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Interaction of cationic surfactants with carboxymethylcellulose in aqueous media

Jitendra Mata [a,*], Jaykumar Patel [a], Nirmesh Jain [b], Gautam Ghosh [c], P. Bahadur [a]

[a] *Department of Chemistry, Veer Narmad South Gujarat University, Surat 395007, India*
[b] *School of Chemistry, University of Sydney, Sydney, Australia*
[c] *UGC-DAE CSR, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*

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Abstract

We have examined the polymer–surfactant interaction in mixed solutions of the cationic surfactants, i.e., dodecyltrimethylammonium chloride, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, tetradecyltriphenylphosphonium bromide, and tetradecylpyridinium bromide and a semiflexible anionic polyelectrolyte carboxymethylcellulose in water and aqueous salt solutions by various techniques: tensiometry, viscosimetry or ion-selective electrode method, and dynamic light scattering. We have investigated the effect of varying surfactant chain length, head group size, counterion, and ionic strength on the critical aggregation concentration (CAC) of mixed polymer surfactant systems and the collapse of the polymer molecule under different solution conditions. The CAC decreases with increasing alkyl chain length. Above a certain surfactant concentration, mixed aggregates start growing until their macroscopic phase separation. The growth is more rapid with greater surfactant tail length and with increasing head group size. This is attributed in both cases to the increasing hydrophobic interaction between polymer and surfactant. Among surfactants with monovalent halide counterions, iodide induces the strongest binding, reflected by the onset of growth of the mixed aggregates at low surfactant concentration. This is perhaps related to the decreasing hydration of the counterion from chloride to iodide. The surfactant concentration at which the viscosity of the solution starts to decrease sharply is smaller than the CAC, and probably reflects polymer chain shrinkage due to noncooperative binding.

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1. Introduction

The study of interactions between polymers and surfactants in aqueous solutions has attracted significant interest in recent years because of their widespread applications and relatively complex behavior. In particular, the association between polyelectrolytes and oppositely charged surfactants, both in bulk and at interfaces, has been extensively studied, and many recent reviews and books covering different aspects are available [1–5].

For these oppositely charged systems, the strong electrostatic attraction between the charged groups leads to bulk complexation above a surfactant concentration called the critical aggregation concentration (CAC), which can be several orders of magnitude below the critical micelle concentration (CMC) of the surfactant. This CAC is usually determined either by surface tension measurements (the tension remains almost constant with increasing surfactant concentration over a range of concentrations above CAC) or by surfactant-specific electrodes that are sensitive to the nonassociated surfactant molecules. It is generally admitted that surfactant micelles start to form much above CAC, decorating the polymer chains, at least when these chains are sufficiently flexible. Recent calorimetry [6] and electrical birefringence [7,8] experiments with cationic surfactants and anionic polymers have revealed that polymer/surfactant association already occurs below CAC. It has been proposed that this binding below CAC is noncooperative, and becomes more cooperative above CAC only. Chatterjee et al. [9] investigated the interaction of a cationic surfactant, CTAB, and an anionic

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[*] Corresponding author. Fax: +91 261 2256012.
E-mail address: jitendramata@yahoo.com (J. Mata).

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surfactant, sodium dodecyl sulfate (SDS), with biopolymers by isothermal titration calorimetry. The onset of CAC and various stages of interaction after CAC were very clearly detected. Langevin and co-workers have examined in detail the influence of polymer charge density [10], polymer molecular weight [11], polymer backbone rigidity [12], and surfactant alkyl chain length on the complexation of C_nTAB with anionic polyelectrolytes [13]. They have shown that complexation is shifted to low surfactant concentration with increasing alkyl chain length. CAC is not affected by the polymer charge density and complete collapse of polymer molecule requires larger amounts of surfactant with increasing charge densities. Hansson predicts that CAC increases with increasing polymer or salt concentration [14]. These effects are in fact similar and due to the increase in ionic strength. Diamant and Andelman [15] also predict that the CAC increases with ionic strength, but is only weakly influenced by polymer charge. Hansson and Almgren found in their study of mixed solutions of alkyltrimethylammonium bromides (C_nTAB) and carboxymethylcellulose (CarboxyMC) that the CAC indeed does not appreciably depend on polyion linear charge density, provided it is large enough [16].

