Multimodal character of shear viscosity response in hydrogen bonded liquids

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The impact of supramolecular aggregate formation on the shear viscosity response of hydrogen bonded liquids was investigated. In particular, we study the shear mechanical response of several monoalcohols showing exponential and non-exponential shape dielectric Debye-like relaxation. In addition to the structural relaxation, distinctive of the glass transition, and the terminal crossover to pure viscous flow, characteristic of simple liquid flow, systematic analysis of complex viscosity curves evidence the presence of an additional intermediate process between those two. While the recovery of pure viscous flow would reflect the complete relaxation of the hydrogen bonded aggregates the intermediate process correlates with the rotational dynamics of hydroxyl groups, pointing to be caused by the breaking of individual hydrogen bonds.

Shear viscosity is a transport property of liquids determined by dynamics and measuring the resistance of the liquid to flow. In addition to its practical importance in chemical engineering and tribology, this fundamental physicochemical property of solvents controls microscopic dynamics such as chemical reactions and molecular diffusion with consequences for the locomotion of microorganisms, flow of blood in vessels and many other bioscenarios. At the molecular scale the ability of neighboring molecules to rearrange and jostle past each other determines the propensity of a liquid to flow, the variation in viscosity of different polymer sizes and architectures being a clear example[1–4].

Yet, it is not always obvious how the macroscopic flow is connected to the atomic/molecular dynamics and complex phenomena can emerge from the presence of different kind and degree of intermolecular interactions between molecules, which, in some cases, result in transient network structures and complicate the molecular scale picture of viscosity. Hydrogen bonding and Coulombic interactions for example are responsible for the mesoscopic structure arising in some monoalcohol (MA) and ionic liquids with long alkyl chains[5–12]. The interest in understanding hydrogen bonded networks is ubiquitous while the need to understand the impact of molecular organization on the physicochemical properties of ionic liquids has both a practical and a fundamental basis. Interestingly, Perera et al. reported the same origin for the structural prepeaks of ionic liquids and high alcohols very recently (2017)[9]. In essence, molecular arrangement of these liquids in polar and non-polar domains resemble the more long-lived structure of surfactant solutions. Since the characteristic mesoscopic structure of surfactant solutions is responsible for their large structural viscosity, the study of the structure and dynamics of these kind of transient networks and their possible influence in the flowing behaviour of liquids has lately drawn a lot of attention[9–21].

Theoretical and molecular dynamics simulation works by Yamaguchi (2016 and 2017)[10,11] show bimodal relaxation modes for shear viscosity in high alcohols and long chain ionic liquids which are assigned to the structural dynamics at the "prepeak" and the main peak. Moreover, experimental observation of mesoscale organization arising from the hydrophobic aggregation of extended alkyl tails has been reported in shear-mechanical and dielectric spectra of a series of bulk alkyl-imidazolium ionic liquids (2017)[16]. The imprint of the mesoscopic network relaxation of the alkyl-imidazolium ionic liquid in the dielectric response as a narrow relaxation slower than the structural relaxation is particularly interesting, as it immediately resembles the famous so called Debye or Debye-like dielectric relaxation of MAs[22]. This process has been the object of intense research throughout the last century and it is broadly accepted to be related to the supramolecular structures or aggregates resulting from hydrogen bond interaction. Xiong et al. also reported a narrow dielectric relaxation slower than the structural one in a supramolecular polymer with triple hydrogen-bonding motifs and bring up its resemblance with the MAs Debye-like relaxation on the discussion[21].

The very intense dielectric Debye-like relaxation observed in MAs is often rationalized invoking chain-like structures explaining the large Kirkwood correlation factor g_k in these systems. As a consequence, analogy to polymer chain dynamics has been used in some contexts to discuss dynamics of MAs chain aggregates[13]. Regarding the shape of this process, although most Debye-like relaxations have been reported to be exponential relaxations Wang et al. reported clearly non-exponential shapes in 2-butyl-1-octanol (2B1O) and 2-hexyl-1-decanol (2H1D)[23]. The closeness of the Debye-like and α-relaxation timescales in MAs, however, poses extra difficulties on their detailed characterization. As a consequence, in previous works we have been exploring new routes for measuring and analyzing the Debye-like and α-dielectric relaxation of MAs with the aim of clarifying i) the cause of the apparently exceptional non-exponential character of the Debye-like relaxation in 2B1O and 2H1D and ii) to which extent one can ex-

