Insights into the non-exponential behavior of the dielectric Debye-like relaxation in monoalcohols

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Insights into the Non-exponential Behaviour of the Dielectric Debye-like Relaxation in Monoalcohols

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More than 100 years after Debye proposed his model for the dielectric relaxation of monoalcohols (MA), some fundamental questions about their dynamics and its relation with the supramolecular structures created by hydrogen bonding remain not fully understood. The recent detection of the dynamics of hydrogen bonded aggregates by techniques other than dielectric spectroscopy is leading to novel insights and opening new questions. In particular it was recently reported that the shear response of some MA present three relaxation components, at variance with their apparent bimodal dielectric response. We show by mixing an archetype MA with LiCl that both shear and dielectric measurements are consistent with the presence of three separated contributions. Results are discussed in the more general context of MAs with non-exponential slow dielectric relaxations. In particular, we propose the recently reported third process as the origin of the unusual broadening of the Debye-like dielectric relaxation of some MAs.

I. INTRODUCTION

Hydrogen bonding has significant impact on the thermodynamics, the structuring and the dynamics of many important fluids with biological or technical applications. From very structured fluids like colloids or surfactants to hydrogen bonded molecular liquids, the emergence of interaction-mediated characteristic mesoscale structures are a paramount ingredient on their particular properties. In this context, deep understanding of the relationship between structure and dynamics is strongly desirable. Monoalcohols (MA) are a typical example of hydrogen bonded liquids with rich dynamics, which have been extensively studied by multiple techniques. Particularly remarkable is their dielectric relaxation, which in addition to the structural relaxation shows an intriguing very intense slower relaxation reported more than 100 years ago, commonly referred to as ‘Debye’ relaxation. Generally, this relaxation is very close to an exponential or time distributed ‘Debye’ relaxations, and therefore, we will use the term Debye-like to refer to the intense slower dielectric relaxation observed in these systems. The typical morphology of the mesoscale structures leading to a pre-peak in the static structure factor of MAs would be chain-like and ring-like structures identified from computer simulations, with the majority of molecules forming chain-like aggregates. The orientational correlation alignment of dipoles forming chains would be at the origin of the intense Debye-like dielectric relaxation, that according to the transient chain model would basically relax through successive loss and/or gain of segments at the end of chains. Although it is broadly accepted that the Debye-like dielectric relaxation is related to supramolecular structures or aggregates resulting from hydrogen bond interactions, there is no evident explanation why this relaxation is broad for some MAs. It has been proposed that the non-exponentiality could emerge due to heterogeneity in the size of hydrogen bonded aggregates. What is clear is that the degree of non-exponentiality of the Debye-like relaxation is correlated with its strength, so that the broader the relaxation the less intense it is.

For long time the observation of the Debye-like process by other techniques than dielectric spectroscopy remained elusive, but slow dynamics additional to that of the structural relaxation have already been reported by a number of techniques and most revealingly by shear modulus measurements. Moreover, very recently and aided by complex viscosity representation of shear data, authors have reported for the first time the presence of an additional process, intermediate between those previously indentified. The timescale of this additional feature observed in the shear viscosity response is consistent with the timescale of the rotational dynamics of hydroxyl groups as seen by NMR. As a consequence, this intermediate process was interpreted as the mechanical imprint of the breaking and forming of individual hydrogen bonds in the framework of the transient chain model. In all, the multimodal shear response of MAs in general shows the following three separate processes: (i) a slow relaxation leading to the recovery of pure viscous flow; (ii) the mentioned additional process at intermediate frequencies; and (iii) a high frequency maximum representative of the structural relaxation involved in the glass transition. Comparison of these results with those obtained by dielectric spectroscopy becomes very interesting. On the one hand, the high frequency peak in matches that of the dielectric α relaxation, confirming its assignment to the structural relaxation. On the other hand, the characteristic time where the liquid recovers pure viscous flow (crossover to ) corre-
lates well with that of the dielectric Debye-like relaxation in many MAs,\textsuperscript{18,20,22,23} supporting the idea that the dielectric Debye-like relaxation reflects the complete relaxation of hydrogen bonded aggregates. The intermediate process observed in the shear response, however, seems to not have a clear dielectric analogue. As commented before, we interpreted\textsuperscript{20} this process as the mechanical imprint of the breaking/forming of individual hydrogen bonds\textsuperscript{7,21}. This dynamics, i.e., the reorientation of individual OH groups attaching and detaching the aggregate could in principle lead to dielectric signal. Interestingly, long before we reported the presence of the intermediate process in the shear response of MAs, we had noticed that when digging into great detail the description of the dielectric relaxation of 2-ethyl-1-hexanol (2E1H) in terms of two processes provided insufficient intensity at the valley between the two relaxations, opening the possibility of an additional dielectric relaxation process in between\textsuperscript{24}. Further exploring these ideas, the purpose of this work was to modify hydrogen bond interactions and structures with several objectives: gain more knowledge on the origin and nature of the mentioned intermediate process; search for possible traces and indications of intermediate process on the dielectric response of MAs; and find an explanation for the non-exponential behavior of some MAs.

