



Self-assembled nano structures of cationic ester-containing gemini surfactants: The surfactant structure and salt effects

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ABSTRACT

The aggregation behavior of ester-containing cationic gemini surfactants, dodecyl esterquat and dodecyl betainate geminis was investigated using tensiometry, conductometry, viscometry, dynamic light scattering (DLS), transmission electron microscopy (TEM) and optical microscopy techniques in the absence and presence of NaBr electrolyte. The effect of chemical structure (*i.e.* the presence of ester bond in alkyl chain and the spacer length) on physicochemical properties and morphology of the surfactants was studied. The results showed that the ester-containing gemini surfactants formed spherical aggregates at dilute concentration (1.1 %wt). At higher concentration (~ 3.7 %wt) the morphology is different depending on the position of ester bond in alkyl chain and the spacer length. Dodecyl betainate gemini with short spacer ($s = 2$) formed gel as a result of the formation of worm-like micelles in the aqueous solution. Dodecyl betainate gemini ($s = 3$) formed large vesicles enclosing smaller ones and dodecyl esterquat gemini ($s = 3$) formed both short cylindrical and spherical micelles. The salt addition induced the growth of micelles and in the case of dodecyl betainate ($s = 2$) gemini changed the morphology from worm-like micelles to lamellar phase.

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1. Introduction

There is a growing interest towards cleavable surfactants, *i.e.* surfactants that have a weak bond in their chemical structure (*e.g.* in alkyl tail close to the head group) and prone to chemical or enzymatic degradation [1]. The main objective behind the development of cleavable surfactants is to improve the rate of biodegradation which has a great importance for development of the new surfactants [2]. In addition to environmental concerns, in some applications, surfactants may be needed in one stage but unwanted at another stage of a process. Thus, the presence of the weak bond in surfactant structure which can accelerate the degradation of the surfactant by a change in pH, enzymatic reaction, heat, ultraviolet

(UV) irradiation, ozone treatment would be advantageous [1,3]. Yet another use of surfactants with limited stability is to have the cleavage product impart a new function. For instance, a surfactant used in personal care formulations may decompose on application to form products beneficial to the skin [4,5]. The pH labile linkages in surfactants result in special applications in industry and biological science such as targeting drug delivery, gene therapy and etc [1].

There are two types of pH sensitive cleavable surfactants (*i.e.* acid labile and alkaline labile). Acetals, ketals, and ortho esters are examples of acid labile bonds in surfactants and esterquats, betainesters are examples of alkaline labile surfactants [2,3]. Esterquats, one of the most common types of cationic surfactants, break down readily under alkaline conditions and exhibit a very good biodegradation profile. The dominating use of esterquats is as fabric softener and the transition from the traditional di(hydrogenated tallow) dimethylammonium chloride, which had been the work-horse softener for more than three decades, to esterquats was made in Europe in the early 1990s as a response to pressure from environmental authorities in the European Union [6].

Both chemical and enzymatic hydrolysis of betainesters yield the amino acid betaine and the starting alcohol, two products that can be regarded as environmentally compatible and possibly even edible [4]. Thus, betainesters are interesting candidates for applications in systems such as cosmetics, food, and feed [1].

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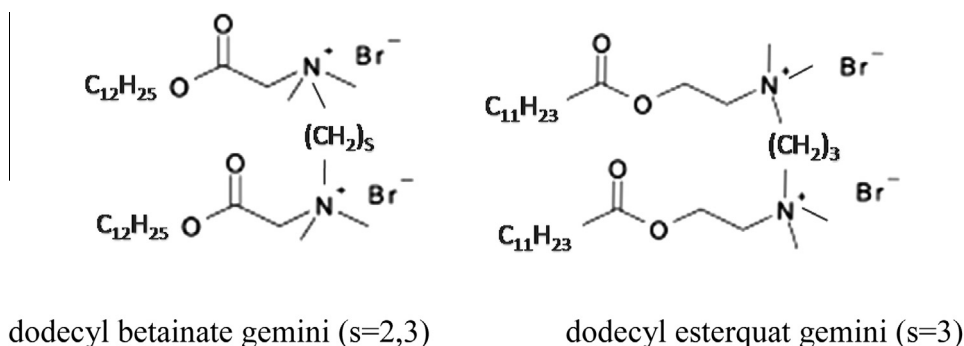
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SCHEME 1. The structure of ester-containing gemini surfactants.

Most studies on betainesters have been performed on substances made from saturated long-chain alcohols [1,7–13]. The physicochemical behavior of betaine esters of long-chain alcohols shows strong similarities to the common, closely related alkyltrimethylammonium surfactants both at low and high surfactant concentration in aqueous solution [9,14].

