

Dielectric secondary relaxation of water in aqueous binary glass-formers†

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Glassy aqueous binary mixtures generally exhibit a water induced dielectric relaxation. The characteristic time-scale of this relaxation follows an Arrhenius temperature dependence with a nearly universal activation energy. We here demonstrate for a series of model aqueous mixtures that the relaxation time also follows a remarkably general exponential dependence on the weight fraction of water. By comparison to literature data we show that this behaviour is shared by a wide range of molecular systems. Neither the detailed nature of the water molecules' glassy environment nor the details of the route of formation of the glassy state has a significant effect on the observed behaviour.

1. Introduction

Water is one of the most important substances on earth, playing essential roles in geology, in chemistry and in most biological systems.¹ The relaxation dynamics of hydration water in proteins, for instance, is believed to control important dynamics of the proteins themselves and thus to influence the process of protein folding and functionality.^{2,3}

Surprisingly, many of the physical properties of water are not well understood and its dynamics, structure and thermodynamics display 'anomalous' behaviour compared to most other liquids; this is believed to be a direct consequence of the strong hydrogen (H-) bonding that characterizes the intermolecular interactions in water.⁴

A problem when investigating pure water and a contributing reason why water is still not well understood is its strong tendency to crystallize. As a consequence, water is very difficult to study in its supercooled regime, where many of its apparent anomalies are located. Below the homogeneous nucleation temperature at ~ 231 K, one has to resort to indirect methods to learn about its behaviour and most studies have been performed either on water in confinement^{5–8} or on water mixed with other liquids.^{9–14}

A liquid in its supercooled state generally displays several molecular relaxation processes. The primary α relaxation is related to the viscosity of the liquid and slows down dramatically as the temperature is reduced, which eventually causes the system to fall out of equilibrium at the glass transition temperature, T_g . In addition, a faster secondary so called β relaxation is generally observed either as a distinct relaxation process or as a high frequency contribution to the α relaxation, a so-called excess wing.¹¹

Moreover, a range of studies^{12–15} have shown that when water is mixed with another glass-forming liquid a new dielectric relaxation process appears, here denoted the w -relaxation. This additional relaxation process shows a number of general features: (i) it follows an Arrhenius temperature dependence in the glassy state, $\tau = \tau_0 \exp(E/k_B T)$, where E is the activation energy and τ_0 the relaxation time in the high temperature limit, (ii) the shape of its response function is symmetric, or very near symmetric, on a logarithmic frequency scale, (iii) E has a value of ~ 0.54 eV (ref. 14 and 16), independent of the system in which water is dissolved or the amount of water that is dissolved¹⁴ and (iv) its relaxation strength increases systematically with increasing water content.

We note that (i) and (ii) are characteristics typical of secondary relaxations in glass-forming systems and the value of the activation energy in (iii) suggests a relatively 'local' character of the observed response; E roughly corresponds to twice the energy of a typical H-bond.¹⁷ Furthermore, it is interesting to note that a secondary relaxation with similar properties (i)–(iii) is observed also for pure water studied in hard confinement, where crystallization can be suppressed.⁸ This, together with the behaviour of its strength (iv), further suggests that the w -relaxation observed in aqueous mixtures is largely a characteristic of the water within the mixtures. It is important to note that the relationship between the dynamics of bulk water and the dynamics of confined water is not well understood. Interestingly, however, the secondary relaxation observed for water in confinement has been interpreted as a β relaxation of pure water, corresponding to the β relaxation observed for most pure glass-formers.^{18–22}

One difference between the w -relaxation observed in aqueous mixtures and most "normal" β relaxations is the quantitative values of its Arrhenius prefactor, τ_0 . Typically, when fitting relaxation data for aqueous mixtures in their glassy state to an Arrhenius expression, values of $\tau_0 \approx 10^{-22}$ – 10^{-16} s are found, which are clearly different from characteristic molecular vibrational time-scales, $\tau_0 \approx 10^{-14}$ – 10^{-12} s. This surprising behaviour demonstrates our present lack of understanding of water in general and of water mixed with

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other liquids in particular and stresses the need for systematic experimental investigations.