The mixing of MAs with other polar and non-polar liquids and even with other MAs has been a usual approach to modify hydrogen bonds and better understand their dielectric response.\textsuperscript{8,25–32} In most cases relaxation in the mixture is broadened with respect to the pure MA and Debye-like process amplitude decreases. One major problem when dealing with such mixtures is that it becomes difficult to distinguish between several broadening scenarios, namely: (i) intrinsic broadening of the Debye-like relaxation of the MA component; (ii) general broadening of relaxations due to mixing effects, a common phenomenology in low molecular weight polymers and polymer blends;\textsuperscript{33–36} and (iii) apparent broadening due overlapping of contributions from different components. In order to avoid the extra level of complexity introduced by the dynamics of a second liquid we have studied in this work the evolution of the mechanic and dielectric response of 2E1H upon LiCl salt addition. In the field of supramolecular polymers for example, the addition of ionic species, strong hydrogen bond competitors, is known to reduce their length and viscosity by breaking non-covalent interactions.\textsuperscript{37} The idea of breaking hydrogen bonds in MAs by adding ionic species has not been fully exploited so far. The early works of Floriano et al\textsuperscript{38} and Power et al\textsuperscript{39} showed that adding strong electrolyte LiClO\textsubscript{4} to 1-propanol decreases the intensity of the Debye-like relaxation and slightly changes its characteristic time distribution, but authors did not explore different concentrations or characterize its mechanic response. In this work the archetype 2E1H was mixed with low amounts of LiCl simple ionic salt with the aim of modifying hydrogen bonds to gain some insight on the effect of such interactions on the dynamics of the liquid. Among different MA the choice of 2E1H results convenient due to the relatively large timescale separation between the structural and the Debye-like relaxation in this MA and its clear multimodal shear response.\textsuperscript{18,20}

As we will see in the following, the addition of ions modifies both the dielectric and mechanic response of the MA and shifts the diffraction structural pre-peak characteristic of mesoscopic structures. These results are discussed in relation to the dielectric imprint of the intermediate process and the intriguing non-exponential slow dielectric relaxation of some MA.

\section{II. MATERIALS AND EXPERIMENTAL}

2-butyl-1-octanol (2B1O), 2-hexyl-1-decanol (2H1D), 5-methyl-3-heptanol (5M3H), 2E1H, propylene carbonate (PC) and LiCl were purchased from Aldrich. The pure molecular liquids were stored with activated molecular sieves for at least one week before any measurement in order to eliminate traces of ionic impurities which could be present in the commercial products. Solutions of LiCl in 2E1H were prepared at 1/30, 1/20, 1/15, and 1/10 LiCl/2E1H molar ratios (between 1% and 3% weight percentage). The resulting solutions were transparent and clear and were characterized by means of: infrared spectroscopy in the near (NIR) and medium (MIR) ranges; small angle X-ray scattering (SAXS); differential scanning calorimetry (DSC); dielectric spectroscopy (DS); and oscillatory shear response.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Infrared absorption spectra and SAXS diffraction curves obtained for pure 2E1H and mixtures with different LiCl content. Panel (a): MIR range; Panel (b): NIR range; Panels (c) and (d) SAXS data normalized to the intensity of the main peak at Q $\sim$1.36 A.}
\end{figure}
Vibrational Spectroscopy

Vibrational spectra of samples were recorded by means of a Jasco 6300 spectrometer in transmission configuration for the NIR range (8000-4000 cm\(^{-1}\)) and in Attenuated Total Reflectance (ATR) configuration for the MIR range (4000-7000 cm\(^{-1}\)) at room temperature. Panels (a) and (b) of figure 1 show detail of the OH stretch absorptions in the MIR and NIR regions, respectively.

