

## Mixed self-assembly of polyacrylic acid and oppositely charged gemini surfactants differing in the structure of head group



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### ABSTRACT

The complexation of a weak polyelectrolyte, polyacrylic acid (PAA) and oppositely charged gemini surfactants 16-6-16 and its hydroxyethylated counterpart 16-6-16(OH) was examined at spontaneous pH. These geminis demonstrate high aggregation capacity and can form micelles in a micromolar concentration range. Only one breakpoint was revealed on the concentration plots of the binary PAA-gemini systems by all the techniques used. The tensiometry and conductometry critical concentrations appeared to be much higher as compared to those revealed by fluorescence ratiometry, with critical aggregation concentration (cac) increasing with an increase in polyelectrolyte concentration in all cases. The cac values of 16-6-16 are higher as compared to 16-6-16(OH). The electrostatic contribution to the gemini-polyelectrolyte complexation is supported by the charge compensation in the systems, in particular by change of zeta potential from ca. -20 to ca. +60 mV with an increase in surfactant concentration, the points of the zero potential being in agreement with the maximum in the turbidity plots. The sizes of aggregates markedly decrease with an increase in surfactant concentration.

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### 1. Introduction

Polyelectrolyte complexes including those with oppositely charged surfactants are of importance from both fundamental and practical viewpoints, and therefore attract much attention in recent years [1–16]. On the one hand these ensembles have biomimetic characters and may provide the information on the properties of their prototypes, i.e. lipid membranes and proteins. On the other, addition of polymers to the surfactant solutions may result in a decrease of critical aggregation concentration (cac) of mixed systems as compared to critical micelle concentration (cmc) of single micellar solutions. This synergistic behavior along with the advanced functional activity is responsible for the wide application of polymer-colloid complexes in biomedicine, cosmetics, protective coatings, oil-recovery, gelatinizing agent, etc. [17].

Oppositely charged polyelectrolytes and surfactants form electrostatically driven complexes, with hydrophobic effect additionally contributed. In the case of strong polyelectrolytes the polyion/counterion exchange followed by a sharp increase in the

entropy of the mixed systems is one of the key factors as well. The structural behavior of these mixed systems is controlled by the nature and concentration of both components and solution conditions (pH, temperature, ionic force, etc.). Primarily, the most significant information on the polyelectrolyte-surfactant interactions was obtained from the binding isotherms with the help of surfactant selective electrode [18]. Typically a marked decrease in cmc of surfactants was observed due to charge compensation of surfactant micelles, which provides a close packing the surfactant molecules and stabilizes aggregates [19]. In accordance with theoretical models [20–24], in the case of hydrophilic polyelectrolytes, the cac values decrease with an increase in charge density, the flexibility of a polymer chain and the hydrophobicity of surfactants. The cac/cmc ratio for flexible polyions is assumed to be about 1/60 versus 1/4 for the rigid one [20]. For the pair polyacrylic acid-alkyltrimethylammonium (TMA-n) surfactants this value is found to be ca. 0.01 [21]. Meanwhile, hydrophobic polyelectrolytes tend to increase the micellization threshold, as it evidenced in Refs. [23,24].

Another commonly used method is the surface tension measurements [25–28], although tensiometry break points reflect not only the bulk phase transition but also adsorption at the air/solution interface [16]. Unlike the uncharged polymer surfactant systems,

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the more complicated surface tension isotherms occur in the case of polyelectrolyte–surfactant systems. While the former are characterized with two critical points, i.e. with cac and concentration of the formation of polymer-free micelles (alternatively they are designated as  $T_1$  and  $T_3$ ), the latter may be characterized by three or four critical points [16]. Strong dependence of the surface structural behavior on the surface age is reported in Ref. [13], with the formation of surface or subsurface aggregates and their morphological transitions postulated.

Much attention is devoted to the cationic surfactant–polyanion interactions, since they model the complexation of DNA with amphiphilic agents. Unlike strong polyelectrolyte systems, those based on weak polyelectrolytes demonstrate the more multiple-factor behavior and are less understood. One of the polyanionic species with the pH dependent behavior is polyacrylic acid (PAA) [18,24,29–39]. The structural behavior of PAA based systems is strongly controlled by the charge density of a polymer chain, with the critical ionization degree  $\alpha_c$  taken into account. This issue received much attention [24,32–34], e.g. the value of  $\alpha_c$  determined in works [33] is found to be 0.3 for PAA–TMA–12 system. Hydrophobic interactions with additional hydrogen bonding prevail prior to  $\alpha_c$ , while electrostatic forces mainly contribute above  $\alpha_c$ . Critical value  $\alpha_c = 0.4$  was determined in Ref. [24] for the PAA–TMA–14 system. Both these results are close to the theoretical value  $\alpha_c$  of about 0.35 derived from the Manning's counterion condensation theory. For mixed system PAA–alkylpyridinium surfactants an increase in ionization degree of polyacid was observed with the addition of the surfactants [18], which is more pronounced at the low charge density. Since the charge character of PAA is a function of pH, the latter may markedly influence the nature of the PAA–surfactant interactions. The transition from basically electrostatic binding mechanism to the hydrogen bonding is postulated for the PAA–surfactant mixture under the solution pH < 4.2 [36]. In its turn, the connection occurs between the solution pH and surfactant counterion binding, which is emphasized in Ref. [37]. Our works focus on the design of nanoreactors and nanocontainers based on surfactants and polymers [40,41], on the complexation of cationic surfactants with nucleic acid [42,43], and on the fabrication of polyelectrolyte nanocapsules through layer-by-layer techniques [44]. Therefore, the polymer–surfactant interactions, and especially the complexation of the oppositely charged polyions and amphiphiles are in sphere of our interest.

