Available online at www.sciencedirect.com
ScienceDirect
Fluid Phase Equilibria 251 (2007) 110–113
FLUID PHASE EQUILIBRIA
www.elsevier.com/locate/fluid

Spectroscopic investigations on the binding of ammonium salt of 8-anilino-1-naphthalene sulfonic acid with non-ionic surfactant micelles in aqueous media

Stephanie A. Moore, Adam A. Harris, Rama M. Palepu *

Department of Chemistry, St. Francis Xavier University, Canada B2G 2W5

Received 11 August 2006; received in revised form 15 November 2006; accepted 15 November 2006
Available online 19 November 2006

Abstract

The anionic dye 8-anilino-1-napthalensulfonic acid ammonium salt, or ANS, was used as a fluorescent probe to investigate the behaviour of dye-surfactant interactions in aqueous solutions of Triton X-100 and the Brij and polyoxyethylene tridecyl ether (POE TDE) series of polyoxyethylene non-ionic surfactants. The fluorescence behaviour of the dye with the non-ionic surfactants was examined in micellar media. The concentration of surfactant was kept well above the cmc to investigate the interaction of the dye with surfactant micelles. In this investigation, the relative fluorescence enhancements, binding constants of the dye to the surfactant micelles and aggregation numbers of the micelles were determined, from the analysis of spectroscopic data.

Keywords: Micelles; Binding constants; Aggregation numbers; ANS; Non-ionic surfactants

1. Introduction

Fluorescence techniques have become widely employed tools in analytical sciences, and are routinely used in the detection, quantization, identification and characterization of inorganic and organic compounds and of biological structures and processes [1,2]. The study of heterogeneous media, biological media and organized media, such as micelles, has been aided by many solvatochromic fluorescent probes whose spectra or quantum yields are sensitive to their environments [3–6].

The 8-anilino-1-napthalene sulfonic acid ammonium salt (ANS) is one of the most frequently used fluorescence probe to determine the relative hydrophobicities of the binding sites in a number of proteins and to detect the protein conformational changes induced by ligand binding [7]. The properties of ANS fluorescence, such as quantum yield, lifetime, and position of fluorescence maximum, are sensitive to the polarity of the immediate environment surrounding the probe (the micropolarity). In solution, surfactants and dyes can interact and form micellar complexes which have characteristic features [8–10].

ANS is an anionic probe which is essentially non-fluorescent in water, but highly fluorescent in non-polar environments or macromolecules (micelles) [10]. Its wavelength of maximum fluorescence intensity varies with its environment, but usually occurs between 450 and 480 nm. Excitation of ANS leads to the formation of an excited singlet state which can then undergo intramolecular charge transfer to form another singlet excited state, and emission can occur from both of these states [11]. Highly polar environments promote the charge transfer transition and the rate of radiative deactivation. Therefore, a more polar environment leads to a smaller quantum yield and a red shift in emission [11].

The surfactants used in this investigation were non-ionic polyoxyethylene (POE) surfactants. These surfactants have an alkyl chain length hydrophobic tail and ethylene oxide head groups as their hydrophilic moiety. Triton X-100 has a phenyl group between the alkyl chain and ethylene oxide head groups. The Brij series has a 12–18 carbon chain length and varying number of ethylene oxide units (20–100), while the POE TDE series has 12–18 ethylene oxide groups and a 13 carbon chain length.

* Corresponding author.
E-mail address: rpalepu@stfx.ca (R.M. Palepu).

0378-3812/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2006.11.009

In this investigation, the excited state spectral properties of the photosensitive dye ANS have been studied in the presence of non-ionic polyoxyethylene micelles to obtain information on the nature and extent of dye-surfactant complex formation in aqueous solutions.

2. Experimental

2.1. Materials

The non-ionic polyoxyethylene (POE) chain surfactants Brij 35 (polyoxyethylene (23) lauryl ether), Brij 58 (polyoxyethylene (20) cetyl ether), Brij 78 (polyoxyethylene (20) stearyl ether), Brij 98 (polyoxyethylene (20) oleyl ether), Brij 700 (polyoxyethylene (100) stearyl ether), POE 12 TDE (polyoxyethylene (12) tridecyl ether), POE 18 TDE (polyoxyethylene (18) tridecyl ether) and Triton X-100 (polyoxyethylene (10) isooctylphenyl ether) were obtained from Aldrich, and were used as received. The probe ANS was obtained from Fisher Scientific Company. Doubly deionized water was used to prepare the solutions.

Solutions of surfactant in ANS were used to determine the equilibrium binding constant, K_M, and the aggregation numbers, N_{agg}. All solutions were prepared so that a constant concentration of dye of the order 10^{-2} mmol/L was present in the mixtures, while the concentration of surfactant was varied.

2.2. Instrumentation

The fluorescence spectra were measured using a JY Horiba Spex Fluoromax-3 fluorimeter, using a 1 cm quartz cuvette. The ANS probe was excited at 346 nm, and studied in the range of 400–650 nm. The excitation and emission bandwidths were 1.05 and 2 nm, respectively. Triplicate measurements were made and mean values were considered for data analysis.

