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Foaming behaviour of polymer–surfactant solutions

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Abstract

We study the effect of a non-ionic amphiphilic polymer (PEG-100 stearate also called Myrj 59) on the foaming behaviour of aqueous solutions of an anionic surfactant (sodium dodecyl sulfate or SDS). The SDS concentration was kept fixed while the Myrj 59 concentration was varied. Measurements of foamability, surface tension and electrical conductivity were carried out. The results show two opposite effects depending on the polymer concentration: foamability is higher when the Myrj 59 concentration is low; however, it decreases considerably when the polymer concentration is increased. This behaviour is due to the polymer adsorption at the air/liquid interface at lower polymer concentrations, and to the formation of a polymer–surfactant complex in the bulk at higher concentrations. The results are confirmed by surface tension and electrical conductivity measurements, which are interpreted in terms of the microstructure of the polymer–surfactant solutions. The observed behaviour is due to the amphiphilic nature of the studied polymer. The increased hydrophobicity of Myrj 59, compared to that of water-soluble polymers like PEG or PEO, increases its ‘reactivity’ towards SDS, i.e. the strength of its interaction with this anionic surfactant. Our results show that hydrophobically modified polymers have potential applications as additives in order to control the foaming properties of surfactant solutions.

1. Introduction

Foams are dispersions of gas bubbles in a liquid or solid phase [1]. They have received a lot of interest in the last years because of their applications in foods, packaging, mineral flotation, etc. However, the study of the behaviour of foams is relevant not only for the design of materials with new physical properties but also for the understanding of fundamental phenomena in complex fluids.

Aqueous foams are made from solutions of amphiphilic molecules which adsorb to the air/liquid interface [1, 2]. Many physical factors are involved in the control of the features

relevant for applications, i.e. foamability, foam stability, and spatial distribution of the liquid inside the foam. In particular, the stability of foams is affected by three mechanisms: drainage, coarsening and film rupture [1]. These mechanisms are controlled by the interfacial and bulk properties of the solution used to prepare the foam: interfacial and bulk viscosity, dynamic and static surface tension, etc. In this way, much effort has been devoted to finding how to modify these factors in order to obtain the maximum foam stability.

One of the experimental systems most widely used to study foam behaviour is formed with the anionic surfactant sodium dodecyl sulfate (SDS) solubilized in water. It has been shown that the characteristics of foams produced with this surfactant depend on the surfactant concentration. In fact, the stability of micelles correlates with the foamability of the SDS solutions. The minimum (maximum) foamability occurs when the SDS micelles are more (less) stable [3, 4].

When surfactants are mixed in solution with other components, several bulk and interfacial properties change as compared to those of the single surfactant solution [2]. For instance, it is known that the use of a cosurfactant, like an alcohol, can enhance the foamability and change the drainage regime of SDS solutions [5–7].

Other approaches have been used in order to modify bulk or interfacial properties and control foam features: for instance, the mixing of surfactants with water-soluble polymers. The addition of this kind of polymer typically increases the bulk viscosity, as well as the surface viscosity, due to the formation of a polymer–surfactant complex. These effects can increase the drainage time and film lifetime, thus increasing the foam stability [8]. Some groups have studied the effect of non-ionic water-soluble polymers, like polyethylene oxide (PEO) [9, 10] and poly(vinylpyrrolidone) (PVP) [11], on the foams produced with SDS solutions. It has been shown that PEO decreases micellar stability, so the foamability of the mixed polymer–surfactant solutions is increased [10]. Similar results have been obtained when PVP was added to the SDS micellar solutions. In this case, at very low surfactant concentrations, association between surfactant and polymer molecules at the air/liquid interface increases the foam stability. However, when these materials form mixed aggregates in the bulk (intermediate surfactant concentration) the foam stability decreases. Finally, at higher surfactant concentrations, the bulk and surface viscosity are significantly increased, and again the foam stability increases [11]. Since PEO and PVP are neutral polymers, their effect on the foaming behaviour of SDS solutions is due to their weak amphiphilic nature. This is at least the case for PEO, which has a slight tendency to adsorb at the air/liquid interface and to aggregate in solution [12]. If a hydrophobic chain is anchored to the polymer backbone, these amphiphilic features can be enhanced, and thus it is expected that the increased hydrophobicity of the polymer will strongly modify the interfacial properties, and the foaming behaviour of the surfactant solutions.

