2C14 Dynamics in Nano-Confined Systems: From Biological Assemblies to Ionic Liquids

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The longstanding goal of chemical dynamics is to unravel dynamics in a complex biological system. In recent years, significant progress towards this end has been achieved using femtosecond laser spectroscopy. In a biological system, water and the reactive species are often confined in a nanocavity. Nano-confinement affects the dynamics, in particular, the ultrafast initial steps. Binding of the water molecules with biological macromolecules greatly restricts its mobility. Solvation dynamics ("dielectric response") of so called "biological water" exhibits an ultraslow component in 100- 1000 ps time scale. This is slower by 2-3 orders of magnitude compared to bulk water. Proximity of the reactants in a confined system results in very fast bi-molecular reactions. We will illustrate this with ultrafast fluorescence resonance energy transfer (FRET) and electron transfer (ET) in an organized assembly. Finally, we will demonstrate that ultraslow solvation causes dramatic retardation of many polar reactions (e.g. proton transfer).

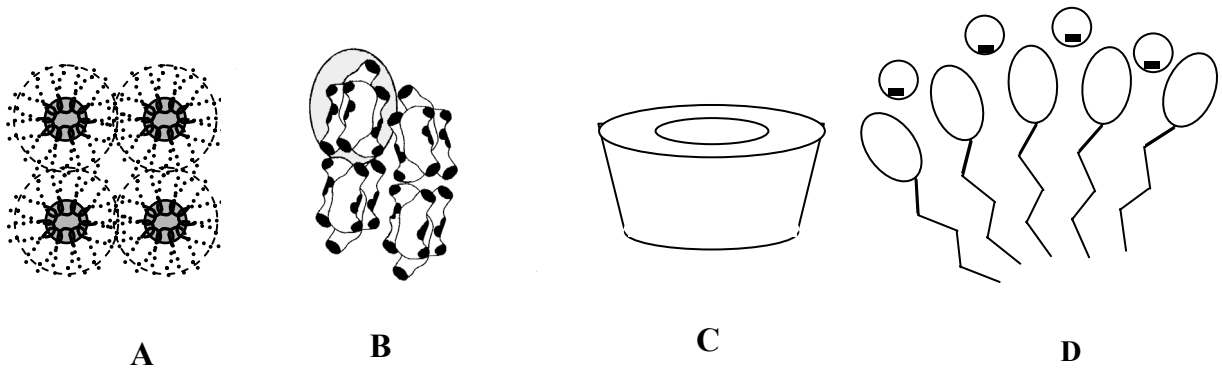

Fig. 1. A) P123 gel; B) bile salt aggregate; C) Cyclodextrin; D) ionic liquid aggregate

We will discuss several examples of ultraslow solvation dynamics in biological systems and their implications. We will show that dynamics of biological water depends on hydrogen bonding using two cyclodextrins (fig. 2a)- one without any OH group (trimethyl-β-cyclodextrin, TMB) and one with one OH pergluocose (dimethyl-β-cyclodextrin, DMB). In DMB, there are seven OH groups at the rim. We show that absence of OH group slows down solvation cinsideranly (in TMB).[1] We found that solvation dynamics vary markedly at two sites of a protein.[2] Solvation

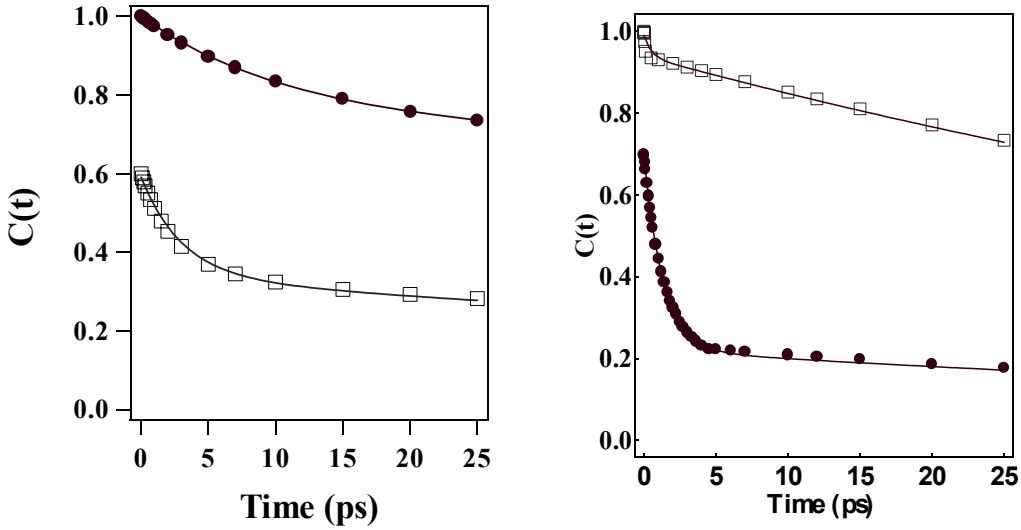

Fig. 2. Solvation dynamics in a) left, TMB (filled circles) and DMB;[1] and b) two partially folded states of cytochrome C.[3]

dynamics in two partially unfolded states of a protein (cytochrome C) are found to be different and slower than that in bulk water.[3] This suggests presence of residual structure in partially unfolded states. We found that by varying excitation wavelength one can selectively probe different regions of a heterogeneous system. Specifically, we have shown that even neat ionic liquid is heterogeneous.[4] An interesting observation is that the buried location of a bile salt aggregate display slower solvation but faster rotational dynamics (anisotropy decay).[5] We also show that FRET in different regions of a heterogeneous assembly may be studied through excitation wavelength dependence. We have reviewed some of these aspects recently.[6]

Reference

1) J. Phys. Chem. A 109 (2005) 9716.

2) Biochemistry 44 (2005) 8940.

3) J. Phys. Chem. B 110 (2006) 1056.

4) J. Phys. Chem. B 111 (2007) 12809.

5) J. Phys. Chem. B 112 (2008) 3575.

6) K. Bhattacharyya, Nature of Biological Water: A Femtosecond Study, Chemical Communications (2008) 2848.