As amphiphilic components, dimeric or gemini surfactants were used herein. Nowadays gemini surfactants attract much attention,

which is conjugated with their superior aggregation capacity and versatile morphological behavior [45–47]. Unlike conventional single head surfactants gemini analogs consist of two head groups bearing two tails bridged with a spacer. Aggregation of geminis in aqueous solution is widely investigated including the *m-s-m* family (here *m* and *s* are the number of carbon atoms in alkyl chains and polymethylene spacer, respectively) [45–47]. Due to their enhanced hydrophobicity geminis demonstrate much lower cmc as compared to conventional surfactants, while the length and nature (flexibility and hydrophilicity) of spacer may serve as a tool for the tuning of their size, shape and morphology, including structural transitions sphere-to-rod or micelle-to-vesicle [47–49]. Due to these features gemini are considered as attractive building blocks in nanotechnological applications, e.g. for the development of nonviral vectors, catalysts, etc. [50,51]. Based on these considerations, two geminis are involved in this study, namely 16-6-16 and its hydroxyethylated analog 16-6-16(OH) (Fig. 1). Functionalization of ammonium groups by hydroxyethyl fragment was reported to result in enhanced aggregation capacity and functional activity [52,53]. Noteworthy, that single head hydroxyethylated surfactants are well studied, while few works are available on the structural behavior of gemini analogs [54,55].

Single PAA solutions are explored in works [56,57], in which surface active properties and rheological behavior are examined. It has been shown that the surface activity of the PAA solutions depends on the charge character [57]. At pH  $\leq 5$  the solutions are surface active, while inactive at higher pH. The interaction of PAA with gemini surfactants of *m-s-m* type was studied in works [58–61]. The effects of surfactant structure, molecular mass of PAA and additive of salts have been elucidated and compared with those of single-chain surfactants and stiffer polyelectrolyte polystyrene sulfonate (PSS). The PAA–gemini interactions are shown to be stronger as compared to conventional monocationic surfactants, with spacer length markedly affecting the interaction. Unlike PSS based systems, molecular mass of PAA slightly influences the PAA–gemini interactions.

Thus, only few works are available on the mixed PAA–gemini self-assembly. They focused on the PAA sodium salt, with all carboxylic groups ionized. Noteworthy, dicationic 12-6-12 was used in each case, and therefore only scarce information is available on the role of structural factor, that was exemplified by the elucidation of the effect of the length of spacer [58]. Herein, the self-organization of mixed systems based on PAA (unbuffered solution) and two gemini surfactants differing in their head groups (Fig. 1) is studied.

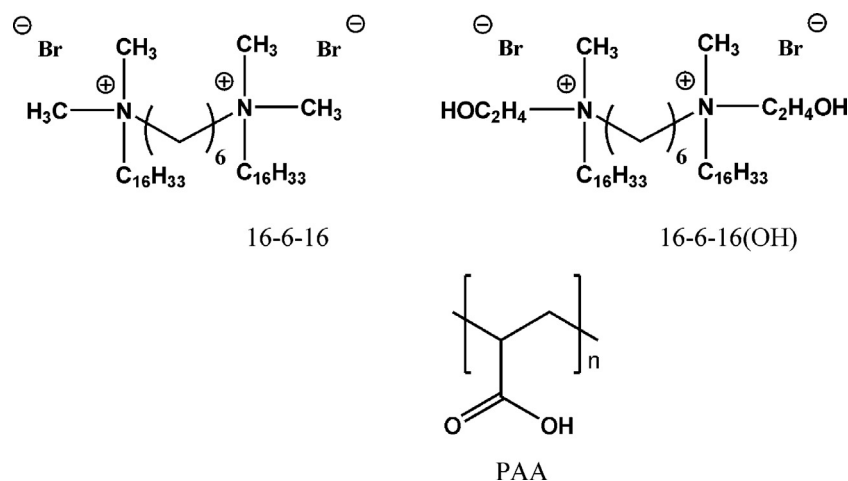


Fig. 1. Structural formulas of PAA and gemini surfactants.

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