Adsorption, aggregation and phase separation in colloidal systems

JING DAI

Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Doctor of Philosophy on Friday the 9th February 2018, at 10:00 a.m. in Sal F3, Lindstedtsvägen 26, Stockholm.
Abstract

The thesis presents work regarding amphiphilic molecules associated in aqueous solution or at the liquid/solid interface. Two main topics are included: the temperature-dependent behavior of micelles and the adsorption of dispersants on carbon nanotube (CNT) surfaces. Various NMR methods were used to analyze those systems, such as chemical shift detection, spectral intensity measurements, spin relaxation and, in particular, self-diffusion experiments. Besides this, small angle X-ray scattering (SAXS) was also applied for structural characterization.

A particular form of phase transition, core freezing, was detected as a function of temperature in micelles composed by a single sort of Brij-type surfactants. In mixed micelles, that phase transition still occurs accompanied by a reversible segregation of different surfactants into distinct aggregates. Adding a hydrophobic solubilizate shifts the core freezing point to a lower temperature. Upon lowering the temperature to the core freezing point, the solubilizate is released. The temperature course of the release curves with different initial solubilizate loadings is rationalized in terms of a temperature-dependent loading capacity.

The behavior of amphiphilic dispersant molecules in aqueous dispersions of carbon nanotubes (CNTs) has been investigated with a Pluronic-type block copolymer as frequent model dispersant. Detailed dispersion curves were recorded and the distribution of the dispersant among different available environments was analyzed. The amount of dispersed CNT was shown to be defined by a complex interplay of several factors during the dispersion process such as dispersant concentration, sonication time, centrifugation and CNT loading. In the dispersion process, high amphiphilic concentration is required because the pristine CNT surfaces made available by sonication must be rapidly covered by dispersants to avoid their re-attachment. In the prepared dispersions, the competitive adsorption of possible dispersants was investigated that provided information about the relative strength of the interaction of those with the nanotube surfaces. Anionic surfactants were found to have a strong tendency to replace Pluronics, which indicates a strong binding of those surfactants.

CNTs were dispersed in an epoxy resin to prepare nanotube-polymer composites. The molecular mobility of epoxy was investigated and the results demonstrated the presence of loosely associated CNT aggregates within which the molecular transport of epoxy is slow because of strong attractive intermolecular interactions between epoxy and the CNT surface. The rheological behavior is dominated by aggregate-aggregate jamming.
Keywords
NMR, chemical shift, spin relaxation, self-diffusion, micelle, core freezing, segregation, solubilization, release, adsorption, binding, surfactant, carbon nanotube, block copolymer, dispersion, competitive adsorption, nanocomposite