



Effect of polymers and temperature on critical micelle concentration of some gemini and monomeric surfactants

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ABSTRACT

The effect of polymers on the physicochemical properties of cationic gemini (16-4-16 MEA, 2Br⁻) and monomeric surfactants (cetyldiethylethanolammonium bromide, (CDEEAB) and cetyldimethylethanolammonium bromide (CDMEAB) have been studied by conductivity measurements. The critical micelle concentration (cmc) value increases by increasing the percentage and molecular mass of polymers (poly (ethylene glycol), PEG-X, where X = 400, 600) while it decreases with higher molecular mass (X = 4000, 6000, 20,000). Thermodynamic parameters (standard Gibbs energy (ΔG_m°), enthalpy (ΔH_m°), and entropy (ΔS_m°), of micellization) have also been investigated. Hydrophobic interactions and the ability to form hydrogen bonds play a role in the polymer–surfactant association. This associative behavior was shown to depend significantly on the polymer and surfactant concentrations. The enthalpies of micellization are much more exothermic for the gemini surfactants than for the monomeric surfactants. All of the surfactants exhibited the enthalpy–entropy compensation phenomenon.

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1. Introduction

Polymers have tremendous application in various fields [1–3]. The interaction between polymers and surfactants in aqueous solutions has played a significant role in the field of technological applications and in fundamental research [4,5]. The polymer–surfactants molecules influence the solution and interfacial properties are controlled by the state of their occurrence in aqueous solutions, namely whether they form mixed aggregates in solution and, if so, the nature of their microstructures [6].

It is well known that solutions of mixtures of certain polymers and surfactant can exhibit molecular interactions that may affect the rheological and physicochemical properties of the solution [7]. These interactions also display features that depend on the polymer and surfactant electrical charges, hydrophobicity of the polymer and nonpolar tail of the surfactant, the structural confirmation and the flexibility of the polymers [8,9].

The polymer/surfactant interactions have become a major topic in colloidal research over the past few decades. Much of the interest in this area has stemmed from the numerous possible industrial applications such as pharmaceutical products, thickening agents, coatings, and cosmetic formulations [10–12]. The interactions of water-soluble polymers and ionic surfactants in aqueous solution are of interest from the fundamental standpoint of special struc-

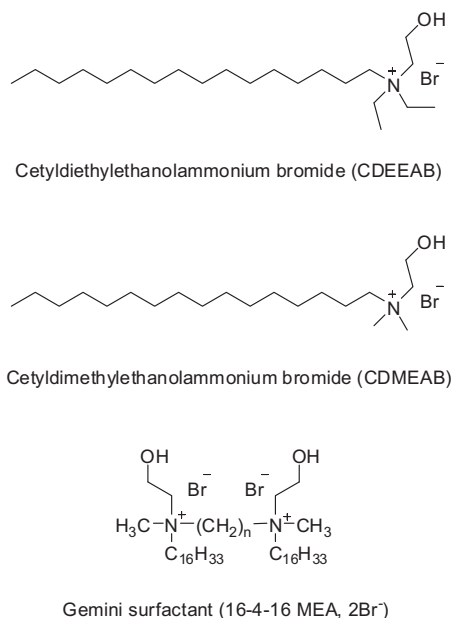
ture and dynamics of polymer/surfactant association and can be used in the process of enhanced oil recovery [13,14]. The ability of surfactants to aggregate and form micelles adds a particular dimension to their interactions with water-soluble polymers [15–22].

Gemini surfactants are surface-active agents having two head groups and two tail group linked by a spacer. Gemini are considerably more surface active than conventional monomeric surfactants [23–26]. These surfactants, because of their unique solution properties such as very low CMC, high detergency, high solubilization and high surface wetting capability, possess a wide range of applications such as in mining, petroleum, chemical, pharmaceutical and biochemical research. Gemini are also utilized as catalysts in several organic and inorganic reactions. They are also used as preservatives, anticorrosives and antimicrobial agents [27–30]. Currently, gemini surfactants have also attracted attention as potential gene delivery agents [31,32].

Recently, Janczuk *et al.* [33] have studied the adsorption properties of nonionic (Triton X-100, 114, 165), anionic (sodium dodecylsulfate) and cationic (tetradecyltrimethylammonium bromide) surfactants at polymethyl methacrylate (PMMA), polytetrafluoroethylene (PTFE)–water and solution–air interfaces. They observed that the adsorption of surfactants at the PTFE, PMMA–solution and nylon 6–solution interface is lower than that at the solution–air interface. Wang and his research group [34] have observed the interactions of cationic ammonium gemini surfactant (C₁₂-6-C₁₂ Br⁻) and single-chain surfactant dodecyltrimethylammonium bromide (DTAB) with anionic polyelectrolytes poly(sodium

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SCHEME 1. Structure of the cationic surfactants studied in this paper.

