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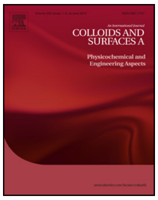

Role of interactions between cationic polymers and surfactants for foam properties

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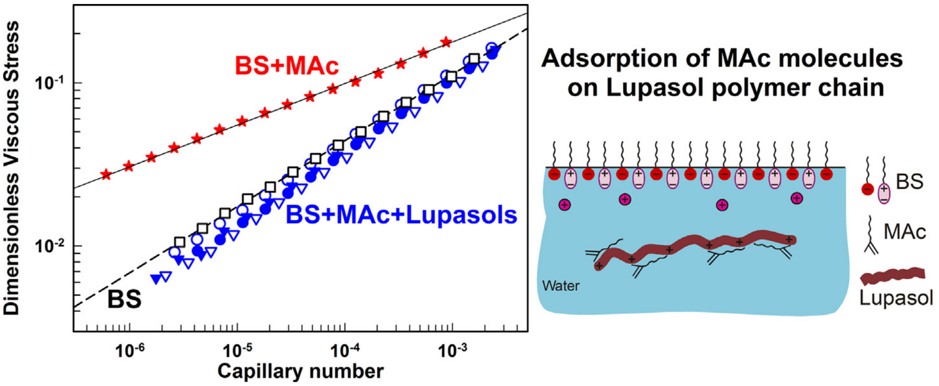
HIGHLIGHTS

- Effect of cationic polymers on foam properties of SLES + CAPB ± MAc was studied.
- Lupasol polymers bind strongly the MAc molecules in the bulk solution.
- Lupasol polymers reduce MAc activity and its adsorption on the bubble surfaces.
- Merquat 740 affects strongly the foam yield stress, foam-wall friction, behavior of BS + MAc films.
- Merquat 100 with very high charge density has week effect on foam properties.

GRAPHICAL ABSTRACT



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ABSTRACT

We study the effect of two classes of cationic polymers, Lupasols (based on polyethylenimine, PEI) and Merquats (based on diallyldimethyl ammonium chloride, DADMAC), on the surface and rheological properties of foams, stabilized with the mixture of anionic (SLES) and zwiterionic (CAPB) surfactants, with and without myristic acid (MAc) present as a cosurfactant. The effects of several polymers from each class, with different molecular mass and charge density, are compared. Polymers from Lupasol series were found to suppress the cosurfactant effect of MAc on all surface and foam properties studied—surface rheological properties, inside foam friction, foam-wall friction, and mean bubble size. The obtained results show that Lupasol polymers bind strongly the MAc molecules in the bulk solution, thus reducing MAc surface activity and adsorption. The cosurfactant effect of MAc could be restored at neutral pH, after increasing MAc concentration to reach a certain weight ratio of MAc/Lupasol. Merquat 740, which is a co-polymer of DADMAC and acrylamide with low charge density, affects strongly the dimensionless foam yield stress, foam-wall friction, and thinning behavior of BS + MAc films. This effect is explained with the strong interactions between polymer molecules and MAc in the mixed adsorption layer at the air–water interface—a relatively thick polymer adsorption layer is formed, able to bridge neighbouring surfaces. In contrast, Merquat 100 with very high charge density (homopolymer of DADMAC) has week effect on foam properties, due to the formation of relatively thin adsorption layers. Thus we observe a variety of possible scenario, depending on (1) the competition between the binding of surfactant/cosurfactant to the polymer molecules in the bulk solution with the polymer adsorption on the bubble surface, and (2) on the ability of the polymer to form thick adsorption layers, bridging the surfaces of neighbouring bubbles.

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1. Introduction

Polymer–surfactant mixtures are widely used in many practical applications, such as the paper industry, and home and personal care products [1,2]. Due to their wide-spread usage and complex physico-chemical properties, these systems have attracted the attention of researchers and they are subject of numerous studies, aimed at determining the role of the surfactant–polymer interactions, both in the bulk and on the solution surface, for the overall system behaviour [1–22]. In the course of these studies, it was shown that presence of polymers in surfactant solutions affects significantly the structure and composition of the adsorption layers [6–8,9–12], the thinning behaviour of the respective foam films [14,15,18,19] and the rheological properties of the formed mixed adsorption layers [8,14,16,17], which in turn affects the foamability and foam stability for polymer–surfactant solutions [21,22].

Other important additives in the practical formulations are the co-surfactants, which are used in relatively low concentration to boost the foam properties. Co-surfactants are usually poorly soluble compounds, which are solubilized in the micelles of the main surfactant and affect the surface and foam properties. In our previous studies [23–25] we found that the addition of fatty acids with chain length between 12 and 16 carbon atoms, as co-surfactants to the mixture of SLES and CAPB (main surfactants, described in Section 2), leads to a significant increase of the dilatational surface modulus of the mixed surfactant solutions [23–25]. This high surface modulus (HSM) was shown to affect significantly the dynamic properties of the foams formed from such triple surfactant mixtures, including foam rheological properties [23–25], the rate and mode of foam film thinning [23], and the rate of bubble Ostwald ripening [26].

