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Origin of ρ^γ/T scaling of primary and secondary conductivity relaxation times in mixture of water with protic ionic liquid†

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Murali *et al.* [*J. Phys. Chem. Lett.*, 2024, 15, 3376–3382] made ambient and high pressure dielectric measurements of a supercooled aqueous mixture of an acidic ionic liquid to find the presence of the primary (σ) conductivity relaxation together with the secondary (ν) conductivity relaxation originating from the water clusters confined by the cations and anions with relaxation times τ_σ and τ_ν respectively. From the isothermal and isobaric conductivity relaxation data found on varying thermodynamic conditions (*i.e.* T and P) at constant τ_σ are the invariance of (i) the frequency dispersion or the Kohlrausch function exponent $(1 - n)$ of the primary conductivity relaxation, and (ii) the ratio of the primary and secondary conductivity times, τ_σ/τ_ν. This co-invariance of τ_σ, τ_ν, and $(1 - n)$ at constant τ_σ was observed before in non-aqueous ionic liquids, but it is found for the first time in aqueous ionic liquids. The new data together with PVT measurements enable Murali *et al.* to show additionally that both τ_σ and τ_ν are functions of ρ^γ/T with a single exponent $\gamma = 0.58$. The Coupling model is the only theory predicting the co-invariance of τ_σ, τ_ν, and $(1 - n)$ as well as the ρ^γ/T scaling of both τ_σ and τ_ν. It is applied herein to address and explain the data of the ionic liquid–water mixture.

1. Introduction

Recently Murali *et al.*[1] studied the conductivity (σ) relaxation in a glass-forming mixture of water and the protic ionic liquid (IL) 1-methyl-3-(3-sulfobutyl)imidazolium *para*-toluenesulfonate ([BMIm-SO_3H][pTS]). They found by isothermal and isobaric dielectric measurements that the primary σ-relaxation is accompanied by a faster conductivity (ν) relaxation contributed from the water clusters confined by ions of the IL. The frequency dispersion of the σ-relaxation is invariant to changes of pressure P and temperature T while maintaining its relaxation times $\tau_\sigma(T,P)$ constant. By itself this property is challenging for an explanation from any theory. Additionally, the secondary conductivity ν-relaxation times $\tau_\nu(T,P)$ are also constant. Hence the ratio $\tau_\sigma(T,P)/\tau_\nu(T,P)$ is also invariant at constant $\tau_\sigma(T,P)$, which is another remarkable property challenging for explanation. These conductivity relaxation properties were brought out by Murali *et al.* from the complex frequency dependent electric modulus spectra, $M^*(f) = M'(f) + iM''(f)$, obtained for different combinations of T and P. The $M^*(f)$ is the reciprocal of the complex permittivity $\varepsilon^*(f)$, and is the representation of choice to characterize the frequency dispersion and to determine the relaxation time τ_σ of ionic conductivity relaxation.[2–4] For example, the electric modulus loss $M''(f)$ obtained by Murali *et al.* at three different combinations of T and P with the same peak frequency $f_\sigma(T,P)$ or the same $\tau_\sigma(T,P)$ shown in Fig. 1 clearly demonstrate the invariance of $\tau_\nu(T,P)$ and the primary frequency dispersion at constant $\tau_\sigma(T,P)$. The findings are remarkable because *a priori* there is no reason why the frequency dispersion of the primary σ-relaxation is unchanged, and why the two conductivity relaxation times τ_σ and τ_ν change in concert to maintain the ratio τ_σ/τ_ν constant on varying T and P resulting in large changes of thermodynamic conditions. The arrow in Fig. 1 indicates the location of the primitive conductivity relaxation frequency f_0 calculated by an equation of the Coupling model (CM)[5–7] to be introduced later in Section 2. The point made here is the approximate agreement between f_0 and the most probable secondary conductivity relaxation frequency f_ν observed experimentally in Fig. 1, as well as in other ionic liquids.[3–13]