tend the analogy of polymer chain dynamics to chain-like aggregate's dynamics[24,25]. Results suggest that the non-exponential character of the dielectric Debye-like relaxation might be a general characteristic in the case of not so intense Debye-like relaxations relative to the α-relaxation. Contrary to the general believing established for many years, the process leading to the intense dielectric Debye-like relaxation is likely to have an imprint on the mechanical properties of these liquids as reported by recent shear modulus investigations[13,15]. With all, it is clear that the characterization of the shear response of MAs and its comparison with other hydrogen bonded and ionic liquids, or their dielectric relaxation is very appealing. In this work we have performed shear-mechanical measurements of several MAs (see figure 1) and a simple liquid and analyzed their complex shear viscosity as a function of frequency (in addition to the more standard shear modulus) with the aim of resolving the non-simple shear viscosity relaxation observed in the simulation works and exploring possible traces of the non-exponential character of the Debye-like relaxation on the mechanical response of MAs.
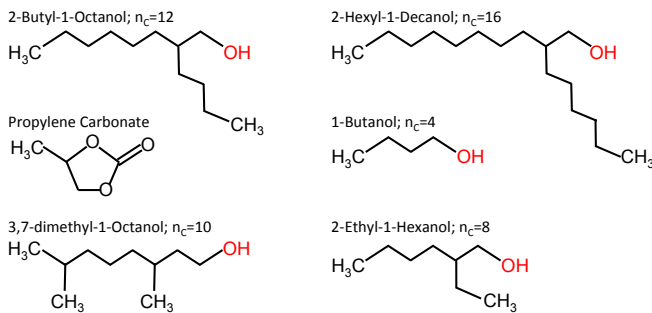

FIG. 1: Molecular structure of the studied samples.

I. EXPERIMENTAL

The complex shear modulus and viscosity were measured with a TA Instruments ARES rheometer with separate motor transducer using invar plates (8mm diameter) in parallel geometry. Each sample was analyzed over a range of temperatures from about 2 degrees below calorimetric glass transition to a temperature high enough for the terminal behaviour to be observed, generally around 15-25 degrees above T_g for MAs. At the lowest temperature dynamic strain sweep tests at $400 rad/s$ were performed to determine the linear regime in which the storage (G') and loss (G'') moduli were constant for each system and a strain in this linear regime was chosen for subsequent measurements which provide torque in the desired range. Dynamic frequency sweeps at a constant strain were run at frequencies between 0.1 and 100 rad/s. Occasionally this range was increased in order to access the glassy range in samples with glass transition near the

low-T limit of the instrument or to avoid cold crystallization.

II. RESULTS AND DISCUSSION

A. Shear and viscosity curves

Figure 2 shows the real (G') and imaginary (G'') parts of the shear modulus ($G^* = G' + iG''$) as a function of angular frequency ω in rad/s for several MAs and a prototype simple liquid propylene carbonate (PC). The broad frequency range showed in the figure is the result of applying time-temperature-superposition to the curves measured at different temperatures. Detailed characterization of Debye-like and α relaxation characteristic times by Broadband Dielectric Spectroscopy (BDS) shows that their ratio is not monotonous[24,26], but as we discuss in detail in the supplementary material, the magnitude of the possible "themorheological complexity" in the shear response would in any case be too small to significantly alter the qualitative features observed in the master curves. At the highest frequencies, recorded values of G' are somewhat lower than expected (below 1 GPa) most probably due to contributions from the torsional compliance of the instrument[27].

The simplest approach to describe the viscoelasticity of glass forming systems is the Maxwell model where

