Complexation behavior of mixed monolayer/mixed micelle formation between cationic noble surfactant-nonionic conventional surfactant in the presence of biocompatible polymer

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ABSTRACT

Herein, we are reporting the interaction of biocompatible polymer polyvinylpyrrolidone (PVP), with gemini, pentamethylene-1,5-bis(hexadecyldimethylammonium bromide) (G5) and TX-114 surfactant mixture. Various thermodynamic parameters are evaluated with the help of regular solution theory (RST) and pseudo-phase separation model. By the addition of PVP, the critical aggregation concentration (cac) value of G5 as well as mixture decreases. A decrease in the cac value mainly credited to the interactions between the polymer and surfactant. The partial negative charged oxygen atoms, present in the amide group of PVP, were believed to be responsible for interaction with cationic head group of gemini surfactant.

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1. Introduction

The interactions between polymer and surfactant have been a subject of extensive studies over the past few decades because they are of importance in a wide variety of industrial, biological, pharmaceuticals and cosmetics [1–3]. In the case of charged polymers, it is comparatively easier to understand the electrostatic interactions between the oppositely charged polymer and ionic surfactants [4,5]. However, in the case of neutral polymers such as polyvinylpyrrolidone, poly(ethylene oxide) and poly(ethylene glycol), the situation is quite intriguing and complex. In these cases, the surfactant–polymer interactions depend upon several factors such as the nature of surfactant head group, nature of the polar groups embedded in the polymer backbone, and polymer hydrophobicity and flexibility [6–11]. The driving force that is responsible for the polymer–surfactant interaction is supposed to be the minimization of the interfacial area between the nonpolar polymer parts and the solvent water by association of these parts with the exposed nonpolar moieties of surfactant molecules. It has also been observed that anionic surfactants have comparatively stronger interactions with the neutral polymers rather than with cationic surfactants [12,13]. Particularly, in the case of cationic surfactants, apart from the electrostatic interactions between the polar head groups of surfactant and neutral polymer systems [14,15], the respective hydrophobic interactions also play a significant role in determining the surfactant–polymer interactions [16]. Therefore, it can be said that the hydrophilic–lipophilic balance between surfactant and polymer moieties plays a vital role in such interactions.

There is a wealth of published literature on surfactants because of their widespread importance in practical applications and scientific interest in their nature and properties [17–19]. The properties of surfactants remarkably improved in complex mixtures. The mixed micelles are often used in the technical, pharmaceutical, and biological fields since they work better than pure micelles [20,21]. The interaction and aggregation behavior of mixed surfactants in solution and at interfaces have been extensively studied using various techniques such as small-angle neutron scattering (SANS), surface tension, conductivity, fluorescence, cyclic voltammeter, and dynamic light scattering [22–27]. Mixtures containing nonionic surfactants are particularly appealing to the formulation technologists due to the surfactant properties including low foaming, superior fiber cleaning and tolerance to water hardness. For instance, pure cationic surfactants are poor detergents since they neutralize the negative charges on fibers or solutes, but it has been shown that their efficiency can be improved in cationic–nonionic mixture [28]. Nonionic surfactants are also known as non-toxic and non-pollutant compounds [17], which are free of phenol and long alkyl moieties. Triton X series is a main class of nonionic surfactants, also called isooctylphenol ethoxylates. Among those, Triton X-114 is one of the most commercially and industrially applied as a detergent and emulsifying agent. The low critical micelle concentration (cmc) value makes

it an excellent choice for studying the behavior of amphiphiles over a wide range of concentrations.

In the last few decades, a new type of surfactants called gemini (dimeric) has been developed. These novel surfactants consisting of two hydrophobic chains and two hydrophilic head-groups are united by a short (rigid or flexible) spacer [29–32]. These kinds of surfactants have a number of unique aggregation properties in comparison to conventional single-chain surfactants, such as smaller critical micelle concentration (*cmc*), much greater efficiency in reducing surface tension than expected, better wetting properties, special aggregate morphology, and other unusual behaviors. Due to their superior performance in applications and their tunable molecular geometry, geminis have been generating increasing interest.

In the present work, we focus on the study of mixed micellization of TX-114 with G5 in the absence and presence of biocompatible polymer (PVP). Polyvinylpyrrolidone (PVP) is an amphiphilic polymer and is soluble in water and in some other important nonaqueous solvents [33]. The presence of a polar amide group is responsible for its hydrophilic character while hydrophobicity is due to the nonpolar methylene and methine groups present in the ring and along its chain. It can be used as an excipient in pharmaceuticals [34]. It is a biocompatible polymer and used in artificial blood preparation [35]. It resembles proteins because of the presence of amide groups.

The aim of this research is to collect the various physicochemical data in order to explore the interaction between cationic gemini and nonionic surfactants with or without PVP, and to see the effect of hydrophobicity and the molecular architecture in such interactions.

2. Materials and methods

2.1. Materials

The cationic gemini surfactant with a five-methylene spacer group, pentanediyl-1,5-bis(dimethylcetylammonium bromide) (G5), was synthesized in our laboratory and the procedure is outlined in reference [36]. For synthesis, 1,5-dibromopentane (98%, Fluka, Switzerland) and N,N-dimethylhexadecylamine (95%, Fluka, Switzerland) were used without further purification. The investigated polyvinylpyrrolidone, PVP K30 (M.W. −40,000, 99.8% Fluka, Switzerland) was used without further purification. TX-114 (Sigma, Germany) was used as received.