Before proceeding further one should distinguish the secondary ionic conductivity relaxation from the more familiar secondary relaxation, often referred to as the Johari–Goldstein β relaxation,[14–17] in ordinary supercooled glass-forming liquids. The distinction is particularly relevant in the present paper on aqueous ionic liquid because water in clusters contribute to the secondary and primary ionic conductivity relaxations. On the other hand, in aqueous supercooled liquids, water contribute to the Johari–Goldstein β relaxation (also called the ν relaxation in some papers) and the primary structural α relaxation.[18–21]

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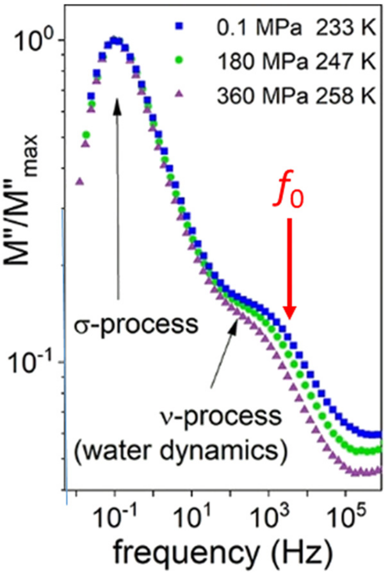

Fig. 1 Representative normalized electric modulus $M''(f)$ data of the primary (σ) and secondary (ν) conductivity relaxations in the IL–water mixture measured at different combinations of T and P. The figure serves to demonstrate the shape of the primary conductivity relaxation as well as the ratio of the two relaxation times τ_σ and τ_ν are invariant to large changes of thermodynamic conditions. The red arrow indicate the location of the primitive conductivity relaxation frequency calculated by the Coupling model equation. Figure taken from ref. 1 and reused with permission from ACS.

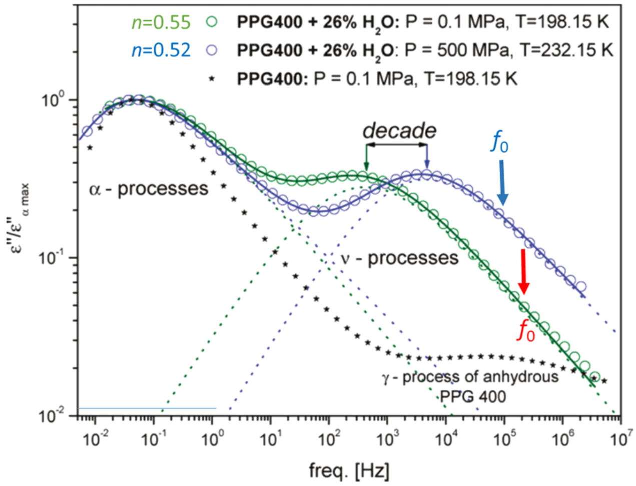

Fig. 2 Comparison of dielectric spectra of a mixture of 26% water with PPG400 having the same structural α-relaxation times obtained at different P and T. Solid lines denote fits of entire spectra as a superposition of the two HN functions (dotted lines). The red and blue arrows indicate the locations of the primitive relaxation frequency f_0 calculated by the Coupling model equation, and shown to demonstrate agreement with the JGβ or ν loss peak frequency is not expected. Shown also is the spectra of anhydrous PPG400. The figure is taken from ref. 20 and reused with permission from ACS.

