

Supplementary Material to

The JG β -relaxation in water and impact on the dynamics of aqueous mixtures and hydrated biomolecules

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1. Comparison of JG β -relaxation of water with the confined water and ν -relaxation in aqueous mixtures

The property (5) of $\tau_{\nu}(T)$ was suggested by the figure 4 in Ref.[S1], where the $\tau_{conf}(T)$ in 20% of water nano-confined in graphite oxide [S2] shorter than $\tau_{conf}(T)$ of water confined in MCM-41 was included. Since this figure is the origin of property (5) and it had inspired others [28, 52], it is reproduced in the Figure S1. For more information see Ref.[S1]: K. L. Ngai, S. Capaccioli, S. Ancherbak, N. Shinyashiki, *Philos. Mag.* **91**, 1809 (2011).

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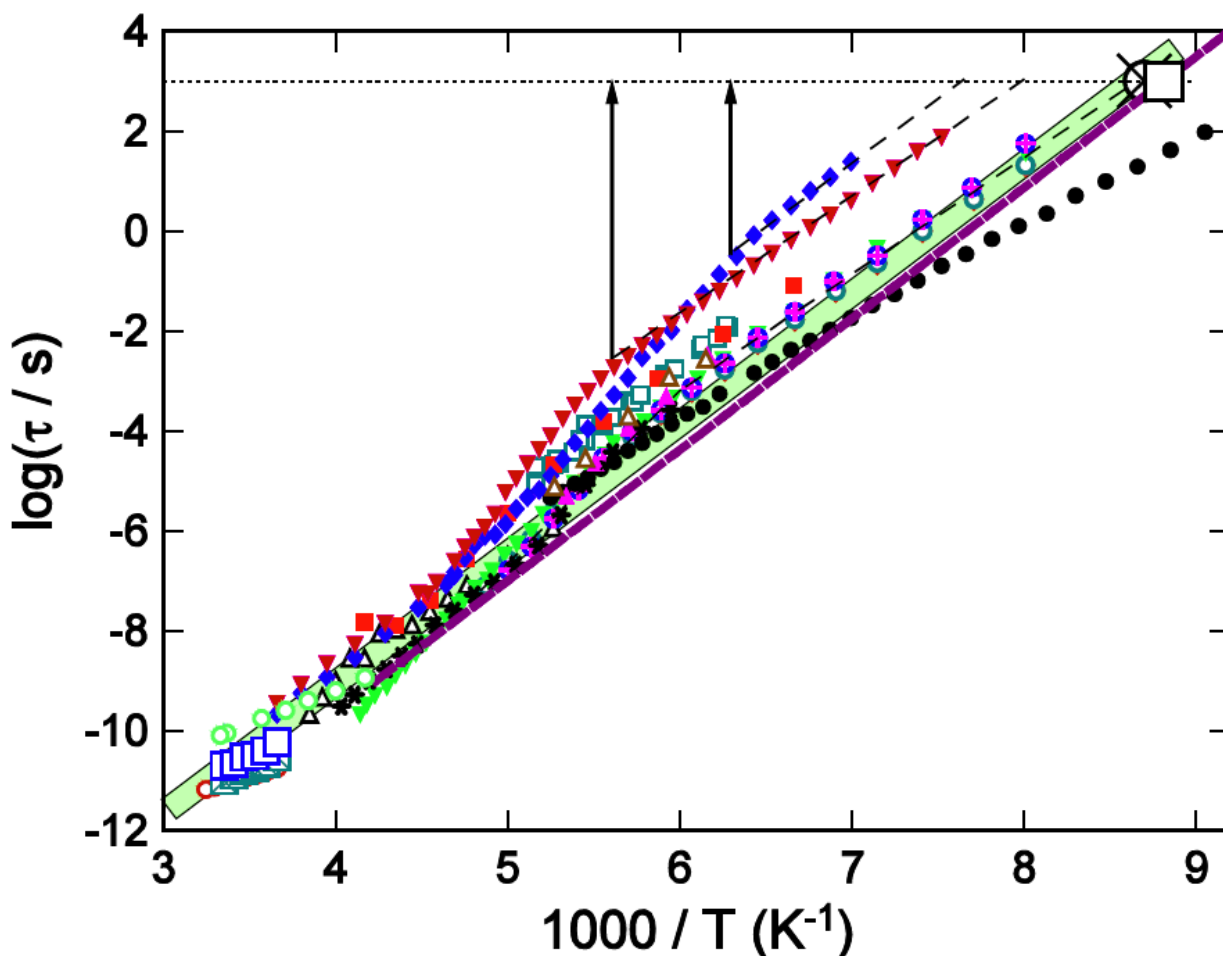


Figure S1. Combinations of all data of $\log_{10}(\tau_i)$ plotted against $1000/T$. Data of the ν -relaxation of water component in various aqueous mixtures are: 35 wt.% water mixture with 3EG (blue closed diamond); 35 wt.% water mixture with PEG600 (purple closed inverted triangle); 50 wt.% water mixture with PVME (red closed squares); 50 wt.% water with PVP (pale blue open squares); 38.6 wt % and 50 wt % of water with PHEMA (brown open triangles and magenta closed triangles respectively); 20 wt.% water with 1-propanol (black \bullet); 90 wt.% water with poly(vinyl alcohol) measured at short times less than 10^{-10} s (pale blue squares with \times inside, located at the lower left corner); and 80 wt.% water with PVP at short times less than 10^{-10} s (blue open squares, located at the lower left corner). All data were obtained by dielectric relaxation spectroscopy. Data of the relaxation times of 20% of water nano-confined in graphite oxide from dielectric relaxation (purple dashed Arrhenius line that fit the data, actual data not shown), and from neutron scattering (green open circles). Dielectric data of relaxation time of water confined in MCM-41 with pore diameter 2.14 nm at three different hydration levels: 12 wt% (small open blue circles each with cross inside), 22 wt% (green inverted triangles), 55 wt% (small open blue circles). The large \otimes located at 10^3 s is the relaxation time of the faster process of water confined in MCM-41 obtained by adiabatic calorimetry. The dielectric relaxation times of bulk water at higher temperatures and shorter times are also shown (small red open circles located at the bottom in the corner). Also shown are the relaxation time τ_ν of water in hydration shell of various proteins: lysozyme from dielectric (black $*$); bovine serum albumin (BSA) from dielectric (black open triangles); myoglobin from neutron scattering (large black closed circles), and NMR (large \times); and c-phyco cyanin (C-PC) from neutron scattering (large brown closed squares, some of which are buried by other data). The lone open square

represents relaxation time of 10^3 s of the faster process of water in the hydration shell of bovine serum albumin (BSA) determined by adiabatic calorimetry. The rectangular box shaded green is added to show all estimates of the secondary relaxation time τ_{JG} of water seem to be located either within or near the box, and hence its relaxation time has approximately the Arrhenius T -dependence over 14 decades with activation energy about 48 kJ/mol. Reproduced from [K. L. Ngai, S. Capaccioli, S. Ancherbak, N. Shinyashiki, *Philos. Mag.* **91**, 1809 (2011).] with the permission of Taylor&Francis Publishing