In this study, we investigate the concentration dependence of the water-related w -relaxation for binary mixtures of water and a series of liquids for which the H-bond density can be systematically varied.²²

2. Experimental

We study oligomeric liquids based on the same monomeric unit, propylene oxide, but varying in chain-ends: $X-[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n-\text{H}$, where $X = \text{HO}$ for propylene glycols (n PG) and $X = \text{CH}_3-\text{O}$ for propylene glycol monomethyl ethers (n PGME). We investigate the monomers with $n = 1$ (PG and PGME), dimers with $n = 2$ (2PG and 2PGME) and trimers with $n = 3$ (3PG and 3PGME), respectively. For both the glycols and the monomethyl ethers, H-bonding plays an important role,²² but as shown in Fig. 1, and discussed below, an increasing water content has a completely different effect on the T_g -values and thus the α relaxations in the two types of liquids.

All samples were purchased from Sigma-Aldrich. They were freeze dried and their purity was confirmed by IR-spectroscopy. The liquids were mixed with distilled milli-Q water (conductivity $< 0.1 \mu\text{S m}^{-1}$) followed by homogenisation for fifteen minutes in an ultrasonic bath.

The differential scanning calorimetry (DSC) experiments were performed on a TA Instrument DSC Q1000. The samples were initially cooled into their glassy states from room temperature at a rate of -30 K min^{-1} . Subsequently, the T_g values were determined as the onset of the heat capacity step upon heating from the glass at a rate of $+10 \text{ K min}^{-1}$.

No sign of crystallisation was observed during the initial cooling for mixtures with water concentrations $C_w < 60 \text{ wt}\%$ (mass of water to total mass of sample) with the exception of the PGME mixtures which showed crystallization at $C_w > 54 \text{ wt}\%$. For the latter samples, crystallization was avoided by submerging of the samples into a bath of liquid nitrogen followed by direct transfer to a pre-cooled cryostat;

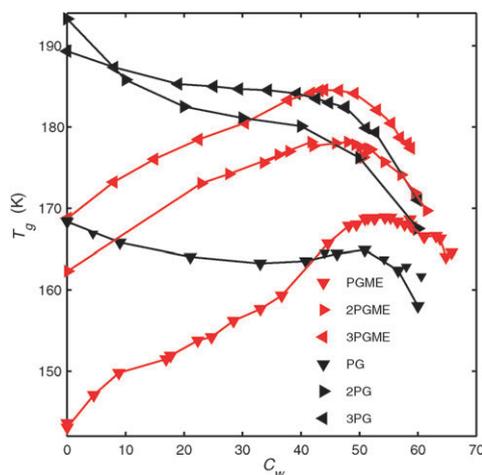


Fig. 1 Calorimetric glass transition temperatures for aqueous mixtures of n PG and n PGME, respectively, as a function of water content. The solid lines are guides to the eye.

for these samples crystallization could not be directly monitored on cooling. However, all samples, both quenched and unquenched, showed one distinct glass transition.

The dielectric response was measured using a Novocontrol Alpha analyser in the frequency range 14 mHz–1 MHz. The 100 micron thick samples, for which the thickness was controlled by silica spacers, were sandwiched between electrodes with a diameter of 20 mm placed within a sealed sample cell. Generally, for all six systems the samples were cooled from room temperature using controlled cryostat cooling at a typical rate of -20 K min^{-1} ; no sign of crystallinity was found for $T < 205 \text{ K}$ using this protocol. The two PGME samples with the highest water fraction were instead quenched by submerging the sample cell into liquid nitrogen followed by placing the sample cell into a pre-cooled cryostat.

