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Structure and phase equilibria of mixtures of the complex salt hexadecyltrimethylammonium polymethacrylate, water and different oils

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Abstract

This work reports on phase diagrams for mixtures of a complex salt formed by a cationic surfactant and an oppositely charged polyelectrolyte, hexadecyltrimethylammonium polymethacrylate, in binary mixtures with water and in ternary mixtures containing water and organic solvents of different polarity ('oils'): decanol, octanol, *p*-xylene and cyclohexane. The liquid crystalline structures formed were identified by small angle X-ray scattering measurements, which also provided information about changes in the size of the aggregates as a function of the system composition. These results are analysed in comparison with others previously reported [Bernardes et al., J. Phys. Chem. B 110 (2006) 10332–10340] for the analog complex formed with polyacrylate and, in general, reveal that the presence of an extra methylene group in the polymer chain does not produce significant changes in the complex phase diagrams nor in the structure of the liquid crystalline phases formed. Additionally, the obtained results confirm once more the approach used to analyze these kinds of systems formed by polymer and oppositely charged surfactant.

Keywords: Phase equilibrium; Polyion–surfactant ion complex salt; Decanol; Octanol; *p*-Xylene; Polymethacrylic acid; Hexadecyltrimethylammonium

1. Introduction

The study of physico-chemical properties of molecules that lead to the formation of supramolecular aggregates is very important for a number of research fields, such as chemistry, physics, biology and nanosciences and nanotechnology in a more general sense [1–4]. One interesting family of such supramolecular structures is the aggregates formed due to self-assembly of amphiphilic molecules in a selective solvent, producing a variety of structures, from spherical micelles to those generically called mesophases, which may include arrays with cubic, hexagonal or lamellar symmetry [5,6].

The association between polyelectrolyte and surfactant leads to a phase separation, resulting in one concentrated phase rich in polyion and surfactant ions, and one dilute phase containing most of the simple counter-ions [7]. The interaction between cationic surfactants with polyacrylic acid (PA) in water being one example of this kind of aggregates, which has been extensively investigated.

The liquid–crystalline phases formed in mixtures of polyeletrolytes and surfactants with opposite electrical charge may display structures that differ from those formed with smaller counter-ions, depending on factors such as: composition, temperature, the presence of additives and features of the polymeric counter-ion. With this respect, important contributions from the presence of the polyelectrolyte are reported both in terms of facilitating the formation of the liquid–crystalline mesophases as well as in modifying their structures [8,9].

The understanding of phase equilibrium in such complex mixtures may be rather complex, as pointed out by Thalberg et al. [13], due to the formation of other chemical species for association of the different ions present, leading to a five chemical species system. A new approach was put forward and thoroughly tested by Piculell and coworkers [8–12], which relies on the preparation of the complex salt (species formed by the association of the surfactant ion with the oppositely-charged polyelectrolyte), allowing then the investigation of true binary or ternary mixtures.

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In a previous study [11] this strategy was used to investigate the phase behavior of ternary mixtures containing alkyltrimethylammonium polyacrylate complex salt, water and an "oil" (*n*-decanol, *p*-xylene or cyclohexane). From the general analysis of their phase diagrams, we concluded that systems containing decanol display a predominance of lamellar phases, while hexagonal phases prevail in systems containing *p*-xylene and cyclohexane. The difference was interpreted as a consequence of the different locations of these oils within the surfactant aggregates. Decanol was incorporated at the aggregate interface, leading to a decrease in its curvature, which favors the appearance of lamellar structures. *p*-Xylene and cyclohexane, on the other hand, were mostly incorporated in the interior of the cylindrical aggregate, as reflected by its swelling as the oil content increases.

In this study, we continue our experimental investigation on the association of polyeletrolytes and oppositely charged surfactants with one major aim in mind: to compare the phase behavior of a slightly more hydrophobic polyanion, polymethacrylate (PMA), with the already investigated systems containing polyacrylate (PA). The presence of an extra methylene group per monomeric unit in PMA with respect to PAA may affect its interaction with the surfactant aggregates for its greater hydrophobicity or larger volume, while keeping the same features of the PA polymeric backbone, such as flexibility and charge density of PA. Phase diagrams and structures were investigated in binary (complex + water) and ternary mixtures (complex + water + oil) for a complex prepared with hexadecyltrimethylammonium polymethacrylate whose features were then compared to those of the analog complex formed with polyacrylate.