$$G'(\omega) = G_p \frac{(\omega\tau_M)^2}{1 + (\omega\tau_M)^2}, \qquad (1)$$

$$G''(\omega) = G_p \frac{\omega\tau_M}{1 + (\omega\tau_M)^2}, \qquad (2)$$

with G_p shear glassy plateau value and τ_M relaxation characteristic time. In the low frequency limit $G'(\omega)$ and $G''(\omega)$ show the so called terminal behavior where $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$ respectively. Although in simple liquids the structural or α-relaxation process is well stretched already, the distribution has little impact in the low frequency flank of the modulus representation so that $\tau_{max} \simeq \tau_M$ to a good approximation, where $\tau_{max} = 1/\omega_{max}$ stands for the maxima of the segmental relaxation in $G''(\omega)$. The shear relaxation of associated liquids and polymers in general is more complex and may involve additional relaxation processes, but the $G'(\omega) \propto \omega$ power law characteristic of pure viscous behavior is still recovered at sufficiently high temperatures and low frequencies. Similar to the previously reported mechanical response of 2-hexyl-1-hexanol (2E1H) and x-methyl-3-heptanol series[13,15], the shear modulus of 3,7-dimethyl-1-octanol (37dM1O), butanol (4OL), 2B1O and 2H1D as well do not conform to that expected for simple liquids (see figure 2). Compared with the response of the prototype simple liquid PC (see figure 2a and references[28,29]) the MAs show a more extended response with an intermediate region between the glassy zone (indicated by the crossing of G' and G'') and the terminal
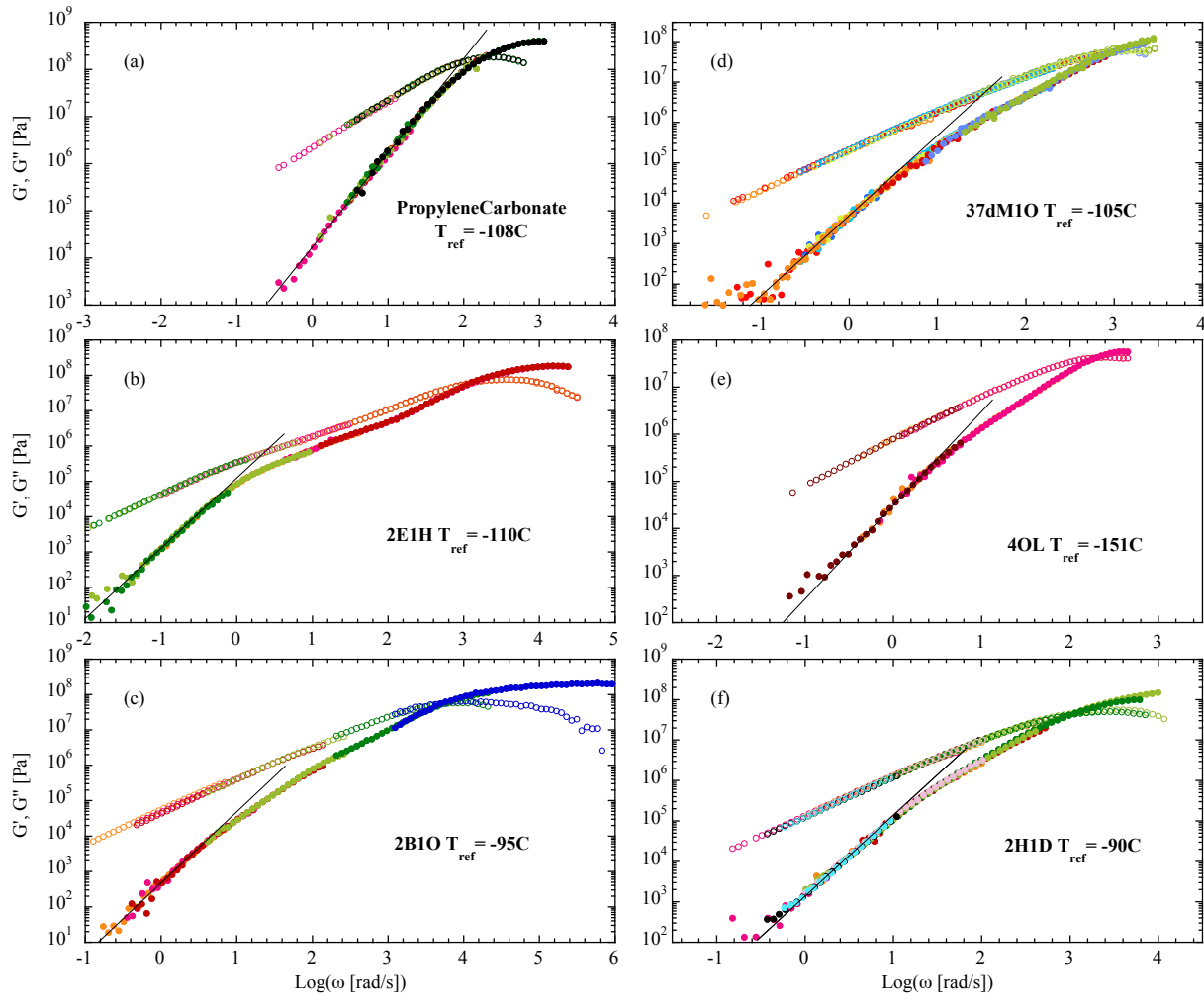
FIG. 2: Master curves for the complex shear modulus of various samples. Filled symbols correspond to real part while empty represent the imaginary part. Solid lines indicate a ω^2 power law characteristic of the so called terminal behavior in $G'(\omega)$.
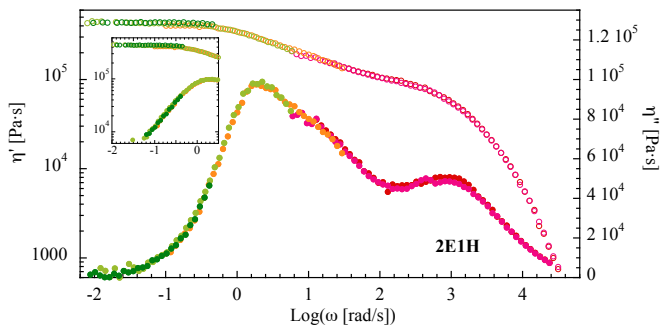

FIG. 3: Shear viscosity master curve for 2E1H.

zone (where $G' \propto \omega^2$ and $G'' \propto \omega$). The extent of this intermediate region does not seem to correlate with the length of the molecule as 4OL and 2H1D for example look similar and 2E1H shows more extended response than 37dM1O. Although the slope of this intermediate region is about 2/3 for G' and G'' in 2E1H (resembling polymer-like behavior as noted in reference[13]) no such trend is reproduced in the rest of the MAs.

