Journal of Colloid and Interface Science 466 (2016) 377–387

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Controlling the phase structures of polymer/surfactant complexes by changing macromolecular architecture and adding n-alcohols

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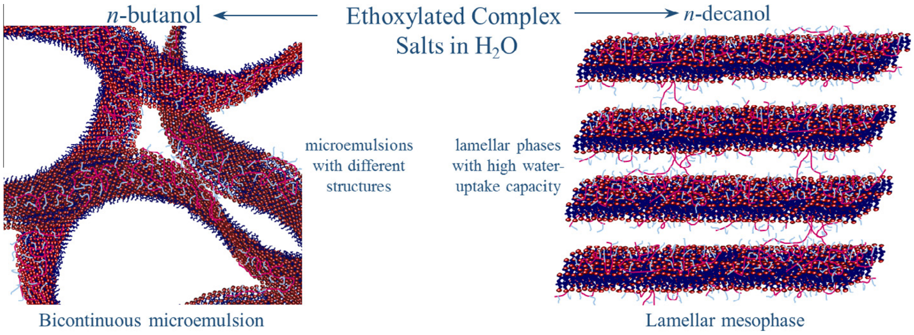
HIGHLIGHTS

- Hydrophilic side chains increase water-uptake capacity of complex salts.
- Ethoxylated complex salts can form new structures.
- *n*-Butanol acts as a cosolvent and *n*-decanol acts as a cosurfactant.
- Phase behavior of complex salts can be tuned by polymer architecture.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 November 2015
Revised 21 December 2015
Accepted 23 December 2015
Available online 24 December 2015

Keywords:
Complex salts
Bicontinuous
Liquid-crystals
Phase equilibria

ABSTRACT

Phase behavior of complex salts formed by a cationic surfactant and different ethoxylated polyions was investigated in water and with addition of two *n*-alcohols of different chain lengths: *n*-butanol and *n*-decanol. The polyion possesses a main chain of methacrylic acid randomly grafted with oligo(ethylene oxide) chains. Strong electrostatic interaction between the anionic main chain and the cationic surfactant hexadecyltrimethylammonium ($C_{16}TA$) leads to the formation of $C_{16}TAP(MA\text{-}MAEO_{\boldsymbol{n}})$ *x*:*y* complex salts. Modifications in polyion structure, such as changes in the proportion of grafted comonomers and in the side chain length caused differences in the overall balance of interactions with water and *n*-alcohols, altering the complex salt solubility and, consequently, the formed liquid–crystalline structures. The role of *n*-decanol as a cosurfactant was verified, but the hydrophilic side chains expanded the capacity of the formed liquid crystalline phases to incorporate water. Additionally, a novel structure, probably cubic bicontinuous (*Pn*3*m*), was observed coexisting with lamellar phases at low water concentration. Because *n*-butanol is known for being a good solvent for poly(ethylene oxide), these side chains intensified the role of this short chain *n*-alcohol as cosolvent for $C_{16}TAP(MA\text{-}MAEO_{\boldsymbol{n}})$ *x*:*y* complex salts, favoring the formation of disordered solutions, including a bicontinuous microemulsion.

1. Introduction

Polyelectrolytes are known to complex with oppositely charged surfactants through strong association, leading to phase separation in water [1–3]. This complexation is governed both by hydrophobic interaction and electrostatic attraction [1,4]. Numerous studies have devoted efforts to understand the interactions involving the formation of the oppositely charged polyelectrolyte/surfactant

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http://dx.doi.org/10.1016/j.jcis.2015.12.050
0021-9797/

complexes over the past few decades [5–13]. The interest on the phase behavior and properties of such systems is still evidenced by their use for different applications (as preparation of responsive films [14], hair care products [15,16], tailored nanostructured materials [17] and for DNA compaction [18]) and is related in recent reviews [4,19–21].

In order to allow a more direct analysis of the phase behavior of polyelectrolyte/surfactant complexes, Svensson et al. developed a new approach to prepare pure and stoichiometric polyion/surfactant ion complex salts, which are free of simple counterions [22]. Surfactant counterions are replaced by polyions by titrating a polyacid with the hydroxide form of a cationic surfactant, which is a way of preparing the so-called complex salts. A recent feature article overviews the general phase behavior of the complex salts and describes the range of possible structures found, their related properties, potential uses and perspectives [23]. In the same article, the importance of the fundamental understanding of the relation between the molecular structure and the obtained properties is highlighted through the comparison of different phase behavior studies [23].

Our group recently showed that the polyion structure is an important factor to modify the self-assembly of surfactants, being a useful tool to control the phase behavior of complex salts and their formed structures. By grafting the polyions with hydrophilic ethoxylated side chains, we prepared water-soluble complex salts and demonstrated that different fractions of grafted monomers or different side chains lengths leads to formation of structures with different properties [24,25].

Another way to control the structures and the phase behavior of complex salts in water is by adding a third component to the system. Janiak et al. investigated the effect of nonionic surfactants with a hydrophilic oligo(ethylene glycol) headgroup, C_nEO_m, on the phase behavior and properties of complex salts (formed by hexadecyltrimethylammonium surfactant and polyacrylate, C_{16}TAPA). Because both the complex salts and the C_nEO_m surfactants form several liquid–crystalline structures in water, interesting structures such as mixed aggregates and an unusual cubic bicontinuous phase (*Ia3d*) were found [26].