2. Experimental

2.1. Chemicals

Sodium polymethacrylate NaPMA, sample with an average molar mass of 6500 $\mathrm{g\,mol^{-1}}$ (ca. 80 monomer units), from Sigma, was used. Cationic surfactant hexadecyltrimethylammonium bromide (C_{16}TABr) with 99% purity was also purchased from Sigma. The organic solvents used were: octanol (from Merck), decanol (from BDH), *p*-xylene and cyclohexane (both from Acros), all of the highest purity available and used as received. Cationic ion exchange resins, Dowex 550OH and Dowex 650H, from Sigma, were activated by washing with 1 $\mathrm{mol\,L^{-1}}$ NaOH and 1 $\mathrm{mol\,L^{-1}}$ HCl, respectively, under stirring for one hour, followed by washing with Millipore water until neutral pH.

2.2. Syntheses of complex salt

The complex salt was prepared following the general procedure developed by Svensson et al. [8], with the slight modification of an extra step, the conversion of sodium polymethacrylate into polymethacrylic acid, which was attained by using an activated ion exchange resin, Dowex 650H.

In the next step the surfactant was converted into its OH form by using the activated ion exchange resin Dowex 550OH. Typically, for 10 g of surfactant, 300 g of resin were used (in three stages). For each stage, 100 g of resin were mixed with surfactant and ca. 100 mL of water, under stirring for 1 h. This mixture was filtered and washed producing ca. 200 mL of C_nTAOH solution. The final solution, ca. 600 mL, was immediately refrigerated to avoid surfactant decomposition. Titrimetric analysis of the bromide content, following previous procedure [7], confirmed that the ion exchange was complete.

The surfactant solution was titrated with an aliquot of a 3.5 wt% solution of polymethacrylic acid with pH measurements using a standard glass electrode. The equivalence point was determined as around pH 9, similar to the one obtained with different polyacrylic acids [7–12]. The polymethacrylic acid solution was added dropwise to the remaining surfactant solution until a pH slightly above the equivalence point was reached. This mixture, containing the white concentrated top phase with the complex salt, was left overnight in a refrigerator. The pH was then adjusted to the equivalence pH by adding more PMA and the complex salt was freeze-dried. The product, hexadecyltrimethylammonium polymethacrylate, CTAPMA, obtained as a white hygroscopic powder, was stored in a desiccator over silica gel, and the uptake of water under these conditions was determined as ca. 10 wt% (this was taken into account in determining exact sample compositions). Similar water uptakes were observed for the complexes with polyacrylate [7–12]. Elemental analyses were performed using a Perkin–Elmer Series II CHNS/O Analyzer 2400 equipment, providing carbon and nitrogen contents within 1% of agreement with a 1:1 (surfactant:MA monomer) complex salt stoichiometry.

2.3. Sample preparation

Appropriate amounts of complex salt, water and oil were weighed into glass tubes. After mixing with a Vortex vibrator, the tubes were flamed sealed. The mixing was continued in a centrifuge at 25 °C, the tubes were turned end over end every 30 min, for several times. The samples were left to equilibrate at 25 °C for, at least, one month prior to analyses.

2.4. Sample analyses

The samples were investigated by visual inspection under normal light and between crossed polarizers to detect the presence of optically anisotropic phases (lamellar, hexagonal and inverted hexagonal).

SAXS measurements were performed in the SAXS beamline (D11A) of the Brazilian Synchrotron Laboratory (LNLS), in Campinas, Brazil. The experimental set-up involved the use of X-rays at the wavelength of 1.608 Å and a sample-to-detector distance of 611.1 mm. For these experiments, a sample cell with mica windows was used allowing temperature control (all measurements were made at 25 °C). Typical acquisition times were around 10 min.