It has been now realized that in ionic micellar solutions, the counterion condensation plays a very important role in deciding the effective charge on the micelle, which in turn influences the formation, structure, and interaction of micelles [17–21]. It has been shown that counterion condensation onto the micelle surface increases with decreasing hydrated size of the counterion. The effect of head group sizes of quaternary ammonium bromides on their micellization in aqueous media has also been investigated [22,23]. However, to the best of our knowledge, much is not known about the influence of head group sizes and variation of counterion of quaternary ammonium surfactants on their complexation with oppositely charged polyelectrolytes.

In this paper, we report studies on binding of quaternary cationic surfactants and anionic polyelectrolyte in aqueous medium. We have investigated how surfactant head group sizes, different halide counterions, and ionic strength of the medium influence the binding between polymer and surfactants. We have determined the CACs of the mixed system by measuring their surface tensions and the size of the mixed polymer surfactant aggregates from dynamic light scattering. We have also used viscosimetry, sensitive to any collapse (partial or total) of the polymer chains induced by progressive binding of surfactants, to see if collapse also begins at the CAC. Binding of alkyltrimethylammonium bromide surfactants and oppositely charged polyelectrolyte is also investigated by potentiometry.

2. Experimental

2.1. Materials

The cationic surfactants, dodecyltrimethylammonium chloride (DTAC), dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), tetradecyltriphenylphosphonium bromide (TTPB), and hexadecyltrimethylammonium bromide (CTAB), were obtained from Aldrich (purity 99%) and were recrystallized three times in an acetone–ethanol (24:1) solution. Tetradecylpyridinium bromide (TPyB) was synthesized in the laboratory by a condensation process between 1-bromotetradecane and pyridine in the presence of acetone. Dodecyltrimethylammonium iodide (DTAI) was prepared by ion exchange of DTAC with sodium iodide (NaI). The product was purified by repeated recrystallization from ethanol. The CMCs of the purified surfactants are in good agreement with literature data. Tetrabutylammonium bromide (TBAB), sodium fluoride (NaF), sodium bromide (NaBr), sodium chloride (NaCl), sodium iodide (NaI), and barium chloride ($BaCl_2$) were highly pure samples from Fluka and were used as received.

CarboxyMC is a water-soluble linear polymer, prepared by partial substitution of the 2, 3, and 6 hydroxyl groups of cellulose by hydrophilic carboxymethyl groups. We have used Blanose sodium carboxymethylcellulose 12M31P, kindly supplied by Aqualon Hercules. No further purification was done before use. Its substitution degree (average number of carboxymethyl groups per glucose unit) is $DS = 1.23$. Triple-distilled water from an all-Pyrex glass apparatus was used for the preparation of solutions. For DLS measurement, second-stage Milli-Q water having specific resistance 18.2 MΩ was used.

2.2. Methods

2.2.1. Surface tension

The surface tension of cationic surfactant solutions in the absence and presence of CarboxyMC was measured by a drop weight method using a modified stalagmometer [24]. The assembly consists of a Pyrex glass bulb of spherical shape with a capillary tube attached at filling and dropping ends. The capillary tube at the dropping end is blown into a two-fold U shape and the tip of the end is grounded in the form of a fine cone. By this way, not only is the formation of drops of uniform shape and size ensured, but also drops are allowed to break under their own weight. A thoroughly stoppered weighing bottle is attached to the dropping end through a rubber septum. The weighing bottle, attached to a dropping capillary tube, was suspended in another closed long glass tube. The stalagmometer assembly, along with the predried and preweighed weighing bottle, was lowered into a thermostatic water bath maintained at $30 \pm 0.1\,^{\circ}C$. A 30-min time of equilibrium was always allowed. Then known numbers of drops (>20) of given solution and reference triple-distilled water were allowed to fall into the weighing bottle in separate runs. The weight of solutions, as well as triple-distilled water drawn from separate runs, was instantly recorded on a single-pan balance. The surface tension of the individual solution was then calculated from known values of surface tension of water and densities and weight of solution and water.

2.2.2. Viscosimetry

The viscosity measurements were carried out using an Ubbelohde suspended-level capillary viscometer. The viscometer was suspended vertically in a thermostat with temperature stability $\pm 0.1\,^{\circ}C$. The flow time for a constant volume of solution through the capillary was measured with a calibrated stopwatch.

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