2. Dielectric Loss Spectra of systems discussed in the present work

This section displays a selection of loss spectra, discussed in the main text, provided by us and not already published or not easily available in literature. The spectra are displayed for the new systems presented in this work, but additional information on systems already studied in literature is provided. The aim of this section is to provide more information on the dielectric response of these systems, whereas only the relaxation times or strengths are discussed in the main article for reasons of brevity.

2.1 Water mixtures with ethylene glycol monomer and oligomers

Among the hydrophilic systems, ethylene glycol (EG) has some interesting properties: miscibility with water is quite high and it has a low glass transition temperature ($T_g=155$ K for the neat system). So it is an interesting candidate to explore the dynamic response in mixture with high quantity of water. We report in the following a selection of spectra for the mixture at 30.3% mol EG in water (60:40 wt. EG:water) (Fig.S2) and 22.5% mol EG in water (50:50 wt. EG:water) (Fig.S3).

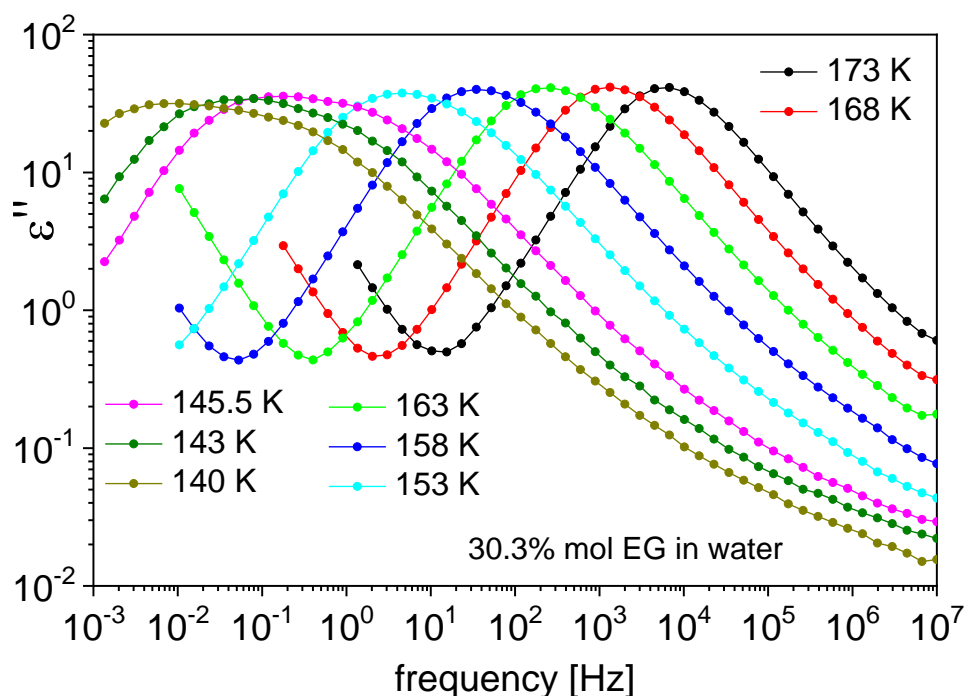


Figure S2. Loss spectra of ethylene glycol 30.3% mole in water at selected temperatures.

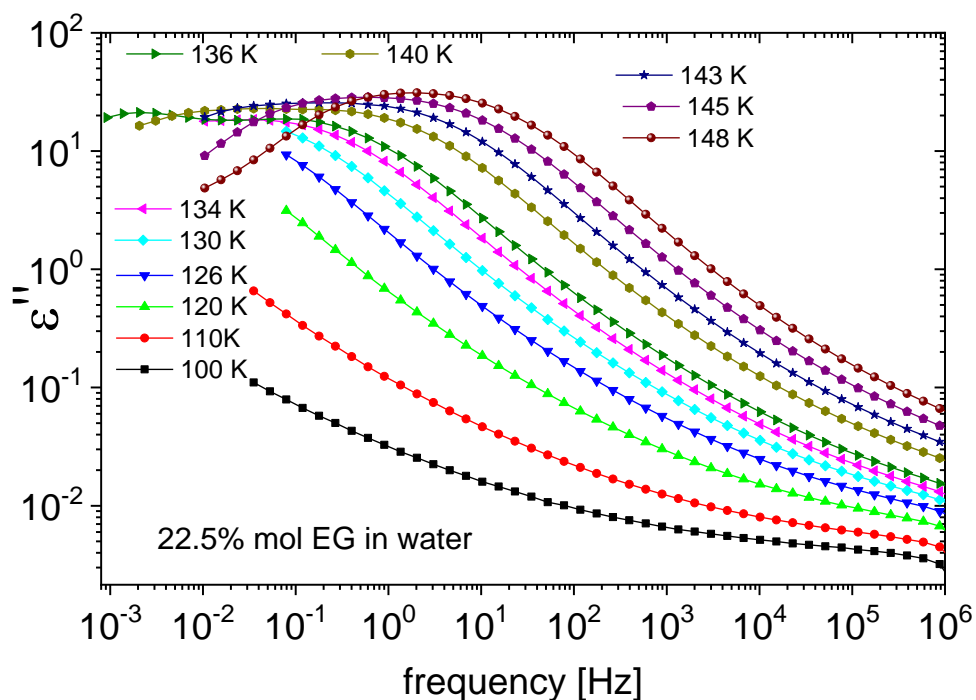


Figure S3. Loss spectra of ethylene glycol 22.5% mole in water at selected temperatures.