Structural Characterization

Small angle X-ray scattering (SAXS) diffraction experiments were carried out by means of a Rigaku 3-pinhole PSAXS-L equipment operating at 45 kV and 0.88 mA. CuKa transition photons of wavelength \(\lambda = 1.54 \text{ Å}\) were produced by a MicroMax-002+ X-Ray Generator System and composed by a microfocus sealed tube source module and an integrated X-Ray generator unit. Flight path and sample chamber in the equipment were under vacuum. A two-dimensional multiwire X-Ray Detector (Gabriel design, 2D-200X) detected the scattered X-Rays. This gas-filled proportional type detector offers a 200 mm diameter active area with ca. 200 micron resolution. The azimuthally averaged scattered intensities were obtained as a function of wavevector \(Q\), \(Q = 4\pi/\lambda \cdot \sin\theta\), where \(\theta\) is the scattering angle. Boron-rich capillaries of 2 mm thickness were filled with sample and placed in transmission geometry with a sample to detector distance of 23 cm. With this configuration the \(Q\)-range covered was 0.07 \(\leq Q \leq 1.7\text{ Å}^{-1}\). All the experiments were carried out at room temperature. Lower panels of figure 1 show the diffraction curves obtained for pure 2EIH and LiCl/2EIH mixtures.

Differential Scanning Calorimetry

Calorimetric glass transition of the samples was determined from the reversible part of the heat flow measured by Temperature Modulated Differential Scanning Calorimetry (Q2000 TA Instruments) at a heating rate of 3K/min and 0.3K modulated amplitude during a 45s period. Salt addition produces a slight increase of the glass transition temperature \(T_g\) -see Supplementary Information (SI)-. The mentioned increase is linear with salt concentration and amounts a maximum of 5-6 degrees above \(T_g\).

Shear Response

The shear response was measured by means of a TA Instruments ARES rheometer with a separate motor transducer using invar plates (8 mm diameter) in parallel geometry. Each sample was analyzed over a range of temperatures from about 2 degrees below the calorimetric glass transition to a temperature high enough for the terminal behavior to be observed, generally around 15 - 25 degrees above \(T_g\). At the lowest temperature, dynamic strain sweep tests at 200 rad/sec were performed to determine the linear regime in which the storage \(G'(\omega)\) and loss \(G''(\omega)\) moduli were constant for each system and a strain in this linear regime was chosen for subsequent measurements which provided torque in the desired range. Dynamic frequency sweeps at a constant strain were run at angular frequencies between 0.1 and 100 rad/sec. Shear data were analyzed paying attention to both the complex modulus \(G'(\omega) = G' + iG''\) and complex viscosity \(\eta^* = \eta' - i\eta''\) representations, which are related as \(G^* = \omega\eta^*\). Although the information contained in both magnitudes is the same, the \(\eta^*\) representation can aid in resolving the presence of different processes by eye as they may appear highlighted in the form of maxima (or more pronounced power law changes or ‘shoulders’).

Dielectric Response

Isothermal dielectric spectroscopy (DS) experiments were carried out by means of Novocontrol Alpha A broad band spectrometer and a Keysight E4991A RF Impedance analyzer. Temperature was controlled by a nitrogen-jet stream with a temperature stability of 0.15 K. Samples were sandwiched between two parallel gold-plated electrodes using Teflon thin strips as a spacer in a specific liquid cell. Results were corrected from stray capacitance of the cell and area of the Teflon strips. Following the procedure applied in our previous works\textsuperscript{10,24} the information from DS experiments was mainly obtained from the analysis of the log-frequency derivative of the real part of the dielectric permittivity \(\varepsilon'(\omega)\). In this way: (i) we minimize the uncertainty in the determination of the parameters characterizing the \(\alpha\) relaxation and its possible influence on the width of resolved Debye-like processes; and (ii) eliminate dc-conductivity contribution from the relaxation peaks. When analyzing the derivative of the real part of the dielectric permittivity we did not assume the approximation \(\varepsilon'(\omega) \sim -d\varepsilon'/(d\log\omega)\), but the complex permittivity was modelled by a sum of Havriliak-Negami (HN) functions\textsuperscript{30} as usual,

\[
\varepsilon(\omega) = \varepsilon_{\infty} + \sum \frac{\Delta \varepsilon_j}{1 + (i\omega\tau_j)^{\alpha_j}},
\]
where each process \( j \) is characterized by its relaxation strength \( \Delta \varepsilon \), its relaxation time \( \tau \), and the shape parameters \( a \) and \( b \) \((0 < a, b \leq 1)\) determining the broadening and asymmetry of the loss curve respectively. For quantitative characterization then the derivative of the real part of the permittivity was fitted to the derivative of the permittivity is not important (see figure S2 in SI), this was modeled by an extra term \( \Pi / \omega^a \), in the derivative of the real permittivity.

