HYDRATION WATER DYNAMICS OF A HYDROPHOBIC OLIGOPEPTIDE

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The role of water on the structure and activity of proteins, DNA and other biological macromolecules is certainly important, although not easily to comprehend.

Depending on its situation, water forms hydrogen bonds, occupies small cavities (pools) or participates to the so-called hydrophobic interaction. The more interesting and realistic approach is the study of aqueous solutions of bio-molecules but, in such samples, the interesting local behaviour is hidden by the molecules of the solvent. Consequently, most of the detailed studies of the behaviour of hydration water have been performed with hydrated powders. Even in this way the results are ambiguous because molecules at different sites contribute in different ways to a global result that is only the average of all the possible motions. The ideal issue would be the selective deuteration of parts of the bio-molecule as it is currently done for example in the study of polymers but, notwithstanding undeniable progresses, this issue remains rare, expensive and not always possible.

We decided to circumvent the problem by the study of a synthesized uniform oligomer formed by five monomers of alanin, which is one of the simplest hydrophobic amino-acids with α-helix potential (figure 1).
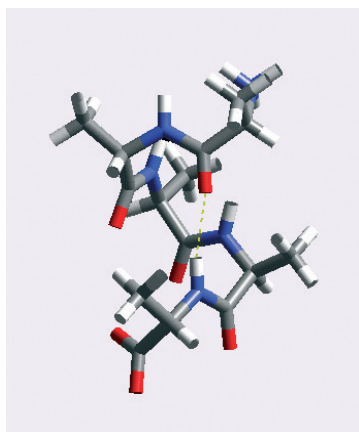

Figure 1. Representation of the structure of penta-alanin (a β-sheet). The broken line represents an internal hydrogen bond.

Quasi-elastic scattered intensity is almost totally due to different motions of hydrogen atoms in water molecules and the minor contribution of the peptide corresponds in intensity to that of three hydrogen atoms.

In a general way, we analysed the scattering function, $S(Q, \omega)$, with the following expression subsequently convoluted with the instrumental resolution:

$$S(Q, \omega) = A\delta(\omega)$$
$$+X\,[B(Q)\delta(\omega)+(1-B(Q))L2(Q, \omega)]$$
$$*[C(Q)\delta(\omega)+(1-C(Q))L1(Q,\omega)]$$

In this expression the first term accounts for the elastic scattering of the peptide and X is the fraction of water contributing to different motions. They are separated into two terms, one representing rotational diffusion, the second the translational diffusion.

Different levels of hydration have been measured according to the following Table:

Hydration (%)	0	7	30	50	90
N total of molecules of water/peptide	0.84	2.8	9.24	14.84	25.84

The dry oligomer contains almost 1 water molecule per peptide. Its dynamics reduces to rotational motions due to the breaking of hydrogen bonds. The signal is a single Lorentzian with a Q independent half-width (0.10 meV). The characteristic time is of the order of 2 ps which corresponds to a life time of hydrogen bonds almost two times longer than in bulk water.

At 7% hydration, there are two more water molecules present. They go preferentially to the only hydrophilic sites at the extremities of the peptide. There motion is confined and is well described by a model of diffusion inside a sphere of small radius [1] as illustrated in figure 2 by the Q dependence of the elastic incoherent structure factor (EISF).

At higher levels of hydration, the translational diffusion is apparent and two Lorentzian quasi-elastic components are necessary to fit the data. The rotational component, yields a value for the hydrogen-bond lifetime equal to 1.3 ps, slightly larger than that (1.1 ps) observed in bulk water at the same room temperature [2]. The half-width of

the Lorentzian $L_1(Q,\omega)$ is plotted in figure 3 for different levels of hydration and compared with bulk water.
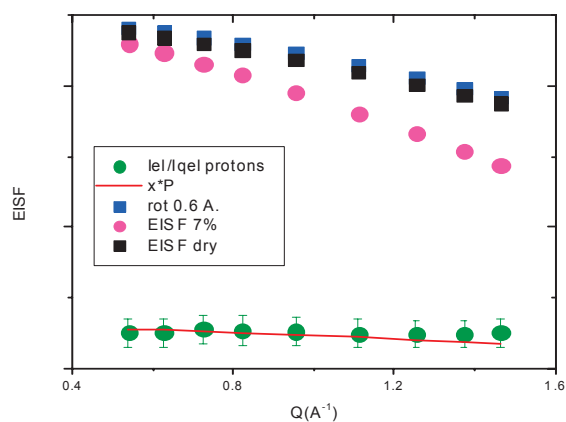

Figure 2. Representation of the Q dependence of the EISF for the dry and 7% hydrated peptide.
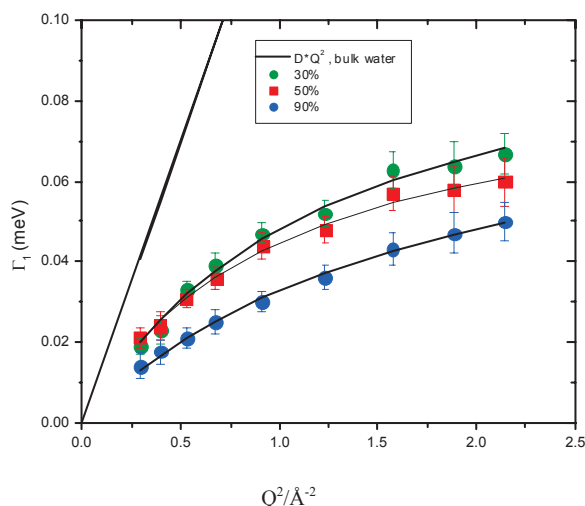

Figure 3. Half width at half maximum of the translational Lorentzian at different levels of hydration plotted as a function of Q^2. The solid line represents DQ^2 for bulk water.

The Table below summarizes the self-diffusion, D, and the residence time, τ_0, that can be deduced from the Q dependence of the half-width, Γ_1,

within a model of jump for the molecular diffusion:

$$\Gamma = DQ^2/(1+DQ^2\tau_0)$$

Higher the hydration and higher the diffusion which tends asymptotically to the self-diffusion in bulk water. Instead, the residence time remains almost constant and much longer than in bulk water, i.e. a behaviour similar to bulk water at a temperature around 30 K lower, as reported previously [3]. The constant jump length, which corresponds to the distance between two neighbouring hydrogen atoms, indicates that the mechanism of diffusion by rotational jumps is always the same.

Hydration	D (10^{-6} cm^2s^{-1})	τ_0(ps)	Jump length
30 %	7.7	7.4	1,5
50 %	13.1	7,4	1,6
90 %	13.6	6,1	1,5
bulk water	22.0	1.2	1.6

This detailed study of the hydration of penta-alanine shows that the dynamical contribution of the first hydration water, of a completely hydrophobic environment, is characteristic of a slow rotational motion with a relaxation time of 2.2 ps.

The addition of two more hydration water molecules shows that the rotational motion of the first water is coupled with diffusive motion. The dynamical profile is described, in first approximation, through a rotational jump model.

At higher levels of hydration, the mobility of water is quite similar to that of bulk water, i.e. translational diffusion by rotational jumps. The 23 water molecules that correspond to the full hydration of the peptide minus the three first hydration waters diffuse in a free way along the peptide. The residence time between successive jumps and the resulting self-diffusion is that of bulk water at a temperature 30° lower.

References
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