On the Electrolyte Induced Aggregation of Concentrated Silica Dispersions
An Experimental Investigation Using the Electrospray Technique

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Göteborg, Sweden, 2011

The thesis will be defended in English on Friday the 30th of September 2011, at 10:15 in lecture hall KB at Kemigården 4, Chalmers University of Technology, Göteborg.

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Abstract

Gels are weak, solid-like structures that arise when colloidal particles aggregate to form a network of particle clusters. A variety of colloidal systems that are important scientifically as well as in industrial applications are capable of gel formation, e.g. globular protein solutions, colloid-polymer mixtures, and metal oxides. Yet, the mechanisms of the gelation process are far from understood, and the investigation of the aggregation and gelation of colloidal dispersions is, therefore, of great importance. Especially, the size distribution and structure of the aggregates are known to affect the gelation, and the main focus of this thesis is to improve our understanding of the initial aggregate formation in concentrated silica dispersions.

The electrospray-scanning mobility particle sizer (ES-SMPS) technique has previously been demonstrated to be a valuable method for size distribution analysis of pure colloidal dispersions. Here, the ES-SMPS method was used to monitor the size distribution variation during electrolyte induced slow aggregation of concentrated silica dispersions. Number size distributions provide information about the primary particles as well as the formed aggregates. The influence of the ion specificity, as well as three initial particle morphologies, on the aggregation behaviour was investigated. Moreover, the aggregate diameters obtained by the ES-SMPS method were compared to the those obtained by other techniques such as scanning electron microscopy (SEM) and in situ small angle X-ray scattering (SAXS).

The initial aggregate formation could be monitored accurately using the ES-SMPS method and compact, nearly spherical aggregates were observed for two of the initial morphologies. It was concluded that these resulted from a dynamic aggregation process where the aggregates broke and reformed several times prior to the gelation. More elongated aggregates were observed in the third dispersion; these aggregates were more rapidly stabilized by interparticle bonds and formed the most stable gel structures. The surface properties of the particles were found to affect the aggregate structure.

Clear ion specific effects were observed; the most stable aggregates were formed in the presence of the least hydrated alkali ions, whereas the rate of gel stability increase was faster in the presence of the more strongly hydrated ions. As expected, the alkali ions adsorbed according to the direct Hofmeister sequence.

A gel layer on the silica particle surfaces was identified for all dispersions investigated. The thickness of these layers were estimated using different techniques and found to be 2-4 nm thick depending on the dispersion.

Keywords: Colloidal silica dispersion, aggregation, gelation, electrospray (ES), scanning mobility particle sizer (SMPS), synchrotron radiation small-angle x-ray scattering (SR-SAXS), electron microscopy (EM), dynamic light scattering (DLS), particle morphology, ion specificity, gel layer