III. RESULTS

We found first evidences of the changes produced by LiCl addition on the hydrogen bonded mesoscopic structure of 2E1H in FTIR and SAXS measurements (see figure 1). On the one hand, LiCl addition modifies OH-group vibrations confirming that ions do interact with hydroxyl hydrogens. The red shift of the stretch band in the MIR indicates further weakening of the OH covalent bond due to dipolar interaction with ions. In the NIR range mixtures show a decrease of both free (~7092 cm\(^{-1}\)) and strongly associated (~6280 cm\(^{-1}\)) OH bonds\(^{41,42}\) consistent with an scenario where ions re-

FIG. 2: Shear master curves (left axis -circles-) and isothermal dielectric measurements (right axis -squares-) at the indicated reference temperature for pure 2B10, 5M3H, 2H1D, 2E1H MAs, LiCl/2E1H mixtures and PC. Solid lines in shear data represent the terminal behavior \( \eta''(\omega) \propto \omega \). Solid, dashed, dotted and dotted-dashed lines in DS data represent total, Debye, intermediate, and structural relaxation fit components, respectively -see SI-.
duce the number of hydroxyl groups available, hampering the formation of strongly bonded associates. Noteworthy, the infrared spectra of all samples both in the NIR and MIR range only differ on the bands related to OH, the rest being indistinguishable. Structural characterization by SAXS on the other hand, shows that the mesoscopic prepeak characteristic of hydrogen bonded aggregates (Q \~ 0.4 - 0.6 Å⁻¹) moves to lower Q values - equivalently, larger characteristic length scales- as LiCl content increases, whereas the main peak characteristic of the intermolecular correlations between CH groups remains invariable. The position of the mesoscopic prepeak in MA (mainly corresponding to O-O correlations) is known to move to lower Q the larger the number of carbons in the main chain. Here being the alkyl chain length the same, a shift to lower Q values is compatible with a decrease in the density of aggregates. An increase of the X-ray scattering contrast due to the presence of ions interacting with end-chain OH-units is also compatible with the observed increase in the relative intensity of the prepeak.

### FIG. 3: Maximum normalized derivative of the real part of the permittivity for different salt concentrations at 215K.

Panels a) to d) of figure 2 show the imaginary part of the shear viscosity \( \eta''(\omega) \) master curves for pure 2E1H and LiCl-containing 2E1H at different concentrations. The y-scale in figure 2 covers only one decade in order to underline different maxima while still being sensible to data \( \propto \omega^p \) power laws. Non-simple, multimodal, relaxation is observed for all the samples. The higher frequency maximum should be representative of the glass transition while the rest of the features presumably originate from mesoscale structures and/or interactions between molecules. As commented, three different processes or components can be identified for pure 2E1H. The addition of LiCl decreases the relative intensity of the slowest and more prominent component in 2E1H, the more, the higher the LiCl content. Regarding dielectric spectroscopy results, mixing mainly results in broadening of the slowest relaxation peak together with a gradual decrease of its intensity (see figures 2, 3 and SI for additional representation of dielectric data). The overall dielectric response of 2E1H/LiCl mixtures thus resembles the not frequently reported non-exponential behavior of the Debye-like relaxation observed for some MA, like 2B1O, 2H1D, or 5M3H illustrated in figure 2 as well together with the simple liquid PC for comparison.

### IV. DISCUSSION

Structural characterization of the samples indicate that salt addition modifies the mesoscale structure formed by hydrogen bond clustering (SAXS pre-peak at \( Q \sim 0.5 Å⁻¹ \) and OH vibrations), but not the microscopic scale (SAXS main peak at \( Q \sim 1.36 Å⁻¹ \)) or the vibrations of other chemical groups. Although the addition of a salt increases dc conductivity, the dielectric relaxation in the mixtures is still dominated by dipolar relaxation. The evolution of the dielectric signal of 2E1H upon LiCl addition confirms that small ions are able to modify the 2E1H aggregates responsible of the prominent slow dielectric relaxation of the alcohol, and therefore act as ‘structure breakers’. Concomitant with the changes in the slow dielectric relaxation and the increase of the characteristic length scale of the mesoscopic structures observed by SAXS, the shear response of 2E1H mixtures also gets modified upon LiCl addition. In this case the shoulder at intermediate frequencies in \( \eta''(\omega) \) (which we will refer to as ‘intermediate process’) seems to gain importance relative to the other two. The effect of ion addition tested by different techniques altogether, leave little room against the interpretation of the Debye-like and shear terminal relaxations as due to the relaxation of hydrogen bonded aggregates.

### FIG. 4: Temperature evolution of the slowest peak of the derivative of the real part of the dielectric permittivity from 265K to 295K every 5K for the 1/15 molar ratio mixture. Curves corresponding to different temperatures were shifted for clarity. Solid line represents the derivative of an exponential (Debye) relaxation for the permittivity.

