

Hydration and self-aggregation of a neutral cosolute from dielectric relaxation spectroscopy and MD simulations: The case of 1,3-dimethylurea

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Abstract

© the Owner Societies 2017. The influence of the amphiphile 1,3-dimethylurea (1,3-DMU) on the dynamic properties of water was studied using dielectric relaxation spectroscopy. The experiment provided evidence for substantial retardation of water reorientation in the hydration shell of 1,3-DMU, leading to a separate slow-water relaxation in addition to contributions from bulk-like and fast water as well as from the solute. From the amplitudes of the resolved water modes effective hydration numbers were calculated, showing that each 1,3-DMU molecule effectively freezes the reorientation of 1-2 water molecules. Additionally, a significant amount of solvent molecules, decreasing from ~ 39 at infinite dilution to ~ 3 close to the solubility limit, is retarded by a factor of ~ 1.4 to 2.3, depending on concentration. The marked increase of the solute amplitude indicates pronounced parallel dipole alignment between 1,3-DMU and its strongly bound H₂O molecules. Molecular dynamics (MD) simulations of selected solutions revealed a notable slowdown of water rotation for those solvent molecules surrounding the methyl groups of 1,3-DMU and strong binding of ~ 2 H₂O by the hydrophilic carbonyl group, corroborating thus the experimental results. Additionally, the simulations revealed 1,3-DMU self-aggregates of substantial lifetime.

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