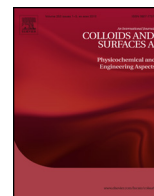




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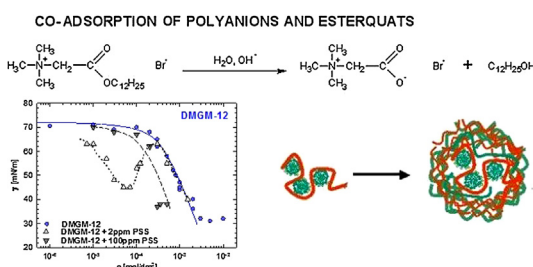
Co-adsorption of polyanions and esterquat surfactants; effect on formation and stability of micellar core nanocapsules

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HIGHLIGHTS

- The co-adsorption of esterquat surfactants and polyanions was investigated.
- Esterquats hydrolysis has an effect on surface charge at water/air interface.
- Surface tension of esterquat/polyanion mixture depends on surfactant hydrolysis.
- Polyanion/esterquat micellar aggregates can be used as cores for encapsulation.
- The micellar aggregates are hydrolytically decomposed under basic conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the co-adsorption at water/air interface of soft cationic surfactants of the esterquat-type, fatty acid quaternary ammonium esters with hydrocarbon chain containing eleven carbons and the amino acid betaine esters with twelve carbons in the chain with polyanions: polysodium 4-styrenesulfonate (PSS), poly-L-glutamic acid sodium salt (PGA), alginic acid sodium salt (ALG) and λ-carrageenan (CAR). The effect of surfactants basic hydrolysis on formation of surfactant/polymer complexes in bulk and at interface was taken into account. We found that the surface charge of the water/air interface originating from the adsorption of fatty acid quaternary ammonium esters decreased as the result of hydrolysis that led to lower co-adsorption of polyanions than in the case of amino acid betaine esters. The optimal conditions for formation of surfactant micelles/polyelectrolyte aggregates were established. These negatively charged aggregates were further used as nanocores for encapsulation by the layer-by-layer (LbL) adsorption of synthetic and natural polyelectrolytes. The average size of nanocapsules was in range 100–200 nm. We observed that stability of micellar cores were dependent on the rate of esterquat hydrolysis, ones formed with fast hydrolysable surfactant were stable under acidic but unstable under basic conditions.

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1. Introduction

Novel therapeutics and drug delivery systems belong to the one of the main disciplines of nanotechnology [1–3]. Nanoscale drug delivery systems are a sub-class of advanced drug delivery vehicles with the sizes mostly below 200 nm. They have become very popular in modern molecular pharmacology and medicine not only

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due to their size but also due to their unique physicochemical and pharmacological properties that may lead to overcoming undesirable side effects of many drugs and hence improving their efficiency in a therapeutic action. Among various nanoscale delivery systems, nanocapsules with shells formed on the emulsion droplets by the sequential adsorption of polyelectrolytes (often referred to as the Layer-by-Layer (LbL) deposition technique) are considered as one of the most promising nanodelivery systems for hydrophobic drugs [4–9] as they can be easily modified by grafted poly(ethylene glycol) chains (so called PEG-ylation) [7,10,11] and functionalized with targeting ligands [12]. Additionally, by loading such polyelectrolyte (PE) shell nanocapsules with other bioactive agents and/or diagnostic species (i.e., optically active small organic molecules, metals and metal oxides, ultrasonic contrast agents, and radionuclides) one can eliminate the problems of poor solubility of such entities and can attain favorable traits such as imaging and trafficking through the cargo of suitable labels in a variety of diagnostics [13] or other biomedical applications [14–19].

Polymer/surfactant mixtures reveal a variety of technological applications as a result of their specific behavior at different interfaces. Surfactants involve the surface and/or interfacial tension reduction, whereas polymers are responsible for the interfacial layers' viscoelastic properties – not provided by surfactants alone. Depending on the type of both surfactant and polymers they can interact by electrostatic, hydrophobic interactions, can form hydrogen bonds, while van der Waals interactions between them are usually of secondary importance. Mixtures of ionic surfactants and polyelectrolytes bearing opposite charges are of major interest since their properties can be tuned by easy to control parameters like ratio of their concentrations, ionic strength and pH of their solution or hydrophobicity of surfactants. Although most polyelectrolytes themselves are not surface active, their aggregation with oppositely charged surfactants may lead to mixtures with high surface activity and interesting surface rheological properties. Developing a better understanding of these systems, in particular for newly synthesized speciality surfactants, is a matter of importance because of their potentially wide use in a variety of emerging applications as new nano- and microcarrier systems, engineered nanostructures or functional interfaces.

