# A FLUORESCENCE METHOD FOR THE DETERMINATION OF CRITICAL MICELLE CONCENTRATION OF IONIC SURFACTANTS

R.R. Moody, K. Nelson, School of Pharmacy, Robert Gordon's Institute of Technology, Schoolhill, Aberdeen, AB1 1FR.

Critical micelle concentration (cmc) determination by measurement of changes in surface tension ($\gamma$) (Elworthy & Mysels 1966) or conductivity (K) (Attwood et al 1974) is difficult because such methods lack the necessary sensitivity required to enhance the detection of the transition to micelle formation occurring around the cmc. This is particularly true for low molecular weight surfactants. We describe the preliminary results of a fluorescence method based on the fact that a fluorophor may show a change in its fluorescence properties (a) due to ion pair or complex formation prior to the cmc or (b) due to solubilisation in the micelles after the cmc (Corrin & Harkins 1947). Dipyridamole (DPD) - $pK_a$ 6.4 - was used for the determination of the cmc values of both cationic and anionic surfactants; 9-anthracene carboxylic acid (AC) - $pK_a$ 3.6 - was used for cationic surfactants. All fluorescence measurements were made using a Baird Atomic ratiometric spectrofluorimeter model RC 200. The temperature was controlled at $25^0$C.

For sodium lauryl sulphate (NaLS), solutions were prepared of molarity 0.001 to 0.020 in deionised water each $7.6 \times 10^{-6}$ molar in DPD. The fluorescence of each was measured relative to a $7.6 \times 10^{-6}$M DPD solution using a $\lambda$ excitation of 400 nm and $\lambda$ emission of 500 nm. The fluorescence increased linearly as the NaLS concentration increased and showed a characteristic sharp, marked, decrease in slope above the cmc. The determined cmc value was $8.0 \times 10^{-3}$M at $25^0$C; cf $\gamma$ ($8.4 \times 10^{-3}$M), K ($8.5 \times 10^{-3}$M) and literature ($8.2 \times 10^{-3}$M) (Florence & Attwood 1982) values. The method was particularly applicable to difficult $\gamma$ and K cmc determinations, e.g. butyric acid (cmc found 0.91M), 1-octanesulphonic acid (cmc found 0.162M).

For cetrimide, solutions were prepared of molarity $5 \times 10^{-5}$ to $5 \times 10^{-3}$ each $1.1 \times 10^{-6}$M in AC. The fluorescence of each was measured relative to a $1.1 \times 10^{-6}$M AC solution using a $\lambda$ excitation of 365 nm and a $\lambda$ emission of 410nm. A similar pattern to that seen with DPD - NaLS was observed. The determined cmc value at $25^0$C was $2.8 \times 10^{-3}$M; cf $\gamma$ ($2.8 \times 10^{-3}$M), K ($2.8 \times 10^{-3}$M - poor change in slope) and literature ($2.9 \times 10^{-3}$M) (Florence & Attwood 1982) values. AC did not show any change in fluorescence with NaLS. DPD in the presence of cetrimide showed no change in fluorescence until the cmc was approached and exceeded (cmc $2.6 \times 10^{-3}$M).

Both the DPD - NaLS and the AC - cetrimide ion pair or complex were extractable with pentane prior to the cmc but not after. DPD was not extractable in the presence of cetrimide. It is suggested that solubilisation of the ion pair or complex in the former and the non-ionised form of DPD in the latter is responsible for the observed changes in fluorescence. The enhancement in fluorescence is probably due to a decrease in collisional deactivation effects (Corren & Harkins 1947). The use of a charged fluorophor is not obligatory; a weak electrolyte such as DPD can be used to determine the cmc of both types of ionic surfactant.

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