Moreover, EG oligomers are available with increasing number of units (2EG, 3EG, etc.) and they all have quite good miscibility of water. So, it is also a good candidate to explore the effect of chain connectivity on the coupling parameter n and on the separation between τ_α from τ_ν . Dielectric spectra of 35 wt% water mixture with ethylene glycols n -mers ($n=2, 3, 4, 5, 6$) can be found in ref.[S3-S5] (relaxation times are shown in Fig.3 of the main article). Here we report a selection of spectra for 35% wt. water mixture with Polyethylene glycol $M_w=600$ Da (PEG600) (relaxation time data are reported in Fig.9 in the main article).

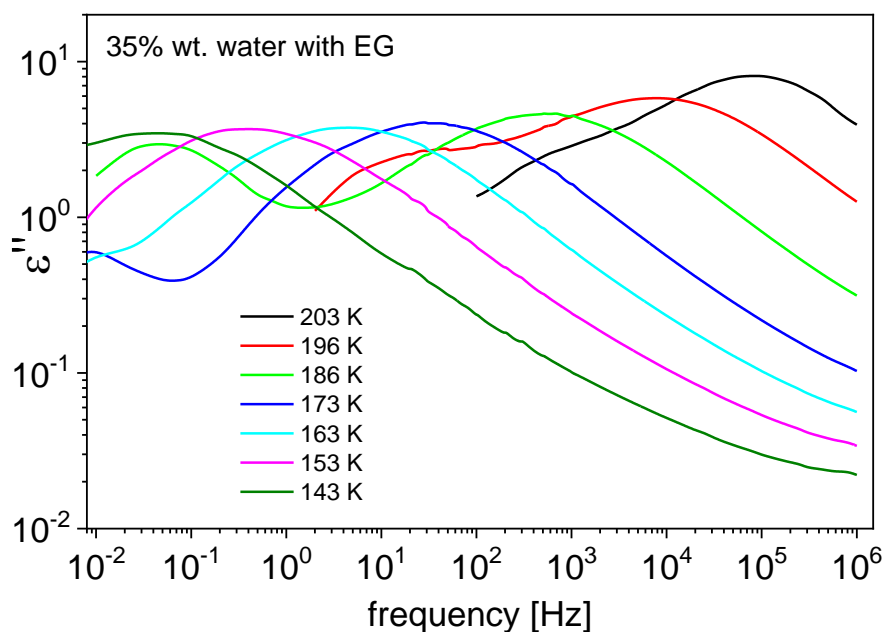


Figure S4. Dielectric loss spectra at selected temperatures for 35% wt. water mixture with Polyethylene glycol Mw=600 Da (PEG600).

2.2 Water mixtures with sugars

We report in the following a selection of spectra for 15, 26, 30, 38% wt. water mixture with glucose (relaxation time and strength data are reported in Fig.4-5 in the main article).

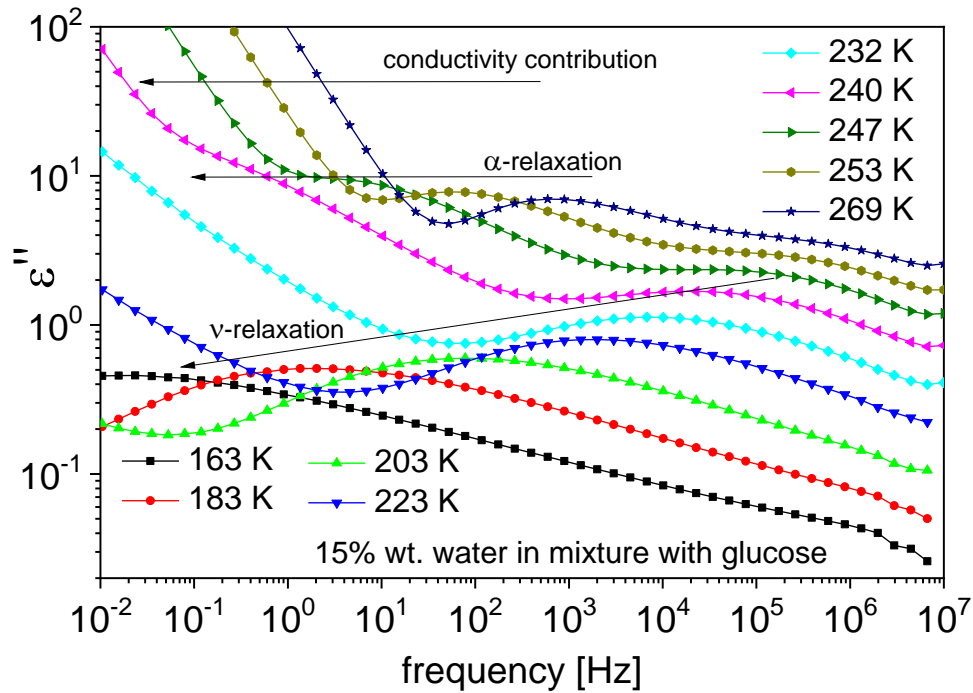


Figure S5. Dielectric loss spectra at selected temperatures for 15% wt. water mixture with glucose. Arrows indicate the different contributions to the loss spectra.

