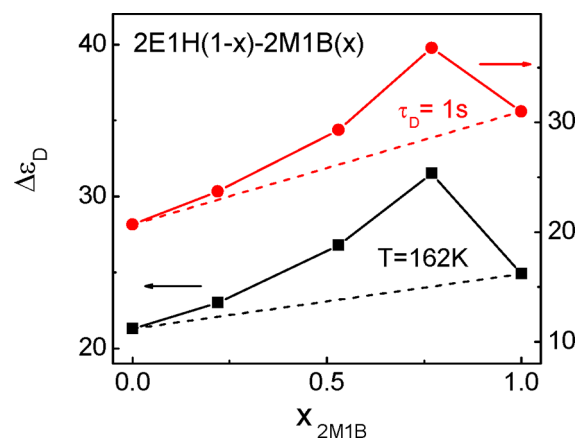


Figure 8. Dielectric strength $\Delta\epsilon_D$ of the Debye relaxation at a temperature and a Debye relaxation time for the mixtures of 2-ethyl-1-hexanol (2E1H) and 2-methyl-1-butanol (2M1B). The dashed line shows the ideal mixing behavior. x is the mole fraction of 2M1B.

Debye relaxation, which has been identified not to relate to the viscous flow and glass transition of monohydroxy alcohols.¹⁸

The dielectric strength of the structural relaxation in liquids is usually explained by the Kirkwood–Fröhlich (KF) equation emphasizing the correlation of dipoles of liquid molecules.³⁶ There are two scenarios regarding the dipole correlation, one being parallel alignment of dipoles induced by specific interactions such as hydrogen-bond interaction in alcohols resulting in an enhancement of the effective dipole moment, and the other antiparallel alignment giving rise to the cancellation of dipole moment. Naturally, the former might lead to an enhanced dielectric strength with an increased effective dipole moment. Intuitively, in the framework of the KF equation the noticeable enhancement of the dielectric strength observed in the mixtures of Debye liquids would, therefore, point to the speculation that newly H-bonded structures form between the unlike molecules via specific interactions with higher effective dipole moments imposed by parallel alignment of dipoles.

In order to examine the speculation, calorimetric analyses of the glass transition are performed in the liquid mixtures aimed at studying the intermolecular interactions of 2E1B and 4M2P molecules since the compositional dependence of T_g is argued to directly correlate with structural variations via specific interactions.³⁷ Figure 9a shows the glass transition heat capacity curves of the mixtures with various mole fractions. The compositional dependence of the calorimetric T_g is presented in Figure 9b. Surprisingly, a negative deviation of the calorimetric T_g from the ideal mixing is observed, strongly contrasting with the results of the dielectric strength of the Debye relaxation shown in Figures 6 and 8. A close analysis shows that the relative change in T_g , $\Delta T_g/T_g$ (where ΔT_g denotes the difference between the calculated values based on the ideal mixing law and the experimentally measured ones), can go up to ~3% at the intermediate concentration, comparable with the result measured in the isomeric mixtures of methyl *o*-toluate and methyl *m*-toluate reported in our recent study.³² The compositional dependence of T_g in binary monohydroxy alcohols has been experimentally studied,^{38–40} and similar negative deviations can be detected in other binary monohydroxy alcohols, such as the mixtures of methanol and 1-butanol.^{38,39} Opposite to the isomeric 2E1B–4M2P system, T_g of 2E1H–2M1B mixtures determined from the T -dependence

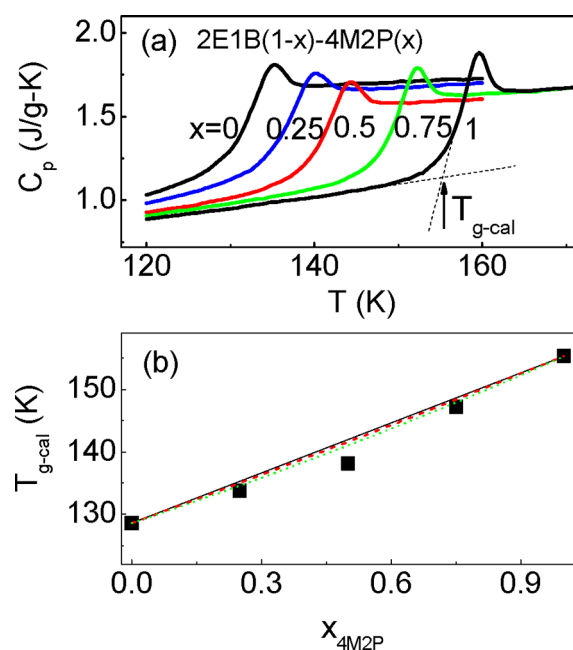


Figure 9. Calorimetric measurements of glass transition in the binary mixtures of 2-ethyl-1-butanol (2E1B) vs 4-methyl-2-pentanol (4M2P). The heat capacity curves are given in the upper panel, and the calorimetric glass transition temperature, T_{g-cal} , is defined. The compositional dependence of T_{g-cal} is shown in the lower panel. The dashed line and dotted line denote the calculated results based on Gordon and Couchman–Karasz models. x is the mole fraction of 4M2P.

