

## Surface properties of fluorinated surfactants

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Surfactants are amphiphilic molecules that have found use in a wide range of pharmaceutical applications either as adjuvants or as the delivery vehicle *per se*. Most pharmaceutical applications to date have utilised surfactants containing hydrophobes composed of hydrocarbon chains. Increasingly however, new classes of surfactant are being developed (such as fluorocarbon and silicone-based molecules) that may have significant advantages over the more commonly used hydrocarbon-based molecules for the purposes of pharmaceutical formulation. For example, as fluorine atoms are known to confer a greater hydrophobicity to a molecule compared to their hydrocarbon counterparts, it would therefore be expected that the fluorocarbon surfactants would exhibit a greater surface activity. A low surface tension is vitally important for the wetting of surfaces and the formation of stable dispersions. However, there is very little data in the literature reporting the surface behaviour of fluorinated surfactants. The aim therefore of the present study is to compare the surface properties of non-ionic fluorinated surfactants with the hydrocarbon surfactants.

Monodisperse fluorinated surfactants (of the general structure  $C_mF_{2m+1}(CH_2)_n(OC_2H_4)_pOH$ , where  $(OC_2H_4)$  is denoted by E) were synthesised according to a scheme adapted from Selve et al (1990) and the pure hydrocarbon surfactants were purchased from Fluka.

Surface tension measurements were carried out using the Wilhelmy plate technique in ultrapure water at 25°C. The table shows the critical micelle concentration (cmc), the area per surfactant molecule just below the cmc, and the surface tension attained at the cmc ( $\gamma_{min}$ ) for some of the surfactants tested. The figure shows a typical surface tension curve obtained.

The results clearly illustrate that the fluorinated surfactants follow the same trend as that reported for hydrocarbon surfactants in that lengthening the fluorophobe decreases the cmc, while increasing the head group increases the cmc. It is also clear that there is a considerable effect on the cmc on replacing the  $CH_2$  group with a  $CF_2$ , as the fluorinated surfactants exhibit much lower cmcs.

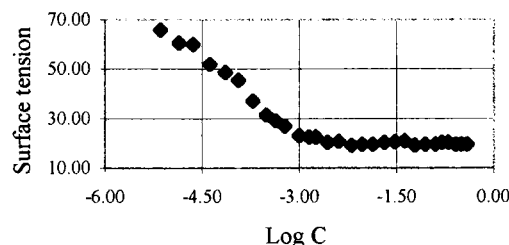
Surface properties data for fluorinated and hydrocarbon surfactants

|                        | cmc $10^3$<br>(moles $l^{-1}$ ) | Area per<br>molecule<br>( $\text{\AA}^2$ ) | $\gamma_{min}$<br>( $mNm^{-1}$ ) |
|------------------------|---------------------------------|--|----------------------------------|
| $C_7F_{15}CH_2E_4$     | 0.24                            | 49.7                                       | 19.5                             |
| $C_6F_{13}CH_2CH_2E_4$ | 1.28                            | 40.5                                       | 19.1                             |
| $C_6F_{13}CH_2E_4$     | 1.80                            | 47.4                                       | 18.6                             |
| $C_7F_{15}CH_2E_6$     | 0.55                            | 44.5                                       | 19.5                             |
| $C_6F_{13}CH_2CH_2E_6$ | 1.70                            | 53.9                                       | 19.5                             |
| $C_6F_{13}CH_2E_6$     | 2.10                            | 46.9                                       | 19.6                             |
| $C_{12}E_4$            | 0.48                            | 47.7                                       | 30.1                             |
| $C_8E_4$               | 1.97                            | 38.6                                       | 32.7                             |

If we examine the data more closely we begin to see a pattern emerging at least in terms of the cmc. That is the emergence of an equivalency rule also proposed by Ravey (1994) suggesting that, within a homologous series, a surfactant containing a fluorophobe is equivalent to a surfactant containing a hydrophobe 1.5 times in length. Here it can be seen experimentally that in terms of their cmc,  $C_7F_{15}CH_2E_4$  is approximately equivalent to  $C_{12}E_4$ . This gives us a ratio of approximately 1.7 (not all data shown).

Finally the fluorinated surfactants possess a much greater surface activity than their hydrocarbon counterparts as demonstrated by the much lower values of  $\gamma_{min}$ .

Surface tension of  $C_7F_{15}CH_2E_4$



Fluorinated surfactants therefore have a potential in the stabilisation of aqueous dispersions.

Ravey, J., Stebe, M.: *Colloids Surfaces A: Physicochem Eng Aspects* (1994), 84, 11-31

Selve, C., Achifelu, S., Mansuy, L.: *Synthetic Communication* (1990), 20, 6, 708-807