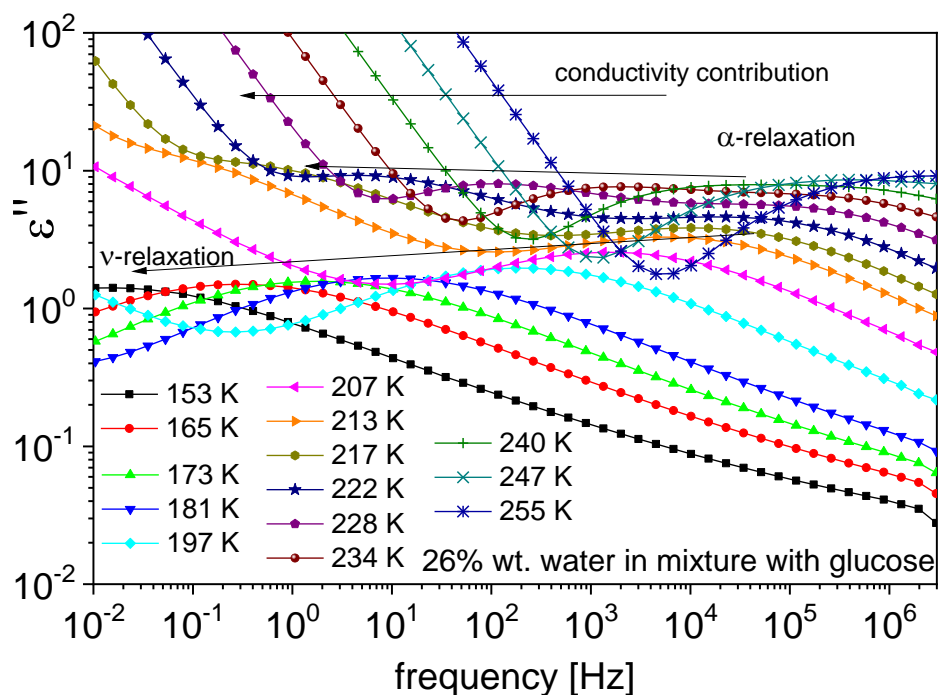


Figure S6. Dielectric loss spectra at selected temperatures for 26% wt. water mixture with glucose. Arrows indicate the different contributions to the loss spectra.

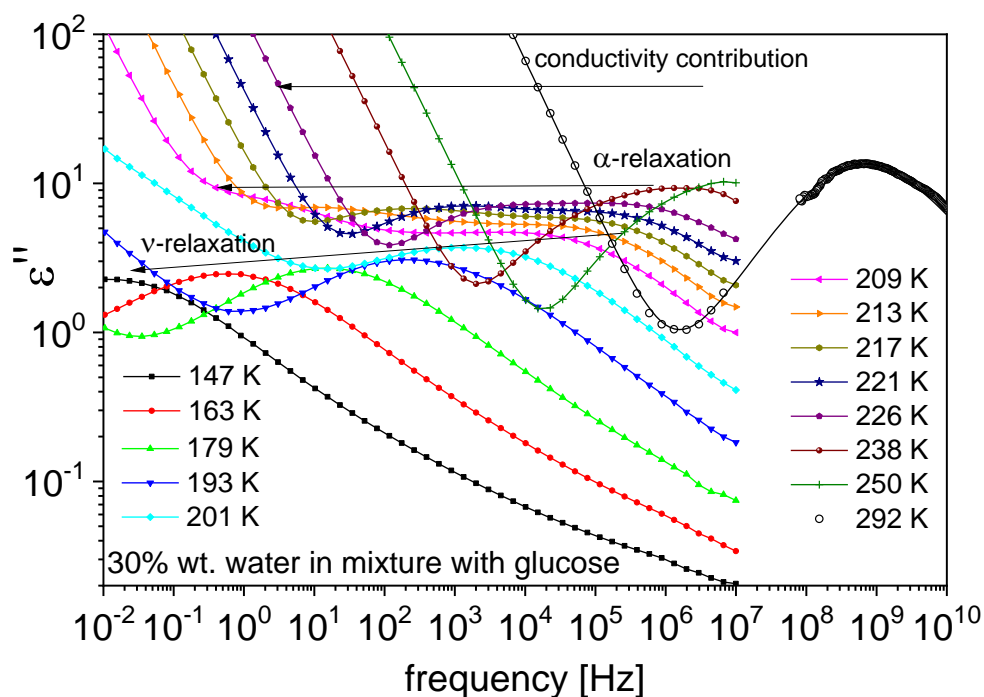


Figure S7. Dielectric loss spectra at selected temperatures for 30% wt. water mixture with glucose. Arrows indicate the different contributions to the loss spectra.

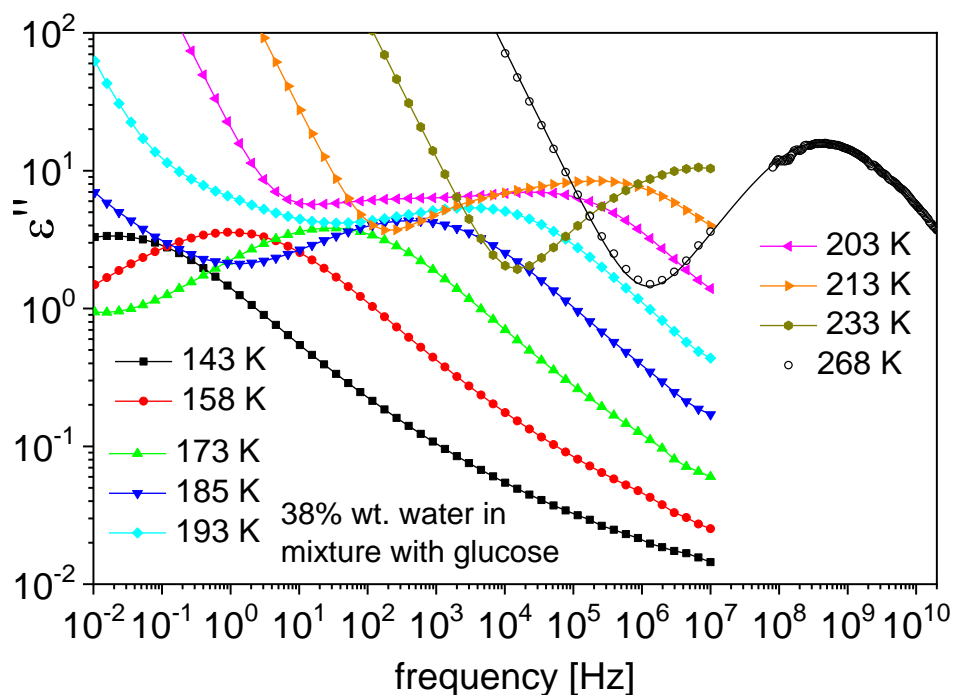


Figure S8. Dielectric loss spectra at selected temperatures for 38% wt. water mixture with glucose.

We report in the following a selection of spectra for 15, 20, 30% wt. water mixture with sucrose (relaxation time and strength data are reported in Fig.6-7 in the main article).