In addition to test the effect of the addition of a
'structure breaker' on the dynamics of 2E1H, in this work we also aimed at modifying the relative contribution of the slowest and intermediate processes to the response obtained by different techniques. In particular, one of the objectives was to make more evident the very subtle sign of the intermediate process in the dielectric relaxation previously proposed by us. For pure 2E1H the width of the slowest dielectric relaxation slightly increases as temperature increases, or otherwise, as intensity decreases. This tendency seems to be quite universal and could be interpreted as an indication of the presence of an underlying process whose contribution appears more clear when the intensity of the slow Debye relaxation decreases due to less or smaller hydrogen bonded aggregates. In principle, if LiCl breaks non-covalent interactions, similar phenomenology could be expected here, that is, a decrease of the intensity together with a broadening of the overall signal due to the presence of an underlying process. In this regard, LiCl/2E1H mixtures present lower intensity slow relaxations together with a progressive broadening of the signal as salt concentration increases. As shown in figure 3, upon LiCl addition there is a significant broadening on the high-frequency flank of the relaxation, i.e. where the contribution of the intermediate process is expected, whereas the low-frequency tail remains more or less the same as long as temperature is not too high. Moreover, for a constant salt concentration the effect of increasing temperature is that previously reported for pure 2E1H, i.e. further broadening of the slow dielectric signal. This is again consistent with the above mentioned picture where the signature of an underlying process (an increase of the relaxation width in this case) appears more clear as the intensity of the slow Debye relaxation decreases. Analyzing results for the 1/15 molar mixture more in detail, one sees that in this sample the broadening and the change of the shape of the slowest dielectric peak as temperature increases is dramatic. This is illustrated for the highest temperatures in figure 4 and for the whole temperature and frequency range in figure 5 of the SI. At the lowest temperatures, although the signal is already broader than that corresponding to a pure exponential relaxation, the broadening mainly affects the high-frequency flank of the relaxation and the a low-frequency side is close to the asymptotic behavior of a Debye relaxation. As temperature increases, the signal continues to broaden only on the high-frequency side for a while. With further heating of the sample, however, the signal also starts to broaden at the low-frequency side so that for the highest temperatures the non-symmetric peak faces now towards the low-frequency flank. This phenomenology would emerge as a consequence of changes in the relative strength of the slow Debye and the intermediate processes with temperature. At the highest temperatures shown in figure 4, even two separate processes could be envisaged in the almost bimodal curves recorded. A reasonable explanation is that the intensity of the slowest Debye-like relaxation decreases to such extent that the underlying additional process (intermediate between Debye-like and $\alpha$ relaxations) appears to dominate the peak as a whole.

The presence of an intermediate dielectric process can rationalize the effect of salt concentration and temperature on the evolution of the shape of the slow dielectric feature in 2E1H/LiCl mixtures and is consistent with the modification of the shear response upon salt addition. As commented before, the timescale for the intermediate shear process in pure 2E1H agrees well with the timescale observed by NMR for the hydroxyl group reflecting the lifetime of a molecule within a transient chain of alcohol molecules. The presence of 'structure breaker' ions would in principle increase the relative number of 'terminal' monomers, increasing the contribution of the breaking of individual hydrogen bonds to the different experimental observables. In order to dig into this idea we made an approach to describe dielectric data in terms of a sum of three processes (see SI for details). Obtained dielectric strengths for 1/15 and 1/10 samples are shown in figure 5. The T-dependence of the strength of both the Debye and the intermediate processes in 1/15 sample shows a change of trend at about 240-250 K (see Figure 5a). This change has been previously reported for the total dielectric strength of 2E1H and other MAs and also for other physical quantities as absorbance of first overtone stretches of OH and chemical shift of the hydroxyl proton measured by NMR. Despite the strength of both processes, Debye and intermediate, reflect changes at ~240-250 K, their temperature behavior is distinct. The strength of the Debye process continuously decreases with temperature, while that of the intermediate process shows a maximum about 240-250 K. The occurrence of a maximum in the strength of the intermediate process associated to the breaking and forming of individual hydrogen bonds on the aggregates would be the result of two competing effects. On the one hand, the decrease of the average chain-like cluster size with increasing temperature and salt concentration increases the relative number of 'terminal monomers', increasing
the contribution of the intermediate process to the different experimental observables. This effect, however, cannot be extended forever. At some point, the gradual extinction of the H-bonded aggregates by itself precludes the occurrence of the intermediate process, which requires cooperation or interaction between OH moieties, as the independent dielectric relaxation of OH groups should reflect the structural α-relaxation. Consistently, the strength of the intermediate process in the 1/10 ratio sample (panel b of Figure 5) remains constant as long as that of the Debye process does, i.e. as long as there is not a significant decrease on the number or size of H-bonded aggregates. Destruction of H-bonded aggregates (decrease of Debye relaxation strength) above ~ 200 K produces an increase in the attaching/detaching of individual hydrogen bonds until the strength of the intermediate process reaches a maximum simultaneous to the change of trend in the decrease of the Debye relaxation strength at ~ 240 K. Although the presented experimental work deals with mixtures of LiCl/2E1H, the proposed interpretation is general and should in principle be extensible to other MAs (and even other H-bonded liquids). Particularly interesting is the generalization for those MAs with modest strength and non-exponential relaxations like 2B1O, 5M3H, and 2H1D shown in figure 2. As in 2E1H, the shear response of these MAs shows three processes. The frequency of the highest and lowest features in the shear response match the maxima of the α and the Debye-like dielectric relaxations respectively. In the proposed scenario, the ‘extra’ broadening of the Debye-like relaxation at the high frequency wing would be nothing else than the dielectric counterpart of the intermediate process seen in the shear response. Once again, the three processes inferred from shear measurements are qualitatively consistent with the dielectric response and its interpretation as due to three separated contributions. Moreover, this rationalization provides a natural explanation for the correlation between the extent of broadness and the strength of the Debye-like relaxation, as the presence of an underlying process becomes more evident the lower the intensity of the slowest pure Debye component.