3. Results and discussion

As water is added to the pure n PG liquids, the T_g values decrease but reach a plateau at $\sim 20 \text{ wt}\%$; the plateau behaviour continues to $\sim 40\text{--}50 \text{ wt}\%$, where an onset of a stronger T dependence takes place leading to a decrease of T_g upon further addition of water. In contrast, for aqueous n PGME, T_g increases strongly upon addition of water and reaches a maximum for $C_w = 45 \text{ wt}\%$ ($55 \text{ wt}\%$ for PGME). For higher C_w , the T_g values decrease rapidly, as shown in Fig. 1. The observed behaviour for the monomethyl ethers with an increasing T_g value for increasing water content is a highly unusual behaviour for aqueous systems. We investigate this behaviour in detail in a separate publication,²³ suggesting that the increase of T_g for low to moderate C_w is an effect of the build-up of H-bond mediated structures and the decrease of T_g for the highest C_w is likely due to a saturation of these structures together with a plasticizing effect due to the excess water.

In the following, we focus primarily on the behaviour of the w relaxation and for this study it is sufficient to recognize the marked difference between the T_g behaviours of the glycol and the monomethyl ether systems.

In addition to the α relaxation, all the anhydrous liquids studied here exhibit a secondary β relaxation at frequencies higher than those characteristic of the α relaxation. For PG this relaxation is submerged under the high frequency flank of the α relaxation and is thus only observed as an excess wing. As water is added, for both n PG and n PGME, a third relaxation process, the w -relaxation, is observed in between the α - and the β relaxations, see Fig. 2a. The strength of this additional process increases monotonically with water content and even for modest water concentrations the contribution of the β relaxation to the dielectric loss, ϵ'' , is negligible. This behaviour makes an analysis of the β relaxations of the mixtures difficult and we therefore restrict our discussion to the α - and the w relaxations. Typical examples of the measured dielectric loss are shown in Fig. 2. Analogous behaviours of the α - and w -relaxations are observed for $n = 1, 2$ and 3 of n PG and n PGME.

We note that for the PGME mixtures with water concentrations corresponding to T_g values above the maximum, we found evidence for an additional relaxation process. This relaxation

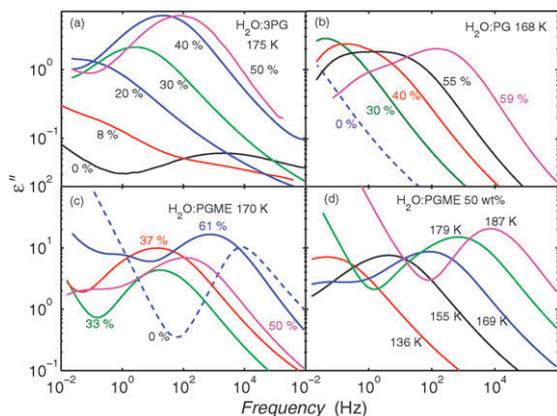


Fig. 2 Dielectric loss spectra. (a) Water–3PG mixtures in the glassy state (175 K) ranging from 0–50 wt% of water. (b) Water–PG mixtures for different water concentrations for $T = 168$ K. (c) Water–PGME mixtures for $T = 170$ K. (d) 50 wt% water–PG mixtures at different temperatures.

is several orders of magnitude slower than the w relaxation, but has approximately the same activation energy. However, due to the difficulty in resolving and thus in quantitatively describing this relaxation process, we will not discuss it further in the following.

We generally fit the dielectric loss spectra with a sum of three terms. The α relaxation is described by a Havriliak–Negami²⁴ (HN) function, $\epsilon''_{\alpha} = -\text{Im}\{\Delta\epsilon/[1 + (i\omega\tau)^a]^b\}$, where $\Delta\epsilon$ denotes the dielectric strength, τ the characteristic relaxation time and a and b describe the symmetric and asymmetric broadening of the relaxation peak respectively. The w -relaxation is described with the symmetric (on a logarithmic frequency scale) Cole–Cole²⁵ (CC) function which equals the HN function for $b = 1$. The loss contribution from dc-conductivity is well described by an inverse frequency term: $\sigma_0/\epsilon_0\omega$, where σ_0 is the dc conductivity and ϵ_0 the vacuum permittivity.