Equivalently the shear mechanical response of the samples can be represented by the complex shear viscosity $\eta^* = \eta' - i\eta''$, which is related to shear modulus as $G^* = i\omega\eta^*$. Very recently Yamaguchi reported bimodal frequency-dependent shear viscosity for several alcohols calculated from the time correlation function of the stress tensor obtained by molecular dynamic simulations[12]. Although the information contained in viscosity data is the same, this 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"). As an example figure 3 shows complex shear viscosity data for 2E1H at a 173K reference temperature. For fluids showing ideally viscous flow the applied deformation energy is completely used up (nothing is stored). For viscoelastic fluids the viscous
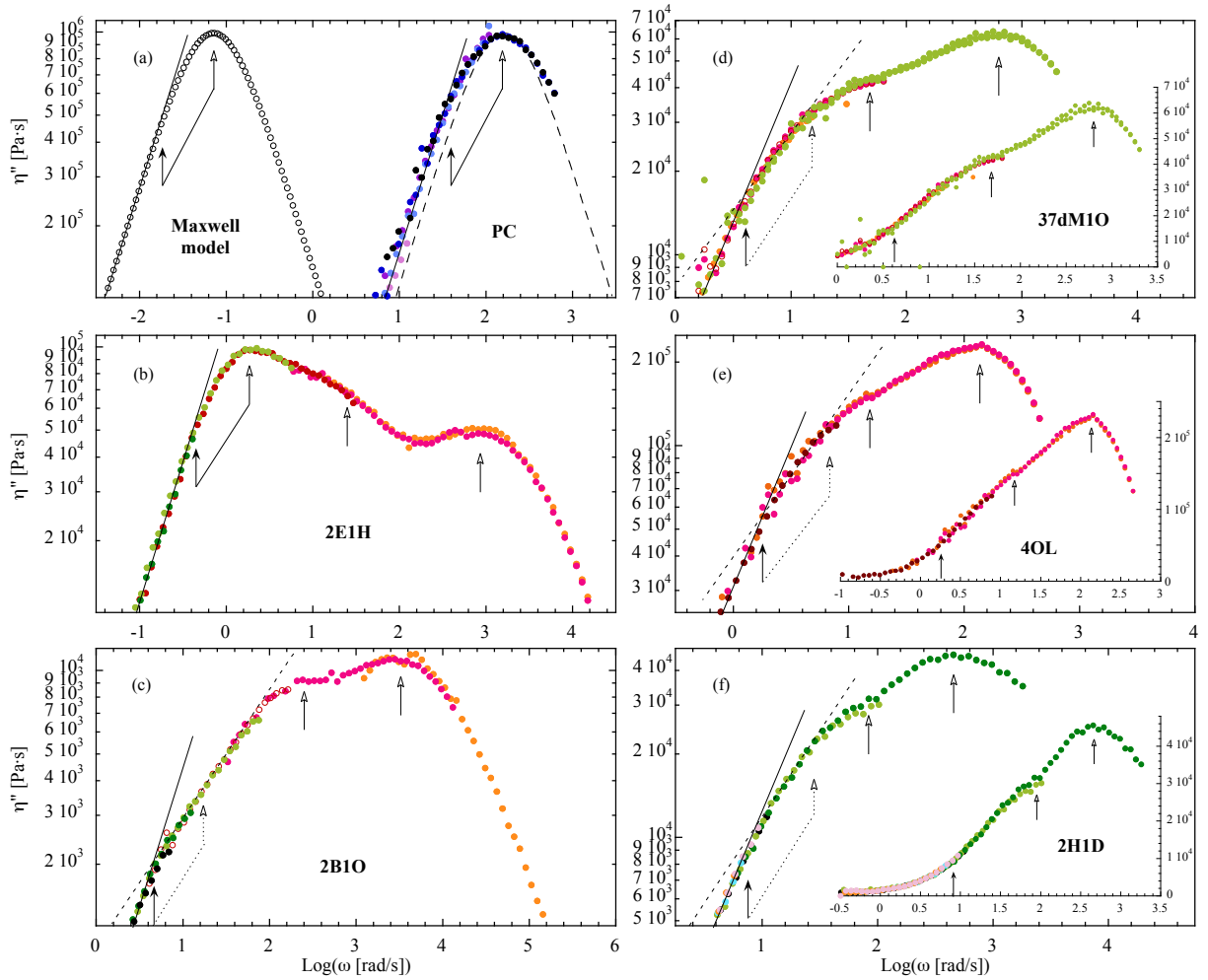
FIG. 4: Imaginary part of the shear viscosity. Open arrows are guides for the eye indicating maxima and shoulders in $\eta''(\omega)$. Black arrows indicate crossover to pure viscous flow. Solid and dashed lines represent $\propto \omega$ and $\propto \omega^{\sim 0.5}$ power laws respectively.

