

Supplementary Material (ESI) for Soft Matter

## SUPPLEMENTARY INFORMATION

### **Polymeric surfactant stabilised air-in-water foams; correlating phase behaviour, molecular structure and foam characteristics**

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#### **Foam assessment**

Foam stability tests were used to quantify the behaviour of aqueous foam stabilised with Pluronic surfactant.

##### *Foam stability*

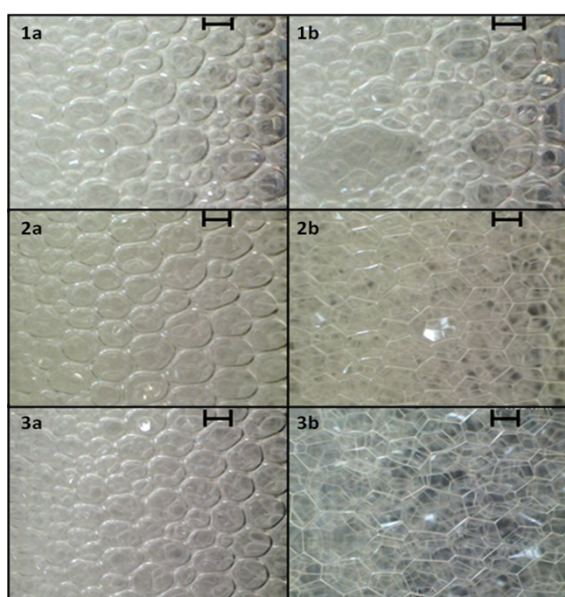
Foam stability tests were performed in a graduated glass column (45cm height and 20mm internal diameter) fitted with a porous fritted disk (nominal porosity of 2 $\mu$ m) situated at the base of the column and insulated with a water jacket to ensure temperature control.

All experiments were performed at  $20 \pm 0.5$  °C with both the column and surfactant solution equilibrated to the desired temperature prior to beginning the measurements. A 2.5 cm<sup>3</sup> aliquot of surfactant solution was inserted into the top of the column above the fritted disk. Nitrogen gas was passed through the disk into the surfactant solution at a constant flow rate of  $0.08 \pm 0.01$  L/min and 0.8 bar pressure. A standard height of foam (15cm) was created for a fixed surfactant concentration (flow rate 0.08 L/min, 0.8 bar) after which the gas flow was turned off and the static foam allowed to drain under gravity. The half-life of the foam ( $t_{1/2}$ ), the time taken for the foam to decay to half of its original height, was recorded. New aliquots of solution were used for each foam test and the column thoroughly rinsed with deionised water between each test, to ensure reproducibility of results.

Images of static foams in the foam column were obtained using a Veho VMS-004 USB microscope at 20x zoom. Images were recorded from the side profile, through the column wall and were taken within 5 seconds of foam formation and sometime after foam formation to demonstrate how foam structure varies with foam age. The time at which the aged foam images were captured varied depending on the half-life of the foam.

## Results and discussion

Visual inspection of foam structure for the Pluronic surfactants, listed in Table 1, indicated that the various surfactants behave rather differently, Scheme 2, and that the structures of the bubbles formed varied markedly with Pluronic. Illustrative data only are presented. For all newly prepared foams, bubbles appeared spherical, separated by thick lamellae walls (Scheme S1, 1a-3a). However, as P123 (and F108 – data not shown) foams aged, the spherical structures distorted into multi-sided polyhedral cells with thinner cell walls (Scheme S1, 3b). This was also observed for PE6800 although to a lesser extent (Scheme S1, 2b), whereas foams of L62 and PE6400 (not shown) broke down before drainage and distortion of cells occurred (Scheme S1, 1b).



Scheme S1; Differences in foam structure for newly prepared foam (left) and aged foam (right) for 5% (w/v) solutions of PE6400 (1a,b), PE6800 (2a,b) and P123 (3a,b) at 20°C. Scale bar is 1mm in all cases.

One approach to quantify this difference in stability is via the half-life, which is strongly dependent on the surfactant composition, figure S1.

