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"Shape Transformations of Dissolved Anionic Polyacrylate Chains in the Presence of Earth Alkaline Ions"

Polymers which are water-soluble because of dissociation in polyions and small co-ions, are called polyelectrolytes. Due to the multiplicity of charges which are covalently bound along the chain, they exhibit both the character of a macromolecule and of an electrolyte.

In the present work, sodium salts of polyacrylic acid (NaPA) with various molecular weights were dissolved in aqueous sodium chloride solutions and investigated by means of different scattering methods. By addition of inert sodium chloride, the repulsions of the equally charged ionic groups along the polyelectrolyte chain are screened and thus allows a coiled conformation of the chain. The amount of sodium chloride governs the solvent quality.

By means of combined static (SLS) and dynamic (DLS) light scattering, one high molecular weight sample was characterized with regard to changes in size and shape as a function of sodium chloride content. Moreover, measurements of the second osmotic virial coefficient allow the determination of the solvent quality. At a sodium chloride content of 1.5 M, the second osmotic virial coefficient was nearly zero, indicating Θ-conditions and therefore the chains being unperturbed. In a further step, several samples with molecular weights between 80,000 and 3,300,000 g/mol were characterized in aqueous solutions with a sodium chloride content of 0.1 M and 1.5 M. The molecular weight dependence of the radius of gyration and of the hydrodynamic effective radius reveals that a sodium chloride content being 0.1 M corresponds to a good solvent and being 1.5 M to a Θ-solvent. These results serve as a reference system in order to estimate the following collapse experiments.

During the collapse experiments, some percent of the sodium ions were replaced by divalent earth alkaline ions (Ca^{2+}, Sr^{2+}, Ba^{2+}) in such a way that the amount of cationic charges remained constant. Measurements were carried out in aqueous solutions with contents of sodium chloride of 1.5 M, 0.1 M and 0.01 M. The divalent cations bind specifically to the carboxylate functions of NaPA. This causes a collapse of the chains. At the end of such a collapse process the PA chains adopt a spherical shape. The amount of sodium chloride influences the mechanism of collapse process. The experiments in aqueous solutions being 0.01 M in sodium chloride gave first hints that formanisotropic intermediate structures were adopted in a collapse series.

In order to enlighten these intermediate structures, the form factor, i. e. the standardized scattering curve, was recorded by means of small angle neutron scattering in the presence of calcium ions and by means of small angle x-ray scattering in the presence of strontium ions. The form factors were at first compared with form factors of spheres. For further data evaluation, the analytic function of a form factor of a pearl necklace was derived and compared with experimental data.