water-alcohol anomalies reflected in the solvency of PNiPAM

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Water and alcohol are well known to form mixtures with properties that are not just a linear combination of the properties of the two components. Remarkably, such anomaly in the solvent properties is also reflected in the solvation behaviour of poly-N-isopropyl acrylamide (PNiPAM) in water/alcohol mixtures. At room-temperature PNiPAM is perfectly soluble in pure water and pure alcohol, but not in certain mixtures of both.

In this contribution we show that this 'co-nonsolvency' phenomenon has to be understood as that the phase behaviour of PNiPAM is governed by two distinct contributions. While the phase behaviour is governed by classical mixing contributions in the alcohol-rich regime, in the water-rich regime the phase behaviour of PNiPAM is determined by the solvent state. This denotes that solvation of PNiPAM in water is primarily governed by hydrophobic hydration, while the PNiPAM-alcohol interactions are largely unspecific.

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