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No Indications of Fragile-to-Strong Transition in Water of Protein Hydration

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1. Introduction

One of the most important features of supercooled liquids is degree of departure of relaxation behaviour from an Arrhenius temperature dependence. Angell proposed classification of the liquids according to this deviation. According to his classification the liquids with Arrhenius like temperature behaviour are called "strong" whereas liquids with strongly non-Arrhenius behaviour are called "fragile"

Bulk water can be supercooled below its melting temperature down to ~235K. Above this temperature water is one of the most fragile liquids. Unfortuantely, below this temperature it inevitably crystalizes. Bulk water can vitrify only by hyperquenching, at rates > 10^5 K s^{-1}. On the basis of the differential scanning calorimetry data, Angell et al. suggest that tempearture of the glass transition of bulk water is located somewhere in the temperature range 160-180K. However real glass transition never can be observed for bulk water due to rapid crystallization at 150K. A way to avoid crystallization is to study water confined in various host materials. Although confinements generally affect the structure and dynamic properties of water, it is nevertheless possible to relate supercooled bulk water to studies of water in severe enough confinement with suppressed crystallization. For example, water could be confined as water of protein hydration. It is believed that ~ 0.4 g. of water per g. of protein is sufficient to cover the whole protein surface and fully activate the protein functionality. However, this hydration level is not sufficient for water crystallization and dynamics of supercooled water could be examined.

Results of recent investigations seem to exhibit new features of supercooled water in confinement. Chen and coworkers showed for water in different confinements that so-called fragile-to-strong transition (FST) occurs at characteristic temperature T_C~220K [1]. Below this temperature water exhibits Arrhenius temperature dependence of relaxation times, τ, or self-diffusion coefficient. This is very unexpected and controversal results. First of all, this kind of transition has not been observed in any other liquid. Second, results from dielectric spectroscopy (DS) experiments presented by Swenson et al. showed that at temperatures above the FST, shape of the structural relaxation peak is asymmetric (as in many other liquids) whereas below the FST peak becomes symmetric. Symmetrically stretched spectral shape as well as activation behavior of relaxation times are characteristic features of so-called secondary relaxation process. Swenson et al. suggested that splitting of the structural and secondary relaxation take place at this temperature and no FST exists in water [2]. Thus, water exhibits some interesting behavior and microscopic nature of the observed anomalies remains unclear.

2. Conductivity in Protein Hydration Water

We perform DS investigations of water confined in lysozyme protein powder. Hydration level was about 0.4 g of water per g of proteins. It is enough to fully activate the protein functionality and to avoid water crystallization. We estimated temperature dependence of conductivity, σ, in the hydrated protein powder. Conductivity originates from translation of small, mobile ions, usually present in liquids. The correlation between τ and σ is often observed. Such correlation is discussed in terms of Debye-Stokes-Einstein (DSE) relation $\sigma\tau = \text{const}$, which expresses a relationship between translational motions of different entities and the viscosity of the liquid. However, it was reported that for some materials decoupling between σ and τ was observed. In this case, the relation between these two quantities can be described by the so called fractional DSE relation (FDSE), $\sigma\tau^s = \text{const}$ where the exponent s is less than 1. It means that σ is less sensitive to temperature changes than τ. Opposite behavior was never observed. As it is visible from Figure 1, for glycerol – lysozyme powder mixture (0.8 g of glycerol per g of protein) temperature dependence of σ follows the common picture described above. However, for water of hydration situation is quite different. σ exhibits normal temperature behavior in the whole temperature range while τ from Chen et al. experiments demonstrates sudden change in temperature dependence at T~220K. This sudden change has been ascribed to FST. Smooth temperature behavior of σ clearly contradicts to this interpretation. It is not possible that sharp change in the temperature dependence of the main structural relaxation will not be reflected in conductivity. The only possible explanation is that the measured τ at low temperatures presents some secondary relaxation process.

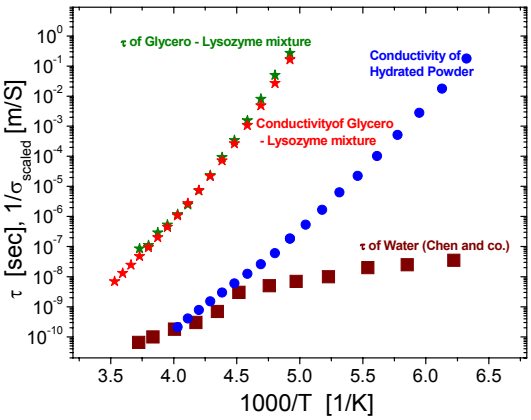

Fig. 1. Arrhenius plot of structural relaxation times and scaled conductivity for hydrated powder and glycerol-lysozyme powder mixture

3. Conclusion

Lack of changes in temperature behaviour of σ suggests that no FST occurs at T~220K in water of protein hydration. Strange temperature behaviour of the relaxation time can be ascribed to splitting of structural and secondary relaxations at this temperature.

References

[1] S.-H. Chen *et al.,* PANS 103 (2006) 9012-9016, *ibid* 103 (2006) 12947-12978;
[2] J. Swenson *et al.,* Phys. Rev. Lett. 96 (2006) 247802.