

Liquid-crystalline structures of core-shell aggregates formed by polymer/surfactant complexes in colloidal dispersions

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Palavras Chave: complex salt, surfactant, block copolymer, liquid-crystalline phase, colloidal dispersion.

Abstract

This communication describes the preparation and characterization of colloidal dispersions of core-shell aggregates with liquid-crystalline cores formed by complex salts of block copolymers. The complex salts are formed by alkyltrimethylammonium (C_nTA^+) surfactants and poly(acrylate-acrylamide). It was possible to achieve different internal phases (cubic, hexagonal, lamellar and reverse phases) depending on the surfactant alkyl chain length and addition of cosurfactant (*n*-alcohols) used. The dispersions are kinetically stable for, at least, 3 months.

Introdução

Polyion-surfactant ion complex salts (CS) are formed by the strong electrostatic association between oppositely charged species in an aqueous medium. The use of block copolymers can originate core-shell structures. The shell is composed by the neutral polar polymeric chains, while the ordered core is composed by surfactant micelles surrounded by the polymeric block of oppositely charge. A method to achieve different internal structures is based on the addition of cosurfactants such as *n*-alcohols in the CS-water mixtures. Our group has investigated the effect of the addition of octanol and decanol on the structures formed by complex salts of dodecyl ($C_{12}TA^+$) and hexadecyltrimethylammonium ($C_{16}TA^+$) surfactants with the symmetric block copolymer P(A_{42} - Am_{42}) (A =acrylate; Am =acrylamide), prepared according our previous work¹.

Resultados e Discussão

The CS dispersions were first analysed by small angle X-ray scattering (SAXS) in order to identify the internal liquid-crystalline structures by indexing the Bragg peaks. The micellar cubic $Pm\bar{3}n$ structure was found for the dispersion prepared employing the $C_{12}TAP(A_{42}-Am_{42})$ CS in water. In the case of the CS dispersion using $C_{16}TAP(A_{42}-Am_{42})$, the internal phase was identified as the hexagonal $p\bar{6}mm$ phase, also in accordance with previous reports¹. In the aqueous dispersions of $C_{12}TAP(A_{42}-Am_{42})$ CS, upon increasing octanol or decanol content, the internal structure of the aggregates changed in the sequence: cubic, normal hexagonal and lamellar phase. For the case of $C_{16}TAP(A_{42}-Am_{42})$ CS particles, as decanol is

added to the dispersion, it is incorporated into the core giving rise to phase coexistence (hexagonal and lamellar). Further addition of decanol leads to a lamellar phase. Through the addition of octanol to this system, the complex salt composing the core of the aggregates self-assembles into lamellar, reverse hexagonal and reverse micellar phases. We were able to reproduce essentially the same phases of the homopolymer CS/water/*n*-alcohol ternary mixtures² in the core of block copolymer CS aggregates dispersed in aqueous medium. These phase transitions are attributed to the effect of the insertion of the *n*-alcohol molecules at the surfactant aggregates composing the core, reducing and further inverting its preferred curvature². The freshly prepared CS dispersions were also studied by means of hydrodynamic radius (R_H) and zeta potential (ζ). Table 1 summarize the results for the aggregates with different internal structures formed by $C_{12}TAP(A_{42}-Am_{42})$ CS aqueous dispersions with octanol.

Tabela 1. – Hydrodynamic radius (R_H) and zeta potential (ζ) values for $C_{12}TAP(A_{42}-Am_{42})$ CS aggregates dispersed in aqueous medium

Internal phase	R_H / nm	ζ / mV
Cubic	110±10	-35±5
Hexagonal	115±10	-25±5
Lamellar	120±10	-25±5

The dispersions are stable for several weeks, depending on the *n*-alcohol content.

Conclusões

We were able to reproduce the same phases of the homopolymer CS/water/*n*-alcohol ternary mixtures in the core of block copolymer CS aggregates dispersed in aqueous medium by the addition of different amounts of octanol and decanol, which act as cosurfactants. The dispersions are kinetically stable for, at least, 3 months.

Agradecimentos

LNLS, CAPES, CNPq.

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