Experimental report

20/11/2015

Proposal:	**9-13-523**	**Council:**	4/2014
Title:	Component Dynamics in Proline Aqueous Solutions at Different Concentrations		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: fully protonated L-proline (C5H9NO2) in D2O at different concentrations
d7-L-proline (C5H7H2NO2) in H2O at different concentrations
d7-L-proline (C5H7H2NO2) in D2O at different concentrations

Instrument	Requested days	Allocated days	From	To
D7	1	2	09/12/2014	11/12/2014
IN16B	4	6	05/12/2014	09/12/2014
			17/12/2014	19/12/2014
IN5	2	2	18/12/2014	21/12/2014

Abstract:

We aim to contribute to the understanding of the dynamic processes in aqueous solutions of an amino acid (proline) at different concentrations. This is a first step toward the case of larger and more complex systems such as proteins. To do this, we want to resolve and characterize the component dynamics of proline and water in the solutions. With the proposed experiments we shall be able to provide a microscopic means to validate (i) the interpretation of previous dielectric results by us and (ii) our cells constructed by MD-simulations. Combining the information offered by these three techniques we have a chance to reach a molecular understanding of the dynamics in this 'simple' biomolecular system.

Component Dynamics in Proline Aqueous Solutions at Different Concentrations

Experiments were performed on proline/water mixtures with different concentrations, corresponding to 4, 6*, 13, 31*, 93 and 190* water molecules / proline molecule. Samples were selectively deuterated in order to be able to isolate the component dynamics: we used systems with deuterated water and protonated proline to follow the H-dynamics of the amino-acid, and mixtures of protonated water and deuterated proline to address the water motions. For the latter labeling, the concentrations investigated were restricted to those marked with an asterisk. Due to the presence of 2 interchangeable protons in this amino-acid, a pre-treatment was performed to substitute them by deuterons in the originally fully protonated proline and by protons in the deuterated proline, before dissolving the amino-acids in D_2O and H_2O respectively. In this way, we avoided uncertainties related to the origin of the signal from the interchangeable atoms.

All samples were investigated at 300K by the three instruments (IN16B, D7 and IN5). On IN16B and IN5, in addition, measurements at 275, 255 and 235K were carried out for both samples with 6 water molecules / proline molecule.

D7 experiments were carried out with an incident wavelength of 3.1461Å. The obtained results are shown in Fig. 1. Two peaks are observed in the Q-range between 0.3 and 2.5Å^{-1} for the samples with deuterated water. The peak at higher Qs is absent in the samples with the opposite labeling. For those samples, the low-Q peak becomes very intense for high proline content. From these qualitative considerations we may attribute the origin of the peak revealing longer distances to correlations involving proline atoms, and the other one to be generated by water/water correlations. This set of data contains a great deal of information that shall be disentangled with the help of the MD-simulations. As a first step, the D7 results will serve as a critical test to validate the simulated cells.

For the IN5 experiments, two incident wavelengths were applied: 5 and 8Å. All the quasielastic data were Fourier transformed to the time domain to obtain the intermediate scattering functions. These were subsequently deconvoluted by division by the corresponding Fourier transformed spectra of the instrumental resolution. All the obtained functions shall be properly combined to obtain full sets of data covering a wide time range from sub pico-seconds to nano-seconds. In a preliminary analysis of the individual IN16B results, the deconvoluted intermediate scattering functions were fitted by single exponentials, which provide a good description without clear signatures of stretching. The obtained characteristic times are represented as function of Q in Figure 2