From our fits, as shown in Fig. 3, we extract the characteristic relaxation times for the α - and w relaxations. The resulting relaxation times for PG and PGME at different hydration levels are shown in an Arrhenius representation in Fig. 4 (the corresponding plots for the dimers and trimers are included in the ESI†). The temperature dependent α relaxation times for all investigated samples are well described by Vogel–Fulcher–Tamman²⁶ (VFT) functions; $\tau = \tau_0 \exp[DT_0/(T - T_0)]$, as expected for α relaxations and demonstrated by the fits in Fig. 4. For temperatures near T_g , the α relaxation generally becomes faster as water is added to the glycols, as shown in Fig. 4. In contrast, the opposite behaviour with a slowing down of the α relaxation for increasing water content is observed for monomethyl ethers up to a certain value of C_w , above which τ decreases. We find that the dielectric T_g values, determined as the temperatures where $\tau_{\alpha} = 100$ s, correspond well to the calorimetric T_g values, shown in Fig. 1.

The characteristic relaxation times for the w relaxations exhibit Arrhenius temperature dependences in the glassy state for all samples. This behaviour changes above T_g , where the VFT behaviour of the α relaxation is approached; this is commonly observed for secondary relaxations in supercooled liquids²⁷ and will not be further discussed here.

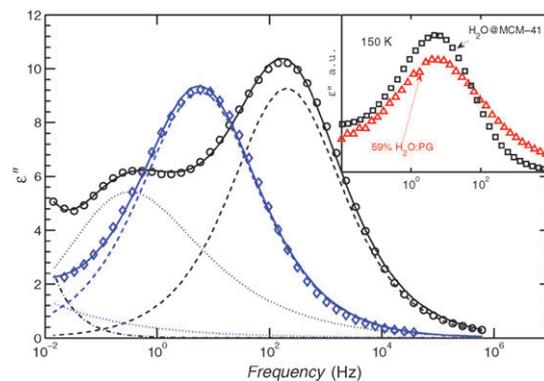


Fig. 3 Examples of the dielectric loss fit for 40 wt% H_2O in 2PG. Circles denote data at $T = 185$ K, where the system is supercooled and both the α - and w -relaxations are observed. Diamonds denote data at $T = 170$ K, where the system is glassy and the response is dominated by the w -relaxation. The total fits are represented by solid lines and the separate contributions as: w -relaxation (CC-function, dashed), α -relaxation (HN function, dotted) and conductivity (power law, dash-dotted). The inset shows dielectric loss spectra at $T = 150$ K for 59 wt% H_2O in PG and water in MCM-41 (diameter 21 Å),⁸ as discussed in the text.