2.2. Synthesis of gemini surfactant

The mixture of alkylbromide and alkanediyl-α, ω-bis(dimethylamine) was refluxed (molar ratio 2.1:1) in ethanol for 48 h. The solvent was removed and then the raw material was recrystallized in ethanol–ethyl acetate mixtures. The crystallization normally repeated four times. The cationic gemini of the hexadecyl series with methyl spacer − (CH$_2$)$_5$ − was prepared according to Scheme 1. All products were checked by ^{1}H NMR spectroscopy using CDCl$_3$ as solvent. For example, the obtained peaks were assigned for protons for G5 and the integrated spectra gave the expected proton contents: δ: 0.858 (t, 6H, alkyl Chain 2 × 1 CH$_3$), 1.257–1.663 (br m, 42 H, alkyl chain 2 × 11 CH$_2$ and spacer chain 1 CH$_2$), 1.728 (crude t, 16 H, alkyl chain 2 × 4 CH$_2$), 2.073–2.126 (br m, 4 H, spacer chain 1 × 2 CH$_2$CH$_2$N$^+$), 3.349 (s, 12 H, 2 × 2 NCH$_3$), and 3.853–3.909 (crude t, 4H, spacer chain 1 × 2 CH$_2$N$^+$). The overall yield was 70–80%.
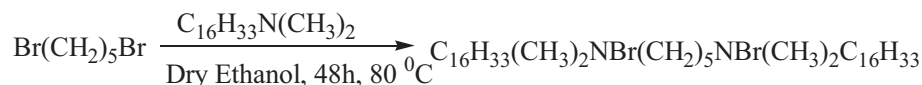
2.3. Surface tension measurements

The surface tension measurements were carried out with Attension Tensiometer (Sigma 701) using a platinum ring at constant temperature (25 ± 0.1 °C). Solutions were contained in a double-walled Pyrex vessel thermostated at 25.0 ± 0.1 °C. Attension Tensiometer operates on the Du Nouy principle, in which a platinum–iridium ring is suspended from a torsion balance, and the force (in mN/m) necessary to pull the ring free from the surface film is measured. Surface tension value was taken when stable reading was obtained for a given surfactant concentration, as indicated by at least three consecutive measurements having nearly the same value. The average of a series of consistent readings for each sample was then corrected to account for the tensiometer configuration, yielding a corrected surface tension value.

3. Results and discussion

3.1. Critical micelle concentration (cmc), critical aggregation concentration (cac) and polymer-bound micelles (C$_p$)

The strong hydrogen bonding among the water molecules is responsible for high surface tension, leading to enhanced cohesive force, which resists the separation of a water column into two. When a surfactant is added in water, surfactant molecules adsorb at interface because of the presence of hydrophobic effect, hence decreasing the surface tension of water. The decrease in the surface tension (γ) value continues until the air/water interface is saturated with surfactant monomers. Beyond this saturation, the added surfactants assemble among themselves to form aggregates to ensure a hydrophilic periphery, hiding the hydrophobic tail within a cage to avoid water. The γ value, therefore, does not change (beyond γ$_{cmc}$) after reaching a certain concentration of surfactant. This concentration of surfactant is called the critical micelle concentration (*cmc*) and is obtained from the break point in the γ versus log [surfactant] profile (Fig. 1).

The interaction between biocompatible polymer and surfactant generally depends on the surfactant tail length, surfactant head-group, polymer hydrophobicity and flexibility. The driving force that is responsible for the polymer–surfactant interaction is supposed to be the minimization of the interfacial area between the nonpolar polymer parts and the solvent water by association of these parts with the exposed nonpolar moieties of surfactant molecules. The surface tension plots of surfactants in water show only one break point (Fig. 1), while in the presence of PVP pure as well as mixture the surface tension plots show double break (Fig. 2). The two break points can be attributed to the occurrence of two kinds of aggregation processes, whereas single break indicates only one kind of aggregation process. The single break in pure water is the *cmc*. In the presence of PVP (0.3 w/v%), the first break at which the surfactants bind to the polymer chain can be regarded as the critical aggregation concentration (*cac*), whereas the second one is at least 2–3 times higher than the first one where the polymer chain is saturated and free micelles are obtained(C$_p$). Table 1 shows that PVP has no significant influence on the *cac* value of pure TX-114, which indicates absence of interaction between polymer and nonionic surfactant. This observation is in complete agreement with the surface tension data classically used to assess for polymer/surfactant interaction. PVP addition does not affect the surface tension of TX-114 solutions, except for a slight decrease in the *cac*. On the other hand on the addition of PVP, the *cac* value of G5 as well as mixture decreases. A decrease in the *cac* value mainly credited to the interactions between

$$\text{Br(CH}_2\text{)}_5\text{Br} \xrightarrow[\text{Dry Ethanol, 48h, 80 }^0\text{C}]{\text{C}_{16}\text{H}_{33}\text{N(CH}_3\text{)}_2} \text{C}_{16}\text{H}_{33}\text{(CH}_3\text{)}_2\text{NBr(CH}_2\text{)}_5\text{NBr(CH}_3\text{)}_2\text{C}_{16}\text{H}_{33}$$

Scheme 1. Protocol for synthesis of gemini (G5) surfactant.