New experimental results on bulk and confined Water

(the transport functions in water-glycerol and water-methanol mixtures)



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We study the role of Water soltions in order to highlight all the possible implications for Supercooled Bulk Water.

Water-Glycerol & Water-Methanol Mixtures in their liquid phase (the Hydrogen bonding & hydrophobicity roles)

The two special temperatures: a) T_W – is the fragile to strong dynamic crossover (FSDC) observed in confined water coincident with Widom line;

b) T^* – is the "magic temperature" in the thermal expansivity of bulk water ($\alpha_P = \delta V \delta S$).

The three proposed scenarios for the confined water FSDC.



- a) The FSDC is due to the HB network that drives, on decreasing T, a continuous evolution of the water structure from a HDL to a LDL liquid phase (Raman-FTIR-Neutron-NMR data).
- b) The low T dynamics is likely due to a crossover from a α -like relaxation above the T_L to a β -like (the Johari-Goldstein). (Dielectric data BDS).
- c) The interfacial water plays the main role, and the FSDC near 225 K results from a reduction of fragility due to a restriction of the accessible volume. The glass transition of interfacial water take place at about 180K (NMR data).

FSDC - The first scenario



This scenario is close to the FSDC proposed to occur for supercooled bulk water and due to the HDL-LDL liquid-liquid transition occurring at ~225 K. Hence, it is generally believed that if correct, it is highly relevant for supercooled bulk water, which should exhibit a similar behavior.

Thus, if the experimental data are correct they are most likely reflecting the thermodynamic properties of supercooled bulk water.

FSDC - The scenario 2



T-dependence of the relaxation times of water confined in ~20 Å pores of MCM-41: QENS (circles) and dielectric spectroscopy (triangles).

INSET: The same for water in aqueous solutions and hard confinement systems. The water relaxation in all types of systems seems to approach a universal (Johari-Goldstein) β -relaxation.

FSDC-The scenario 3



Water relaxation times in silica (MCM-41 C10) and myoglobin (MYO, h=0.35, 0.45 g/g).

a) ²H NMR spin-lattice relaxation (SLR) and stimulated-echo experiments (STE) data for heavy water in MCM-41 and MYO; BDS data deal with water in MCM-41 and MYO, wheras QENS data represent water in MCM-41-S.

(Data of hydrated collagen (triangles up) and hydrated elastin (trianglel down), are also reported. The arrow marks the interfacial water glass-transition.)

(b) ²H NMR SLR and STE data for heavy water in MCM-41 C12 and C14.

Implications of the three FSDC scenarios for Supercooled Bulk Water

- Scenario 1: confined and bulk water have essentially the same physical behavior. The HB clustering imposes the formation of the HDL and LDL phase with a possible liquid-liquid critical point. The FSDC represents the locus of the maxima fluctuations (the Widom line).
- > Scenario 2: The crossover from an α relaxation to a Johari-Goldstein implies that the impossibility of a fully development of the HB network. In other words, the length-scale of the cooperative *a*-relaxation is prevented to grow indefinitely.
- Scenario 3: The corresponding findings imply that it is not straightforward to draw definite conclusions about bulk water based on confined water results. In the weakly supercooled regime, the confinement properties influence the system dynamics i.e. the correlation times of the α process. On these bases, one may expect that there are also implications on the thermal evolution from a HDL-like to a LDL-like water structure.

In this frame, role and effects of confinement should be clarified.

The Boson Peak (BP) in confined water (NEUTRON DATA)

A marked difference characterizes the BP of strong and fragile glasses: if compared with fragile glasses the BP spectra of Strong glasses are narrow if compared with fragile.

So that at the dynamical-crossover or Widom line must be observed a BP narrowing.

The BP narrowing at the Widom line (450 bar).



1.2 kbar.







The Water Boson Peak and the Widom line (water in MCM)



T^{*} – the magic temperature

Bulk water isothermal compressibility

P.W. Bridgman, Proc. Am. Acad. Art. Sci. 1912, 47, 441-558



a minimun, for every P, at $T^* \sim 315$ K



T^{*} – *the magic temperature*







 T^* is also the crossover from an Arrhenuis ($T > T^*$) to a super-Arrhenius ($T < T^*$) behavior for the transport parameters.

Local order

The water Self-Diffusive dynamics is governed by the Configurational-Entropy





 T^* – these data suggest that this temperature signals the water transition from a normal simple liquid to that governed by the well known thermodynamic anomalies. And the Stokes – Einstein is violated.

Water-Glycerol & Water-Methanol Mixtures in their liquid phase

(the Hydrogen bonding role studied on considering the concentration dependences)

 T_L and T^*



Relaxation times of glycerol (3 – OH groups) , water and methanol (1 - OH)

In comparison with the glycerol, the little methanol has also a more effective hydrophobic CH₃ group (able to perturb the HB network).

The merged Water-Glycerol relaxation times



Erice-Water 16

bulk wat. NMR





High T (normal liquid)

In both there is a not linear behavior (dotted line):

- a) the components are not miscible indicating the presence of liquid pools of different composition;
- b) The excess, negative, $\Delta t_{\alpha}(T)$ is always located at the glycerol molar fraction $X_{Gly} \sim 0.7$.



