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SHORT COMMUNICATION

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Study of polymer-surfactant interactions via surface tension measurements

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Abstract Interactions between a polymer and a surfactant were studied via surface tension measurements. Poly(ethylene glycol) and sodium dodecyl sulfate were used as a polymer and a surfactant, respectively. The addition of polymer affected the CMC value of the surfactant. The interpretations of the data and theoretical plots of polymer-surfactant interactions are discussed using a theoretical model.

Key words Surface tension · Polymer · Surfactant · Interactions

Introduction

The field of polymer-surfactant interactions has attracted much interest both academically and industrially [1, 2]. Although the subject has been studied over a period of several decades, extensive research is continuing on many fronts owing to the ongoing interest in enhanced oil recovery, drug delivery, cosmetic formulation, etc. [3–6]. The focus of these investigations may be divided into two categories, i.e., those which are "polymer-centered" and those which are "surfactant-centered." In the first case, a polymer molecule is believed to possess sites that may bind surfactant molecules. The assumption is that polymer-surfactant interaction constitutes a strong perturbation to the bulk surfactant medium. In the latter case, polymer-surfactant complexation is mainly a matter of surfactant micellization. Although there are several theories, all researchers recognize that polymer-surfactant complexation results in a surfactant micellization though perturbed in the presence of polymer [7–12]. Polymer-surfactant association is a cooperative phenomenon where surfactant binds to the polymer in the form of aggregates.

The poly(ethylene glycol) (PEG)-sodium dodecyl sulfate (SDS) polymer-surfactant system was selected for this study. This system has been investigated by various researchers [13–15]. The nature of the interactions is the same in the cases of PEG-SDS and poly(ethylene oxide)-SDS systems [16–18]. Although the repeating unit is the same for both polymers, they have different end groups.

Experimental

Sodium dodecyl sulfate (SDS) of high purity grade was obtained from BDH Chemical Ltd and was used as received. Poly(ethylene glycol) (PEG) was supplied by Fisher Scientific Company and had a weight average molecular weight of 6000. The Wilhelmy plate apparatus (Krüss Process Tensiometer Model K-12) was used to measure the surface tensions. The measurements were conducted at 25 °C and atmospheric pressure.

Theoretical

For a given total surfactant concentration [S_T] a partitioning occurs into free surfactant, polymer bound surfactant, and micellized surfactant as noted by Nagarajan [8]:

$$[S_T] = \left[S_f\right] + [S_b] + m[S_m] \tag{1}$$

where [S_f] is the concentration of the free surfactant molecules, [S_b] is the concentration of the surfactant molecules bound to the polymer, and [S_m] is the concentration of the micellized surfactant molecules in the solution. The extent of this partitioning depends on the intrinsic binding constant (K_b), the micellization equilibrium constant (K_m), the critical or optimal micelle size (m), the size of the surfactant clusters bound at a polymer binding site (λ), and the number of binding sites per polymer molecule (n):

$$[S_T] = [S_f] + [P_T]\frac{n\lambda K_b[S_f]^{\lambda}}{1+K_b[S_f]^{\lambda}} + mK_m[S_f]^{m} \qquad (2)$$

In the present calculations the value of K_b was arbitrarily taken to be twice that of K_m in recognition of the fact that surfactant/polymer binding occurs more readily than surfactant micellization. Theoretical predictions of bound surfactant concentration, free surfactant concentration, and surface tension vs total surfactant concentration were shown in the Nikas and Blankschtein model [12]. In their calculations, two or more types of micelles were considered whereas in the case of Nagarajan's model [8] only one type of micelle occurs.

Results and discussion

Figure 1a represents the surface tension vs surfactant concentration plot both in the presence and absence of polymer. As the surfactant concentration increases in the absence of polymer, the surface tension monotonically decreases to a certain concentration of the surfactant, and thereafter remains constant. That break point is called the critical micelle concentration (CMC) of the surfactant. In the presence of polymer, the CMC value is shifted to the higher concentration region. The schematic representation of surface tension vs surfactant concentration for both the presence and absence of a polymer is shown in Fig. 1b. The surface tension behavior of the polymer-surfactant system may be divided into three regions according to the prevailing surfactant concentration, i.e., the monomer region, the polymer-surfactant complex region, and the micellization region. In the polymer-surfactant mixed system, the surface tension initially decreases and then rises again. After that, the surface tension decreases with increasing surfactant concentration. The first break point is called the critical association concentration (CAC) of the polymer and the second transition point is due to the shifted value of the CMC. The surface tension increases slightly in the intermediate region due to complex formation. As the polymer is also involved in the structure of the micelles, the slope of the curve is different from that for surfactant alone.

