Water Dynamics in Aqueous Poly(*N*-isopropyl acrylamide) Solutions with a Methanol Cosolvent

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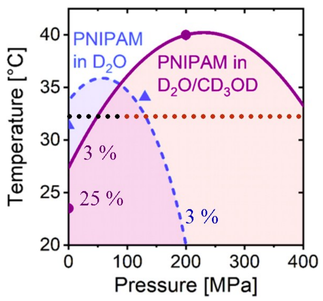
Summary

Cooperative dehydration is a major driving force for the demixing transition in poly(N-isopropylacrylamide) (PNIPAM), causing the polymer chains to collapse at the cloud point, followed by aggregation in aqueous solution. The motion of the hydration water is slowed down compared to bulk water and it is crucial in the solvation behavior in the presence of a co-solvent such as methanol. QENS measurements were conducted on PNIPAM in a 80% H2O / 20% methanol mixture at variable temperature and pressure with the time-of-flight spectrometer TOFTOF. Hydration water is partially released at the demixing transition. The release and adsorption of solvent by the polymer chains correlate with a change in effective solvent composition as evidenced by the diffusive properties of bulk water. At high pressure the solvent phase is enriched with methanol near the cloud point implying that water is preferentially adsorbed.

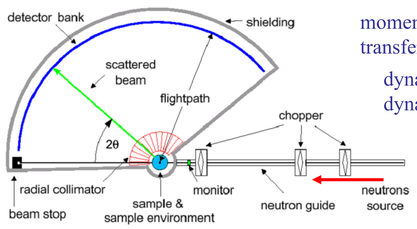


High pressure has a substantial effect on the lower critical solution temperature (LCST) and on the phase behavior of PNIPAM. In a water-methanol mixture the one phase region is hugely expanded along the pressure axis compared to purely aqueous solutions.

Experimental approach

- Poly(*N*-isopropylacrylamide) with a molar mass M_n = 36 kg mol^{-1} in 25 wt% in H_2O and in 80:20 wt% H_2O/CD_3OD
- Quasi-elastic neutron scattering (QENS) at FRM II, TOF-TOF. Incoherent scattering dominant due to ^{1}H. Elastic energy resolution ~ 30 μeV. λ = 6 Å. Al pressure cell. Background correction (empty cell), calibration: vanadium standard

Time-of-flight of scattered neutrons energy loss (gain)



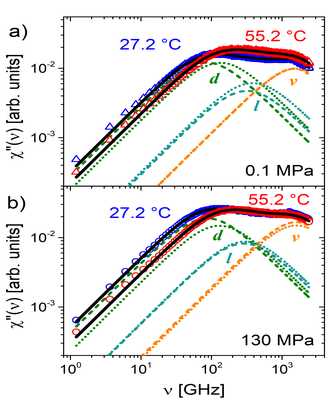
momentum transfer $q = \frac{4\pi}{\lambda}\sin\theta$

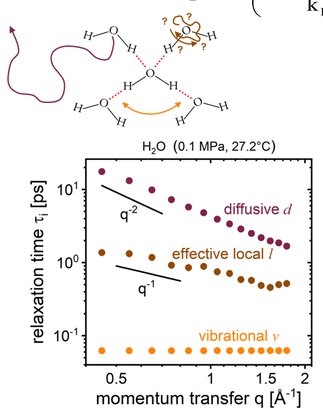
dynamic structure factor $S(q,\nu) \rightarrow$ dynamic susceptibility $\chi''(\nu)$