Based on the key property of the invariance of $\tau_\sigma(T,P)/\tau_\nu(T,P)$ to changes of thermodynamic conditions at constant $\tau_\sigma(T,P)$, Murali *et al.* performed the PVT measurements of the IL–water mixture, and applied them to show that both $\tau_\sigma(T,P)$ and $\tau_\nu(T,P)$ are functions of ρ^γ/T with $\gamma = 0.58$ and ρ is the density. The success of thermodynamic scaling of $\tau_\sigma(T,P)$ and $\tau_\nu(T,P)$ in the IL–water mixture involving the conductivity ν-relaxation of water is novel and significant. Firstly, it was found in an aqueous ionic liquid and for the first time. Secondly, in aqueous supercooled liquids the Johari–Goldstein β relaxation times $\tau_\beta(T,P)$ originating from water changes on varying T and P while the structural relaxation time $\tau_\alpha(T,P)$ is kept constant, and thus ρ^γ/T scaling of both relaxation times is not possible. An example is the polypropylene glycol of molecular weight $M_w = 400$ g mol^{-1} (PPG400) mixed with water at several concentrations studied by dielectric spectroscopy.[11,12] Compared in Fig. 2, the loss spectra taken at $T = 198.15$ K and $P = 0.1$ MPa and at $T = 232.15$ and $P = 500$ MPa have the same α-loss peak frequency, but the ν-loss peak frequencies differ significantly. Moreover, the shape of the structural α-loss peak changes and becomes narrower at high pressure, and unsurprisingly the primitive relaxation frequency f_0 calculated by the Coupling Model equation are far different from the ν-loss peak frequency. The Arrhenius plots of the $\tau\nu(T,P)$ and $\tau_\alpha(T,P)$ at $P = 0.1$ MPa and $P = 500$ MPa presented in Fig. S1 of ESI† demonstrate the relation between the two relaxation times changes on elevating pressure.

In view of the novel and significant finding of the conductivity relaxation times $\tau_\sigma(T,P)$ and $\tau_\nu(T,P)$ in the IL–water mixture are co-invariant at constant $\tau_\sigma(T,P)$ to changes in thermodynamic condition and consequently both obey ρ^γ/T scaling with the same γ, a theoretical explanation of the experimental data is required. The explanation has to be consistent with the fact that the co-invariance of the structural $\tau_\alpha(T,P)$ and $\tau\nu(T,P)$ does not hold in the other aqueous mixtures such as that shown in Fig. 2. The objective of this paper is to provide such an explanation. It is given in the Sections to follow.

2. Explanation of co-invariance of $\tau_{\sigma\alpha}(T,P)$, $\tau_{\sigma\beta}(T,P)$, and $n(T,P)$ at constant $\tau_{\sigma\alpha}(T,P)$

The properties of the σ and ν conductivity relaxations of the IL–water mixture are analogous to the primary ($\sigma\alpha$) and secondary ($\sigma\beta$) conductivity relaxations found in ionic liquids without the presence of water.[4–13] One example is procainamide HCl, a protic ionic liquid[9] shown in Fig. S2 in ESI.† The frequency dispersions of the conductivity α-relaxation taken at two combinations ($T = 308$ K, $P = 0.1$ MPa) and ($T = 323$ K, $P = 160$ MPa) with the same $\tau_{\sigma\alpha}(T,P)$ are well fitted by the Fourier transform of the Kohlrausch stretched exponential correlation function,

$$\varphi(t) = \exp - (t/\tau_{\sigma\alpha})^{1-n} \tag{1}$$

with $(1 - n) = 0.64$. The $\sigma\beta$ relaxation times $\tau_{\sigma\beta}(T,P)$ under the two different thermodynamic conditions are also the same. Another case is the ionic liquid composed of a silicon-substituted imidazolium cation, 1-methyl-3-trimethylsilylmethylimidazolium ([Si-MIm]$^+$) and tetrafluoroborate anion ([BF4]$^-$).[13] Fig. S3 in ESI† shows isochronal superposition of $M''(f)$ data of both the primary ($\sigma\alpha$) and the secondary ($\sigma\beta$) conductivity relaxations obtained at a fixed conductivity α-relaxation time $\tau_{\sigma\alpha}$, for two different combinations of

(P = 600 MPa, T = 253 K) and (P = 0.1 MPa, T = 213 K). Clearly the ratio $\tau_{\sigma\alpha}(T,P)/\tau_{\sigma\beta}(T,P)$ is invariant at constant $\tau_{\sigma\alpha}(T,P)$. The inset show isochronal superpositioning at two more constant values of $\tau_{\sigma\alpha}$. The lines are the fits by Fourier transform of the Kohlrausch function with $n = 0.43$ independent of T and P at constant $\tau_{\sigma\alpha}$. So, what is the explanation of the existence of this remarkably general co-invariance of the three quantities, $\tau_{\sigma\alpha}(T,P)$, $\tau_{\sigma\beta}(T,P)$, and $n(T,P)$ at constant $\tau_{\sigma\alpha}(T,P)$ found also in the IL–water mixture by Murali *et al.*[1] As far as the author knows, the only explanation of the co-invariance is provided by the predictions of the Coupling Model (CM),[4–12] which are briefly reviewed in this Section. The data of the IL–water mixture offer another chance to test the predictions, and the results are described in Section 3.