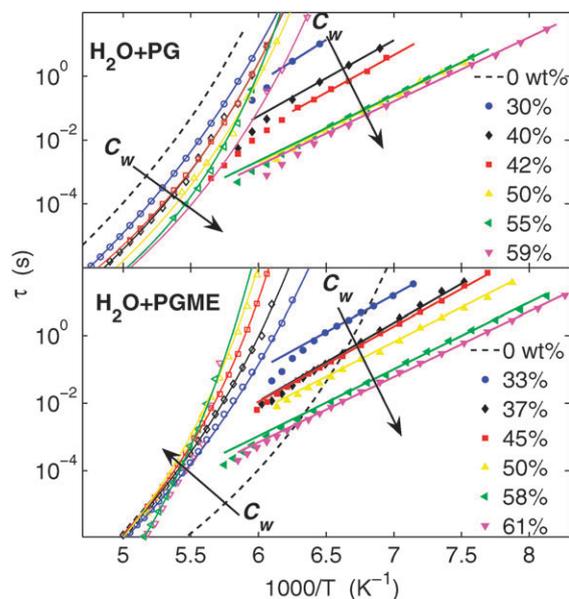


Fig. 4 Dielectric relaxation times of the water–PG mixtures (top) and water–PGME mixtures (bottom). The dashed black lines denote the α relaxations of the anhydrous samples. The solid symbols denote the relaxation times for the w relaxation and thick lines are the fits to the Arrhenius equation. The open symbols denote the relaxation times of the α relaxation and the thin lines denote the results of VFT fits. The arrows indicate the direction of increasing water content.

Here we focus on the behaviour of the w relaxation within the glassy state.

Remarkably, in marked contrast to the very different behaviours of the α relaxations for PG and PGME, the w relaxation shifts systematically towards shorter times as more water is added for both systems. We find the same behaviours for the dimers and trimers, as shown in the ESI.†

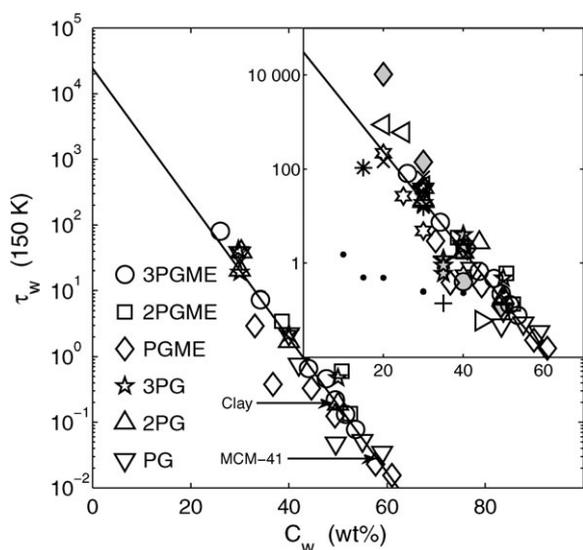


Fig. 5 Dielectric relaxation time of the w -relaxation, τ_w , at 150 K for all systems in this study against C_w . The inset shows τ_w for literature data on a wide range of different systems including glycerol²⁸ (\blacklozenge), sorbitol (\blacksquare), nEG¹⁴ (\star), fructose²⁹ (\times) and sucrose²⁹ (\blacktriangle), glucose³⁰ (\ast), ribose (\otimes) and deoxyribose³¹ (\triangleleft), hemoglobin (\blacktriangleright) and myoglobin³² (\blacktriangledown), PVP³³ (\bullet), PVME (\bullet) and PEG600¹⁴ ($+$). Solid lines are exponential fits to the data (excluding PVP). Arrows indicate the relaxation times for pure water confined in clay⁷ and MCM-41.⁸

The activation energy of the w relaxation is highly similar for all investigated systems with only a weak decrease observed for increasing C_w ; values within the range $E = 0.46 \pm 0.06$ eV (44 ± 6 kJ mol⁻¹) were found for all mixtures, which are consistent with the previously reported values for the w relaxation available in the literature.¹⁴

To investigate this behaviour further we plot the w relaxation time at a fixed temperature, $T = 150$ K, as a function of C_w for all six systems in Fig. 5; at this temperature all samples are in their glassy states. Surprisingly, we find that all systems show the same quantitative exponential decrease of $\tau_w(150$ K) with C_w . We recall the markedly different C_w dependence of the α relaxations for the different liquids and we thus establish that for these systems the w relaxation is essentially insensitive both to the route of glass formation and to the detailed nature of its glassy environment.

Even more surprising is the fact that the observed correlation holds for an even wider range of different liquids. In the inset to Fig. 5, we have included all, to our knowledge, available literature data for the w relaxation in aqueous binary systems that are glassy at 150 K. The quantitative agreement between the different data sets is surprising, particularly since we expect the spatial distribution of water to be different for different systems. Decreased interactions between water and the matrix molecules due to the formation of water clusters at higher C_w could lead to faster dynamics, but such an effect should depend on the density of water clusters and not on the overall water content, C_w .