behaviour is rendered by the real part of the viscosity ($\eta' = G''/\omega$) while the elastic behaviour (energy storage) is rendered by the imaginary part ($\eta'' = G'/\omega$). At low frequencies or equivalent high temperatures the monoalcohol in figure 3 behaves as a liquid with a well defined constant viscosity while the elastic component decreases rapidly (terminal behaviour for $\eta'' \propto \omega$ -see inset in figure 3-). As frequency increases or temperature decreases the elastic component of the viscoelastic response becomes progressively dominant till the system glassifies and behaves as an elastic solid so that no viscosity remains. The imaginary part of the complex viscosity in figure 3 (represented in the linear scale to highlight different maxima and "structure") evidences at a glance the presence of more than one process contributing to the elastic storage. The hint of a plateau in the real part of the viscosity around 2 rad/s is clearly underlined as a minimum in the imaginary part. Figure 4 displays $\eta''(\omega)$ master curves for all the samples studied. The y-scale covers only one decade in order to underline different maxima while still

being sensible to data's $\propto \omega^x$ power laws. Non-simple, multimodal, relaxation is easily discernible in all MAs, either as a shoulder in 4OL, 2H1D and 37dM1O, or as well separated peaks in 2B1O and 2E1H (as a guide for the eye maxima and shoulder in $\eta''(\omega)$ are indicated by solid open arrows). Higher frequency maximum should be representative of the glass transition while the rest of the features would presumably originate from mesoscale structures and or interactions between molecules. The experimental complex viscosity curves qualitatively resemble those obtained at higher temperatures by simulations in reference[12]. In that work the relaxation frequency of the slowest mode of $\eta''(\omega)$ agreed well with that predicted from the intermediate scattering function at the prepeak, supporting the relation between the slowest mode and the dynamics of the hydrogen-bonded structure. The shear viscosity representation of these systems enhances what otherwise seem subtle differences in modulus. For example, 2E1H's shear response definitely differs from the others, showing a prominent slow relaxation

dominating the complex frequency response while for the rest the structural relaxation is the prevailing feature.

In addition to qualitative features, quantitative measures of the impact of molecular organization and hydrogen bonding on the viscosity are possible for example by comparing the Maxwell time ($\tau_M = \eta_o/G_p$, where $\eta_o = lim_{\omega \to 0}[\eta'(\omega)]$) and the time corresponding to the maximum loss of shear modulus for segmental relaxation τ_α.[13,30,31] For the case of a Maxwell relaxation one has $\tau_M/\tau_{max} = \frac{\eta_o G'_\alpha}{\eta''_\alpha G_p} = 1$, which still holds to a good approximation for van der Waals simple liquids. As an alternative, we have quantified the viscosity enhancement due to processes other than the structural relaxation directly by the ratio between η_o and $\eta''_\alpha = G'(\omega_\alpha)/\omega_\alpha$, which does not stand on extrapolation or fitting of the modulus values at high frequencies. For a Maxwell relaxation $\eta_o/\eta''_\alpha = 2$. Taking the crossing point of G' and G'' as ω_α an experimental value of $\eta_o/\eta''_\alpha = 2.3$ was obtained for PC in this work. The viscosity increase over simple viscous behavior quantified as η_o/η''_α is about a factor of ~ 9 in 2E1H, ~ 5 in 2B1O, ~ 4 in 4OL and ~ 3 in 37dM1O and 2H1D.[32] Measured values of η''_α might be affected by the compliance of the measuring system but we can expect this effect to be similar for all the samples so that estimations are still valid for comparative purposes at least.

Regarding the terminal behavior, all samples reach the $\eta'' \propto \omega$ ($G' \propto \omega^2$) limit at low frequencies. In this concern, the crossover to pure viscous flow (to $x = 1$ exponent power law in η'' at low frequencies) is a reference feature of the spectra that immediately precedes in frequency (~ 0.6 *decades* in that scale, see figure 4a) the maximum of the imaginary shear viscosity of a Maxwell relaxation. In the case of PC, the maximum following the terminal crossover corresponds to the glass transition while in the case of 2E1H would correspond to the ultimate dynamic relaxation of the hydrogen bonded structures (see connected arrows in figure 4a and b). In this respect, the crossover to terminal behavior in the rest of the samples would presumably indicate the presence of an underlying and overlapped maximum in η'', in concordance with the multimodal and asymmetric aspect of the spectra. Interestingly however, the crossover to pure viscous flow in 2B1O does not "immediately" precede the slower maximum in $\eta''(\omega)$ at ~ 2.2 rad/s. The position of the maximum expected from the terminal crossover (dashed open arrow in figure 4c) is much below the $\eta''(\omega)$ maximum at ~ 2.2 rad/s and instead, a well defined intermediate power law extends for about 2 decades. Close inspection of the data reveals that this phenomenology is similarly repeated in 4OL, 37dM1O and 2H1D. Although no clear second maxima is resolved in these cases, the position of a virtual maximum (dashed open arrows) following the pure viscous flow crossover (black arrows) locates at a frequency well below the emerging shoulder on the low frequency side of the structural relaxation. Moreover, in the case of 2E1H, although a well defined maximum does follow the terminal crossover of $\eta''(\omega)$ at