Figure 2 represents the calculated surface tension vs the surfactant concentration plot at several different polymer concentrations. Figure 3 represents the bound surfactant concentration vs total surfactant concentration curves, also at several polymer concentrations. Similarly, Fig. 4 represents the free surfactant concentration vs surfactant concentration curves in various polymer concentrations. In Fig. 2, as the concentration of polymer increases the CMC value of the surfactant also increases. It is interesting to note that the CAC value of the polymer is independent of the surfactant concentration. As the polymer concentration increases, the bound surfactant concentration also increases as shown in Fig. 3. However, the free surfactant concentration depends upon the polymer concentration. For example, at high polymer concentration, the free surfactant concentration initially increases and then in a certain range it remains almost independent with increasing surfactant concentration. It then again increases with surfactant concentration until it reaches a constant value.

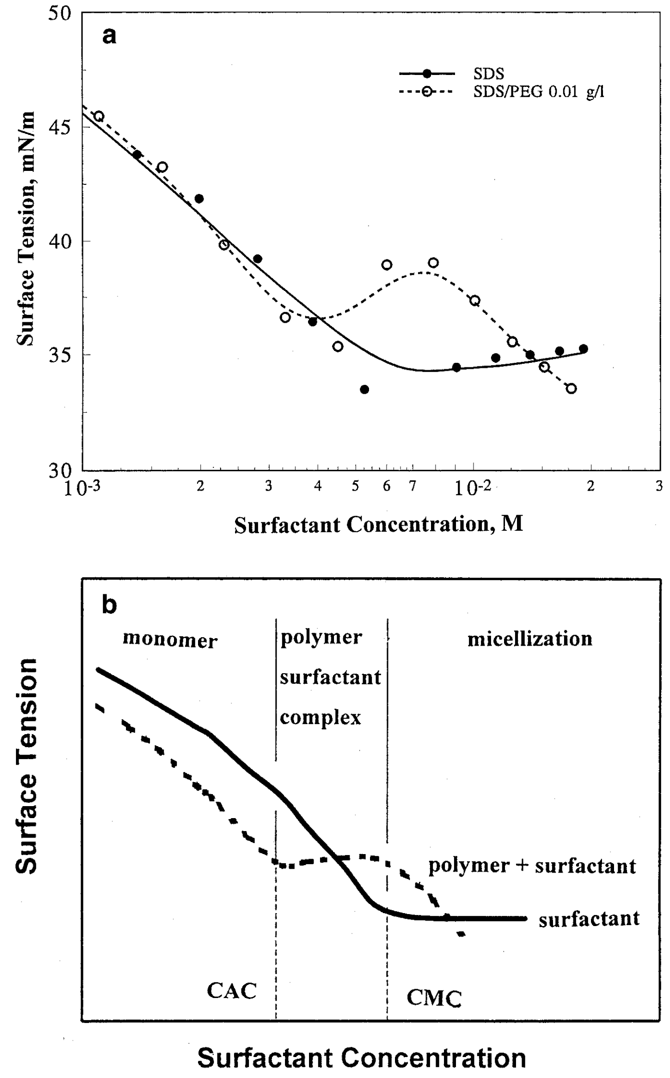

Fig. 1 **a** Surface tension as a function of surfactant concentration in the absence and presence of polymer: (●) without poly(ethylene glycol); (○) with 0.01 g/l poly(ethylene glycol). **b** Schematic representation of surface tension as a function of surfactant concentration: (——) without polymer; (– –) with polymer

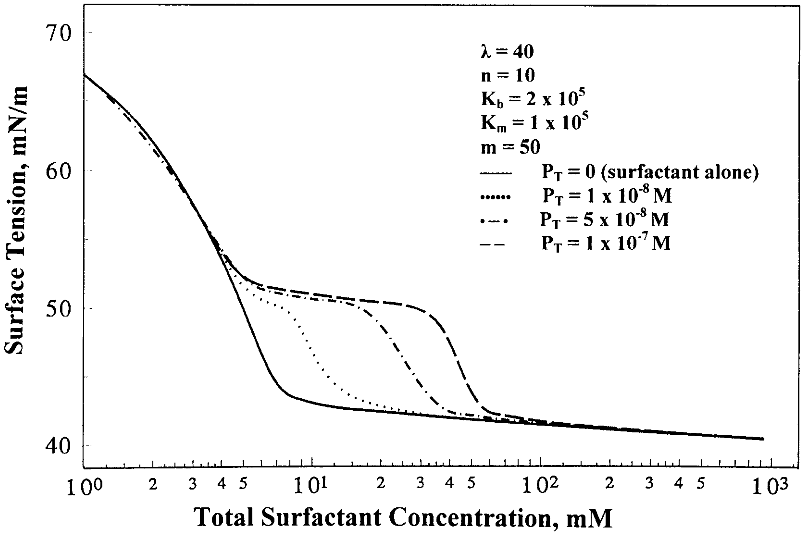

Fig. 2 Theoretical predictions of surface tension as a function of total surfactant concentration: (——) without polymer; (· · · · ·) polymer concentration 1×10^{-8} mol/l; (·—·—·) polymer concentration 5×10^{-8} mol/l; (- - - -) polymer concentration 1×10^{-7} mol/l