First of all, generally the good fit of the frequency dispersion of the conductivity α-relaxation and the structural α-relaxation by the Fourier transform of the Kohlrausch function in ionically conducting materials[13–17] is consistent with one of the predictions of the CM.[19–21] The other prediction is the relation between $\tau_{\sigma\alpha}$ and the primitive relaxation time $\tau_{\sigma0}$ given by

$$\tau_{\sigma\alpha}(T,P) = [t_c^{-n}\tau_{\sigma0}(T,P)]^{1/(1-n)}, \qquad (2)$$

derived from the crossover of the correlation function from $\exp(-t/\tau_0)$ to $\exp-(t/\tau_{\sigma\alpha})^{1-n}$ at t_c = 1 to 2 ps predicted by the CM.[6] The crossover is evidenced by quasielastic neutron scattering experiment in a typical ionic liquid [bmim][PF$_6$][22] and by high frequency dielectric measurements in other ionic conductors.[5,6] In eqn (2) the primitive relaxation time $\tau_{\sigma0}$ and the stretch exponent $(1-n)$ are independent physical quantities of different origins and properties, and there is no connection or correlation between their separate dependences on T and P. Thus, on varying T and P while keeping $\tau_{\sigma\alpha}(T,P)$ on the left-hand-side of eqn (2) constant, in all likelihood $\tau_{\sigma0}(T,P)$ and $(1-n)$ on the right-hand-side of eqn (2) have to maintain constant individually. In other words, the co-invariance of $\tau_{\sigma\alpha}(T,P)$, $\tau_{\sigma0}(T,P)$, and $n(T,P)$ at constant $\tau_{\sigma\alpha}(T,P)$ follows naturally as a consequence of the CM eqn (2). It also explain why the shape of the conductivity α-relaxation or its Kohlrausch exponent $(1-n)$ is invariant to changes in thermodynamic conditions while $\tau_{\sigma\alpha}(T,P)$ is kept the same in so many different ionic conductors[19,20] and now including the IL–water mixture of Murali *et al.*

Furthermore the primitive conductivity relaxation is part of the $\sigma\beta$ relaxation, and hence their relaxation times $\tau_{\sigma0}$ and $\tau_{\sigma\beta}$ are approximately equal,[5,6,16,17] *i.e.*,

$$\tau_{\sigma\beta}(T,P) \approx \tau_{\sigma0}(T,P) \qquad (3)$$

The value of $\tau_{\sigma0}(T,P)$ calculated from $\tau_{\sigma\beta}(T,P)$ by eqn (2) with the known value of n and t_c = 1 to 2 ps has been compared with the experimental $\tau_{\sigma\beta}(T,P)$. The prediction given by the eqn (3) is generally verified[4,8–12] and as shown by the examples in Fig. S1 and S2, and also in Fig. 1 for the IL–water mixture.[1] By combining eqn (3) with co-invariance of $\tau_{\sigma\alpha}(T,P)$, $\tau_{\sigma0}(T,P)$, and $n(T,P)$ at constant $\tau_{\sigma\alpha}(T,P)$ from eqn (2), one has an explanation of why both $\tau_{\sigma\beta}(T,P)$ and $\tau_{\sigma\alpha}(T,P)$ from experiments are simultaneously invariant to change in thermodynamic conditions.

