H-bond Interactions in Heterogeneous Systems

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Crowding disrupts solvent hydrogen bond networks and modulates the hydration levels of biomolecules and osmolytes. Although the effect of additives on biomolecular structure and stability has been extensively studied, the role of crowding and heterogeneity is not well understood. Dimethyl sulfoxide (DMSO) is important small organic solvent in adaptable applications, such as protein destabilization, cryopreservation, and drug permeation. In particular, DMSO disrupts the hydrogen-bond networks of water in DMSO/water binary mixtures. Here, vibrational spectroscopy combined with molecular dynamics simulations (MD) and quantum chemistry models was used to describe the mechanism by which H-bond interactions of DMSO/water mixtures and crowding effects these heterogeneous systems. Based on directly quantifying H-bond populations using the S=O stretching vibration of DMSO, we show that crowding stabilizes hydrogen bonding in aqueous DMSO. Specifically, we use formamide and dimethylformamide (DMF) as molecular crowder, and map hydrogen bond populations of the S=O and C=O groups in DMSO/water/formamide or DMF ternary mixtures. Further, we use temperature-dependent C=O stretching 2D IR spectroscopy to quantify H-bond solvation dynamics, in binary mixtures. The results are as follows; 1. hydrogen bonds are formed and broken through a “step-in” mechanism, which involves hydrogen bonding between water and the DMSO aggregate species. 2. amide additives increase the amount of water within the DMSO first solvation shell, 3. lower temperature increases inhomogeneity of binary mixtures at varying concentrations.