For this reason, in this work we study the effect of a hydrophobically modified neutral polymer (PEG-100 stearate also called Myrj 59) on the foaming behaviour of SDS solutions. Myrj 59 is an amphiphilic molecule; its polar head is composed of 100 monomers of polyethylene glycol (PEG), whereas its hydrophobic tail is an 18 carbon-long hydrocarbon chain. Its interaction with SDS should be stronger than that of PEO since both polymers have the same monomer, but Myrj 59 has a hydrophobic tail which should bind to the surfactant micelles. In fact, it is well known that the ‘reactivity’ of a polymer towards anionic surfactants, i.e., the strength of its interaction with the surfactant, correlates with its own surface activity [8]. PEO or PEG are relatively weakly surface-active polymers; on the other hand, hydrophobically modified polymers, like Myrj 59, are markedly surface active. Thus, we expect a stronger effect of Myrj 59 on the foaming properties of SDS solutions. In fact, the Myrj surfactant family has been used in several applications in pharmacy [13] and drug delivery [14] because

of its surface activity and micellization properties [15]. Note that in the literature there is a report on the effect of a hydrophobically modified polymer (HM-polyacrylamide) on the foaming behaviour of sodium dodecylbenzene sulfonate (SDBS) solutions [16]. However, in this case the interaction between the cationic polymer and the anionic surfactant has two components: a strong electrostatic attraction and an attraction due to the hydrophobic effect. In the Myrj 59–SDS system studied in our work, the interaction has only the component due to the hydrophobic effect. However, this interaction could be strong enough to promote the formation of a polymer–surfactant complex and thus modify the foamability of the surfactant solutions.

We have performed foaming experiments with foams made with a fixed surfactant concentration, but different polymer content. We have also measured some physicochemical properties of the polymer–surfactant solution in order to correlate their modifications with the behaviour of the studied foams. The paper is divided as follows. In section 2, we describe the experimental techniques. In section 3 we present and discuss our results, and in section 4 we draw some conclusions.

2. Materials and methods

Sodium dodecyl sulfate (SDS 99% purity) was chosen as anionic surfactant. We also used PEG-100 stearate (Myrj 59), a non-ionic amphiphilic polymer. Both materials were supplied by Sigma-Aldrich and were used as received. All solutions were prepared using freshly ultra-purified water (Millipore); its resistivity was $18 \text{ M}\Omega \text{ cm}^{-1}$. We fixed the SDS concentration at 25 mM ($cmc \approx 8 \text{ mM}$) and varied the Myrj 59 concentration. The SDS–Myrj 59 molar ratios studied varied from 30 750:1 to 8:1. The molecular weights of the polymer and surfactant are 4684 g mol^{-1} and 288.4 g mol^{-1} , respectively.

We produced the foams by the air bubbling method. We injected air ($74 \text{ cm}^3 \text{ min}^{-1}$) through a single capillary into 10 ml of the required polymer–surfactant solution contained in a Plexiglas column (diameter 3.2 cm, height 80 cm). With this technique we produced foams with bubbles of initial diameter $D = 5 \text{ mm}$. We recorded the height of the foam produced during two minutes of air supply. We performed at least three experiments with each sample in order to assure that the results were reproducible. The reported values are averages of the measured values.

Surface tension was measured by the pendent drop method (Tracker IT Concept apparatus). For the electrical conductivity measurements we used a conductivity meter (Radiometer Analytical CDM210). All the experiments were performed at $25 \text{ }^\circ\text{C}$.

3. Results and discussion

We studied the foamability behaviour of SDS micellar solutions as a function of the polymer content. In figure 1(a) we show the height after 2 min of the foams produced by the bubbling method as a function of Myrj 59 molar concentration. The horizontal line in the picture represents the height of foam produced with a pure SDS solution. Note that this value (adjusted for different gas flow and tube diameter) agrees within experimental error with the result reported in reference [5].