the expected frequency position, hints of an additional intermediate feature are also observed at around 1.2 rad/s in between the two well resolved maxima, pointed out by the asymmetry, broadness and non-monotonous ω^x power law of the high frequency wing of the slower maximum. Summarizing, we can say that all MA samples display complex features in their $\eta''(\omega)$ response, which point to the presence of an intermediate relaxation process between the terminal pure viscous flow and the structural relaxation.

B. Comparison of different techniques and timescales

The understanding of the phenomena and properties arising from hydrogen bond interactions is a complex problem that requires the use of different approaches. The information obtained from different experimental techniques is often complementary and gathering different contributions usually provides forward steps. From structural analysis the formation of mesoscale structures in many systems containing hydrogen bonds in general and in MAs in particular is clear. From a dynamical point of view, dielectric techniques provide good characterization of timescales over a broad frequency and temperature range, but structural information is obtained indirectly and only by virtue of its coupling with dipolar fluctuations so that microscopic interpretation is not always straightforward. Nuclear Magnetic Resonance (NMR) measurements in addition to dynamics can procure spatial and microscopic information, which often require selective labeling. Dynamic mechanical testing on the other hand is intrinsically highly sensitive to structure. We have followed several approaches in order to assess quantitative timescale to the dynamics observed by shear oscillatory measurements. Timescales where determined as $\tau = 1/\omega$ from: i) $G' = G''$ crossing, τ_{cross}; ii) the crossover to pure viscous flow or $\eta'' \propto \omega$ power law regime, τ_x; and iii) η'' maxima and shoulder, τ_{max}. Note that for the determination of τ_{cross} and τ_x only isothermally recorded data were used. τ_{max} were determined either from isothermal curves by eye inspection (red symbols), either from time-temperature-superposition master curves by fitting the shear response to the sum of three Maxwell processes for G* $\left(\eta* = \sum G_{pk}\tau_k/(1 + i\omega\tau_k)\right)$. In general, squares, diamonds and circles were used to depict slowest, intermediate and fastest process respectively, observed by mechanic response. The characteristic times obtained after applying time-temperature-superposition mechanical shift factors to the dielectric characteristic times are separately indicated by crosses (see supplementary information). As an example figure 5 gathers together the characteristic times determined from the response of 2E1H and 4OL to several excitation, i.e. to several experimental techniques. For all the MAs, τ_{cross} and the highest frequency τ_{max} are in good agreement with the characteristic times for the di-

electric α-relaxation and the glass transition temperature measured by calorimetry[25], evidencing that the high frequency peak in $\eta''(\omega)$ is due to the structural relaxation ultimately leading to the glass transition. With the exception of 2E1H, this faster relaxation dominates the complex shear viscosity response so that flowing behavior is still very much dictated by short range intermolecular correlations.

On the other hand, and also for all the MAs, the characteristic time where the liquid recovers pure viscous flow (crossover to $\eta'' \propto \omega$) coincides with that of the dielectric Debye-like relaxation. As the pure viscous flow should be recovered in a time/length scale where the effects of the mesoscopic structures do not longer play a role, this coincidence strongly supports the idea that the dielectric Debye-like relaxation reflects the complete relaxation or lifetime of hydrogen bonded aggregates. With respect to the intermediate feature between the terminal pure viscous flow and the structural relaxation, as expected it lays in between the dielectric Debye-like and α relaxations. Trying to shed new light on the origin of the Debye-like relaxation in MAs some years ago Böhmer et al conducted NMR measurements on isotopically labeled 4OL and 2E1H. They found that the correlation times of the alkyl group (main chain) correspond well with those of the dielectric α-relaxation while those of the hydroxyl group are much slower while still faster than the dielectric Debye-like relaxation[14,33]. They proposed the existence of an intermediate time scale related to the reorientation of individual OH groups attaching and detaching the aggregate, while the Debye-like relaxation would be caused by fluctuations of the supramolecular dipole of the aggregate. The hydroxyl group rotation as seen by NMR (taken directly from figures 3 in references[14,33]) is consistent with the intermediate processes observed in the shear viscosity of 2E1H and 4OL (see figure 5). At the molecular scale viscosity is nothing more than the ability of neighbouring molecules to rearrange and jostle past each other, therefore it is not surprising that the reorientation of hydroxyl groups interfered by hydrogen bond interactions also shows its imprint on the viscosity response. The fact that an intermediate process has been observed by mechanic and NMR techniques makes it a sounder result. Moreover, in a previous work we showed that when digging into great detail the description of the Debye-like and structural dielectric relaxations of 2E1H in terms of a Cole-Davidson (CD) and a Kohlrausch-Williams-Watts (KWW) function provide insufficient intensity at the valley between these two processes, opening the possibility of an additional relaxation process[24]. Note that the mentioned effect is very tinny but systematic and can only be noticed when looking at the differences between fit curves and data in the linear scale. Motivated by mechanical and NMR results we have fitted dielectric data of 2E1H with two exponential (Debye) and a KWW function. The introduction of an additional process provides excellent fitting and what is more relevant, the characteristic times obtained for this ex-