$$\frac{1}{\pi}\chi''(\nu) = \frac{S(q,\nu)}{n_B(\nu)+1}$$

$$n_B(\nu) = \left(\exp\left(\frac{h\nu}{k_B T}\right) - 1\right)^{-1}$$

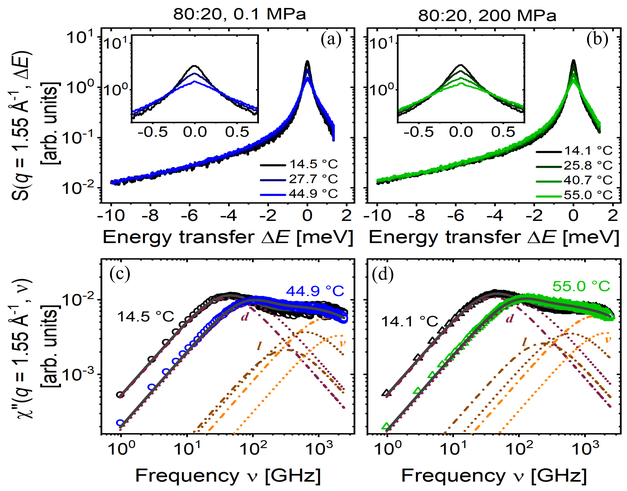
Pure water (bulk) $\chi''(\nu)$





Relaxation times of the diffusive process (d, Debye), the effective local process (*l*), and vibrational process (v)

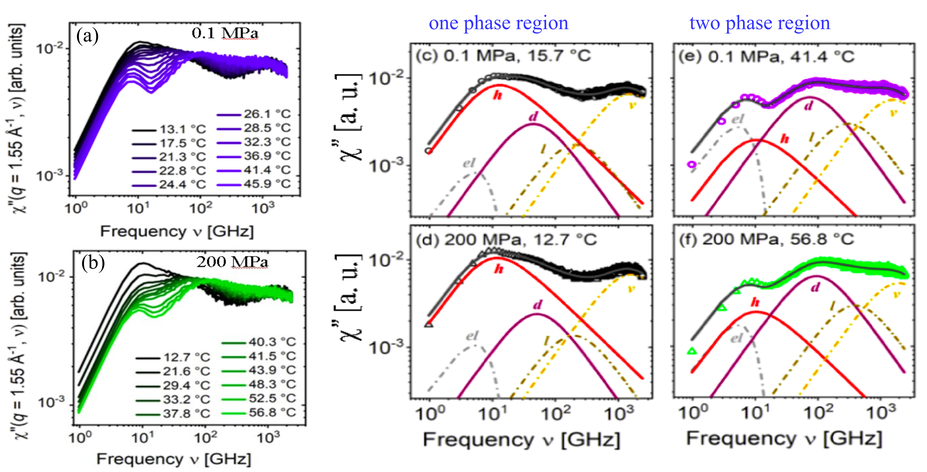
80:20 H_2O/CD_3OD



Dynamic structure factors, $S(q,\Delta E)$, of the 80:20 v/v H_2O/CD_3OD solution obtained at q = 1.55 Å^{-1} at 0.1 MPa (a) and 200 MPa (b).
(c), (d) deconvolution: diffusive process of bulk water ***d***, effective local process of bulk water ***l***, and vibrational process ***v***.

Susceptibility spectra

PNIPAM in 80:20 H_2O/CD_3OD



Temperature dependence of the susceptibility $\chi''(q,\nu)$ of the 25 wt% PNIPAM solution in 80:20 v/v H_2O/CD_3OD obtained at q = 1.55 Å^{-1} at 0.1 MPa (a) and (b) 200 MPa.
Deconvolution at temperatures below and above the respective cloud point at ambient and high pressure.
Elastic fraction ***el***, hydration water ***h***, diffusive process of bulk water ***d***, effective local process of bulk water ***l***, and vibrational process ***v***.