In figure 1(a), we see that low concentrations of polymer ($c \leq 0.20 \text{ mM}$) increase the foamability of the solutions as compared with the pure SDS solution. The foams produced with these polymer concentrations reached heights 17% higher than that of the pure surfactant solution. On the other hand, when the polymer concentration is $c > 0.2 \text{ mM}$, the foamability of the solutions decreases abruptly. For these polymer concentrations, the heights of the foams

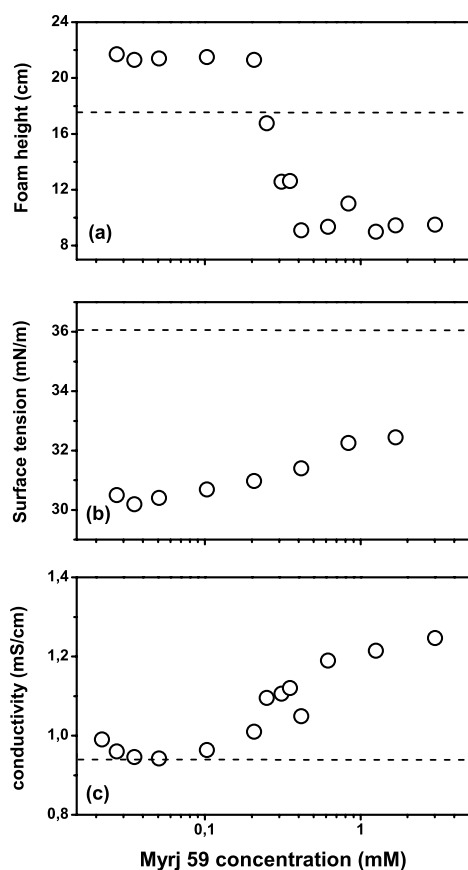


Figure 1. Changes on the properties of SDS solution with the concentration of Myrj 59 (a) foam height, (b) surface tension and (c) electrical conductivity. The SDS concentration was fixed at 25 mM (~ 3 times the CMC). The dashed line is the value for the SDS solution without polymer.

are smaller by 48% than that of the pure surfactant solution. Thus, the polymer concentration plays an important role in the foamability of the solutions.

The different foamability behaviour of the polymer–surfactant samples is due to modifications in the surface and bulk properties of the system. In figure 1(b), we plot the surface tension of solutions of fixed SDS concentration but increasing Myrj 59 concentration in the range where the foamability modification occurs. The broken line represents the surface tension of a pure surfactant solution. At low polymer concentration, the surface tension is about 16% lower than that of a pure SDS solution, indicating a strong adsorption of the polymer to the air/liquid interface. This low surface tension explains the high foamability at these polymer concentrations. In fact, the energy necessary to create the foam is related to the air/liquid interfacial area A by

$$E = \gamma A \quad (1)$$

where γ is the surface tension. Since γ is low, the flux of air through the solution produces large interfacial areas when the polymer concentration is low.

As the polymer concentration increases, the surface tension increases progressively, increasing the energy associated with the air/liquid interface and thus reducing the foamability

Table 1. Typical $t_{1/2}$ times of foams with different polymer concentrations.

Myrj 59 concentration (mM)	$t_{1/2}$ (s)
0	660
0.000 81	1120
0.027	1140
0.41	125
1.68	240

of the solutions. Note however that the increase in surface tension is not enough to explain why the foamability for higher polymer concentrations is lower than that of pure surfactant solutions. A similar effect has been observed with the same surfactant but different counterions [17]. This is due to the competitive action of three mechanisms: interfacial area expansion, surfactant monomer diffusion and breakdown of micelles.

In fact, the increase in surface tension with increasing polymer concentrations indicates that amphiphilic molecules (probably polymer and surfactant) leave the interface and form aggregates in the bulk. This result agrees with measurements of the electrical conductivity of the same polymer–surfactant solutions. In figure 1(c), we observe that the electrical conductivity has a constant value for polymer concentrations $c \leq 0.2$ mM. After this concentration, the electrical conductivity increases and reaches a value 32% higher than that of the SDS solution. These variations indicate modifications in the bulk structure of the solutions. As the Myrj 59 molecule is neutral, the increase in electrical conductivity of the solution can only be due to the presence of surfactant molecules in the bulk. Note that the polymer concentrations over which the surface tension and electrical conductivity change agree with those where the foamability decreases (figure 1).