All stated in the above for conductivity relaxation are valid for structural relaxation involving the times $\tau_\alpha(T,P)$, $\tau_0(T,P)$, $n(T,P)$, and the Johari–Goldstein (JG) β-relaxation time $\tau_\beta(T,P)$.[16,17,23–25] Again the crux of explaining the co-invariance of $\tau_\alpha(T,P)$, $\tau_\beta(T,P)$, and $n(T,P)$ at constant $\tau_\alpha(T,P)$ found in many glass-forming liquids and mixtures by the CM are the relations $\tau_\beta(T,P) \approx \tau_0(T,P)$ and $\tau_\alpha(T,P) = [t_c^{-n}\tau_0(T,P)]^{1/(1-n)}$, the counterparts of eqn (2) and (3). An example for a mixture of 10 wt% of quinaldine (QN) in tristyrene measured for different T and P combinations but the same τ_α = 0.67 s.[25] The α-loss peaks are well fitted by the Fourier transform of the Kohlrausch function with $\beta_K \equiv (1-n) = 0.53$. The data are presented in Fig. S4 of ESI† to exhibit the same co-invariance property as Fig. 1 from the IL-mixture and Fig. S1 and S2 (ESI†) of the other ionic liquids.

3. Application of the CM explanation to IL–water mixture

The previous sections have made clear that the CM is the only theory providing an explanation of the co-invariance of $\tau_{\sigma\alpha}(T,P)$, $\tau_{\sigma\beta}(T,P)$, and $n(T,P)$ at constant $\tau_{\sigma\alpha}(T,P)$, observed generally in conductivity relaxation of ionic liquids not containing water. The same explanation applies to the co-invariance of $\tau_\sigma(T,P)$, $\tau_\nu(T,P)$, and $n(T,P)$ to changes of thermodynamic conditions at constant $\tau_\sigma(T,P)$ found in conductivity relaxation of the IL–water mixture. The co-invariance property is of primary importance because if it holds then the ρ^γ/T scaling of both $\tau_\sigma(T,P)$ and $\tau_\nu(T,P)$ are obtained routinely with the addition of PVT data as made available by Murali *et al.* The intriguing aspect of the co-invariance is the origin of the relation between the ν-relaxation and the σ-relaxation that makes possible for the ratio $\tau_\sigma(T,P)/\tau_\nu(T,P)$ to remain invariant to changes of the T and P combinations at constant $\tau_\sigma(T,P)$. In the CM explanation, the crux is eqn (3), which in the case of the IL–water mixture takes the form of

$$\tau_\nu(T,P) \approx \tau_{\sigma0}(T,P) \qquad (4)$$

Here $\tau_{\sigma0}(T,P)$ is the relaxation time of the primitive conductivity relaxation related to $\tau_\sigma(T,P)$ in analogy to eqn (2) by

$$\tau_\sigma(T,P) = [t_c^{-n}\tau_{\sigma0}(T,P)]^{1/(1-n)} \qquad (5)$$

In verifying eqn (4), the primary electric modulus loss peaks in $M''(f)$ of the IL–water mixture at ambient pressure (same as given in Fig. 2a of ref. 1) are fitted by the Fourier transform of the Kohlrausch function $\varphi(t) = \exp-(t/\tau_\sigma)^{1-n}$ to determine n. Some of the data at several temperatures are shown in Fig. 3 together with some representative fits to data at lower temperatures to determine the value of $n = 0.40$. The primitive $\tau_{\sigma0}(T,P)$ are calculated with τ_σ obtained from the fits using eqn (5) for six temperatures, and the locations of the corresponding primitive frequencies $f_{\sigma0} = 1/2\pi\tau_0$ are indicated by the six black arrows pointing to the respective $M''(f)$ data. At lower temperatures the secondary conductivity ν-relaxation shows up as a smaller loss peak in Fig. 3 with peak frequency slightly lower than $f_{\sigma0}$, and thus verifying eqn (4). At higher temperatures the ν-relaxation appears as a shoulder and $f_{\sigma0}$ is higher than the inflection point by a decade or less. In either case the proximity

