Hydrophobic hydration of amphiphilic molecules by extended depolarized light scattering (EDLS): the case of tert-butyl alcohol (TBA) and trimethylamine N-oxide (TMAO)

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The molecular dynamics of aqueous solutions of two amphiphilic biorelevant solutes, tert-butyl alcohol (TBA) and trimethylamine N-oxide (TMAO), has been investigated by Extended Depolarized Light Scattering (EDLS) experiments. This approach has proved to be suitable to probe dynamical processes in a frequency range going from fractions of GHz to tens of THz, providing detailed information on relaxation processes of both solute and solvent [1-3]. TBA and TMAO are water-soluble small polar molecules with rather similar shape and volume. Since a large fraction of their solvent-exposed surface area is related to the presence of three methyl groups, these molecules are widely employed as simple models for the study of hydrophobic hydration and interactions [4,5]. Notably, in spite of their similarities, TBA is a denaturant that decreases the thermal stability of globular proteins, whereas TMAO stabilizes their native state [4]. From our experiments, two solvent relaxation processes at the picosecond time scale have been identified and assigned to hydration and bulk water. It is found that both molecules slow down the structural dynamics of water by a factor of *ca.* 4 and that this perturbation is limited to the first hydration shell. This indicates that the probed retardation is mainly due to the hydrophobic portion of these molecules. It is worth noting that larger perturbation factors have been revealed by EDLS in a number of systems, including sugars, peptides, amino acids and proteins [1]. At increasing solute concentration, the average number of perturbed water molecules decreases in both systems due to shell superposition effects; however, in the case of TMAO the hydration behavior can be fully explained by considering a random mixing process, while for TBA a tendency towards self-aggregation is evidenced [2,3]. This difference might be related to the higher propensity of TMAO to form strong hydrogen bonds with water through the polar NO group [6]. A comparative analysis of the spectral region related to intermolecular resonant modes (10-350 cm^{-1}) reveals specific signatures of these interactions in TMAO mixtures, in agreement with Raman results [4].

References

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