V. CONCLUSIONS

We have proved that LiCl ionic salt mixed with 2E1H acts as a ‘structure breaker’, modifying both the dielectric relaxation and the mechanical response of the MA and shifting the diffraction structural pre-peak characteristic of mesoscopic structures. All the experimental observations agree with an scenario where the presence of ions limits the formation of strongly associated hydrogen bonded aggregates. The impact of LiCl addition on the three relaxation components identified in the shear response is uneven, and the evolution of the dielectric signal with temperature and LiCl concentration is consistent with the presence of three separated contributions in the dielectric response as well. Generalization of the proposed scenario provides a natural explanation for the unusual spectral broadening of some MAs, which would just reflect the dielectric signature of the intermediate process observed in the shear response. In a more general context, it is reasonable to think that similar dynamic processes can also take place in other hydrogen bonded systems, where structural relaxation, individual hydrogen bond forming and breaking and complete relaxation of the hydrogen bonded aggregates should to a greater or lesser extent dictate their dynamic response depending on the bonding lifetime and architecture of the structures formed.

Sample CRedit author statement

S. Arrese-Igor Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Visualization. A. Alegría Data curation, Resources, Writing - Review & Editing. J. Colmenero Resources, Writing - Review & Editing, Supervision, Project administration. A. Arbe Investigation, Resources, Writing - Review & Editing. J. Colmenero Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

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Supporting Information

Supporting information available: Differential Scanning Calorimetry results, and extended analysis of Dielectric Spectroscopy data.

3 M. Tomsšič, A. Jammik, G. Fritz-Popovski, O. Glatter, and L. Víček. Structural properties of pure simple alcohols from ethanol, propanol, butanol, pentanol, to hexanol: com-


To be precise, the asymptotic behavior for the derivative of the real part of a Debye type relaxation for the permittivity, as we are representing $-d\epsilon'/d(\log\omega)$...
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SUPPORTING INFORMATION

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I. DIFFERENTIAL SCANNING CALORIMETRY

Figure S1 shows the temperature derivative of the reversible heat flow for pure 2E1H and LiCl/2E1H mixtures at 1/30, 1/20, 1/15, and 1/10 molar ratios measured by temperature modulated differential scanning calorimetry.

Figure S1: Derivative of the reversible heat flow for pure 2E1H and LiCl/2E1H mixtures at 1/30 (purple), 1/20 (pink), 1/15 (orange), and 1/10 (brown) molar ratios.

II. DIELECTRIC RESPONSE

Figure S2 shows dielectric results for 2E1H and its mixtures with LiCl at 180K. As expected, addition of salt increases the low frequency conductivity contribution in the representation, the more the higher the LiCl content. Despite the presence of important conductivity contribution the presence of the Debye relaxation is clearly distinguishable for all but for the 1/10 concentration sample.

Figure S3 illustrates now in the linear scale how by representing the derivative of the real part of the permittivity slow relaxation peaks are nicely resolved and well separated from electrode polarization effects. The spectra in figures S3 and S4 show the decrease of the relaxation strength of the slowest peak upon salt addition, which is relatively larger at low temperatures (or larger characteristic time scales) than at high temperatures (or shorter characteristic timescales). Complementary to figure 4 of the manuscript, figure S5 shows the change in the shape and broadness of the slowest dielectric peak for 1/15 mixture in the whole frequency range covered. Figure S6 summarizes the evolution of the di-
electric strength of the samples parametrized as \((\epsilon_0 - \epsilon_\infty)\) where \(\epsilon_\infty\) was taken as the high frequency value of \(\epsilon'\) measured at the lowest temperature (125 K), and \(\epsilon_0\) as the low frequency plateau value of \(\epsilon'\) at each temperature. The so obtained dielectric strength does not discriminate among the different contributions to the relaxation of the polarization but it is model independent, unlike the dielectric strengths \((\Delta \epsilon)\) obtained from fitting procedures.