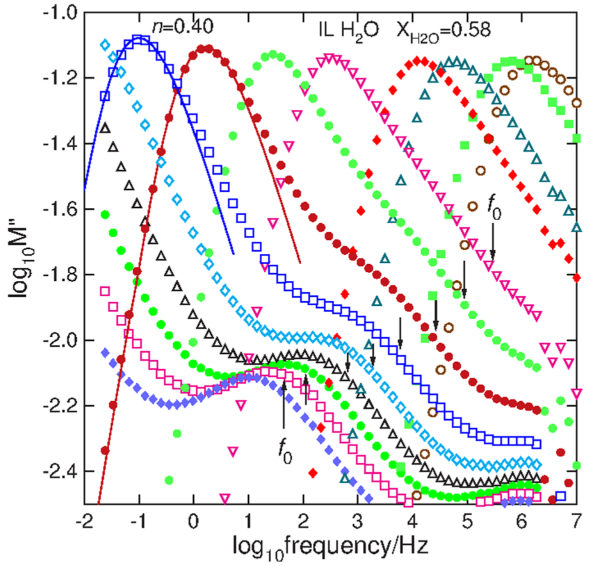

Fig. 3 Representative dielectric spectra of IL–H_2O mixture presented in modulus formalism at ambient pressure and different temperatures. From left to right, T = 203, 209, 215, 221, 227, 233, 239, 245, 257, 269, 275, 281, and 287 K. The lines are the Fourier transforms of the Kohlrausch function with n = 0.40 used to fit the primary loss peaks in $M''(f)$. The secondary conductivity relaxation appears as smaller loss peaks at lower temperatures and as excess wing at higher temperatures. Each of the short vertical black arrows with its head ending near data points at a certain temperature indicates the location of the primitive frequencies f_0 calculated by the CM eqn (5) for the same temperature.

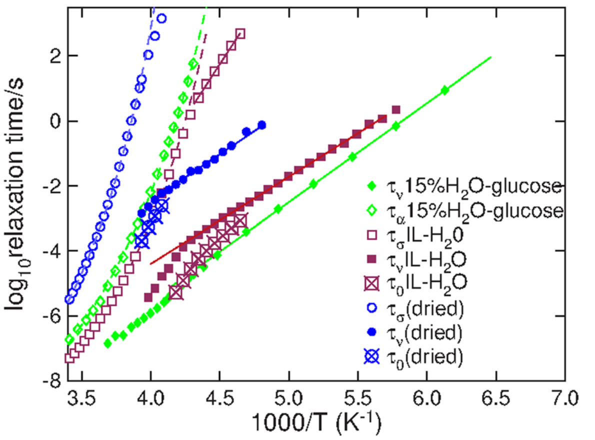

Fig. 4 Relaxation map showing the temperature variations of the conductivity relaxation times $\tau_\sigma(T)$ and $\tau_\nu(T)$ of the IL–water and the dried sample at ambient pressure. Dashed lines are the VFT fits (above T_g) and solid lines are Arrhenius fits (below T_g) fits of dielectric experimental data. The primitive relaxation times $\tau_0(T)$ are calculated by the CM eqn (5). Added are the $\tau_\alpha(T)$ and $\tau_\nu(T)$ of a glucose–water mixture.

of the primitive $\tau_{\sigma 0}(T,P)$ in relation to the most probable $\tau_\nu(T,P)$ verifies the approximate relation (4). Notwithstanding, Murali *et al.* fitted the relaxation spectra by the sum of two Havriliak–Negami functions representing the σ-relaxation and the ν-relaxation. This way of fitting the spectra assumes the two relaxations are independent, which is untenable because $\tau_\sigma(T,P)$ and $\tau_\nu(T,P)$ are co-invariant. Their fits also tend to obtain a longer $\tau_\nu(T,P)$ if the ν-relaxation is not resolved as a loss peak but instead appears as a shoulder or excess wing at higher temperatures in Fig. 3.