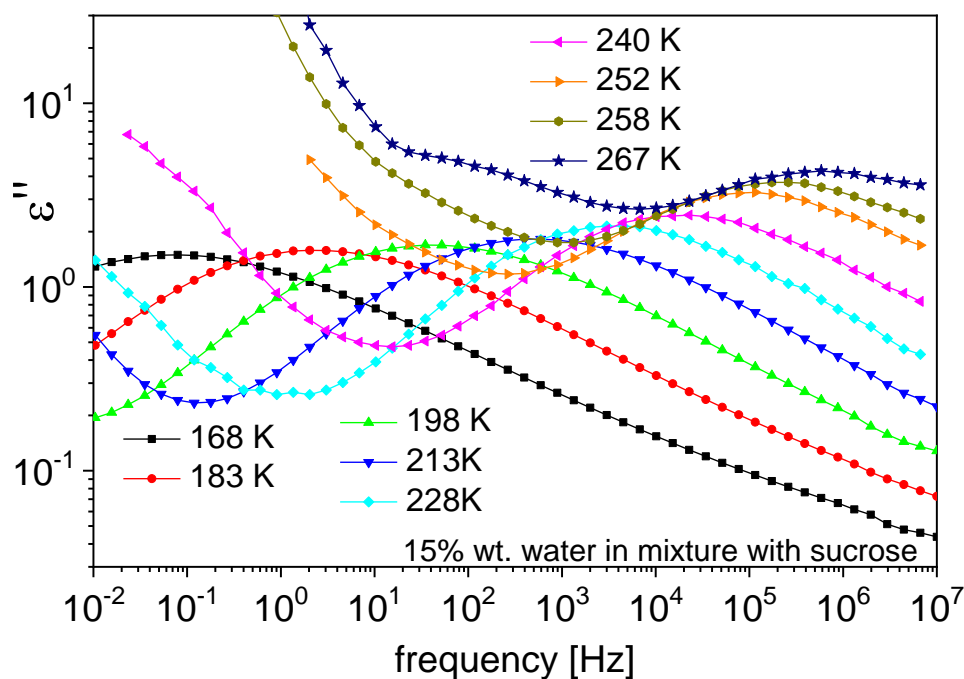


Figure S9. Loss spectra at selected temperatures for 15% wt. water mixture with sucrose.

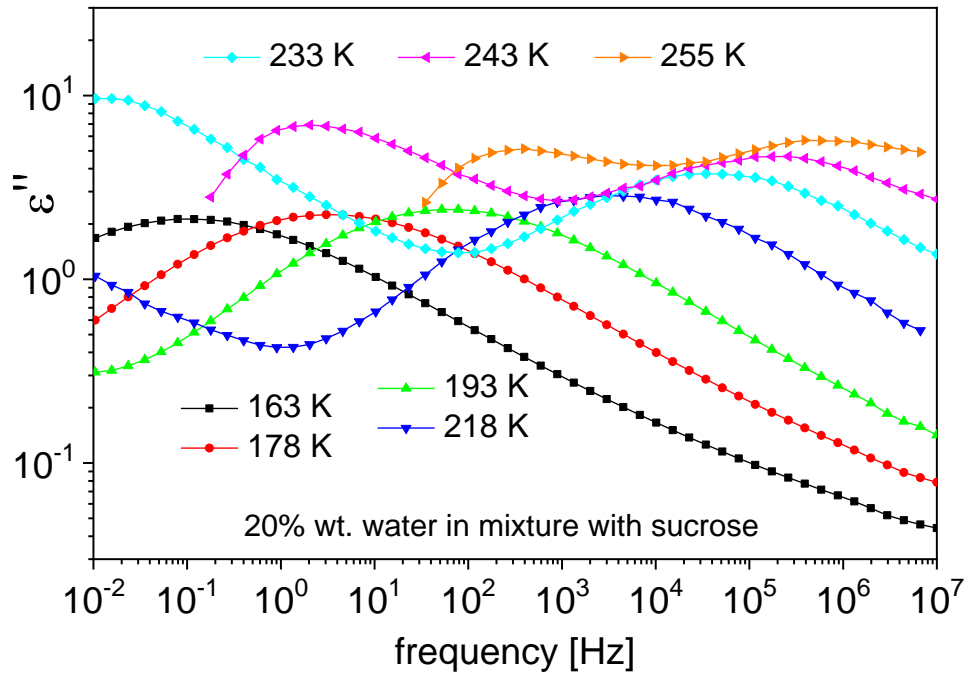


Figure S10. Loss spectra at selected temperatures for 20% wt. water mixture with sucrose.

Similarly to what usually occurs in dielectric spectroscopy studies on aqueous mixtures, at higher water content the low frequency part of loss spectra at high temperature is dominated by a strong dc conductivity contribution $\sigma_{dc}/(\epsilon_0\omega)$. That is what occurs for mixture with 30%wt. water in sucrose. Taking advantage from the fact that complex permittivity has been measured, we calculated a quantity that approximates the dielectric loss spectra that is proportional to the logarithmic derivative of the real part of permittivity, following the procedure illustrated in Ref.[S6], that helps to gain information on the low frequency part of losses minimizing the conductivity contribution.

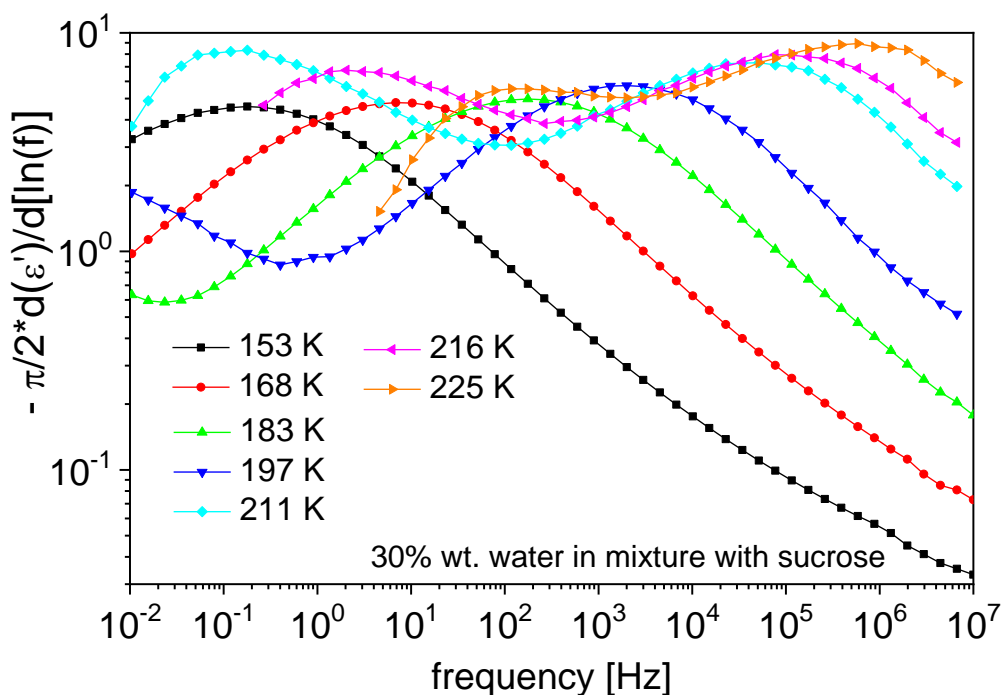


Figure S11. Loss spectra at selected temperatures for 30% wt. water mixture with sucrose.