Susceptibility spectra of PNIPAM solution modelled with

$$\chi''_q(\nu) = \chi''_{q,el}(\nu) + \chi''_{q,h}(\nu) + \chi''_{q,d}(\nu) + \chi''_{q,\ell}(\nu) + \chi''_{q,v}(\nu)$$

elastic: measured resolution function × amplitude; Hydration water: Cole-Davidson α = 0.7; diffusive, local, vibrational: bulk water

$$\chi''_{q,h} = -\mathrm{Im}\left(C_{q,h}\frac{1}{(1+2\pi i\,\tau_h\nu)^{\alpha}}\right)$$

Variation of bulk and hydration water with T and P

Relative fractions f_i of water species from amplitudes $f_i = \frac{C_i}{C_h + C_d + C_l}$

Ambient pressure $T \geq T_{cp}$: **abrupt polymer dehydration**

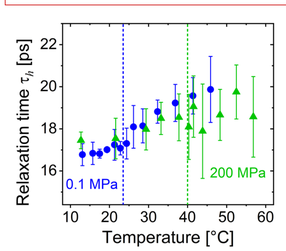
High pressure (200 MPa) $T < T_{cp}$: weakly decreasing hydration
$T > T_{cp}$: continuous weak dehydration

Relaxation time of H_2O diffusive mode

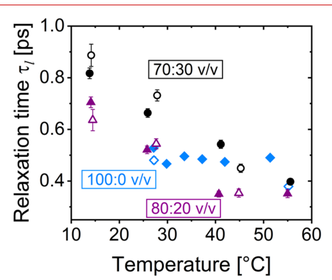
Effective solvent composition depends on amount of bound water / methanol

At 200 MPa the relaxation time τ_d for PNIPAM in 80:20 H_2O/CD_3OD at T_{CP} = 40 °C, is about the same as in H_2O/CD_3OD with composition 70:30

At high pressure, the solvent phase is enriched with methanol near T_{cp}water is preferentially adsorbed on the chains

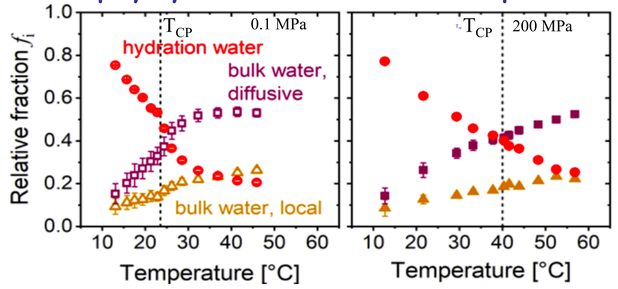


Relaxation time τ_h of hydration water.
25 wt% PNIPAM in 80:20 v/v H_2O/CD_3OD at 0.1 MPa (blue circles) and 200 MPa (green triangles) The dashed vertical lines mark the cloud points at both pressures.

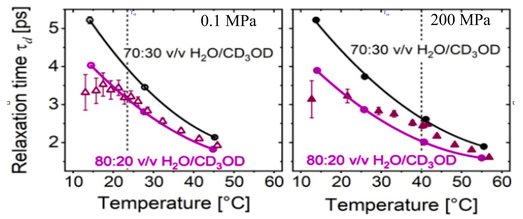


Relaxation time τ_l of the local mode of H_2O at q = 1.55 Å^{-1}. 25 wt%. PNIPAM in 70:30 v/v H_2O/CD_3OD, 80:20 v/v H_2O/CD_3OD and in neat H_2O. t 0.1 MPa (open symbols), 200 MPa (closed symbols)

Interplay hydration - bulk solvent composition



Deconvolution of τ_d → hydration and bulk water fractions



Bulk water relaxation time τ_d ↔ effective solvent composition

Conclusions

- QENS reveals the dynamics of bulk and hydration water that is partially released across the LCST transition
- Release and adsorption of cosolvent molecules by the polymer chains correlate with a change in effective solvent composition as evidenced by the diffusive properties of bulk water
- At high pressure the solvent phase is enriched with methanol near T_{CP} ↔ water is preferentially adsorbed

References

[1] B.-J. Niebuur et al. , *Macromolecules* 2019, 52, 1942
[2] B.-J. Niebuur et al., *Macromolecules* 2021, 54, 4387

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