The values of $\tau_\sigma(T,P)$ given by Murali *et al.* over a range of temperatures above and below the glass transition temperature T_g can be used directly to calculate the primitive $\tau_{\sigma 0}(T,P)$ by eqn (5). The results of $\tau_{\sigma 0}(T,P)$ are shown in the relaxation map of Fig. 4, and compared with the values of $\tau_\nu(T,P)$ deduced by Murali *et al.* There are good agreements of $\tau_{\sigma 0}(T,P)$ with $\tau_\nu(T,P)$ at lower temperatures where the ν-relaxation exhibits loss peaks, and the peak frequency directly determines $\tau_\nu(T,P)$. At higher temperatures, the values of $\tau_\nu(T,P)$ from Murali *et al.* becomes shorter than $\tau_{\sigma 0}(T,P)$ by one decade or less. Part of the deviation is due to overestimating $\tau_\nu(T,P)$ in the fit by the sum of two Havriliak–Negami functions mentioned in the previous paragraph. Added in Fig. 4 are the structural α-relaxation times $\tau_\alpha(T)$ and the JGβ water ν-relaxation times $\tau_\nu(T)$ of 15% water in glucose.[19] The $\tau_\nu(T)$ of this mixture has magnitude and activation energy in the glassy state close to that of $\tau_\nu(T)$ of the IL–water mixture.

It is relevant to recall the ρ^γ/T scaling with the same γ for both the structural α relaxation time $\tau_\alpha(T,P)$ and the JG β relaxation time $\tau_\nu(T,P)$ in supercooled glass-formers that has been established by experiments before, and reviewed.[26] Examples include methylated derivative of ketoprofen,[27] ternidazole,[28] and diglycidyl ether of bisphenol-A.[29] Evidences are given in ref. 26 to conclude that the origin of ρ^γ/T scaling is not from the structural α-relaxation times τ_α. Instead it comes from its precursor, the Johari–Goldstein β-relaxation or the primitive relaxation of the Coupling Model, and their relaxation times τ_β or τ_0 respectively. Similar conclusion can be made that ρ^γ/T scaling of the conductivity τ_σ originates from τ_ν in the ionic liquids with or without water.

4. Discussions

As pointed out in the Introduction, in mixtures of hydrophilic materials with water changes are usually observed in both the frequency dispersion of the structural α-relaxation and the ratio $\tau_\alpha(T,P)/\tau_\nu(T,P)$ with changing T and P while keeping $\tau_\alpha(T,P)$ constant. In contrast the conductivity relaxation in the IL–water mixture of Murali *et al.*[1] shows the opposite behavior of having both the ratio $\tau_\sigma(T,P)/\tau_\nu(T,P)$ and the frequency dispersion or the Kohlrausch exponent $(1 - n)$ invariant to changes of T and P while keeping $\tau_\sigma(T,P)$ constant. The question posed before is why the behavior of the processes in these two aqueous mixtures are so different. To answer this question it is worthwhile to consider dielectric data of mixtures of two components without hydrogen bonding such as 10 wt% of the quinaldine (QN) in tristyrene[25] shown in Fig. S3 (ESI†) before. Both the α-relaxation and the primitive/JG β-relaxation combined can be traced to the motion of the polar quinaldin molecules in the presence of the nonpolar tristyrene. The CM equations relating these two processes apply, and the predictions of $\tau_\beta(T,P) \approx \tau_0(T,P)$ and the co-invariance of $\tau_\alpha(T,P)$, $\tau_\beta(T,P)$, and $n(T,P)$ to changes of thermodynamic conditions at constant $\tau_\alpha(T,P)$ are verified in the quinaldin mixture with tristyrene as shown in

Fig. S3 (ESI†), and in many other mixtures without hydrogen bonds, and in pure molecular glass-formers.[6,7]

On the other hand, in aqueous mixture with some hydrophilic compounds such as the oligomers of propylene glycol, the small water molecules are homogeneously hydrogen bonded to the host molecules. The structural α-relaxation probed is contributed by host and water together. Thus the width of its frequency dispersion or $n(T,P)$ and its relaxation time $\tau_\alpha(T,P)$, have no bearing on the primitive/ν-relaxation of water. The relations, $\tau_\alpha(T,P) = [t_c^{-n}\tau_0(T,P)]^{1/(1-n)}$ and $\tau_\nu(T,P) \approx \tau_0(T,P)$ no longer hold even at ambient pressure as evidenced by the dielectric data of mixture of water with PPG400 in Fig. 2. Furthermore, applications of pressure accompanied by increase in temperature to maintain the same $\tau_\alpha(T,P)$ tend to break hydrogen bonds, alter the intermolecular interaction, and changes $n(T,P)$. All these factors cause the breakdown of co-invariance of $\tau_\alpha(T,P)$, $\tau_\beta(T,P)$, and $n(T,P)$ in aqueous mixtures as observed. Notwithstanding the possibility of other aqueous mixtures in which water are present as clusters instead of homogeneously bonded to the host cannot be excluded. Candidates include fructose–water mixtures[30] and hydrated poly(vinyl pyrrolidone)[31] as suggested by the demonstration of the validity of the relation $\tau_\nu(T,P) \approx \tau_0(T,P)$.