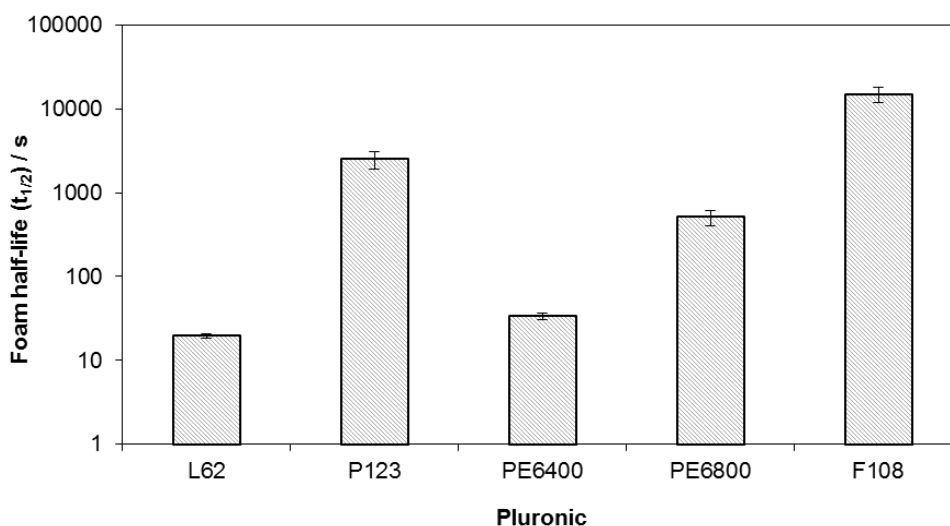


Figure S1; Stability of the air-in-water foams as a function of Pluronic type; [Pluronic] = 5% (w/v), flow rate 0.08 L/min, 0.8 bar. The stability of the foam presented on a logarithmic scale is quantified in terms of the foam half-life,  $t_{1/2}$ , as described in the Experimental section. At the stated concentration, P123 is the only surfactant above its critical micelle concentration (CMC). All other surfactants are far below their CMC.

From this relatively simple assessment, two conclusions are apparent. Firstly, those surfactants with largest hydrophobic block, P123 (PPO 4000 $\text{g}\cdot\text{mol}^{-1}$ ) and F108 (PPO 3250 $\text{g}\cdot\text{mol}^{-1}$ ) produce significantly more stable foams as can be seen in their longer lifetimes. It is generally accepted that polymeric surfactants of this type adopt a conformation at the interface in which the hydrophobic block is anchored at the surface whilst the hydrophilic blocks, with their strong affinity for water, protrude into the aqueous phase.<sup>1-3</sup> Polymeric surfactants with larger PPO block have been shown previously<sup>4</sup> to occupy a smaller area at the interface forming a more tightly packed layer. This was previously observed for poly(ethylene oxide) alkyl ether surfactants<sup>5</sup> in which the most stable foam was produced for surfactant with the smallest area per molecule and longest hydrocarbon chain. Reported values for surface area per molecule for both P123 and F108 at 25°C are 50 and 150 Å<sup>2</sup> respectively<sup>4</sup> so on this basis alone one would expect that P123 with its larger PPO mass and smaller area per molecule would provide the greatest degree of stabilisation. However, F108 produces the most stable foam and it is this simple argument that requires elaboration. Firstly, it is necessary to look further at the surfactant structure and consider the size of the PEO blocks (and thus the overall molecular weight). Sedev et al<sup>1</sup>, determined that the adsorbed layer thickness increases with number of EO segments in the PEO chain suggesting that F108 (130 EO segments, compared to 20 EO segments in P123) will exhibit a thicker adsorbed layer at the interface. It is also well known that at separations comparable to twice the surfactant adsorbed layer thickness, long chain PEO groups repel each other providing steric stabilisation; the effect increasing with increasing length of EO chain.<sup>6</sup> Results here

correlate to the findings of Rippner Blomqvist et al<sup>7</sup> who determined that stability increases with the overall size of the polymer and longer PEO chains produce greater foam stability. They suggest that for block copolymer systems good foam stability requires long range steric repulsion. Secondly, the phase behaviour of the copolymers also needs to be considered. At 5%w/v concentration, P123 has is above its CMC and therefore micelles are present in solution suggesting their presence promotes foam stability. Similar findings were observed for dodecyl stabilised foams<sup>8</sup> in which surfactants which formed the most stable micelles produced the most stable foam. This has been attributed to the findings of Wasan and co-workers<sup>9, 10</sup> who established that micelles located within the lamella walls form ordered structures which enhance foam stability by a step-wise film thinning mechanism.

A much less notable increase in foam lifetime is also observed for those surfactants with constant PPO molecular weight and increasing PEO molecular weight (L62, 20% PEO; PE6400, 40% PEO; PE6800, 80% PEO) with foam stability following the order PE6800 > PE6400 > L62. As discussed previously, it is predicted that of this series PE6800 will produce the thickest adsorbed layer due to the larger size of the PEO block (and greater overall molecular weight).

It is worth highlighting that foam stability displays a greater dependence on the overall molecular weight of the polymeric surfactant, rather than the size of the hydrophobic block, and the presence of micelles in solution promotes stability as can be seen by the longer lifetime of P123. In fact, L31 (molecular weight 1100gmol<sup>-1</sup>), the surfactant with lowest molecular weight of those commercially available displayed such poor foaming ability that it was not possible to record the foam lifetime, demonstrating the importance of parameters such as molecular weight and degree of hydrophobicity on foam behaviour.

## References

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