tra process (open diamonds in figure 5a) perfectly match the intermediate process observed in the shear viscosity response and is consistent with the OH group motion observed by NMR. The mentioned tiny mismatch between measured and fitted (two process) curves also occurs for 2B1O, but this is even less evident than for 2E1H, as in 2B1O the Debye-like relaxation is much broader and in addition closer in time to the α-relaxation. If we attempt to fit the dielectric data of 2B1O with a CD, an exponential and a KWW function for Debye-like, intermediate and structural relaxations respectively, the description of data is very good, and the resulting characteristic times for the intermediate process match those for the intermediate process observed in shear mechanical experiments of 2B1O. We should note however, that this result should be taken more as a test for consistency than as an evidence, because the effect is very small and obviously models with higher number of parameters generally attain better description of data. Finally, if the intermediate process is explained by the motion of hydroxyl groups or breaking of H-bonds, one should expect not to be constrained to primary MA and to see some broadened viscosity response also in Hydrogen bonded systems not showing dielectric Debye-like relaxation. Interestingly a very recent work has reported the existence of a slow rheological mode in neat glycerol[30].

One of the aims of this work was to check if the exceptional broadening of the dielectric Debye-like relaxation observed in some MAs had its imprint on the mechanical relaxation of the alcohols. We could not observe any clear differential characteristic feature on the mechanical response of 2B1O and 2H1D relative to other MAs. One could contemplate the possibility that the unusual broadening of the Debye-like relaxation in 2B1O was related to the prominent intermediate process observed in its shear viscosity response (maximum at $\sim 2.2 \, rad/s$ in figure 4c). To check this possibility we tried to describe the dielectric Debye-like relaxation in terms of two exponential relaxations. The resulting description, however, having one more free parameter is even worse than that provided by a single CD and in addition, the characteristic times inferred for the intermediate process are much slower than those observed in the shear viscosity response. We thus conclude that the broadening of the Debye-like relaxation in 2B1O does not seem to have its origin or be related to the intermediate process of shear viscosity and the individual reorientation of OH bonds, and therefore remains a puzzle.

In a transient chain model scenario, considering that the orientation of an OH is essentially fixed as long as it is part of a chain and that the timescale at which molecules attach to and detach away from the chain ends can be approximated by $\simeq \tau_{cross} \simeq \tau_\alpha$, the timescale for OH reorientation $\tau_{OH} \simeq N\tau_{cross}$, where N stands of the number of chain segments[14]. If the intermediate process observed by viscosity measurements was indeed a signature of the mentioned attaching and detaching or reorientation of OH molecules, the ratio between its timescale and that
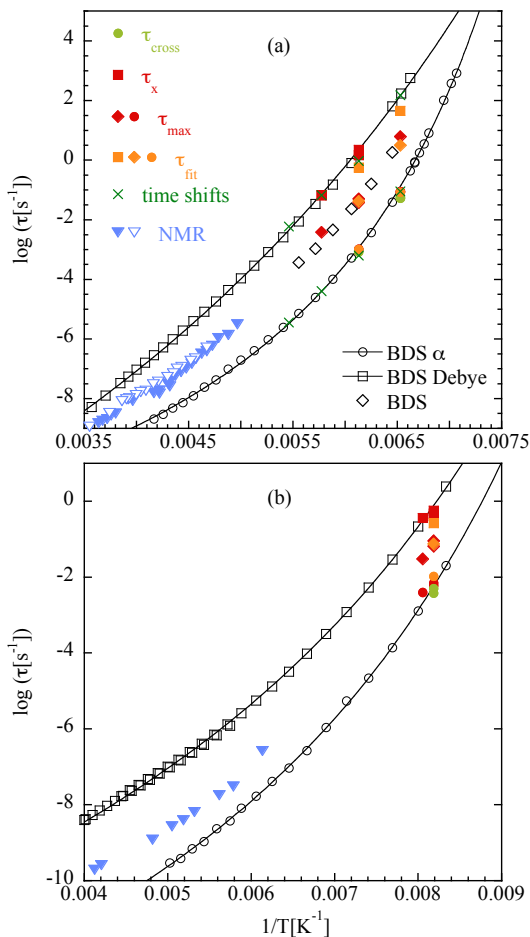
FIG. 5: Characteristic times for 2E1H (a) and 4OL (b). Squares, diamonds and circles represent slowest, intermediate and fastest process respectively, observed by mechanic and dielectric techniques. τ_{cross} represent characteristic times obtained from $G' = G''$ crossing; τ_x from the crossover to pure viscous flow; τ_{max} from the position of maxima and shoulder in $\eta''(\omega)$; τ_{fit} from fitting the shear response to the sum of three Maxwell processes; times represented by crosses were obtained after application of time-temperature-superposition shift factors to dielectric times; and triangles represent characteristic times obtained by NMR from references[14,33].