of the α -relaxation time at a temperature where $\tau_\alpha = 100 \text{ s}$ ²³ shows a positive deviation.

The studies of the compositional dependence of the calorimetric T_g have been a subject of liquid dynamics in miscible mixtures, and the deviation of T_g from the ideal mixing law lies, in part, in the variation of the heat capacity jumps at T_g , ΔC_p , of two pure components in terms of Gordon³⁸ and Couchman–Karasz⁴¹ models. When using the ΔC_p values of 0.52 and 0.55 J/g-K for the isomeric 2E1B and 4M2P, the calculated compositional dependence of T_g is shown in Figure 9b by the dashed (Gordon model) and dotted lines (Couchman–Karasz model). Unfortunately, the calculated results do not coincide with the experimental values, suggesting that the variation in ΔC_p between the two alcohols does not generate such a big deviation. The nonideal behavior of the compositional dependence of T_g has been pointed out as a consequence of the balance of enthalpic and entropic factors,^{42–45} and a strong interaction between components with a large and negative entropy (or enthalpy) of mixing would result in strong and positive deviations from the predicted values by models such as Gordon or Couchman–Karasz equations, while a positive entropy of mixing has the effect of shifting T_g to a lower value.⁴⁶ Recently, Kalogeras systematically compared the theoretical or semiempirical equations describing the compositional dependence of T_g and drew a similar conclusion emphasizing the enthalpic contributions imposed by specific interactions such as hydrogen bonding to the strong and positive deviations of T_g from the ideal mixing rule.⁴⁷ Our recent studies of the mixtures with various intermolecular interactions justify this conclusion with the observation of remarkable positive deviations of T_g for the alcohol–amine mixtures with large and negative mixing heat,

and a negative deviation in the case of isomeric molecular mixtures.³² Consequently, the noticeably more negative deviation of the calorimetric T_g observed in the 2E1B–4M2P mixtures than what would be expected by the models does not provide direct evidence of the favorable interactions between 2E1B and 4M2P molecules, and the calorimetric measurement might not be compatible with the above-mentioned speculation of the formation of newly H-bonded structures between the unlike molecules.

The finding of the new dielectric feature in the Debye relaxation of monohydroxy alcohols allows for further understanding of the origin of the special dynamics. Models have been proposed to interpret the Debye relaxation in pure monohydroxy alcohols, and common to the models is the clustered structures imposed by hydrogen bonding such as transient (linear) chains,²² cyclic multimers,⁴⁸ and self-assembly micelle.⁴⁹ For the mixtures of Debye liquids studied here, although the striking enhancement in dielectric strength might be ascribed to new associated structures formed by the unlike molecules with higher effective dipole moments, the calorimetric result of the noticeably negative deviation of T_g in the isomeric mixtures of 2E1B and 4M2P seems to provide little support of the formation of the H-bonded chain structures. More structural analyses of the glass-forming monohydroxy alcohols and their mixtures in supercooled liquid regions are in need for a complete interpretation.

V. CONCLUSION

The dielectric strength of the Debye relaxation in monohydroxy alcohols is studied by focusing on binary mixtures of 2-ethyl-1-butanol and 4-methyl-2-pentanol. Enhanced relaxation strength is experimentally observed in the mixtures. The data analyses of the previously reported dielectric measurements of 2-ethyl-1-hexanol and 2-methyl-1-butanol mixtures reproduce the observation. The unusual behavior of the dielectric strength in binary Debye liquids is proven to be a new feature of the Debye relaxation, greatly different from the mixing behaviors in non-Debye liquids. The calorimetric measurements of the glass transition temperatures in 2-ethyl-1-butanol and 4-methyl-2-pentanol mixtures reveal the negative deviation from the ideal mixing law. The analyses of the calorimetric results provide little support to the explanation that the enhanced dielectric strength of the Debye relaxation arises from the formation of newly H-bonded structures of unlike molecules in mixtures with higher effective dipole moments.

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Notes

The authors declare no competing financial interest.

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