

Interfacial hydration dynamics in cationic reverse and regular micelles using 2D-IR

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We use thiocyanate ions to probe interfacial hydration dynamics in regular and reverse micelles using ultrafast 2D-IR. The affinity of the anion for the cationic interfaces enables examination of dynamics independent of surface curvature.

Extended biomacromolecular interfaces perturb to some degree the orientational and translational dynamics of the nearby water molecules. Even relatively distant interfaces ($< 40 \text{ \AA}$) [1–3] can disrupt the hydrogen bonding network and alter the probability of dynamic molecular jumps [4] between hydrogen bonded partners thereby causing it to appear to slow down. In biological systems where interfacial environments predominate, hydration dynamics are expected to be dictated by the collective influence of these interfacial constraints. From relatively flat membranes formed by lipids to sharp grooves in proteins, curvature is likely to influence hydration dynamics differently. Two-dimensional infrared (2D-IR) spectroscopy is capable of delineating the dynamical fluctuations in the hydration environment of a vibrational probe by quantifying the decay of the frequency fluctuation correlation function (FFCF). We access interfacial water dynamics in a model system of reverse ($W_0 = [Water]/[Surfactant]$) and regular micelles prepared using surfactants with cationic head groups (Dodecyltrimethylammonium bromide, DTAB) and introducing thiocyanate (NaSCN) as a vibrational probe. The placement of our probe on the extreme chaotropic end of the Hofmeister series allows for its preferential association [5] with the interface. An interface selective probe of water dynamics independent of surface curvature enables us to explore the collective hydration mechanisms inside confined assemblies.

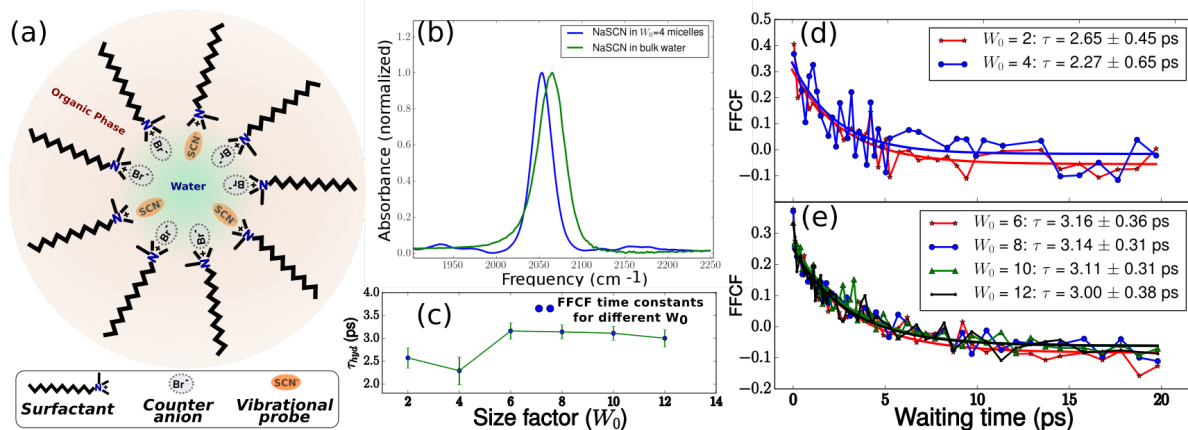


Figure 1: (a) Diagram showing reverse micelles prepared using DTAB with dichloromethane as the organic phase. The vibrational probe (SCN^-) is preferentially associated with the head group. (b) Linear absorption spectra of NaSCN in bulk water and inside $W_0 = 4$ size reverse micelles. A 12 cm^{-1} red shift is attributed to proximity of SCN^- to the cationic interface. (c) FFCF time constant values obtained after fitting for different reverse micelles sizes showing a transition between $W_0 = 4$ and $W_0 = 6$. (d)-(e) Experimental FFCF data points for different reverse micelle sizes along with their respective fits. Smaller reverse micelles are prone to noise due to low overall concentration of NaSCN.

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