

## Interfacial and foaming properties in film-forming cationic mixtures

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### Introduction

Mixtures of cationic and anionic surfactants have attracted great interest because of their strong synergism in bulk and interfacial properties. A great variety of aggregation morphologies can be found in these kind of systems, e.g. mixed micelles, stable vesicles, lamellar, hexagonal and cubic liquid-crystalline phases. It has been reported that solid thin film formation occurs at the air/water interface from cationic surfactant mixtures and hydrophilic polymers [1]. In this work we investigated the interfacial and foaming properties of the cationic system, namely cetyltrimethylammonium bromide (CTAB) / sodium dodecyl sulphate (SDS) mixtures at different molar ratios, in the range below 1.0%wt, and in the absence of polymer. Interfacial behavior was determined using surface tension measurements, and the results were correlated with bulk aggregation, using conductivity and fluorescence techniques. Foaming properties were also investigated using a modified Ross-Miles method.

### Results and Discussion

Surface tension isotherms were obtained and interfacial parameters (surface excess and area per molecule) were calculated. The values evidenced the formation of a more compact monolayer at the air/solution interface in the cationic systems, compared to individual surfactants. Aggregation in bulk showed two distinct stages with increasing concentration (Fig. 1), likely related to different phase transitions in the microheterogeneous system.

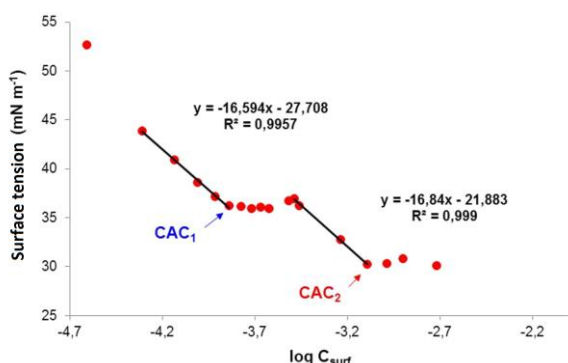


Figura 1. Surface tension profile of C:S (90:10).

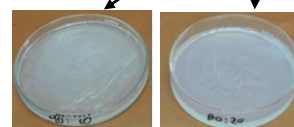
This result was confirmed by three different techniques (Table 1), correlating surface process with aggregation in solution. The CAC values are smaller than those in the pure systems.

Table 1. Aggregation in cationic systems

Technique	CMC (mol L <sup>-1</sup> )		CAC <sub>1</sub> (mol L <sup>-1</sup> )		CAC <sub>2</sub> (mol L <sup>-1</sup> )	
	CTAB (C)	SDS (S)	C:S (90:10)	C:S (80:20)	C:S (90:10)	C:S (80:20)
Conductivity	1.0	7.9	-	-	1.2	0.12
Surface tension	0.81	6.2	0.071	0.014	1.0	0.070
Fluorescence	1.0	-	0.20	0.9*	1.0	1.0

\* estimated

Solid film formation was observed in mixtures with cationic excess (0.75%wt), which suggests a need for an excess of CTAB in the mixture, either because the positive charge or the higher hydrophobicity of the aggregates.



The mixtures also showed a synergy in the interfacial properties, yielding more stable foams than those obtained using the individual surfactants.

Table 2. Foamability and stability (@CMC)

	CTAB (C)	SDS (S)	C:S (90:10)	C:S (80:20)	C:S (60:40)
h <sub>0</sub> (cm)	6.4	6.2	7.3	6.5	3.9
R <sub>5</sub> (%)	73	93	89	94	18
R <sub>30</sub> (%)	39	85	82	89	13

### Conclusions

Cationic mixtures of SDS and CTAB have a synergy in the interfacial properties and bulk aggregation in relation to the pure surfactants, due to reduced repulsion between surfactant heads. These effects occur even in the dilute regime (<1%wt). Phase transitions can occur in these systems, and in the mixtures with excess CTAB, spontaneous formation of solid films at the air/solution interface occurs, without the need of polymer in the system. Best results regarding stability and foamability were also obtained in mixtures with excess cationic surfactant (10:90 > 20:80 > 40:60), which indicates that the monolayer at the interface has greater cohesion, due to attractive interactions.

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<sup>1</sup> B.M.D. O'Driscoll, E.A., K.J. Edler, *Chem. Commun.* **2007**, 1068.