Experimental report

31/07/2026

Proposal: EASY-1180 **Council:** 4/2023

Title: Relaxation Spectrum of a Polymer-Associated and Bulk Solvent in Poly(N-isopropylacrylamide) in Methanol

Research area: Soft condensed matter

This proposal is a new proposal

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Experimental team:

Local contacts: Jacques OLLIVIER

Samples: 25 wt% poly(N-isopropylacrylamide) in methanol

Instrument	Requested days	Allocated days	From	To
IN5	8	8	06/11/2023	07/11/2023

Abstract:

The adsorption of methanol to poly(N-isopropyl acrylamide) (PNIPAM) is discussed as a possible reason for the co-non-solvency effect of PNIPAM in mixtures with water. In an experiment with quasi-elastic neutron scattering at IN5, we wish to measure the solvent dynamics in a solution of PNIPAM in neat methanol to detect and characterize possible polymer-adsorbed methanol. This would complement our previous QENS measurements in neat H2O, in H2O/CD3OD and D2O/CH3OH. We propose to do room temperature measurements of a PNIPAM solution in CH3OH and of neat CH3OH within the Easy Access mode.

Relaxation Spectra of Polymer-Associated and Bulk Solvent in Poly(*N*-isopropylacrylamide) Solutions in Methanol

Abstract:
Our aim is to probe relaxation processes in a PNIPAM solution in CH_3OH, in particular to investigate if there is a relaxation process due to polymer-associated methanol. This result is important in the context of the co-nonsolvency effect, where the rreferential adsorption of methanol or water on the polymer plays a key role.

The thermoresponsive polymer poly(*N*-isopropylacrylamide) (PNIPAM) possesses a sharp demixing transition in an aqueous environment with a lower critical solution temperature near 32 °C, which is exploited in applications as sensors or switches, e.g. in microfluidics. Cooperative dehydration is a major driving force, causing the polymer chains to collapse at the cloud point, followed by aggregation. The hydration behavior of PNIPAM and the dehydration process are not only essential for an understanding of the solvation of the polymer in aqueous solution, but also the molecular basis of the co-nonsolvency effect of PNIPAM, i.e. the depression of the cloud point in, for instance, water-methanol mixtures [1]. Preferential binding of water or the cosolvent to the polymer is of major importance in driving the conformational transition of the polymer upon addition of the cosolvent. An ideal tool to investigate the fraction and dynamics of water bound to the polymer [2-4] is quasi-elastic neutron scattering (QENS) as it is sensitive to the hydrogen motion.

The present study focuses on the dynamics of PNIPAM in a pure methanol solution to complete our experiment. Similar to water, methanol is a hydrogen-bonding liquid with strong intermolecular correlations [5,6]. The key question is whether there is an additional slower relaxation process in a solution of PNIPAM in methanol that may be caused by methanol adsorbed to the polymer chains. Quasielastic neutron scattering experiments were conducted at the IN5 time-of-flight spectrometer over a q-range from 0.65 to 1.85 A^{-1}. The dynamic structure factors $S(q,\Delta E)$ were measured on a sample of pure methanol and a 25 wt% PNIPAM solution in methanol at a temperature of 24 °C (Figure 1a).

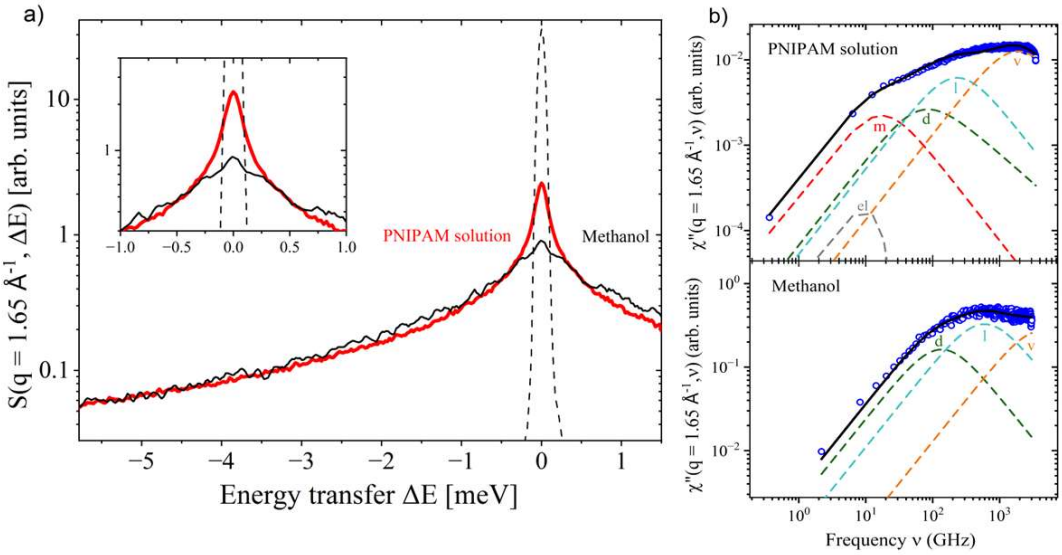

Figure 1. (a) Dynamic structure factors $S(q,\Delta E)$ at q = 1.65 Å^{-1} of pure methanol (full black line) and of the 25 wt% PNIPAM solution (full red line) at 24 °C at ambient pressure. Broken black line: resolution function. The inset shows a zoom around the elastic line. (b) Corresponding imaginary parts of the dynamic susceptibilities $\chi''(q,\nu)$ at q = 1.65 A^{-1} (symbols). ν denotes the frequency. Top: PNIPAM solution, bottom: pure methanol. Full black lines: overall fits, broken colored lines: contributions to the fit: (el) elastic line, (m) adsorbed methanol, (d, l, v) diffusive, local and vibrational process of bulk methanol.