The “dilution” effects of the micellar surface charge on the alkaline hydrolysis rate of a betaine ester surfactant have been investigated for a mixture of decyl betainate and a non-ionic surfactant with similar CMC values [7].

The dilute aqueous mixture of dodecyl betainate and hydrophobically modified hydroxyethylcellulose (HM-HEC) have been studied by Karlberg *et al.* By preparing a mixture of a surface active betaine ester and HM-HEC in a solution buffered at a pH where the surfactant is hydrolyzed, it is possible to make a gel with a time-dependent viscosity [10].

Surface active betaine esters can be also used as temporary bactericides [8,12,15] and pharmaceutical excipients (pharmaceutical helper molecules) [9].

Owing to the remarkable properties of gemini surfactants (*i.e.* lower CMC [16], better solubilizing power [17], much lower Krafft points [16,17], and better wetting [18] than the corresponding conventional monomeric surfactants) considerable effort has been invested in the design of new gemini surfactants and studying the relationship between their molecular structures and their aggregation morphologies in aqueous solution [19,20].

The purpose of this work is to evaluate the physicochemical and structural properties of cleavable cationic gemini surfactants with ester bonds inserted between the hydrocarbon tails and the positively charged head groups. The ester bonds were either with the ester carbonyl group away from the positive charge (esterquat type arrangement) or facing the positive charge (betaine ester type arrangement). The structures of these surfactants are shown in scheme 1. To best of our knowledge, the thermodynamic data for micelle formation, size and morphology for these compounds have not been reported yet. A precise knowledge of the mentioned quantities is important for various applications of the studied compounds. We used techniques including surface tension, conductometry, viscometry, dynamic light scattering (DLS), transmission electron microscopy (TEM) and optical microscopy. First, the critical micelle concentration (CMC), surface excess (Γ_{\max}), mean molecular surface area (A_{\min}), degree of counterion dissociation (α), and the thermodynamic parameters of micellization were determined from the surface tension and conductance data. Second, the viscometry, DLS measurements, TEM and optical microscopy enabled the investigation of the size and morphologies of the surfactant aggregates and the phase transition. By comparing the results for these surfactants, we determined not only the effects of varying the position of ester bond in alkyl chain on the solution properties of ester-containing gemini surfactants but also

the effects of varying the hydrophobicity of the spacer chain on micelle formation. Finally, in order to explore whether the electrolyte is able to cause significant morphological changes, NaBr solutions were used at various concentrations.

2. Experimental

2.1. Materials

A collection of the chemicals used are shown in table 1. The procedure for synthesis of dodecyl betainate gemini ($s = 3$) can be found in the Supplementary material. Dodecyl esterquat gemini ($s = 3$) and dodecyl betainate gemini ($s = 2$) were synthesized according to the previous report [21]. Doubly distilled deionised water was used for sample preparation and dilution. A fresh surfactant solution was prepared for each series of measurements.

2.2. Methods

2.2.1. Surface tension measurements

Surface tension measurements were made with Krüss K12 tensiometer under atmospheric pressure by the ring Method [22]. The platinum ring was thoroughly cleaned with acetone and then flame dried before each measurement. The uncertainty of the measurements was $\pm 0.1 \text{ mN} \cdot \text{m}^{-1}$. At least three measurements were carried out for each data point and the standard deviation did not exceed $0.08 \text{ mN} \cdot \text{m}^{-1}$. The temperature was maintained constant by circulating thermostatted water through a jacketed vessel containing the solution. The temperature was controlled within $\pm 0.1 \text{ K}$.

2.2.2. Electrical conductivity measurements

Conductivity measurements of surfactant solutions were made by a conductometer (model Jenway 4510) using a water bath with stirring to control the temperature. For each series of measure-

TABLE 1
The name, purity and provenance of chemicals used.

Chemical	Mass fraction purity	Provenance
1-Dodecanol	0.98	Sigma-Aldrich
Bromoacetyl bromide	>0.98	Sigma-Aldrich
Dichloromethane	>0.995	Sigma-Aldrich
Acetone	>0.995	Sigma-Aldrich
N,N,N',N'-tetramethyl-1,2-Ethanediamine	0.99	Sigma-Aldrich
N,N,N',N'-tetramethyl-1,3-propanediamine	0.99	Sigma-Aldrich
2-Dimethylaminoethanol	>0.995	Sigma-Aldrich
Lauroyl chloride	0.98	Sigma-Aldrich
2-Bromoethanol	0.99	Sigma-Aldrich
1,3-Dibromopropane	0.99	Sigma-Aldrich
Sodium bromide	0.99	Merck

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