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Water Dynamics in Aqueous Poly(N-isopropylacrylamide) Solutions with a Methanol Cosolvent

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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 [1]. 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.

[1] B.-J. Niebuur et al., *Macromolecules* 54, 4387 (2021)

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