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Interaction of bovine serum albumin with cationic monomeric and dimeric surfactants: A comparative study

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ABSTRACT

The interaction of bovine serum albumin (BSA) with a single chain cationic surfactant, dodecyl trimethylammonium bromide (DTAB) and three dimeric surfactants viz., butanediyl-1,4 bis(dimethyldodecylammonium bromide ($12–4-12,2Br^{-}$), 2- butanol-1,4-bis(dimethyldodecylammonium bromide) ($12–4(OH)-12,2Br^{-}$), 2,4-dibutanol-1,4 bis(dimethyldodecylammonium bromide) ($12\text{-}4(OH)_2\text{-}12_,2Br^{-}$) have been investigated by means of surface tension, conductance, viscosity, fluorescence and UV–Visible spectroscopic measurements. The results obtained depict that the hydroxyl group substitution in linker of gemini surfactants affects the BSA-surfactant interactions. As compared to single chain cationic surfactants, gemini surfactants show more interactions with BSA. The negetive values of thermodynamic parameters viz., Gibbs free energy of micellization ($\Delta G°_m$), Gibbs free energy of adsorption ($\Delta G°_{ads}$) and Gibbs free energy of quenching process ($\Delta G°_q$) showed spontaneity of micellization process.

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1. Introduction

Protein–surfactant interactions carry greater importance since they are more relevant in the fields of detergents, cosmetics, biosciences, foods and pharmaceuticals [1,2]. The marginal stability of the native globular conformation of proteins which is a delicate balance of various interactions in the proteins, is influenced by the pH, temperature and additives such as substrates, activators, coenzymes and inhibitors [3, 4]. Studies on the interactions of surfactants with globular proteins can contribute towards an understanding of the action of surfactants as denaturants and as solubilizing agents for membranes of proteins and lipids. Surfactant can be broadly classified according to their binding nature towards proteins [5]. Some of the surfactants only bind to protein and leave their tertiary structure intact while some are initiate protein unfolding known as denaturing surfactants [6]. Commonly used ionic surfactants such as sodium dodecyl sulfate and cetyltrimethylammonium bromide, generally denature proteins whereas non-ionic surfactants do not [7,8]. Binding of surfactants to proteins could either stabilize the structures of these proteins or denature them. Ionic surfactants usually interact strongly with proteins and denature them [9]. The denaturation mechanism of surfactant is different from that of urea and guanidinium chloride. It usually occurs at very low concentration, making them much more efficient than traditional chemical denaturants. Except for few nonionic surfactants, most of them usually do not denature the proteins [10,11].

The most abundant protein in plasma is serum albumin. Serum albumin is synthesized in liver and exported as non-glycosylated protein [12]. They bind to a variety of hydrophobic ligands and thus used as model proteins for many studies like biophysical, biochemical and physico-chemical [13,14]. Albumin plays an important role in the transportation and deposition of a variety of endogenous and exogenous substances in the blood [15,16] and are also used in peritoneal dialysis in fighting against the harmful effect of antibiotics [17]. Studies have shown that the distribution and metabolism of a large number of biologically active compounds, such as metabolites, drugs, and even some toxins, in blood are dependent to a larger extent on their affinities towards serum albumin [18,19]. Bovine serum albumin (BSA) is an expedient and widely studied model globular protein not only for its important roles in biological processes due to its unique ligand binding properties, but also for its structure being well established [20,21]. In its native state, it contains 583 amino acids and 17 disulfide bonds with one free cystein group [22]. It is highly water soluble because of their distribution of amino acid (hydrophobic inside, hydrophilic outside) and large number of ionized amino acids [23].

From the last decades considerable attention have been paid from researchers across the globe to study the interaction of BSA and surfactant of different kind viz., ionic, nonionic, gemini etc. [24–27]. However, most researches mainly focused on the interactions of protein with traditional surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium

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bromide and the researches on gemini surfactants, a new generation of surfactants, with proteins are relatively limited [28]. In general, the gemini surfactants show comparatively stronger interaction with the BSA molecule than the single-chain surfactants [25]. Gemini surfactants are made up of two polar headgroups and two hydrophobic alkyl tails linked by a spacer at the level of headgroups or close to the headgroups. This unique structure makes gemini surfactants to possess different protein binding behaviors than the conventional surfactants [29–33].

