Electronic Supplementary Information (ESI)

Dielectric secondary relaxation of water in aqueous binary glass-formers

Johan Sjöström, Johan Mattsson, Rikard Bergman, Erik Johansson, Karin Josefsson, David Svantesson, and Jan Swenson

Department of Applied Physics, Chalmers University of Technology, SE-41296 Göteborg, Sweden.

Fitting results for the dimers and trimers

Figure 4 of the corresponding article shows the temperature dependent relaxation times for the α and *w* 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 α and *w* 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 α relaxation times for all investigated samples are well described by VFT functions, as shown by the solid lines. At temperatures near T_g, the α 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 α 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 α relaxation speeds up. The α relaxation behaviour for both the dimers and trimers are consistent with the results from calorimetry, as shown in Fig. 1 in the article. The *w* 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 α relaxation for the glycols and monomethyl ethers, the *w* 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±0.06 eV.

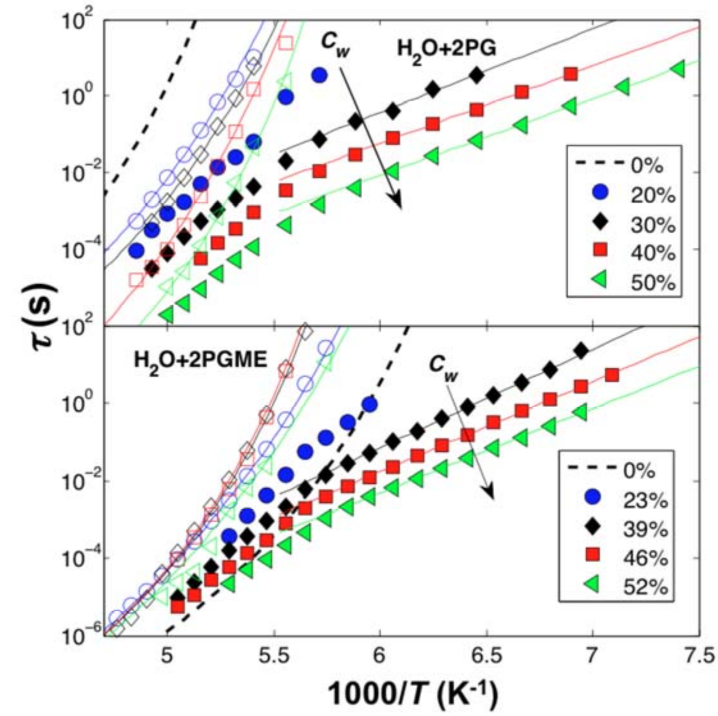

Fig. S1. Dielectric α and w relaxation times, marked in open and closed symbols respectively, of water-2PG mixtures (top) and water-2PGME mixtures (bottom). The solid lines through the open symbols show the results of fits using a VFT expression. The relaxation times for the anhydrous samples are shown with a dashed black line. The Arrhenius fits to the w relaxation in the glassy state are shown as solid straight lines. The arrows indicate the trend of increasing water content.

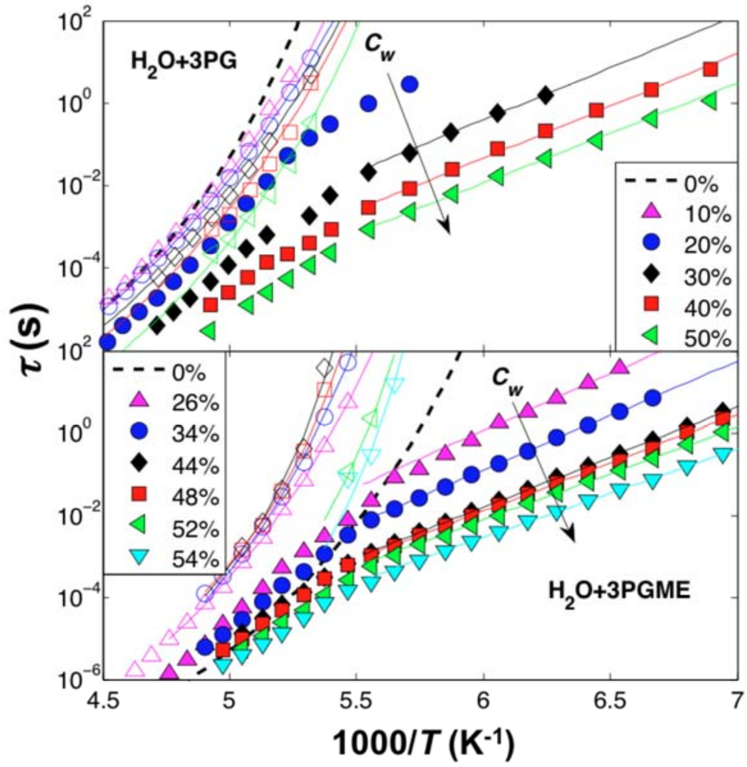

Fig. S2. Dielectric α and w relaxation times, marked in open and closed symbols respectively, of water-3PG mixtures (top) and water-3PGME mixtures (bottom). The solid lines through the open symbols show the results of fits using a VFT expression. The relaxation times for the anhydrous samples are shown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