In biosystems, water is a component of a multicomponent fluid mixture with various biomolecules, small organic molecules, variety of ions (monoatomic or molecular), charged species etc. The dissolution of solutes (biomolecules, ionic compounds and charged chemical species) in water is accompanied by formation of hydration shell (layers) around them. The dynamical coupling between biomolecules and their hydration water is long recognized as a major determinant of protein stability and macromolecular functions. In chemical and biological environments, water exists mainly as interfacial water, which is located in the close vicinity of different types of interfaces and is mostly confined in cellular cavities and interstitial voids as isolated water molecules. These environments may contain from millions to only a few tens of water molecules. The attractive/repulsive interaction between the interface and water molecules, as well as the geometrical constraint by the environment, causes significant changes in local and long-range water structure. As a result, chemistry in aqueous biomolecular systems and in organized molecular assemblies differs markedly from that in a homogeneous fluid medium. An attempt to unravel the dynamical states and energetics of water in bulk state and in presence of ions have been made by studying the solvation dynamics of coumarin 500 (C500) which performs the dual role of a solvation reporter and a mimic for small moieties like amino acid residues. The activation energy of bound to free water interconversion has been estimated to be 3.6 kcal mol^{-1}. The increased solubility of C500 in water indicates preferential interaction of the probe with GdmCl (guanidinium hydrochloride). The results indicate that the reporter probe C500 is located in the solvation shell of the Gdm cation comprising of loosely bound water molecules. The residence of the probe in the solvation shell of the Gdm cation has been confirmed through the increased microviscosity of the probe environment, compared to the bulk viscosity of the solution. We have

also explored the dynamical evolution of isolated water clusters in the non-aqueous dioxane continuum as a function of water concentration; we have used femtosecond/picosecond-resolved solvation dynamics and fluorescence anisotropy techniques. Solvation dynamics becomes faster with increasing temperature for the concentrated system due to the breakage of tetrahedral hydrogen bond network in the clusters. The activation energy for the process has been calculated to be 3.1 kcal mol^{-1}, which is smaller than the hydrogen bond energy in bulk water, but larger than the water-dioxane hydrogen bond energy, confirming the presence of both kinds of bond at the cluster interface.

In order to explore confined water dynamics systematically, we have used "microreactor" where hydration can be tuned in a systematic manner within the structural integrity of the system. Precise measurement of the different dynamical states of water molecules at the AOT (sodium bis(2-ethylhexyl) sulfosuccinate) reverse micellar interface with various degrees of hydration is achieved through temperature dependent solvation dynamics of coumarin 523 (C523). Applying Arrhenius model to the solvolysis of BzCl (benzoyl chloride) shows that the difference between the activation energy barrier for the solvolysis at different w_0 values are attributed to the formation and availability of free type water molecules at the interface, which in turn depends upon w0.

In another study, we have attempted to correlate the change in water dynamics in a reverse micellar (RM) core caused by the modification of the interface by mixing an anionic surfactant, AOT and a nonionic surfactant, tetraethylene glycol monododecyl ether (Brij-30), at different proportions and its consequent effect on the reactivity of water, measured by monitoring the solvolysis reaction of benzoyl chloride (BzCl). Solvation dynamics of coumarin 500 (C500) becomes faster with increasing XBrij-30. Also the solvolysis of BzCl becomes faster with XBrij-30 indicating the increased nucleophilicity of the entrapped water caused by the faster diffusion of water molecules as evidenced from the solvation studies. In another work, we have explored the slow dynamics of water confined in AOT lamellar structures and RM with various degrees of hydration based on two criteria: similar surface-to-surface distance ($d = l$, where d is the diameter of the RM nanopool and l is the interlayer distance in the lamellae) and having the same number of water molecules per AOT molecule ($w_0 = L_0$, where w_0 and L_0 are the water to surfactant molar ratio in RM and lamellae, respectively) using picosecond-resolved fluorescence spectroscopy. It is observed that the relaxation dynamics of water of the lamellar systems are slower for the $w_0 = L_0$ systems but faster or comparable for the $d = l$ systems.

To understand the energetic contributions from various steps of a diffusion controlled reaction, we have attempted to explore the molecular mechanism associated with a diffusion controlled reaction at a polymer hydration region by monitoring temperature dependent solvolysis reaction of benzoyl chloride (BzCl) in water-polyethylene glycol mixture at low water concentration. Temperature dependent solvolysis allows estimating the overall Arrhenius type

activation energy barrier associated with the reaction. To estimate the relative contribution of hydration and diffusive motion on the overall activation energy, we have studied the temperature dependent picosecond-resolved solvation dynamics using a fluorophore coumarin 500 (C500). The activation barrier for microviscosity as applicable to the Kramers model has been estimated from temperature dependent rotational anisotropy study. The activation energy barriers estimated from the temperature dependent solvation dynamics and microviscosity studies are correlated with the overall solvolysis reaction activation energy.

In order to investigate the role of water molecules on the substrate binding and functionality of a very commonly studied enzyme α-chymotrypsin (CHT), we have studied its catalytic activity in the presence of different concentrations of PEG 400 (polyethylene glycol with average molecular weight of 400). Our results show that the enzymatic activity of CHT decreases with the addition of PEG 400. A detailed energetic calculation shows that the entrance path for the substrate is stabilized (decrease in KM, Michaelis-Menten constant) whereas the exit channel is destabilized (decrease in kcat, turnover number) with increasing osmotic stress (OS). The overall secondary and tertiary structures of CHT determined from far-UV and near-UV CD (circular dichroism) show no significant change in the studied osmotic stress range, ruling out the possibility of massive structural reorientation of the overall enzyme being responsible for the altered catalytic activity. We have also investigated the dynamical evolution at the active site of CHT as well as the hydration shell surrounding the enzyme using picosecond-resolved fluorescence anisotropy of a substrate mimic (inhibitor) proflavin and ANS (1-anilino-8-naphthalenesulfonic acid, ammonium salt).

Recently, there has been a surge of interest in the research to explore the intermediate states of protein folding/unfolding and measuring molecular distances using FRET (Förster resonance energy transfer) between organic dye molecules. However, organic fluorophores suffer from unavoidable photobleaching and also have relatively faster excited state lifetimes, which are inefficient to monitor slow biophysical processes. In contrast with conventional organic fluorophores/dyes, inorganic metal nanocrystals have many advantages such as size-dependent emission, exceptional photostability, longer florescence lifetimes etc. Apart from being fluorescent, metal nanoclusters can have magnetic properties as well. In one of our works, we have incorporated a molecular magnet V_{15} (polyoxovanadate $[V_{15}As_6O_{42}(H_2O)]^{6-}$ cluster) into a protein (human serum albumin, HSA) cavity and used it as a local probe for the thermal denaturation of HSA at elevated temperatures using FRET between tryptophan of HSA (donor) and V_{15} (acceptor). Combining the florescence and magnetic properties into a nanosphere of a single material would lead to new applications in biological systems. In one of our studies, we have synthesized and characterized a luminescent and superparamagnetic Ni-nanoparticle conjugated to CHT.