The interaction of polyelectrolyte/surfactant mixtures has been discussed in terms of complex formation, competitive adsorption between surface active polyelectrolyte/surfactant complexes and polymer/surfactant aggregation in solution [20–31]. Surfactant hydrophobicity determines the surface properties of polyelectrolyte/surfactant mixtures since their surface behavior can be explained by formation of surface active complexes, which compete with aggregation in bulk [32]. The group of Penfold and Thomas [20,31], proposed the macroscopic model of the surface tension of ionic surfactant/polyelectrolyte mixtures and discern two types of behavior, however, Campbell, Varga et al. [33–36] demonstrated that the origin of the differences between them is the kinetics of surfactant/polyelectrolyte complex formation and its reorganization in the adsorption layer. Ionic surfactant/polyelectrolyte complexes in the bulk and at interfaces play a crucial role of the construction blocks of nanostructures [20,21,37]. They stabilize the nanoemulsion drops that serve as cores for the further encapsulation by the LbL technique. Therefore, determination of the bulk and interfacial properties of surfactant polyelectrolyte mixtures is important for the design of the nanoemulsion based delivery systems.

In our previous paper we investigated adsorption properties of four esterquat surfactant, i.e., cationic surfactants with ester bond between quaternary ammonium head-group and hydrophobic hydrocarbon tail. Namely, they were: (i) fatty acid aminoesters, i.e., N,N,N-trimethyl-2-(dodecanoyloxy)ethaneammonium bromide (DMM-11) and

N,N,N-trimethyl-2-(dodecanoyloxy)-1-methylethaneammonium bromide (DMP2M-11), with the carbonyl carbon of the ester bond R11-CO-O- facing the hydrophobic tail that contained eleven carbon atoms and, (ii) the amino acid betaine (trimethylglycine) esters, dodecyloxycarbonylmethyl-N,N,N-trimethylammonium bromide (DMGM-12) and dodecyloxycarbonyl-1-ethyl-N,N,N-trimethylammonium bromide (DMALM-12), with the opposite orientation of the ester bond, i.e., with the bridging oxygen of R12-O-CO- facing the tail with twelve carbons (see [38] for the details of their structure). Adsorption of these surfactants at air/water interface was described in terms of the theoretical model that considered decomposition of esterquats by the base catalyzed hydrolysis, which mechanism is widely described in the literature [39–41]. The reaction results in the formation of simpler surface active compounds, dodecanol and dodecanoic acid/dodecanoate anion that can adsorb in the synergistic manner together with the esterquats leading to the increase of overall surface activity. The elaborated by us theoretical model allowed explaining the observed dependence of esterquats surface activity on the degree of their hydrolysis determined by the molecular structure and pH of their solutions [42].

The present study is an attempt for applying the esterquat surfactants mixtures with oppositely charged polyelectrolytes to form surfactant/polyelectrolyte complexes to use them as cores for nanocapsules prepared by the sequential adsorption of polyelectrolytes. We investigated the co-adsorption of cationic esterquat surfactants, DMM-11, DMP2M-11, DMGM-12 and DMALM-12 with synthetic: polysodium 4-styrenesulfonate (PSS), poly-L-glutamic acid sodium salt (PGA) and natural polyanions, alginate sodium salt (ALG) and carrageenan (CAR). Then, the selected systems were used for the formation of surfactant micelles/polyelectrolyte aggregates, which were further used to form capsules with polyelectrolyte shells. Since the esterquats undergo hydrolytic decomposition the possibility of pH triggered destabilization of nanocapsules was examined.

2. Experimental section

2.1. Materials

2.1.1. Quaternary ammonium bromide surfactants – esterquats

Materials, methodology and synthesis of N,N,N-trimethyl-2-(dodecanoyloxy)-ethaneammonium bromide (DMM-11), dodecyloxycarbonylmethyl-N,N,N-trimethylammonium bromide (DMGM-12) and N,N,N-trimethyl-2-(dodecanoyloxy)-1-methylethaneammonium bromide (DMP2M-11) and dodecyloxycarbonyl-1-ethyl-N,N,N-trimethylammonium bromide (DMALM-12), as well as the methods to obtain the spectroscopic and analytical data of cationic ester-containing surfactants, the results concerning the elemental analysis and the NMR ^1H chemical shifts were collected in our previous paper [38] in the accompanying “Supplementary material”.

2.1.2. Polyelectrolytes

The polyelectrolytes used in our studies were: polycations: poly(diallyldimethylammonium) chloride – PDADMAC (MW ~100 to 200 kDa), poly-L-lysine hydrobromide – PLL (MW ~15000–30000) and polyanions: polysodium 4-styrenesulfonate – PSS (MW ~70 kDa), alginic acid sodium salt – ALG (MW ~90 kDa) and poly-L-glutamic acid sodium salt – PGA (MW ~15000–50000) and λ -carrageenan – CAR. All polyelectrolytes, coumarine-6 (98%), and sodium chloride were obtained from Sigma-Aldrich. All materials were used without further purification. The distilled water used in all experiments was

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