Dielectric secondary relaxation of water in aqueous binary glass-formers

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Fitting results for the dimers and trimers

Figure 4 of the corresponding article shows the temperature dependent relaxation times for the \( \alpha \) and \( \omega \) relaxations, as plotted in an Arrhenius representation for aqueous PG and PGME. In this ESI we show that an analogous behaviour is found also for nPG and nPGME with \( n=2 \) and 3. The \( \alpha \) and \( \omega \) relaxation relaxation times for aqueous 2PG and 2PGME are shown in Fig. S1 and for aqueous 3PG and 3PGME in Fig. S2, respectively. The temperature dependent \( \alpha \) relaxation times for all investigated samples are well described by VFT functions, as shown by the solid lines. At temperatures near \( T_g \), the \( \alpha \) relaxation generally becomes faster as water is added to the glycols (2PG and 3PG). In contrast, the opposite behaviour, with a slowing down of the \( \alpha \) relaxation for increasing water content is observed for the monomethyl ethers (2PGME and 3PGME) up to a certain value of \( C_w \), above which the \( \alpha \) relaxation speeds up. The \( \alpha \) relaxation behaviour for both the dimers and trimers are consistent with the results from calorimetry, as shown in Fig. 1 in the article. The \( \omega \) relaxation times exhibit Arrhenius temperature dependences in the glassy state for all samples. In marked contrast to the very different \( C_w \) behaviours of the \( \alpha \) relaxation for the glycols and monomethyl ethers, the \( \omega \) relaxations shift systematically towards shorter times as more water is added. Moreover, the activation energy, \( E \), is highly similar for all systems with values within the range \( E=0.46\pm0.06 \) eV.
**Fig. S1.** Dielectric $\alpha$ and $\omega$ relaxation times, marked in open and closed symbols respectively, of water-2PG mixtures (top) and water-2PGME mixtures (bottom). The solid lines through the open symbols show the results of fits using a VFT expression. The relaxation times for the anhydrous samples are shown with a dashed black line. The Arrhenius fits to the $\omega$ relaxation in the glassy state are shown as solid straight lines. The arrows indicate the trend of increasing water content.

**Fig. S2.** Dielectric $\alpha$ and $\omega$ relaxation times, marked in open and closed symbols respectively, of water-3PG mixtures (top) and water-3PGME mixtures (bottom). The solid lines through the open symbols show the results of fits using a VFT expression. The relaxation times for the anhydrous samples are shown with a dashed black line. The Arrhenius fits to the $\omega$ relaxation in the glassy state are shown as solid straight lines. The arrows indicate the trend of increasing water content.