The arrangement of water molecules in the IL–water mixtures of Murali *et al.* are different from aqueous mixtures with some hydrophilic molecules like oligomers of propylene glycol.[2] They form sizeable clusters confined by the cations and anions of the IL as found by several molecular dynamics simulations of a few mixtures of water with other imidazolium-based ILs.[32–35] The [BMIm-SO$_3$H][pTS] ionic liquid studied by Murali *et al.*[1] has sulfonate/sulfonic acid group located in the chemical structure of ions to form an extensive hydrogen-bonding network and conductivity is *via* fast proton transport between ionic species and water molecules in the clusters. The water in clusters are involved in proton hopping in generating the primitive/ν conductivity relaxation at shorter times and also in the cooperative σ relaxation at longer times. Confined in cages, the water clusters retain their identity with changes of T and P. The favorable conditions imply applicability of the CM to this IL–water mixture, and it is verified by the experimental $\tau_\nu(T,P)$ and the calculated $\tau_0(T,P)$ have approximately the same values as shown in Fig. 3 and 4. In turn the CM equations further explain the observed co-invariance of $\tau_\sigma(T,P)$, $\tau_\nu(T,P)$, and $n(T,P)$ to changes of thermodynamic conditions at constant $\tau_\sigma(T,P)$. A natural consequence of the co-invariance of $\tau_\sigma(T,P)$ and $\tau_\nu(T,P)$ with changes of T and P is the density scaling of both $\tau_\sigma(T,P)$ and $\tau_\nu(T,P)$ to become two different functions of ρ^γ/T but with the same γ after the PVT data have been acquired and incorporated.

5. Conclusion

Found in the conductivity relaxation of a IL–water mixture by Murali *et al.* is the co-invariance of $\tau_\sigma(T,P)$, $\tau_\nu(T,P)$, and $n(T,P)$ to changes of T and P while maintaining $\tau_\sigma(T,P)$ constant. The shape of the primary conductivity σ relaxation as well as the ratio $\tau_\sigma(T,P)/\tau_\nu(T,P)$ do not change. The co-invariance property found is exactly the same as that of the conductivity relaxation in other ionic liquids without water, and is the analogue of the structural α-relaxation and the Johari–Goldstein β-relaxation in mixture of two molecular glass-formers without hydrogen bonds. The predictions of the Coupling Model are applied to explain the co-invariance property of the IL–water mixture quantitatively in the same manner as given before for the other ionic liquids without water and van der Waals glass-forming liquids and mixtures. In contrast to conductivity relaxation in the IL–water mixture, co-invariance had not been seen before in structural relaxation in aqueous mixtures with hydrophilic compounds, where the shape of the structural α-relaxation and the ratio $\tau_\alpha(T,P)/\tau_\beta(T,P)$ are not invariant to changes of thermodynamic conditions. The difference is attributed to water in the IL–water mixture form clusters that are confined by the cations and anions of the IL–water mixture.

Data availability

Data for this article, including Fig. 1–4 are available at [American Chemical Society, ACS Publications] at **https://doi.org/10.1021/jz100154u**, and **https://doi.org/10.1021/acs.jpclett.4c00356**. Data of Fig. S1, S2, S3, and S4 in ESI† are taken respectively from **https://doi.org/10.1016/j.jnoncrysol.2010.07.054**, **https://doi.org/10.1063/1.4705274**, **https://doi.org/10.1021/jp207291k**, and **https://doi.org/10.1021/jp800764w**.

Conflicts of interest

There are no conflicts to declare.

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