for the structural relaxation would indicate roughly 10-15 chain segments for 4OL, 37dM1O and 2B1O and around 40 for 2E1H at temperatures close to the glass transition.

The complex shear viscosity of 2E1H definitely differs from others showing a prominent slow relaxation dominating the complex frequency response while for the rest of the MAs the structural relaxation is the prevailing feature. Summarizing figures, 2E1H presents the highest η_o/η_α, τ_{OH}/τ_α and $\Delta\epsilon_D/\Delta\epsilon_\alpha$ ratios. However, there is not straightforward relationship between these quantities for different MAs. 2B1O, 4OL and 37dM1O have similar values of η_o/η_α and τ_{OH}/τ_α, but the $\Delta\epsilon_D/\Delta\epsilon_\alpha$ ratio of 2B1O is significantly lower than that for 4OL or

37dM1O. It seems that the hydrogen bond driven molecular aggregation in 2E1H occurs in such a way that it enhances both dielectric and stress correlations. In contrast, although the structures formed in 2B1O seem to be as effective as those in 4OL or 37dM1O at increasing the viscosity of the liquid (similar η_o/η_α values), they result in a more modest degree of dielectric strength (much lower $\Delta\epsilon_D/\Delta\epsilon_\alpha$ values for 2B1O). This finding would support the idea that the geometry of the supramolecular structure plays a bigger role than its size on explaining the dielectric strength of the Debye-like relaxation[15,34,35]. If a distinct architecture of supramolecular structures in 2B1O was the reason for its low $\Delta\epsilon_D/\Delta\epsilon_\alpha$ in comparison with other MAs with similar viscosity increase, this could also be the at the origin of the outstanding broadening of its dielectric Debye-like relaxation.

III. CONCLUSIONS

The shear mechanical response of several MAs showing exponential and non-exponential dielectric Debye-like relaxations was tested. Although it was not the first time that the mechanical response of some of the MAs here studied was measured special attention was paid to the analysis of the data in the shear viscosity representation, which result revealing. The complex viscosity representation of shear data has proven to be particularly appropriate to highlight and characterize the non simple flow behaviour of these hydrogen bonded liquids. The Imaginary part of the shear viscosity presents non simple, multimodal, response in all the MAs proving the dynamics of mesoscopic structures formed by hydrogen bonds. The measured response qualitatively resemble those predicted by molecular dynamics simulations. By systematic analysis of $\eta''(\omega)$ curves we found enough evidence for an intermediate process between the terminal pure viscous flow and the structural relaxation of the studied MAs.

Combination of these results with those obtained by other techniques results particularly interesting. In all the cases τ_{cross} and the τ_{max} corresponding to the highest frequency maxima the are in good agreement with the characteristic times for the dielectric α-relaxation, evidencing that the high frequency peak in $\eta''(\omega)$ is due to the structural relaxation ultimately leading to the glass transition. On the other hand, the characteristic time where the liquid recovers pure viscous flow (crossover to $\eta'' \propto \omega$) coincides with that of the dielectric Debye-like relaxation, supporting the idea that the dielectric Debye-like relaxation reflects the complete relaxation of hydrogen bonded aggregates. Intermediate features observed in the shear viscosity response are consistent with the rotational dynamics of hydroxyl groups as seen by NMR and therefore point to be the mechanical imprint of the breaking of individual hydrogen bonds.

Among all MAs studied 2E1H presents the highest η_o/η_α, τ_{OH}/τ_{alpha} and $\Delta\epsilon_D/\Delta\epsilon_\alpha$ ratios. However, we could not find a straightforward relationship between vis-

cosity enhancement, the size of the aggregates and the dielectric strength of the Debye-like relaxation. 2B1O having similar degree of viscosity increase as 4OL or 37dM1O stays out of the line showing low strength and markedly non-exponential Debye-like relaxation. A distinct architecture for the supramolecular structures in 2B1O could be at the origin of these dissimilarities.

Supplementary Material

See supplementary material for comments on the application of time-temperature superposition and on dielectric and calorimetric measurements.

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