Data were represented as a function of the inverse of the frequency of the maximum of the Debye-like relaxation \((\omega_{\text{max}} = 1/\tau_{\text{max}} = 2\pi f_{\text{max}})\) to eliminate the effect of the weak slowing down of the dynamics with with salt concentration.

Finally, figure S7 shows the effect of LiCl concentration on the broadening of the slowest relaxation of the mixtures. For this purpose we chose to represent Full Width at Half Maximum (FWHM) value of the derivative of the real part of the permittivity, which is a model-free parameter. As commented in the body of the manuscript, the width of the slowest dielectric relaxation for pure 2E1H slightly increases as temperature increases, or otherwise, as intensity decreases\(^3\). Note that this tendency for 2E1H is not well captured when the width is quantified in terms of FWHM, as the broadening is low and it occurs at the high-frequency tail of the relaxation. Data in figure S7 were again represented as a function of the inverse of the frequency of the maximum of the Debye-like relaxation \((\omega_{\text{max}} = 1/\tau_{\text{max}} = 2\pi f_{\text{max}})\) to eliminate the effect of the weak slowing down of the dynamics with salt concentration.

A. Modelling of the dielectric response

Quantitative description of dielectric data was done as follows. As in our previous works, when analyzing the derivative of the real part of the dielectric permittivity we did not assume the approximation \(\epsilon' \sim d\epsilon'/d\log \omega\), but the complex permittivity was modeled by a sum of Havriliak-Negami (HN) functions\(^5\) as usual,

\[
\epsilon*(\omega) = \epsilon_\infty + \sum_{j} \frac{\Delta\epsilon_j}{1 + (i\omega\tau_j)^{a_j}b_j},
\]

where each process \(j\) is characterized by its relaxation strength \(\Delta\epsilon\), its relaxation time \(\tau\), and the shape parameters \(a\) and \(b\) \((0 < a, b \leq 1)\) determining the broadening and asymmetry of the loss curve respectively. The derivative of the real part of the permittivity was then fitted.
to the derivative of the former expression as

$$-\frac{d\varepsilon'(\omega)}{d\log \omega} = \text{Re}\left\{ \frac{1}{\text{Im} \varepsilon} \sum_j \frac{\Delta \varepsilon_j a_j b_j (i\omega \tau_j)^{a_j}}{[1 + (i\omega \tau_j)^{b_j}](b_j + 1)} \right\},$$

so that the parameters obtained from the fittings can be directly compared with those obtained from $\varepsilon'(\omega)$ and/or $\varepsilon''(\omega)$ fittings. Although the contribution of Maxwell-Wagner-Sillars-type processes to the real part of the permittivity is not important (see figure S4), this was modeled by an extra term $P/\omega^2$, in the derivative of the real permittivity.

As at first sight at least dielectric relaxation shows only two relaxations (apart from a faster secondary relaxation not discussed in this paper), a first approach would be the phenomenological description of these two relaxations by the HN expression. Therefore, in first instance two functions were used to describe data: a HN for the slower relaxation (i.e. free $a$ and $b$); and a Kolrausch-Williams-Watts-equivalent Havriliak-Negami ($\text{HN}_{K\text{WW}}$) function for the faster structural relaxation. In the $\text{HN}_{K\text{WW}}$ function the $a$ and $b$ shape parameters are related to each other as $b = 1 - 0.8121(1 - a)^{0.387}$, and to the equivalent stretching parameter $\beta_{K\text{WW}}$ as $\beta_{K\text{WW}} \approx (a + b)^{0.813}$. This ‘two HN process approach’ describes well the measured data for low temperatures and LiCl concentrations but otherwise shows systematic deviations. Figure S8 shows examples of such fittings for 1/15 sample. As it can be seen, the quality of the fittings gets worse the higher the temperature and the broader the relaxation. At the highest temperatures shown in figure 4 of the manuscript and figure S5 of the present SI the two HN model is not valid any more, an expected result in view of the asymmetry and shape of the experimental relaxation data.

Figure S6: Evolution of dielectric strength for different salt concentrations.

Figure S7: Full Width at Half Maximum (FWHM) of the derivative of the real part of the permittivity for different salt concentrations. Dashed line indicates FWHM for a Debye (exponential) relaxation for the permittivity function.