The dynamic structure factor $S(q, \Delta E)$ of pure methanol shows at least two contributions. In the PNIPAM solution, the scattering near the elastic line is enhanced, pointing to additional slow dynamic processes. For the analysis, we chose the representation of the data as the imaginary part of the dynamic susceptibility, $\chi''(q,\nu)$ (Figure 1b), as in our previous works on aqueous PNIPAM solutions [2, 3]. In the range $\nu = 10^2 - 5\times10^3$ s^{-1}, it shows several maxima. In the hydrogen-bonded liquid methanol, similar to pure water, three relaxation processes can be distinguished, namely a diffusional process (marked *d* in Figure 1b) centered near 10^2 GHz. Two more relaxation processes at higher frequencies may be attributed to local and vibrational motions (marked *l* and *v* in Figure 1b).

In the PNIPAM solution, an additional low-frequency relaxation process is observed (peak frequency ca. 10 s^{-1}) that is absent in pure methanol. This feature indicates that a population of methanol molecules is present whose motion is significantly slower than that of the bulk solvent. Such slowing is consistent with methanol molecules remaining associated with the polymer over longer time scales (or "adsorbed"), which may be attributed to significant polymer-methanol interactions. Previous molecular dynamics simulations demonstrated that liquid methanol forms an extended hydrogen-bond network composed of chains and rings and featuring bifurcated hydrogen bonds [6]. Together, these results suggest that the adsorbed methanol forms a hydrogen-bonded solvation shell surrounding PNIPAM.

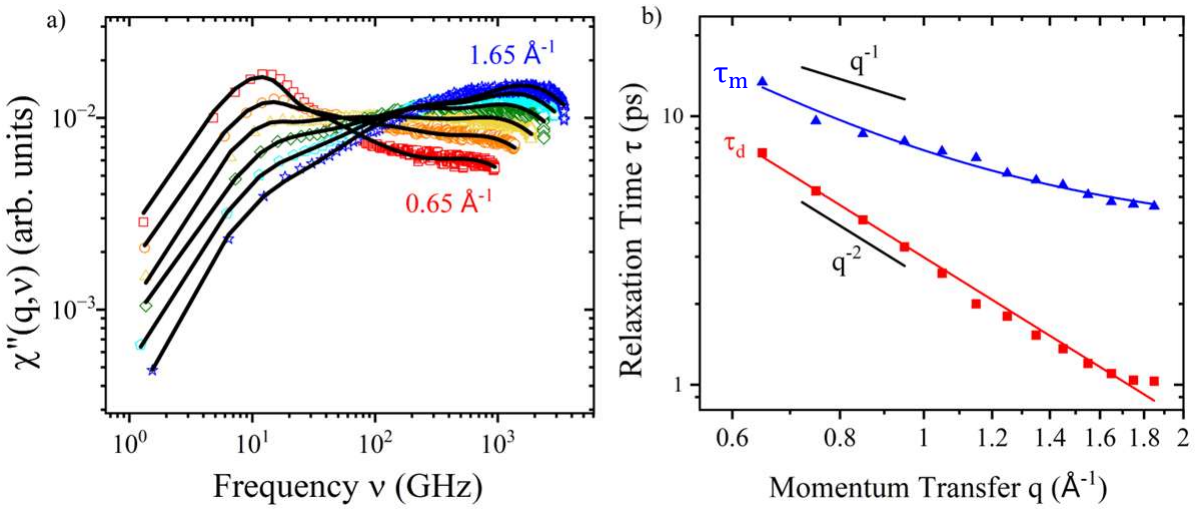

Figure 2. (a) Dynamic susceptibilities of the PNIPAM solution over a range of q-values. (b) Relaxation times for the bulk diffusive process and the hydration water obtained from the deconvolution of the susceptibility spectra for the PNIPAM solution.

Figure 2 further illustrates the q dependence of the relaxation spectra for the PNIPAM solution. As q increases, the bulk diffusive process of methanol shifts more strongly along the frequency axis than the polymer-associated relaxation, indicating different types of molecular motions. The relaxation times τ extracted from the peak frequencies of the deconvolution (Figure 1b) are shown in Figure 2b. The bulk diffusive process follows approximately a dependence $\tau_d \propto q^{-2}$ over the entire q-range studied, which is characteristic of the expected translational diffusion, while the q-dependence of the relaxation time of the polymer-associated methanol is significantly weaker and exhibits an approximate dependence $\tau_m \propto q^{-1}$, which is consistent with, e.g., jump diffusion. Overall, these results indicate that a fraction of the methanol molecules remain associated with PNIPAM, forming a solvation shell around the polymer.

In summary, we have observed an additional slow relaxation process in a solution of PNIPAM in methanol compared to the pure solvent which is consistent with polymer associated methanol.
We thank Dr. Jacques Ollivier for carrying out this very successful experiment.

References

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