Fluorescence Probe Studies on Alkylcarbazolesulphonates in Aqueous Solution

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The fluorescence probe properties of sodium 9-alkylcarbazolesulphonate and sodium ω-carbazol-9-ylalkanesulphonate (alkyl = $C_{10}H_{21}$ or $C_{12}H_{25}$) in micellar solutions have been examined, and their excimer formation confirmed.

When a fluorescent substance is merely solubilized with a surfactant, the exact location of the substance in the micelle and the amount of solubilization can not be determined. In order to overcome these problems, functional micelles with an attached chromophore as the head group have been studied. The micellar properties and photochemical processes of sodium 9-alkylcarbazolesulphonate,[1] sodium 12-phenothiazin-10-yldodecanesulphonate,[2] n-(9-anthroyloxy)-fatty acid,[3] methyl viologen derivatives,[4] and sodium 10-dodecyl-9-anthrylmethanesulphonate[5] have been reported. We report here the synthesis of two surfactants in which the carbazole group is located either in the rim or in the core of the micelle. Their micellar aggregation properties have been compared by fluorescence spectrum measurements. This type of study will be useful for the determination of the photo-induced charge separation mechanism.

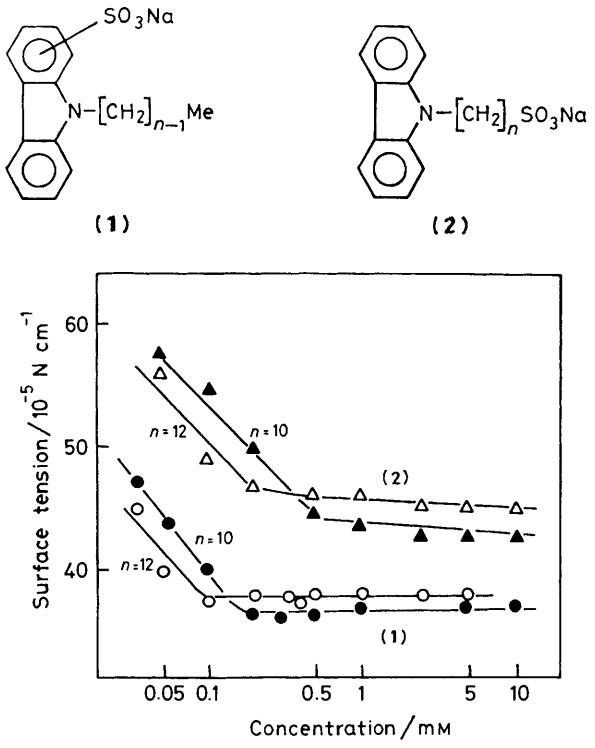

Figure 1. Relationship between surface tension and concentration at pH 10.5 and 36 °C. The surface tension was measured by the Wilhelmy vertical plate method with a Shimadzu ST-1 tensiometer.

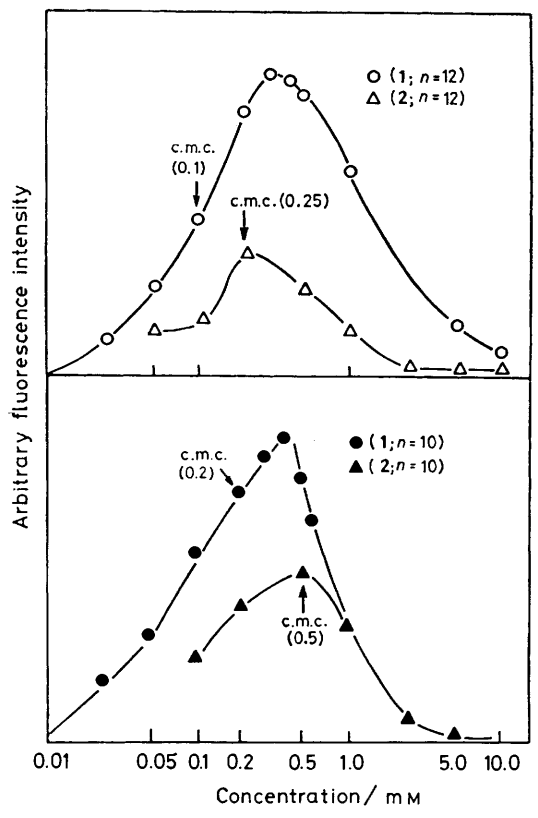

Figure 2. Relationship between fluorescence intensity I_m at 371 nm excited by radiation of wavelength 331 nm and concentration.

The surfactants were prepared as follows. After conversion of carbazole (0.18 mol) into the *N*-sodium salt by treatment with 0.18 mol of sodium hydride in 150 ml of hexamethyl phosphoramide under an atmosphere of nitrogen at 0 °C, 0.18 mol of 1-bromodecane or 1-bromododecane was added according to Rubottom's method.[6] This was followed by sulphonation with chlorosulphonic acid and neutralization with sodium hydroxide to give sodium 9-alkylcarbazolesulphonate (**1**) (alkyl = $C_{10}H_{21}$ or $C_{12}H_{25}$), on recrystallization from ethanol {i.r. (cm^{-1}): 1200(S=O), 1330, 1115(O=S=O), 1600(C=C), 730, and 750 (carbazolyl); ^1H n.m.r. (Me_2SO) δ: 0.87(–CH_3), 1.25 (–$[CH_2]_n$–), 1.80(N–CH_2–CH_2–), 4.42 (N–CH_2–), and 7.50—8.42 (carbazolyl)}.