Figure S8: Fitting of the derivative of the real part of the permittivity of the 1/15 sample to a sum of a HN for the slowest peak and a $\text{HN}_{K\text{WW}}$ for the faster structural $\alpha$ relaxation. Insets show detail of the fittings at the linear scale evidencing systematic disagreement at the peak maximum.

Figure S9 shows the characteristic times for the maxima of the slow peak and the structural $\alpha$ relaxation for pure 2E1H and its mixtures with LiCl. Despite the fact that for some concentrations the description of experimental data in terms of two processes is not satisfactory,
the frequency of the maxima for each peak is a rather well defined and thus quite independent of the model used to describe data. In concordance with DSC results, structural relaxation becomes slower the higher the salt content. Likewise, the slower peak also slows down with salt addition. Apart from the mentioned slow down the T-dependence of the relaxations does not change appreciably. This is corroborated in panel b) of figure S9 where temperature was normalized to the glass transition temperature measured by calorimetry (position of the maxima in figure S1). Thus, while the amplitude and the shape of the slowest relaxation considerably changes with salt addition, it has little impact on the relation between the alpha and the slow relaxation characteristic times or on their T-dependence. This result supports the idea that salt addition does not change appreciably the mechanism or basic physics behind the observed relaxations.

Separate relaxation components resulting form such fits were shown in figure 2 of the manuscript. Temperature evolution of the dielectric strength of the Debye and intermediate processes were also included in figure 4 of the manuscript for the most favorable cases i.e. 1/15 and 1/10 molar ratio samples. For these two samples, 1/15 and 1/10 LiCl/2E1H molar ratio samples, best fits were obtained by a CC function for the intermediate process. In the case of pure MAs, although a CC function also provides good fits at high temperatures where the Debye-like relaxation is broad, numerical minimization sometimes produces physically meaningless outcomes at low temperatures. This is because at low temperatures the relatively narrow character of the Debye-like relaxation does not provide sufficient numerical resolution to obtain a meaningful separate characterization of each component. In these cases, the intermediate process was characterized by a CD function, which somehow limits the characteristic times of this process to a frequency range intermediate between that of the Debye and α processes.

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Figure S9: (a) Characteristic times corresponding to the maxima of the relaxation peaks for 2E1H and the mixtures. (b) Same as in (a) but normalized to the glass transition temperature measured by DSC.

At the light of the conclusions drawn in the paper a quantitative description of data in terms of a model comprising three different processes would be more physically meaning and consistent. Unfortunately, for low concentration samples, the great overlap existing between the slowest relaxation attributed to supramolecular H-bonded structures and the intermediate process prevents the obtention of reliable parameters characterizing each of the relaxations independently. In any case we tested a three process approach as follows. On the one hand, as the low temperature Debye-like relaxation of pure 2E1H is almost an exponential one (equivalent Debye in the frequency domain), the shape of the slowest component was fixed to a Debye function (HN with $a = b = 1$). For the structural relaxation the previously mentioned HN$_{KWW}$ function was used. In view of the great extent of the overlap between different processes we estimated convenient to minimize the number of free parameters with the aim of limiting numerically correct but physically meaningless outcomes. For this reason, in the case of the intermediate process a symmetric Cole-Cole (CC) - HN with $b = 1$ - or an asymmetric Cole-Davidson (CD) - HN with $a = 1$ - function was used. All in all:

$$\epsilon \ast (\omega) = \epsilon_{\infty} + \frac{\Delta \epsilon_{\text{debye}}}{1 + (i\omega\tau_{\text{debye}})^a} + \frac{\Delta \epsilon_{\text{int}}}{1 + (i\omega\tau_{\text{int}})^a} + \frac{\Delta \epsilon_{\alpha}}{1 + (i\omega\tau_{\alpha})^a} \left[1 - 0.8121(1 - a_a)^{0.587}\right]$$

Separate relaxation components resulting form such fits were shown in figure 2 of the manuscript. Temperature evolution of the dielectric strength of the Debye and intermediate processes were also included in figure 4 of the manuscript for the most favorable cases i.e. 1/15 and 1/10 molar ratio samples. For these two samples, 1/15 and 1/10 LiCl/2E1H molar ratio samples, best fits were obtained by a CC function for the intermediate process. In the case of pure MAs, although a CC function also provides good fits at high temperatures where the Debye-like relaxation is broad, numerical minimization sometimes produces physically meaningless outcomes at low temperatures. This is because at low temperatures the relatively narrow character of the Debye-like relaxation does not provide sufficient numerical resolution to obtain a meaningful separate characterization of each component. In these cases, the intermediate process was characterized by a CD function, which somehow limits the characteristic times of this process to a frequency range intermediate between that of the Debye and α processes.