styrenesulfonates) (NaPSS) and poly(sodium acrylates) (NaPAA) with different molar masses by microcalorimetry, turbidity and steady-state fluorescence measurements. They observed that polyelectrolytes show a remarkable interaction with the cationic surfactants. Compared with DTAB, C₁₂-6-C₁₂ Br⁻ can bind to NaPSS and NaPAA at a very low concentration and has stronger interactions with NaPSS and NaPAA. Larson *et al.* [35] have focused the effect of sodium *n*-dodecyl sulfate (SDS), *n*-dodecyl trimethylammonium chloride (DTAC), of *n*-dodecyl ammonium chloride (DAC) and its headgroup size, charge and structures of poly(ethylene oxide) (PEO)-micelle interaction. They observed that direct electrostatic interactions between the polymer and micelle are most responsible for the preference for interaction with anionic micelles. The synthesis and physicochemical behavior of alkanediethylethanolammonium bromide and alkanedimethylethanolammonium bromide (R = C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃) have been studied by Palepu *et al.* [36]. Their micellar properties in binary aquo-organic solvent mixtures [37,38] as well as studies on their mixed surfactant systems have also been reported [39,40]. Significant contributions were also made by Manna [41] and Oliveira *et al.* [42] in this context.

Our research group studied the effect of polymers on micellar properties of surfactants [43] and observed acidic hydrolysis of hydroxamic acid in single and mixed systems [44]. To our knowledge, studies of the effects of polymer-surfactant mixture on the physicochemical behavior of cationic gemini and monomeric surfactants in presence of polymers have not been reported, previously. In the present work, two series of combinations of PEG polymers with cationic surfactants of: (i) monomeric, *i.e.*, cetyldiethylethanolammonium bromide and cetyldimethylethanolammonium bromide and (ii) gemini surfactant (16-4-16 MEA, 2Br⁻) (scheme 1) head groups have been selected. The choice of these

surfactants is based on the fact that the alkanol amine surfactants are considered to be having amine and hydroxyl groups and gemini surfactants having bis(hydroxyethylammonium) head groups. Hence it is expected that the micellar behavior of both kinds of surfactants with polymers would be quite different from each other. The aim of the present work is to study the effect of a series of polymer with different molecular mass (PEG-400, PEG-600, PEG-4000, PEG-6000 and PEG-20,000) on the micellization of cationic gemini (C₁₆-4-C₁₆ MEA, 2Br⁻) and monomeric surfactants (cetyldiethylethanolammonium bromide (CDEEAB), cetyldimethylethanolammonium bromide (CDMEAB)).

2. Experimental

2.1. Materials

The gemini surfactant was synthesized and the purity of the surfactant was checked using ¹H NMR, as previously reported [45a–46]. Cationic surfactants cetyldiethylethanolammonium bromide (CDEEAB) and cetyldimethylethanolammonium bromide (CDMEAB) were prepared in the laboratory of Prof. RM. Palepu, St. Francis Xavier University, Canada. The purity of these surfactants was checked employing conductometric titration of bromide ion with a standard silver nitrate solution. In all the cases, surfactants were found to be >0.995 mass fraction purity [45b]. Polyethylene glycols, *i.e.*, PEG-400, PEG-600 were obtained from Sigma-Aldrich and PEG-4000, PEG-6000 and PEG-20,000 were purchased from Merck and used without further purification. The purity of samples are given in table 1. All the solutions were prepared in triple distilled water.

2.2. Conductivity method

The conductivity of aqueous solutions of surfactants were measured using a Systronics direct reading conductivity meter (Type 304 and 306). The conductometer was calibrated with KCl solutions of appropriate concentration range. A concentrated solution of surfactant was progressively added to 10 cm³ of medium in a thermostat container (having a temperature accuracy of ±0.01 °C) using a micropipette. Measurements were taken thorough mixing and allowing time for thermal equilibration. The fitting of experimental specific conductivity data vs surfactant concentration was performed with the program Table Curve, using a Levenberg–Marquardt procedure.

3. Results and discussion

3.1. Physicochemical properties

The physicochemical properties (CMC and α) for every surfactant were analyzed with and without the addition of polymers in aqueous solution. The % (w/v) of PEG used were 1, 3 and 5. Figure 1 shows the curve of specific conductivity vs concentration for the surfactants CDEEAB in the presence of 1% (w/v) PEG-400 at *T* = 300 K. The CMC values can be determined by the intersection of the two straight lines above and below the inflection point as can be seen in table 2. Table 2 also shows the degree of micellar

TABLE 1
Provenance and purity of procured compounds.

Chemical Name	Source	Mass fraction purity	Purification method	Analysis method
Polyethylene glycol (400, 600)	Sigma-Aldrich	>0.99	Chemical used without further purification	IR ^a
Polyethylene glycol (4000, 6000, 20000)	Merck	>0.99	Chemical used without further purification	IR ^a

^a IR = infra red spectroscopy.

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