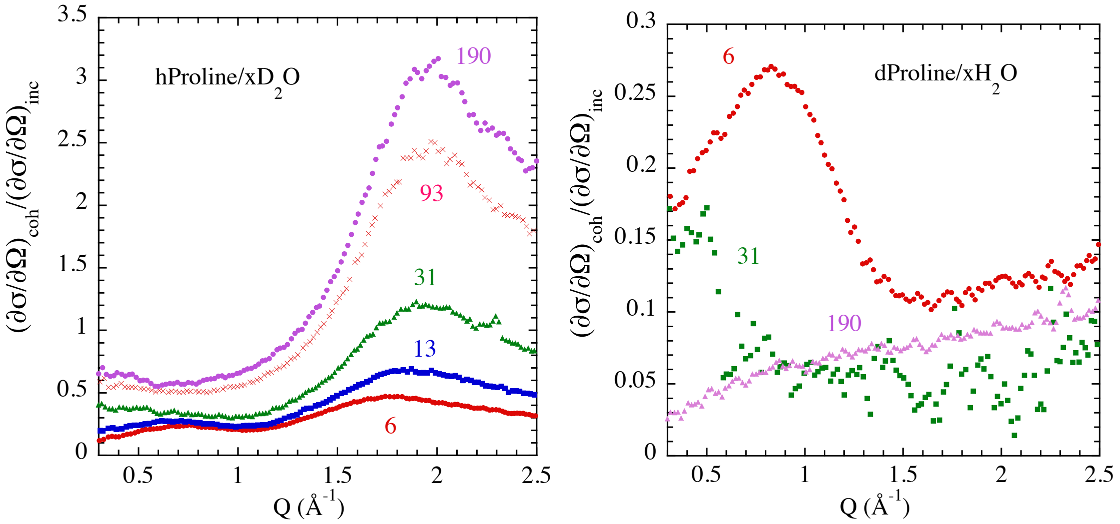

Figure 1: Ratio between coherent and incoherent differential cross sections obtained by D7 at room temperature on samples with protonated proline and deuterated water (left) and deuterated proline and protonated water (right) with the number of water molecules / proline molecule (x) indicated.

for the sample where proline dynamics in an environment of 6 water molecules / proline molecule is followed at 255K. We observe the coincidence of the results for the two lowest Q-values accessed by IN16B. This was observed for all IN16B measurements. The reason for this problem in the two lowest-angle detectors could not be elucidated during the experiment. Assuming that the problem was on the lowest Q-detector, the data can be well described in a first approach by the Q-dependence expected in the jump-diffusion model, with a residence time of 80 ps and a jump length of about 0.5Å, as can be seen in the figure.

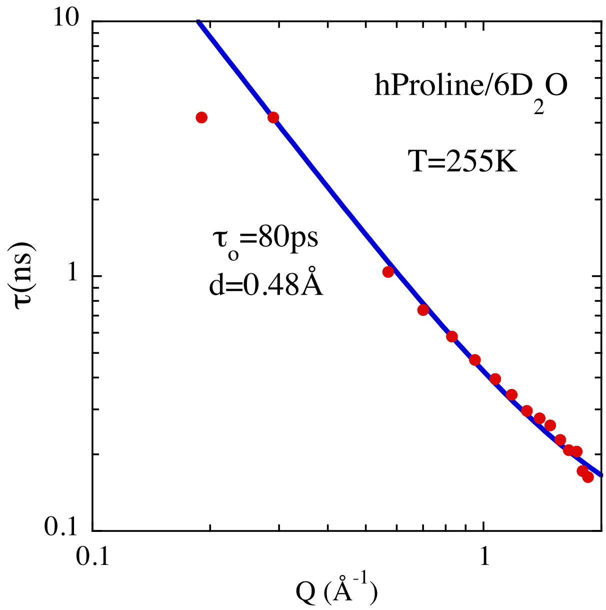

Figure 2: Q-dependence of the characteristic times obtained from IN16B measurements on hProline/6D$_2$O sample revealing the amino-acid dynamics. Solid line is a fit of the jump diffusion model $\tau = \tau_o[1+(dQ)^{-2}]$ to the data.

The dynamic information will also be combined with the MD-simulation results to characterize the motions of both components in the mixtures at the different concentrations investigated.