DYNAMICS OF CONFINED WATER

Traditionally, the dynamics of interfacial water has been studied by nuclear magnetic relaxation techniques. Halle and coworkers (64–66) have used water ^{2}H and ^{17}O spin relaxation to study water dynamics in the hydration layers of small peptides, globular proteins and in living cells of two microorganisms which is a particularly suitable method for investigating the single-particle dynamics of interfacial water and thus the protein-water interaction.

They have characterized the dynamical heterogeneity of hydration water by performing relaxation measurements over a wide temperature range, extending deeply into the supercooled regime, or by covering a wide frequency range. Protein hydration layers can be described by a power-law distribution of rotational correlation times with an exponent close to 2. This distribution comprises a small fraction of protein-specific hydration sites, where water rotation is strongly retarded, and a dominant fraction of generic hydration sites, where water rotation is as fast as in the hydration shells of small peptides. The generic dynamic perturbation factor is less than 2 at room temperature and exhibits a maximum near 260 K. Water in living cells behaves as expected from studies of simpler model systems, the only difference being a larger fraction of secluded (strongly perturbed) hydration sites associated with the supramolecular organization in the cell. Intracellular water that is not in direct contact with biopolymers has essentially the same dynamics as bulk water. There is no significant difference in cell water dynamics between mesophilic and halophilic organisms, despite the high K^{+} and Na^{+} concentrations in the latter. This finding is different from a recent report on anomalously slow water diffusion in *Haloarcula marismortui* cells (67).

The free hydration layer studied here differs qualitatively from confined water in solid protein powder samples. With regard to the solvent diffusion constant near protein and silica surfaces, there are reports from other groups showing that it is reduced by a factor of about 5 compared with that of bulk water (68).

An ideally microscopically detailed method for exploring the change in hydrogen bonding patterns as well as the translational and rotational diffusion constants and residence times of water molecules, when they are near surfaces is computer molecular dynamics (CMD). For example, Rossky and coworkers (32,33,35–37) have investigated changes of the structure, hydrogen bonding and dynamics of water molecules when they are adjacent to an atomically detailed hydrophobic surface and to a hydroxylated silica surface. Results of CMD simulations (32,33,35–37) generally indicate that the dynamics of water molecules on protein and silica surfaces where hydrophilic interactions are dominant suffer only a mild slowing down compared with bulk water. More specifically, it has been reported that the retardation is by a factor of ~ 2 in the protein case and about a factor of 5 in the silica case. Residence times of water in the first hydration layer are typically of the order of 100 ps.

Linse (69) made a similar simulation for water near a charged surface with mobile counterions constituting an electric double layer such as in the interior of a reverse micelle formed by ionic surfactants in oil. He reported that water in the aqueous core of reverse micelles has a reduced rate of translational and rotational motions by a factor of 2 to 4.

These CMD results are still qualitative and somewhat conflicting with the available experimental data (65), largely because of the simplified models used