Therefore, both polymers and co-surfactants can affect significantly the surface and foam properties for mixed polymer/surfactant/co-surfactant solutions. In our recent study [27] we investigated the effect of two cationic polymers, Jaguar C13s and Merquat 100, on the rheological properties of foams, stabilized by the mixture SLES + CAPB, in presence of five different co-surfactants. We showed that the addition of Jaguar to the foaming solutions leads to: (1) significant increase of the foam yield stress for all systems studied; (2) presence of consecutive maximum and minimum in the rheological curve stress vs. shear rate, for foams stabilized by co-surfactants with high surface modulus; (3) presence of significant foam-wall yield stress for all foaming solutions. These effects were explained with the formation of polymer bridges between the neighbouring bubbles in slowly sheared foams (for inside foam friction) and between the bubbles and the confining solid wall (for foam-wall friction). However, the addition of Merquat 100 did not affect noticeably any of the foam rheological properties studied. The foam film observations and surface tension measurements showed that this polymer adsorbs on the bubble surfaces, but forms thin adsorption layers which do not bridge the surfaces of the foam and wetting films.

To clarify the key molecular characteristics of the polymers, which lead to this very different behaviour of Merquat 100 and Jaguar containing foams, for the current study we performed systematic experiments with a series of cationic polymers, which differ in their chemical structure, molecular mass, and charge density—see Table 1 for description of the polymers studied. We used the same main surfactant base, as in our previous studies—a 2:1 mixture of sodium lauryl-oxyethylene sulfate (SLES) and cocoamidopropyl betaine (CAPB), designated as BS (from “Basic surfactants”). This system exhibited excellent foamability and foam stability, and low surface modulus of the bubbles. To obtain systems with high surface modulus, myristic acid (MAc) was added to the BS solution, as in our previous studies [23–27].

Along with the foam rheological measurements (viscous friction inside foam, foam-wall friction), we determined the viscosity and surface tension of the used solutions, and the size of the bubbles after foam shearing under controlled shear rate, which are all quantities needed to interpret the foam rheological data. Experiments with foam films were also performed to determine the effect of the studied polymers on the film thinning behaviour and on the equilibrium film thickness. In addition, the effects of polymers on the surface rheological properties of BS and BS + MAc solutions were studied by oscillating drop method (ODM).

The paper is organized as follows. The methods and materials are described in Section 2. In Section 3.1 we describe the bulk properties of the solutions studied. In Section 3.2 we describe their surface properties. In Section 3.3 we discuss the effect of polymers on the film thinning behavior. In Sections 3.4–3.5 we describe the results for the effects of polymers on the foam properties. The main conclusions are summarized in Section 4.

2. Materials and methods

2.1. Materials

Two series of polymers are studied, according to their chemical content: (1) Merquat series which contains co-polymers of polydiallyldimethylammonium chloride (DADMAC) and acrylic acid or acrylamide, and (2) Lupasol series which is based on polyethylenimine. Merquat polymers are products of Nalco, whereas Lupasol polymers are products of BASF. The polymer properties are described in Table 1, along with their chemical structure (when available). Merquat 100 is a cationic homopolymer of DADMAC, whereas all other polymers are heteropolymers. Polymers from Merquat series have charge density between 2.6 and 6.2 meq/g and molecular mass between 1.2×10^5 and 1.5×10^6 g/mol. Lupasol molecular mass varied between 800 and 2×10^6 g/mol. Polymers from Lupasol series are highly charged with charge density in the range between 8 and 17 meq/g (the charge density is determined by the producer at pH 4.5). The charge density of Lupasol polymers decreases significantly with increasing pH, but no information from the producer is available for the charge density at pH 10 (the natural pH of these polymers).

The basic surfactant system, denoted as “BS”, is a 2:1 mixture (in weight) of the anionic surfactant sodium lauryl-oxyethylene sulfate, SLES (product of STEPAN Co., with commercial name STEOL CS-170) and the zwitterionic surfactant cocoamidopropyl betaine, CAPB (product of Goldschmith, with commercial name Tego Betaine F50). To increase the surface modulus of the BS system, we added myristic acid (MAc).

The procedures for solution preparation were the following: First, we prepared a stock solution of SLES + CAPB (BS). The weight ratio of the active SLES and CAPB in the studied BS-mixtures was fixed at 2:1 and the total surfactant concentration was $C_{TOT} = 10$ wt%. Mixtures of BS + MAc were prepared by dissolving 0.5 wt% MAc in the concentrated BS solution, under mild stirring and heating at 60 °C. For the foaming experiments, these solutions were diluted 20 times with de-ionized water (1 part of the stock solution of BS and 19 parts of de-ionized water). In the prepared BS or BS + MAc stock solutions, we dissolved up to 2 wt% of Lupasol polymers, applying vigorous stirring on magnetic stirrer. The stirring continued until a homogeneous solution was obtained (at least for 1 h). These stocks solutions were kept at room temperature for further studies. The final solutions of BS ± MAc + Lupasol were prepared by direct dilution of 1 g of the concentrated surfactant-polymer solution with 19 g of de-ionized water (1:20 dilution). Therefore, the concentration of the BS mixture in the foaming solu-