In a recent study, we were able to investigate the effect of oligo (ethylene oxide) chains in a different way: by synthesizing poly (methacrylic acid) randomly grafted with oligo(ethylene oxide) side chains, P(MAA-MAEO$_{\boldsymbol{n}}$), preparing the respective ethoxylated complex salt, C_{16}TAP(MA-MAEO$_{\boldsymbol{n}}$) [25]. The great advantage of this family of complex salts over the mixture of C_{16}TAPA with C_nEO_m is that, in the first case, the hydrophilic EO chains are covalently attached to the complex salt, forming only one species and being necessarily part of the formed aggregates. Hence, the hydrophilic EO side chains favor the formation of micelles with high curvature and, above a minimal weight fraction of EO groups in the molecular structure, they improve the solubility and hinder the phase separation of complex salts in water. Additionally, we observed that variations in the proportion or length of side chains directly affect the surfactant phase behavior in water, resulting in the observation of different structures, including a hierarchical micellar system [25].

Because of their amphiphilic structure containing a hydroxyl group and a hydrophobic chain, *n*-alcohols present properties similar to those of non-ionic surfactants without forming either micelles or liquid–crystalline phases in water. Bernardes et al. reported a systematic study on the phase behavior of systems formed by the same C_{16}TAPA complex salts with water but with *n*-alcohols of different chain lengths (from ethanol to *n*-decanol) [27]. In that study, it was observed that long chain *n*-alcohols, which are water-insoluble, behave as cosurfactants: alcohol molecules enter the complex salts aggregates, intercalating with the surfactant molecules and reducing the aggregate curvature. On the other hand, short chain alcohols, can be partially or totally miscible with water, changing the solvent polarity, and acting as cosolvents, what favors the formation of inverted aggregates in organic disordered systems [27]. Other studies with the same surfactant (C_{16}TA) but with different polyions confirmed the general roles of some *n*-alcohols. Although the main trends are kept, these studies showed that the polymer structure affects the interaction of the complex salts with these *n*-alcohols, and consequently, their phase behavior [28–31].

In the present study, by using ethoxylated complex salts, the C_{16}TAP(MA-MAEO$_{\boldsymbol{n}}$), and adding water and *n*-alcohols, we have been able to obtain ternary phase diagrams and to study the effect of the ethylene oxide groups and *n*-alcohols simultaneously. More importantly, this study demonstrates how the variations in the grafting degree and in the side chains length have direct effects on the interaction with the *n*-alcohols, on their roles in the phase behavior, on the aggregates geometry and, as a consequence, on the system properties.

2. Experimental section

2.1. Materials

For the synthesis of the copolymers, the comonomers poly (ethylene glycol) monomethyl ether methacrylate with molar masses of 300 and 1100 g/mol (MAEO$_{\mathbf{5}}$ and MAEO$_{\mathbf{24}}$, Sigma–Aldrich) and the free radical initiator Azobis(isobutyronitrile) (AIBN, ⩾98% GC, Fluka) were used as received. The comonomer methacrylic acid, (99%, Sigma–Aldrich) was vacuum distilled and the solvent tetrahydrofuran (THF, Inhibitor free, HPLC grade, Tedia) was distilled over $LiAlH_4$ and redistilled over Na.

For preparation of complex salts, hexadecyltrimethylammonium bromide (C_{16}TAB, ⩾98%, Sigma–Aldrich) was converted to the hydroxide form (C_{16}TAOH) by complete ion-exchange using the anionic resin Dowex® Monosphere® 550A (hydroxide form, Sigma–Aldrich).

Water purified by a Milli-Q® system (0.2 μm filter, resistivity of 18.2 MΩ cm) was used throughout this study.

2.2. Synthesis of copolymers and complex salts

The synthesis and characterization of copolymers poly (methacrylic acid-co-methacrylate ethoxylated), P(MAA-MAEO$_{\boldsymbol{n}}$) *x:y* is described in details elsewhere [24,25]. The general chemical structure of the products is shown in Scheme 1 and Table 1 provides chemical characteristics of each studied copolymer.

The methodology developed by Svensson et al. [22] was used to prepare three different complex salts: C_{16}TAP(MA-MAEO$_{\mathbf{5}}$) *72:28* (a white powder), C_{16}TAP(MA-MAEO$_{\mathbf{5}}$) *36:64* (a gel) and C_{16}TAP(MA-MAEO$_{\mathbf{24}}$) *69:31* (a white powder). This methodology consists of titrating a polyacid with a surfactant in its basic form (C_{16}TAOH) up to the equivalence point, forming a pure stoichiometric salt (which is called complex salt), free of simple counterions. The pure complex salt acts as one component in truly binary (with water) or ternary (with addition of a third component) phase diagrams. Here, a freshly prepared aqueous solution of C_{16}TAOH was used to titrate a solution of 15 g of P (MAA-MAEO$_{\boldsymbol{n}}$) *x:y* copolymer in 100 mL of water. The titration was conducted up to the equivalence point (previously checked). The final solution was freeze-dried to remove water. The complex salt stoichiometry and purity were confirmed by elemental analyses and ^{1}H NMR.