By a similar procedure, ω-bromoalkylcarbazole was derived from the sodium salt of carbazole and 1,10-dibromodecane or 1,12-dibromododecane. This was followed by sulphonation with sodium sulphite to give sodium ω-carbazol-9-ylalkanesulphonate (**2**). Recrystallization from ethanol gave the pure product {i.r.(cm^{-1}): 1200(S=O), 1300, 1115(O=S=O), 1600 (C=C), 730, and 750(carbazolyl); ^1H n.m.r. (D_2O) δ: 1.25 (–$[CH_2]_n$–), 2.05(N–CH_2–CH_2–), 2.54(–CH_2–SO_3Na), 4.26 (N–CH_2–), and 7.70—8.50(carbazolyl)}.

The maxima in the u.v. spectra of carbazole and its derivatives are as follows: λ_{max}^{EtOH} carbazole 323, 337; decylcarbazole 330, 344.5; bromodecylcarbazole 331, 344.5 nm. *N*-Alkylation of carbazole resulted in a shift to longer wavelength. Sulphonation caused only a small shift of the two peaks [(**1**; $n = 10$), $\lambda_{max}^{H_2O}$ 331, 347.5 and (**2**; $n = 10$) $\lambda_{max}^{H_2O}$ 331, 347.5 nm]. The molar absorption coefficient (ε) at 347.5 nm was measured at concentrations on either side of the critical micelle concentration (c.m.c.). The value decreased with increasing concentration and at a concentration above the c.m.c. value the following definite values were obtained: $\epsilon = 2.45 \times 10^3$ for (**1**; $n = 10$), $\epsilon = 2.60 \times 10^3$ for (**1**; $n = 12$), $\epsilon = 0.89 \times 10^3$ for (**2**; $n = 10$), and $\epsilon = 1.38 \times 10^3$ dm^3 mol^{-1} cm^{-1} for (**2**; $n = 12$). These results reflect the difference between the monomeric state below the c.m.c. and the aggregated ground-state form above the c.m.c.

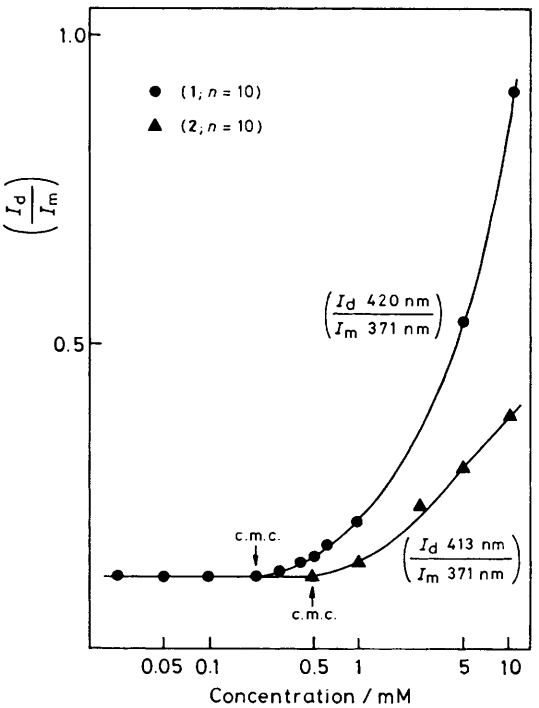

Figure 3. The ratio I_d/I_m for probes (**1**; $n = 10$) and (**2**; $n = 10$) as a function of concentration, where I_d is the fluorescence intensity of the excimer band and I_m is the maximum fluorescence intensity at 371 nm.

The relationship between surface tension and concentration is shown in Figure 1. The C_{12}-derivative has a lower c.m.c. than the corresponding C_{10}-derivative. The c.m.c. and surface tension of (**1**) are lower than for (**2**). The c.m.c. values were 0.2 mM for (**1**; $n = 10$), 0.1 mM for (**1**; $n = 12$), 0.5 mM for (**2**; $n = 10$), and 0.25 mM for (**2**; $n = 12$).

The fluorescence intensity at 371 nm plotted against concentration of surfactant is shown in Figure 2. The concentration at the maximum fluorescent intensity for (**2**) coincides with the c.m.c. value. Compound (**1**; $n = 10$) exhibited maximum fluorescence intensity at 0.4 mM, greater than the c.m.c. value (0.2 mM), followed by a 'concentration quenching.' Similarly (**1**; $n = 12$) gave the maximum intensity at a concentration (0.3 mM) higher than the c.m.c. value (0.1 mM). As the concentration of surfactant increased further, the intensity of the peak was quenched. From these results, it can be seen that it would be optimum to employ approximately c.m.c. for an efficient redox system. The two structureless bands [420, 437 for (**1**; $n = 10$) and 413, 435 nm for (**2**; $n = 10$)] at wavelengths longer than 371 nm are attributed to excimer formation.

Figure 3 shows the dependence of concentration on the ratio of the intensities at 420 nm or 413 nm due to the excimer and 371 nm due to the monomer (I_d/I_m). No excimer formation was observed in the solution prior to micelle formation but the excimer appeared at the c.m.c. or above. A consideration of the geometrical structure of the carbazole group suggests that it should locate at intervals like a sandwich, to form the micelle.[7] Excimer formation is easier for the derivative having the carbazole group in the rim of the micelle than for the derivative with the carbazole group in the micelle core. Therefore, the opportunity for the correct alignment of pairs of carbazole entities in the core, by conformational changes of methylene segments, is more limited. From the results of light scattering experiments reported by Anacker *et al.*,[8] it is deduced that the c.m.c. is inversely proportional to the aggregation number of the micelle. Since (**2**) exhibited a higher c.m.c. than (**1**), (**2**) should have a smaller aggregation number than (**1**).

In conclusion, since the micellar core-location of carbazole entities limited the conformational changes, excimer formation was difficult. On the other hand, the micellar rim-location of carbazole entities facilitated excimer formation.

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