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A Small-Angle Scattering study of the behaviour of polyelectrolytes in organic media

Polyelectrolytes are a class of material that have appealed to researchers in many different areas owing to their versatility and potential applications. The existing studies mostly deal with their behaviour in aqueous solutions due to their lack of solubility in other media. Here we have utilized carboxymethyl cellulose (CMC), which is widely available as a sodium salt, NaCMC. The solubility of CMC in organic media was enhanced by replacing the hydrophilic Na+ with the hydrophobic tetrabutylammonium (TBA^+) counterion. In this study, a series of SANS and SAXS measurements were conducted to explore the behaviour of TBACMC by determining the correlation length (ξ) as a function of concentration (c) and solvent dielectric constant (ε). We have combined these techniques with rheology to determine other properties such as the overlap (c*) and entanglement (c_e) concentrations in the different solvents. It was found that* c and c_e scale as $\approx \varepsilon^{-1}$ and $\approx \varepsilon^{0}$ respectively. Also, conductivity measurements were conducted to determine the degree of uncondensed counterions (f) in the different media. We are trying to utilize the knowledge of f to explain the deviation observed in SANS and SAXS behaviour in some of the systems. It is observed that in solvents with a higher dielectric constant, a greater deviation between SAXS and SANS results is observed, presumably due to the higher values of f and the difference in the origin of contrast for the two techniques (the polyelectrolyte backbone (SAXS) and the counterion (SANS)).

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In addition, a better understood polystyrene sulfonate (PSS) system with the same hydrophobic counterion has been explored using SANS. Owing to the low polydispersity obtainable in TBAPSS, we have also used it to study the effect of degree of polymerization (N) on properties such as c* in different solvents. These explorations allow us to draw parallels between the CMC and PSS systems and to expand our understanding of the polyelectrolytes.

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