In Figure 8 and in the discussion of the article mention to data from water mixtures with threolose fructose, and deoxyribose is done. More details can be found in ref. [S7]. The following figure shows spectra for 25% wt. water mixture with threolose.

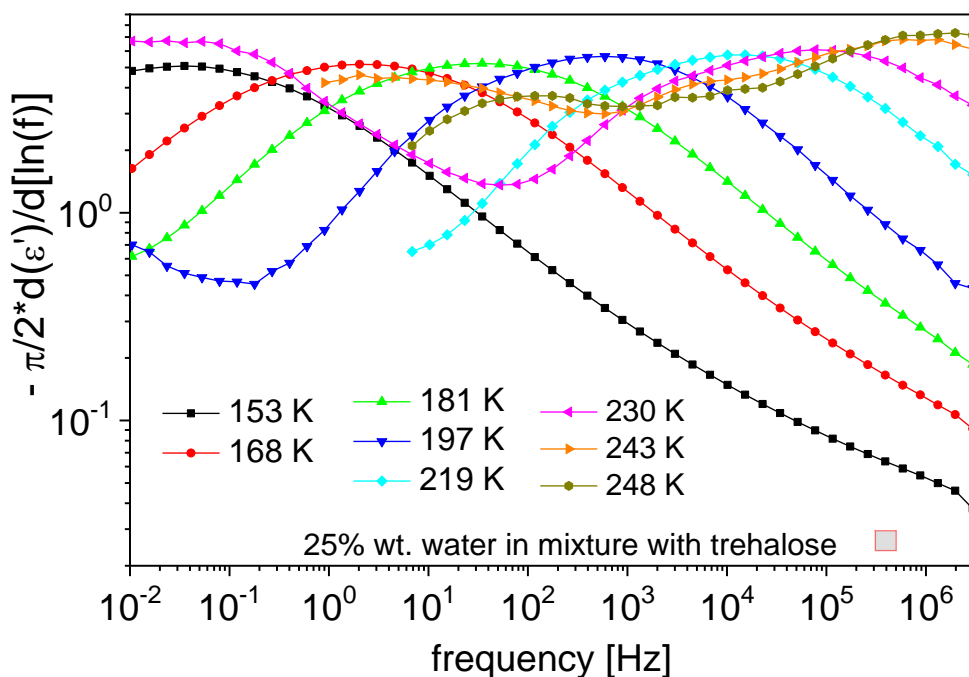


Figure S12. Loss spectra at selected temperatures for 25% wt. water mixture with trehalose.

We report here some spectra and comparison of the dynamics of sugars with the same water concentration, showing that while the ν -relaxation is less affected, the α -relaxation, due to motions of water and solvent molecules coupled together is strongly affected by the molecular weight of the solvent molecules.

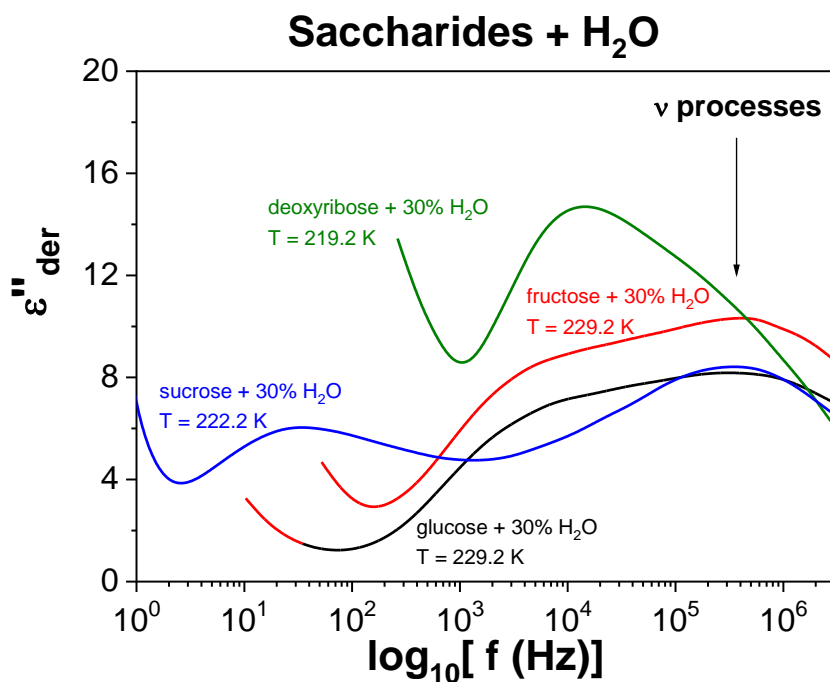


Figure S13. Conductivity free losses (derivative of ϵ' (see ref.[S6])) vs. frequency for mixtures of different saccharides with 30 wt.% of water.

Moreover, water mixtures of fructose and glucose with similar concentration show similar spectra and relaxation maps.