- ✓ By increasing the glycerol content, the water relaxation time, in principle, must increase linearly. Instead, up to $X_{Gly} \sim 0.7$ there is a moderate increase accompanied by a jump towards the glycerol values. The observable minimum evidence pools of different composition around it: namely for $X_{Gly} < 0.7$ water dominates.
- ✓ In the bulk liquid water region the $\Delta t_{\alpha}(T)$ is at maximum of about one order of magnitude (e.g. $2e^{-8} 1e^{-7}$ sec for T = 253K), in the no man's land such a variation become much larger ($2e^{-4} 9e^{-4}$ sec for T = 215K) by decreasing T.
- ✓ For pure bulk water the T decrease means the onset of the LDL phase (the HB percolating network that becomes more and more stable, inside the no man's land, by decreasing T).
- ✓ The addition of the glycerol (molecular weight 92.06 and three OH groups) results in a perturbation of the water HB network, that become dominant at X_{Gly} ~ 0.7 (3 water molecules and 7 of glycerol).
- ✓ By decreasing T the corresponding $\Delta t_{\alpha}(T)$ must have a strong and progressive increase because the water LDL becomes more and more stable.

The previuos analysis on the excess of the relaxation time $(|\Delta t_{\alpha}(T)|)$ due to the glycerol effects on the water HB network (LDL phase) is reflected in the two relevant water temperatures $T_L = T_W$ and T^* .



Water-methanol relaxation times



The Water-methanol relaxation times in the stable liquid phase



On the contrary of the water-glycerol, where for all the temperatures there is a negative excess in the mixture relaxation time, for water-methanol case for $T > T_L \Delta t_{\alpha}(T)$ is positive. The figure evidences this.

The Water-methanol relaxation times for different temperatures as a function of the methanol molar fraction (log scale left side – linear on the right).





High T (normal liquid) Positive Excess Hydrophobicity?

Also in this case there is a not linear behavior (dotted line) but:

- a) For $T > T_L$ the $\Delta t_{\alpha}(T)$ is positive becoming negative in the deep supercooled regime;
- b) The negative excess, $\Delta t_{\alpha}(T)$, is located at the molar fraction $X_{met} \sim 0.3$, whereas the positive one at about 0.5.

Low T (no man's land) Positive Excess Hydrophilicity The water-methanol (molecular weight 32.04 and one OH group) relaxation time behavior in the low T regime is consistent with the previous interpretation of the water-glycerol data: a perturbative effect of the water HB network, that becomes dominant at $X_{met} \sim 0.3$ (7 water molecules and 3 of methanol). This perturbation is due to the methanol hydrophobicity, CH₃ groups, that influence the HB's and their network



On the contrary in the High T region, where the HB becomes progressively strongless, if compared to the hydrophobic contribution, there is the onset of transient methanol-water clusters.

Such a picture is consistent with many MD and experimental studies.

Also in this case the system properties must be linked to the two temperatures object of our study.

The excess of the relaxation time ($|\Delta t_{\alpha}(T)|$) in the liquid phase of the water-methanol solutions evidences the dominant role of T^* and T_L in the water dynamics. Due to the HB stability in the supercooled regime the change at T_L is more dramatic







The Stokes Einstein violation (Water_Gly)

The liquid-liquid transition (Water_Gly)



The Stokes Einstein violation (Water_Gly)



New NMR (self difffusion) data and the comparison with of 1/D_s and the viscosity (multiplied for a factor of 10⁻⁵) Erice-Water 16





The Stokes Einstein violation (Water_Gly) at the different molar fractions



Water-Glycerol transport parameters.



 $1000/T (K^{-1})$

The liquid-liquid transition

The glycerol molar fraction dependence of the main relaxation time at the different temperatures in a log-log representation.

Two well different behaviors are evident for the low and high X_{gly} .

In the second case the beahavior is that of a power law.









The locus of a liquid-liquid transition*.

Erice-Water 16

K.Murata & H. Tanaka Nat.Mat. 11, 436 (2012)

The Tanaka work report direct experimental evidence for a genuine (isocompositional) LLT without macroscopic phase separation in an aqueous solution of glycerol.

The liquids I and II differ in density, refractive index, structure, hydrogen bonding state, glass transition temperature and fragility, and that the transition between the two liquids is mainly driven by the local structuring of water rather than of glycerol, suggesting a link to a plausible LLT in pure water.

The liquid I transforms into liquid II by way of two types of kinetics: nucleation and growth, and spinodal decomposition.

Although liquid II is metastable against crystallization, we could access both its static and dynamical properties experimentally.

The power law exponent



Summary

The study of water liquid solutions in a wide temperature range (from the stable bulk phase to well inside the no man's land) as a function of the concentration well clarify the transport properties of the system.

We studied the mixtures water-glycerol and water-methanol obtaining information on the role of the two main water temperatures: that of the fragile to strong glass forming dynamical (FSDC) transition T_w and that of the thermodynamical singularity T*.

In both the mixtures the existence of the FSDC comes out unambigously from the experimental value of the transport parameters.

Our data highlight a continuity between the water in the bulk phase and the confined one, showing that among the three possible scenarios for the FSDC in confined water, the one related to the existence of the liquid polymorfism may be the most appropriate.

A lot of Thanks











Water-Glycerol transport parameters.





X_{GLY}