Different types of physicochemical techniques have been employed to investigate the interactions between cationic and anionic surfactants with proteins in vitro [34–36]. The mechanism of such type of interactions has become an essential field of research in colloidal science. Li et al. [27] have reported that the cationic gemini surfactant stabilizes the secondary structure of bovine serum albumin (BSA) at low surfactant concentration, while the corresponding monomeric surfactant (dodecyltrimethylammonium bromide) did not show such effect. Ahluwalia et al. [1] have studied the conformational changes induced by conventional anionic surfactants. Niu et al. [37] have also done some spectroscopic studies on interaction of BSA and gemini surfactant with different spacer length. Recent studies revealed that gemini surfactants interact more efficiently with proteins and denature them at lower concentration as compared with conventional surfactants [30,31]. Owing to superior performance of gemini surfactants, they have been creating special interest in the field of protein–surfactant studies. The present study is aimed to explore the interactions of BSA with structurally different monomeric and gemini surfactants.

In the present investigation, we have performed a comparative study to evaluate the binding efficacy of hydroxyl group substituted gemini surfactants with BSA against conventional monomeric cationic surfactants. Structure of the surfactants are presented in Scheme 1.

2. Materials

The gemini surfactants, 12-4-12, $2Br^-$, 12-4(OH)-12, $2Br^-$ and 12-4$(OH)_2$-12, $2Br^-$ were synthesized following the same method as reported in the literature [38,39]. Bovine serum albumin (BSA) with the molar mass of 66.4 kDa and DTAB were purchased from Sigma Aldrich and used as received. Millipore water was used for preparing the solutions. The BSA concentration was determined by Varian Cary 50 UV–visible spectrophotometer, using a molar extinction coefficient of 4.4×10^4 cm^{-1} at 280 nm [27].

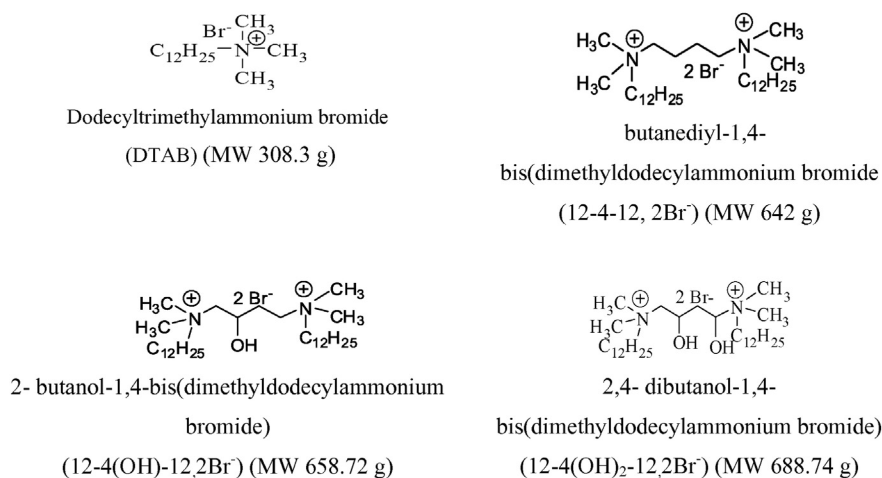
3. Method

3.1. Conductivity

Conductometric measurements were carried out using a Systronics direct reading conductivity meter (Type 306). The conductivity cell constant was calibrated with KCl solutions in appropriate concentration range. The temperature of the solution was carefully controlled by a thermostat (having a temperature accuracy of ± 0.01 °C). A concentrated protein–surfactant solution was added in 10 ml of aqueous medium using a micropipette. After ensuring temperature equilibration, the specific conductance (κ) was measured. At each concentration, the conductivity measurement was repeated three times and the average value was obtained.

3.2. Surface tension

The surface tension measurement was measured using surface tensiometer (Jancon, India) employing ring detachment technique at



(Source: RCSB Protein Data Bank)

Scheme 1. Structure of surfactants and protein.

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