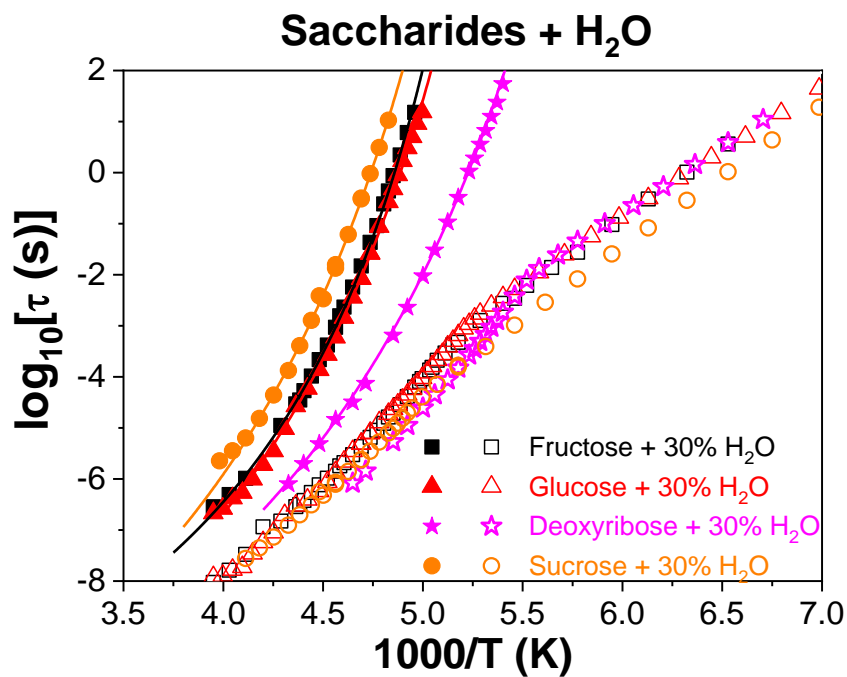


Figure S14. Plot of relaxation times vs. reciprocal temperature of 30 wt.% of water in mono- and di-saccharides: fructose (black squares), glucose (red triangles), deoxyribose (magenta stars), sucrose (orange circles). Close and open symbols indicate α - and ν - process, respectively. Solid lines are the VFT function fit.

2.3 Water mixtures with propylene glycols oligomers

In figure 8 of the main article mention to some oligomers of propylene glycols. We report here some spectra and a comparison between 3PG (trimer) and PPG400 (heptamer) with similar water concentration.

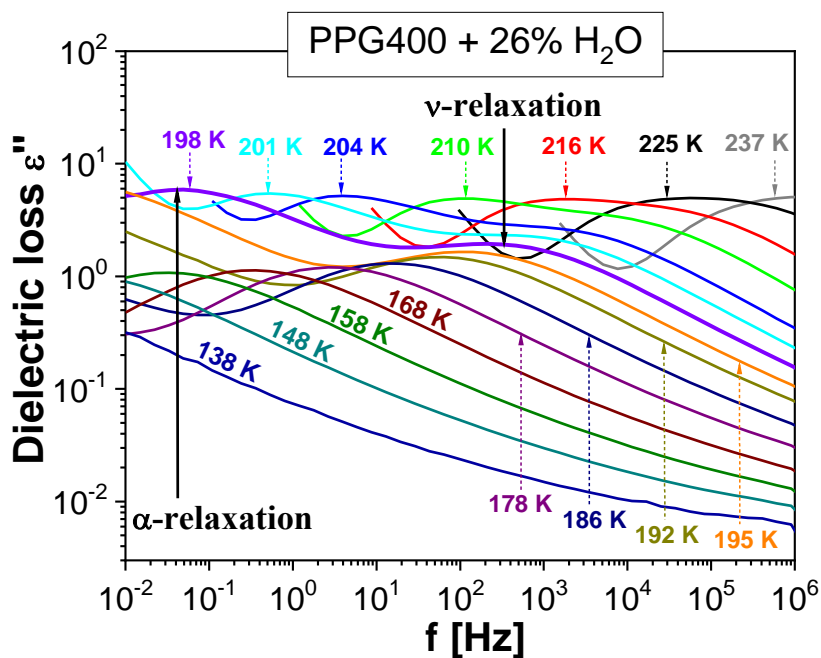


Figure S15. Dielectric spectra of PPG400-water mixtures with mass fraction of water $c_{H_2O} = 26.0\%$.

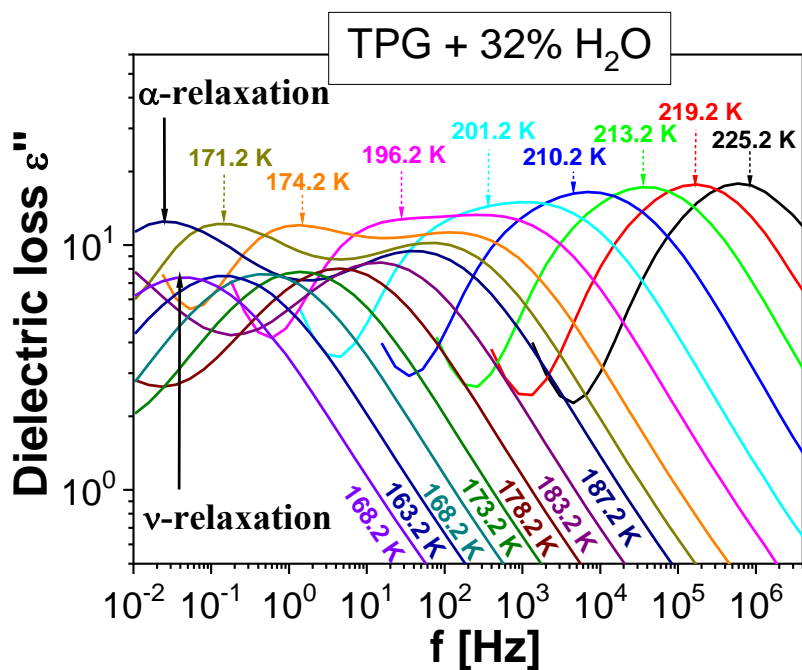


Figure S16. Dielectric spectra of triPG-water mixtures with mass fraction of water $c_{H_2O} = 32.0\%$.