However, as seen from the inset to Fig. 5, some large molecular weight systems do display a clearly different behaviour, at least at low (< 35 wt%) hydration levels; this is most evident for PVP. This difference in behaviour might be due to a highly

uneven distribution of water, which would lead to local water concentrations significantly different from the average values reported in Fig. 5, making direct comparisons difficult. We also note that the w -relaxation has been reported for more complex materials, such as bread and purple membranes,^{18,34} where the matrix is a complicated multi-component system. We exclude these here, however, due to the obvious difficulty in direct comparison of water concentrations.

The fact remains that the observed correlation is remarkably general and excluding PVP from the discussion, we can describe all systems by the same exponential behaviour, as demonstrated by the solid line in Fig. 5; this behaviour generally correlates overall water concentrations and τ_w within an accuracy of a decade in time.

4. Conclusions

We have thus found that the secondary dielectric relaxation of water in glassy binary mixtures: (i) follows an activated Arrhenius temperature dependence with an almost system independent activation energy and (ii) its relaxation time at a fixed temperature decreases exponentially with increasing weight fraction of water. Thus, the main cause of the change in τ_w is a decrease of the concentration dependent ‘attempt’ time scale, $\tau_0(C_w) = \tau' \exp(-C_w/C_w^*)$, where τ' is the time scale for $C_w = 0$ and C_w^* characterizes the speeding up of τ_0 with increasing C_w . An extrapolation of the exponential behaviour in Fig. 4 to $C_w = 0$ gives $\tau' = 4 \times 10^{-14}$ s, consistent with a typical vibrational time-scale expected for a pure glass-former and we find that $C_w^* \approx 10$ wt%.

It is interesting to note that for water concentrations < 50 – 55 wt% we obtain relaxation times corresponding well to those observed for pure water measured in ‘hard’ confinement, where the confining volume is as large as possible whilst still hindering crystallization.^{7,8} To demonstrate this we have included the values of $\tau_w(150$ K) determined from dielectric measurements of water within two different confinements, a porous glass (MCM-41) and a clay,^{7,8} respectively, in Fig. 5.

To further illustrate the similarities in behaviour, we show the dielectric loss spectrum of water at $T = 150$ K confined within MCM-41 (pore diameter 21 Å) in the inset of Fig. 3 together with the spectrum for a 59 wt% mixture of water and PG. The observed relaxation processes clearly exhibit nearly identical characteristic relaxation times even though the MCM-41 data are slightly distorted due to the heterogeneous nature of the matrix.³⁵ Thus, for MCM-41 pore sizes corresponding to ~ 7 water molecules across the pores, the dielectric relaxation time of water coincides with the w relaxation times for aqueous mixtures at $C_w \approx 50$ – 55 wt%.

It is also interesting to note that at $C_w \approx 50$ – 55 wt% a strong change in behaviour is observed in the T_g vs. C_w dependence, observed either as a maximum (monomethyl ethers) or as a rapid decrease (glycols). This suggests that the characteristic behaviours, observed for the α relaxation, are related to the onset of some degree of ‘bulk-like’ water properties in the mixtures and suggests a possible saturation of the w relaxation time for higher water concentrations if crystallisation could be avoided.

In summary, we demonstrate that the unique secondary relaxation observed in binary aqueous mixtures exhibits a remarkably general dependence on the overall water weight fraction. We determine a quantitative relationship, which describes this dependence for a wide range of aqueous mixtures. We find that this near 'universal' effect is unrelated to the highly system dependent effects of water content on the structural relaxation time. The generalities presented in this work are important for a better understanding of the role played by 'local' water dynamics in biology and in many industrial processes, such as the cryopreservation of biomolecules.

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