Note that the stability of the foams is also different when the polymer content is modified. In order to estimate the stability of the foams, we followed the time evolution of the foam height after stopping the air flow. Then we measured the time taken by the foam to decay to half the original height, $t_{1/2}$. It can be appreciated that the foam produced with the pure surfactant solution disappears at a moderate rate, while the foams produced with polymer–surfactant solutions exhibit different behaviours. When the polymer concentration is low ($c < 0.2$ mM), the foams have an increased lifetime, i.e. they are more stable than those of pure SDS solutions. On the other hand, when the polymer concentration is higher ($c > 0.2$ mM) the foams disappear faster. In table 1 we give typical $t_{1/2}$ times. Small polymer concentrations increase the lifetime of the SDS foams by almost 70%, while higher polymer concentrations decrease it until 64% of the pure SDS value.

Note that other possible factors could play a role in the observed modifications of foamability and foam stability in our system. Among these factors we can list variations in gas solubility, solution viscosity and equilibrium film thickness, as well as the effect of depletion forces. These properties can change with polymer concentration and thus affect the foamability of the solutions. However, we can conclude by different means that this is not the case in our system.

For instance, it is well known that an increase in gas solubility may enhance the coarsening of air bubbles due to gas diffusion related with different Laplace pressures in bubbles of different sizes [1]. However, since the bubbling method produces foams with monodisperse bubbles, this effect is not very important in our system. In addition, if coarsening due to gas solubility were important, breakage of bubbles would occur with a random distribution throughout the foam, and bubble coalescence would be homogeneous in space, an effect not observed in our foams, which always break at the top.

On the other hand, variations in liquid viscosity can modify the rate of drainage and thus the rate of foam production. We measured the bulk viscosity as a function of polymer content. The measured values have a slight dependence on the polymer concentration, from $\eta_r = 1.05$ for the less concentrated sample, to $\eta_r = 1.10$ for the highest polymer concentration. $\eta_r = \eta_s/\eta_w$ is the relative viscosity of the solution (η_s) to that of water (η_w). This small increase on the liquid viscosity could reduce the liquid flow rate through the plateau borders. However, this effect would contribute to an increase in foam stability in a similar way as water-soluble polymers [8], and does not explain the observed behaviour. In addition, preliminary free-drainage results showed no dependence on the polymer concentration, indicating that variations in solution viscosity do not affect our experiments.

Finally, note that addition of the polymer and the formation of the polymer–surfactant complexes could give rise to depletion interactions between bubbles. Such interactions could affect the foamability in our system. These kinds of ‘structural’ forces are present in surfactant films of ionic surfactants at concentrations above the *cmc*, where micelles are formed. The confinement of the micelles between the films induces a layering of the aggregates which induces a damped oscillatory disjoining pressure [18]. However, it has been found that effective volume fractions of at least 20 vol% of ionic surfactants (CTAB, AOT) are required to observe these structural forces [19, 20]. In the case of SDS, no oscillations are observed at small concentrations (9 mM); ‘structural’ forces are present at high concentrations (100 mM), when the surfactant layers approach at distances below 50 nm [21]. We can rule out the influence of depletion interactions in our study because the surfactant and polymer concentrations are low. In addition, since the foam is not dry at the end of the foamability experiment, the liquid film thickness has not reached the value at which such forces are present.

4. Conclusions

We have studied the effect of a non-ionic amphiphilic polymer (Myrj 59) on the foaming behaviour of solutions of the anionic surfactant SDS. Our results show that the polymer concentration controls the foamability of the surfactant solutions. Low polymer concentrations ($c < 0.4$ mM) increase the foamability of the solutions as compared with the pure SDS solution. On the other hand, higher polymer concentrations ($c > 0.4$ mM) decrease the foamability. This behaviour is due to modifications in the surface and bulk properties of the polymer–surfactant system. Surface tension and electrical conductivity experiments show that for polymer concentrations $c > 0.4$ mM, polymer–surfactant aggregates are formed in the bulk. Thus, foamability is decreased because less amphiphilic molecules are available for stabilizing air/liquid interfaces, and because the polymer–surfactant aggregates are stable enough to diminish the flux of amphiphilic molecules necessary to stabilize new air/liquid interfaces. The observed behaviour is due to the amphiphilic nature of the hydrophobically modified polymer. The increased hydrophobicity of Myrj 59, compared to that of water soluble polymers like PEG or PEO, increases its ‘reactivity’ towards SDS, i.e. the strength of its interaction with this anionic surfactant. Our results show that hydrophobically modified polymers have potential applications as additives in order to control the foaming properties of surfactant solutions.

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