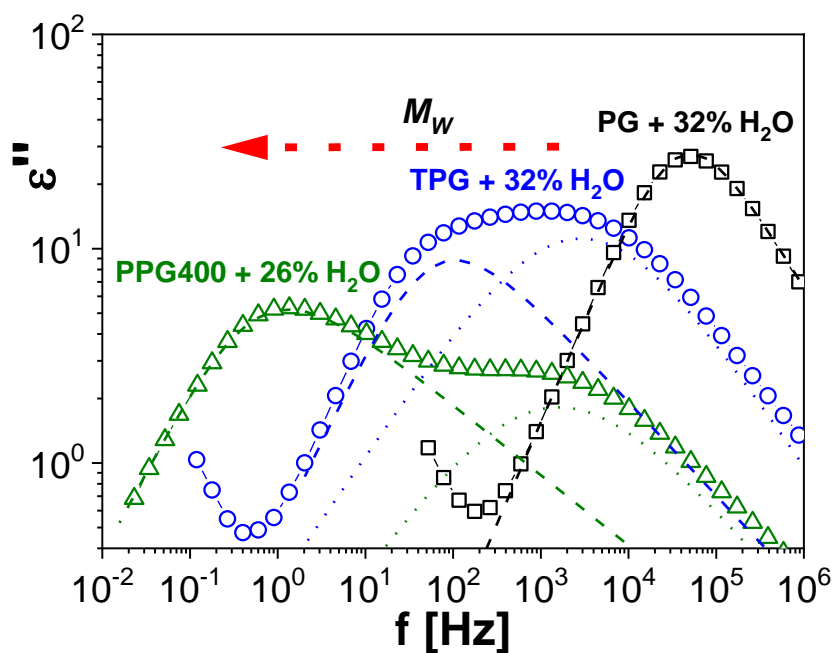


Figure S17. Comparison of dielectric loss spectra at $T \approx 202$ K for similar mass fraction of water in various n-PG oligomers: propylene glycol+32 wt.% water (squares), TPG+32 wt.% water (circles), PPG400+26 wt.% water (triangles).

2.4 Hydrated biomacromolecules: glycogen

Fig.10 of the article reports relaxation time data for 23 and 34% wt. water mixture with glycogen. We reported here some dielectric loss spectra for both systems for the temperature range investigated.

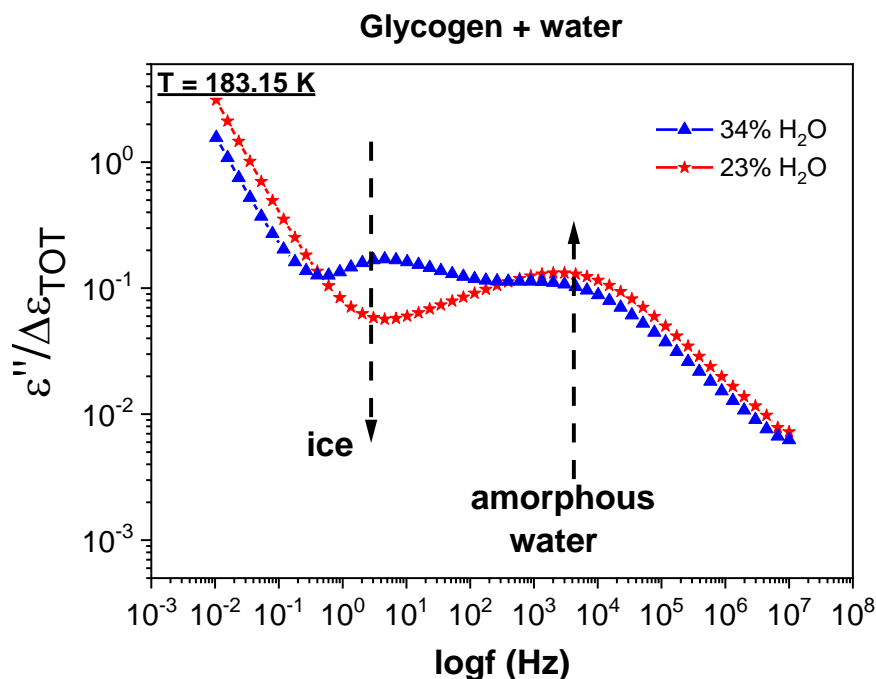


Figure S18. Comparison of dielectric loss spectra at $T=183.15$ K for for 23 and 34 % wt. water mixture with glycogen. The dielectric loss has been normalized to the total dielectric strength, that is proportional to the number of active dipoles (and related to concentration of water). The presence of ice relaxation at lower frequency is detected for water concentration of 34% wt..

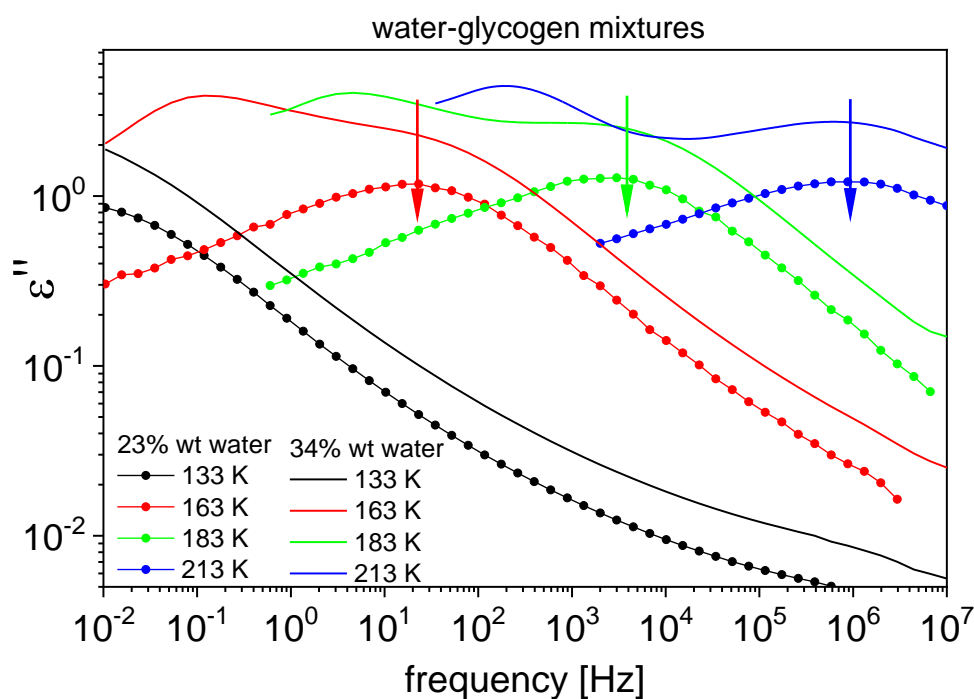


Figure S19. Loss spectra at selected temperatures for 23 and 34 % wt. water mixture with glycogen. The pointing down arrows show the frequency of the ν -relaxation from uncrystallized water.

References

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