

## Critical micelle concentration measurement in aggregation behaviour studies

This application note illustrates how the Attension Sigma Force Tensiometer can be used to study aggregation behaviour.

### Introduction

Critical micelle concentration (CMC) is defined as the concentration of surfactants in which micelles are spontaneously formed. Below the CMC point surfactant molecules tend to accumulate at the interface, reducing surface tension. At CMC, the surface tension of the solution does not change but remains constant, as the gas-liquid interface is already saturated with the surfactant molecules. Above the CMC point most of the surfactant molecules are inside the bulk, aggregating into micelles. When this occurs, the addition of surfactants just increases the number of micelles and the surface tension becomes independent of surfactant concentration.

There are several factors affecting the CMC point of a surfactant. These include the amphiphile chain length, dissolved salts, the structure of the head group, temperature, the structure of the alkyl chain and polar additives. The effects of chain length, salts and alcohol on the critical micelle concentration have been widely studied [1]. The exact molar weight and impurities in the surfactant also influence the CMC, and therefore a careful purification of the surfactant is relevant. A common and much studied surfactant found in many detergents is sodium dodecyl sulfate (SDS). SDS is easily hydrolyzed to dodecanol, which can be seen as a possible contaminant [2].

The critical micelle concentration is a useful measure also in pharmacology. Silicon surfactants are important in pharmaceutical and cosmetic industry due to their low price and technological advantages [3]. Liposomes can be used to carry non-polar drug molecules in blood where as polymeric nanoparticles are found to be useful in selective delivery of cancer drugs [4]. Studies on interfacial properties of these drug carrying compounds require the full understanding of the molecule's CMC.

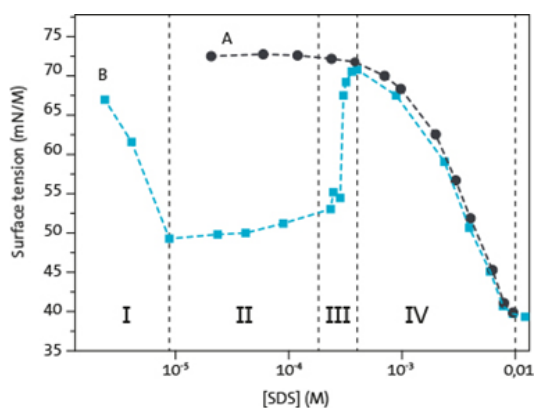


### Case study: Aggregation behaviour of porphyrins in presence of surfactants

Porphyrins are naturally occurring heterocyclic macrocycles that are recently found to have a wide variety of applications especially in therapeutic drugs and targeting agents as well as molecular electronics. One of the best known porphyrins is heme, the pigment in red blood cells. Dissolved porphyrins have a tendency to form aggregates through noncovalent bonding. It is known that strong intermolecular interactions occur between porphyrins and surfactants. The nature of these interactions have been studied,

however the cause of the aggregation process has remained unknown. Yaffe et al. [5] have studied the aggregation behavior of Fe(III)tetrakis(4-N-methylpyridinium)porphyrin (Fe(III)TMPyP) when sodium dodecyl sulfate (SDS) is present. A new species of Fe(III)TMPyP with SDS has been reported at submicellar surfactant concentrations. These results are significant in the applications of Fe(III)TMPyP in bionics and medicine.

Yaffe et al. [5] used Sigma 70 tensiometer (Attension, previously KSV Instruments) to study surface tension of aqueous solutions of pure SDS as a function of concentration. The same measurement was conducted with a constant concentration ( $6 \times 10^{-5}$  M) of Fe(III)TMPyP in the solution. No change in the SDS critical micelle concentration was observed due to the porphyrin. At SDS concentration of around  $2 \times 10^{-4}$  M macroscopic precipitation of aggregates was observed, but some of the porphyrin still remained surface active. Two possible results are suggested: the addition of SDS causes the change in the properties of the colloid, or causes the colloids to break up to smaller particles.



[Figure 1]: Surface tension of aqueous solutions of SDS as a function of concentration (curve A) and of SDS solutions containing  $6 \times 10^{-5}$  M Fe(III)TMPyP (curve B). The circle indicates the concentration of SDS at which precipitation precipitation is observed. Dashed vertical lines indicate regions with different surface behavior.

## Conclusion

Critical micelle concentration studies have been known to be important for decades in all areas containing surfactants. Surfactants are relevant in many chemical manufacturing processes and therefore precise and accurate results of CMC studies are essential in order for these processes to be successful. CMC studies also play an important role in targeted drug delivery development.

## References:

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