IR pump-probe, MD simulation, and graph theoretical studies of high salt solutions

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Critical aggregation phenomena are ubiquitous in many self-assembling systems. Ions in high salt solutions could also spontaneously form larger ion aggregates, but their effects on hydrogen-bonding structures of water in aqueous salt solutions have not been fully understood yet. Recently, we have proposed a hypothesis on the mechanism of ion aggregation processes in very high salt solutions (1,2). Carrying out femtosecond IR pump-probe measurements of HDO in aqueous salt solutions, ^{13}C-NMR measurements of $S^{13}CN^-$ in various salt solutions, and extensive MD simulations with a few different sets of forcefield parameters, we have shown that the ion aggregate structures can be classified either ion clusters resembling molten salt-like structures or ion networks fully intertwined with water H-bonding networks, depending on the nature of dissolved anions (1). Although ions can be fully solvated separately from other counter-ions or form a variety of ion pairs at relatively low salt concentrations in water, as certain salt concentration increases up to its solubility limit in water, the dissolved ions tend to form large ion aggregates but the morphological structure could be different from each other depending on the nature of ions, i.e., chaotrope or kosmotrophe. To quantitatively describe and distinguish the cluster-like and network-like ion aggregate structures in high salt solutions, we used a spectral graph analysis theory and examined various spectral graph theoretical quantities reflecting connectivity patterns between ions and water molecules (2). Furthermore, since the most widely used IR probe for studying water dynamics in those aqueous salt solutions is O-D stretch mode of HDO, we have developed a novel vibrational solvatochromism theory for HDO in very high salt solutions (3). Moreover, the distributions of degree (connection) and path length of water H-bonding networks and ion aggregates are examined in terms of scale free or random network characteristics. This series of works combining time-resolved IR study, MD simulation, and graph analyses show the importance of morphological variation of ion aggregate structures from ion cluster to ion network in high salt solutions, which is in turn interrelated to the onset of macroscopic aggregate formation and the water hydrogen-bond structure making and breaking processes induced by Hofmeister ions.

References

[1] S. Kim, H. Kim, J.-H. Choi, and M. Cho, "Ion aggregation in high salt solutions: Ion network versus ion cluster" J. Chem. Phys., 141, 124510 (2014)
[2] J.-H. Choi and M. Cho, "Ion aggregation in high salt solutions: II. Spectral graph analysis of water hydrogen-bonding network and ion aggregate structures" J. Chem. Phys., 141, 154502 (2014)
[3] J.-H. Choi, H. Kim, S. Kim, S. Lim, B. Chon, and M. Cho, "Ion aggregation in high salt solutions: II. Computational vibrational spectroscopy of HDO in aqueous salt solutions" J. Chem. Phys., submitted (2015)