

Slow and Fast Dynamics in Glycerol-Water Mixtures

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Understanding the liquid-glass transition and its related dynamics is one of the most important and challenging problems in modern condensed matter physics. Glycerol and its mixtures with water are hydrogen-bonded (H-bonded) liquids, which are widely used as models to study the cooperative dynamics and also glass transition phenomena in complex liquids. It is well known that the dc-conductivity process, the main relaxation process, and a high frequency relaxation (the so-called “excess wing”) are observed by broadband dielectric spectroscopy (BDS) measurements of glycerol in supercooled or liquid phases. The presentation of our experimental results in terms of so-called “master plots”, in which the data and the correspondent frequency axis are normalized to the value of relaxation peak maximum and the corresponding frequency, shows that all the data for pure glycerol, for example, in the temperature range 196 to 250 K are condensed to a single function (See Fig.1). It means that both of the excess wing and the dc-conductivity are characterized by the same temperature dependence as the main process, which is described by the Vogel-Fulcher-Tammann (VFT) law. Moreover, the same behavior was also found in glycerol-water mixtures in the glycerol rich region (50 to 100 mole % of glycerol). In addition, it is possible to normalize the frequency dependencies of ϵ'' for different glycerol-water mixtures at a constant temperature. Such normalization demonstrates that the excess wing and the main dielectric dispersion have the same dependency on the composition of glycerol-water mixture over the comparatively wide range of concentrations: from 50 up to 100 mole %. All these results indicate that the dc-conductivity, the main relaxation process and the excess wing have the same molecular origin [1].

The universality in the master plots of dielectric spectra for glycerol and glycerol-water mixtures, with respect to the changes of both concentration and temperature, is related to the same origin of elementary molecular processes which is most probably a “defect” formation and its percolation in H-bond network;

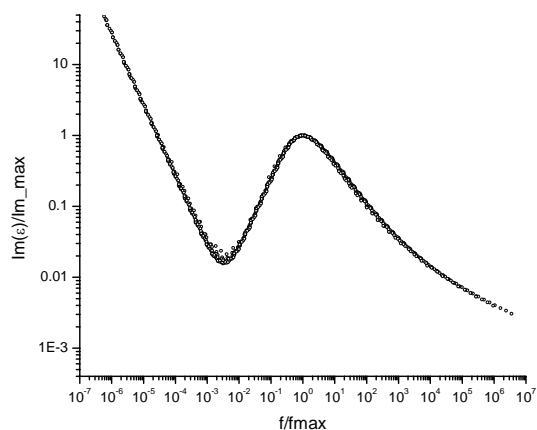


Figure 1 Master-plots of the imaginary parts of the dielectric spectra for pure dehydrate glycerol measured in the temperature intervals 202 - 292 K,

This universality disappears through a further decrease of glycerol content (below 40 mole %). This result is likely explained by appearing of the so-called cooperative domains of glycerol and water, respectively. In the water rich region glycerol molecules cannot provide all the water molecules with H-bonds. The critical mole fraction (x_g) would be related to the numbers of H-bonds of the glycerol molecule ($n_g \approx 6$) and the water molecule ($n_w = 4$) namely $x_g = 100\% \cdot n_w / (n_w + n_g) = 40\%$ [2]. An x-ray diffraction study performed at room temperature also indicated the change of the static structure of glycerol-water mixtures at the 40 mole % of glycerol.

A new phenomenological relationship for complex dielectric permittivity is proposed in order to provide a comprehensive fitting of our experimental data both for conductivity, main process and excess wing. The structural and dynamic properties of the molecular dynamics of the water/glycerol mixtures are discussed in terms of the Kirkwood correlation factor, cage dynamics and defect percolation in H-bonded network.

REFERENCES

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- [2] Y. Hayashi, A. Puzenko, I. Balin, Ya. E. Ryabov, and Yu. Feldman, *J. Phys. Chem. B*, **109**, (2005) 9174.