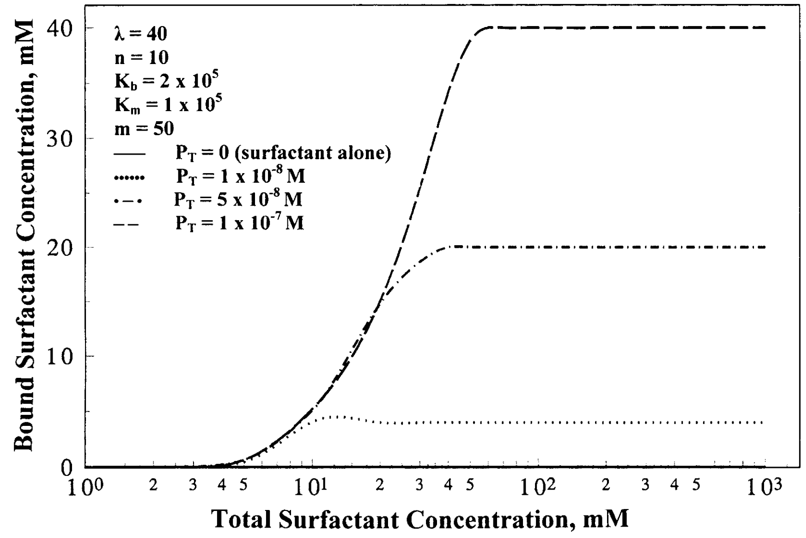

Fig. 3 Theoretical predictions of bound surfactant concentration as a function of total surfactant concentration: (——) without polymer; (· · · · ·) polymer concentration 1×10^{-8} mol/l; (·—·—·) polymer concentration 5×10^{-8} mol/l; (- - - -) polymer concentration 1×10^{-7} mol/l

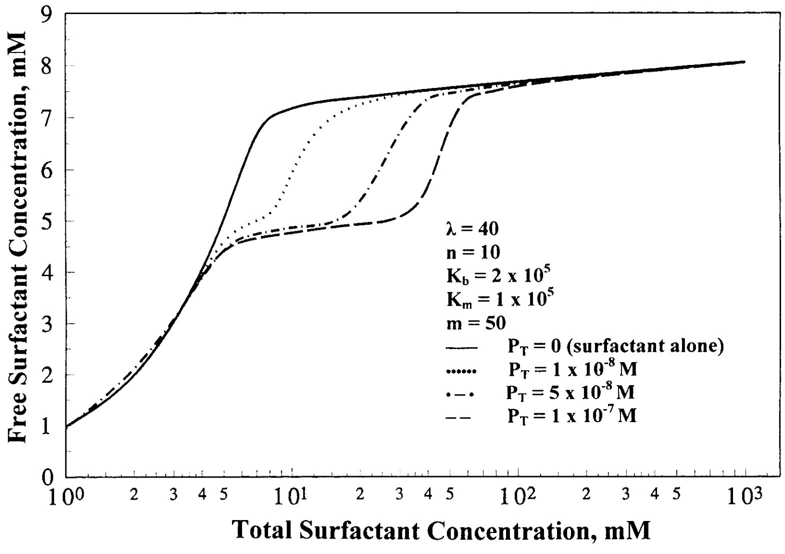

Fig. 4 Theoretical predictions of free surfactant concentration as a function of total surfactant concentration: (——) without polymer; (· · · · ·) polymer concentration 1×10^{-8} mol/l; (·—·—·) polymer concentration 5×10^{-8} mol/l; (- - - -) polymer concentration 1×10^{-7} mol/l

Conclusions

The surface tension of sodium dodecyl sulfate was investigated as a function of poly(ethylene glycol) concentration using a Wilhelmy plate tensiometer. The addition of polymer affected the critical micelle concentration (CMC) of the surfactant, such that the CMC of the surfactant concentration increases with increase of the polymer concentration. The behavior of this polymer-surfactant complex could be closely predicted using the Nagarajan model.

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