Using Scattering to Probe Superchaotropic Anion Adsorption to Nonionic Polymers

Patrick Denk [a], *Max Hohenschutz* [a]

[a] *RWTH Aachen University, Institute of Physical Chemistry, Landoltweg 2, 52074 Aachen, Germany*

denk@pc.rwth-aachen.de

Classical anions are categorized into kosmotropes ("water structure makers"), such as F^- and SO_4^{2-}, and chaotropes ("water structure breakers"), such as I^- or SCN^-. A high charge density results in kosmotropic behavior, while a low charge density results in chaotropic behavior. The even lower charge density of nanometer-sized ions, such as $B_{12}Br_{12}^{2-}$ and $SiW_{12}O_{40}^{4-}$ (Fig. 1b), leads to more pronounced "superchaotropic" behavior: Strong salting-in of hydrophobic solutes and large shifts in the lower critical solution temperature (LCST) of thermosensitive polymers, such as poly *N*-isopropylacrylamide (PNIPAM) or hydroxypropylcellulose (HPC, Fig. 1b). An important aspect of this behavior is the adsorption of (super)chaotropic anions to the uncharged solutes [1]. Adsorption constants of classical chaotropes to these polymers are typically in the range of $1 < K_A < 10\ M^{-1}$ (very weak binding) [2–4], and orders of magnitude higher for superchaotropes, $200 < K_A < 2000\ M^{-1}$ (weak to intermediate binding) [5–7]. Due to the much stronger binding, interactions of polymers and superchaotropes are experimentally easier to examine. Such superchaotrope-nonionic polymer systems are therefore also good model systems to elucidate non-additive salt effects, seen for example in the LCST behavior of HPC as a function of $H_4SiW_{12}O_{40}$ (HSiW) concentration with NaCl as background salt (Fig. 1a).
Typically applied methods like LCST measurements, isothermal calorimetry, or NMR (chemical shifts), all yield somewhat different apparent association constants. Here we explore the possibility of using small-angle scattering and dynamic light scattering to determine the association constant, while at the same time obtaining information on structural changes of the polymer.

Keywords:
superchaotrope, light scattering, small-angle scattering, salt effects, ion adsorption

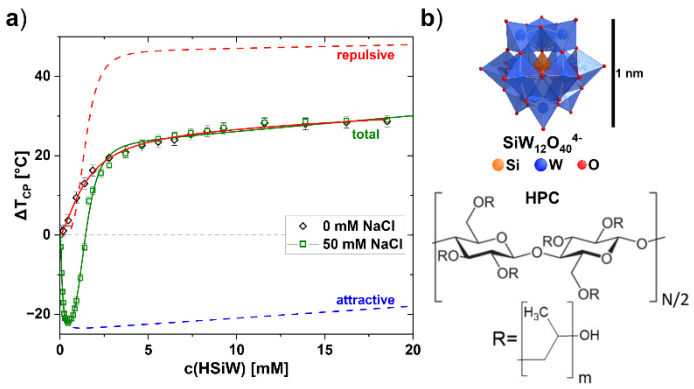

Fig. 1. a) Increase of the LCST of 26 mM HPC in water due to adsorption of HSiW without added NaCl and non-additive behavior in presence of 50 mM NaCl. b) Structures of HSiW and HPC.

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