3. Results and discussion

In aqueous solutions, ANS is almost non-fluorescent. The addition of Brij, and the other non-ionic surfactant, to the aqueous ANS solution caused an increase in the fluorescence intensity. Fig. 1A and B represent the relative fluorescence intensity of ANS in arbitrary unit (au) as a function of Brij 35 and POE 18 TDE surfactant concentration. These plots indicate that the very weak fluorescence intensity of ANS in aqueous solution (F_0) rapidly increases with surfactant concentration and reaches a plateau at higher concentrations (F_{max}) of the surfactants (Fig. 2A–C). The values of the relative increase of fluorescent intensities (F_{max}/F_0) are shown in Table 1. The plateau indicates that all the dye is interacting with the surfactant micelles and occurs at only at sufficiently high concentrations of surfactant. In this study, surfactant concentrations were kept well above the critical micellar concentration (cmc) to maximize the interaction between ANS and the surfactants.

If it is assumed that the dye molecules are exclusively in a 1:1 complex with the non-ionic micelles [13], the $F_{max} - F_0$ values

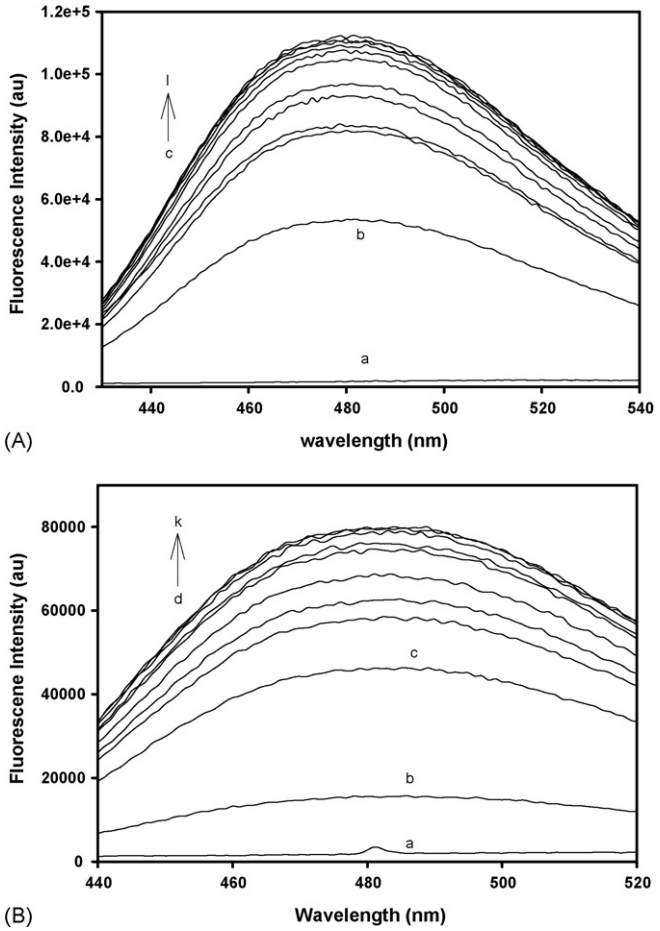

Fig. 1. Plot showing the fluorescence emission spectra of ANS in (A) aqueous Brij 35 at 298 K when Brij 35 is: (a) 0 mM, (b) 0.5 mM, (c) 1.25 mM, (d) 2 mM, (e) 2.5 mM, (f) 3.75 mM (g) 5 mM, (h) 7.5 mM. (i) 10 mM, (j) 12.5 mM, (k) 17.5 mM and (l) 25 mM. (B) Aqueous POE 18 TDE at 298 K when POE 18 TDE is: (a) 0 mM, (b) 0.5 mM, (c) 1.25 mM, (d) 2 mM, (e) 2.5 mM, (f) 3.75 mM (g) 7.5 mM. (h) 10 mM, (i) 12.5 mM, (j) 17.5 mM and (k) 25 mM.

can be taken to be proportional to $[D_{complex}]$,

$$F_{max} - F_0 = K_M[D_{complex}] \quad (1)$$

where K_M is a proportionality constant, $[D_{complex}]$ is the concentration of the dye in the complex form, F_{max} and F_0 are the maximum and initial fluorescence intensities, respectively. The F values at any other value than F_{max} can be related similarly to

Table 1
Values of the relative increase in fluorescence intensity, binding constant, K_M, and aggregation number, N_{agg} determined for the Brij and POE TDE non-ionic surfactant series, as well as for Triton X-100

Surfactant	F_{max}/F_0	K_M	N_{agg}
Brij 35	55.5	177,188	56
Brij 58	65.1	198,827	49
Brij 78	76.5	264,048	58
Brij 98	68.2	145,557	49
Brij 700	53.7	725,536	61
POE 12 TDE	40.0	323,118	148
POE 18 TDE	23.0	229,711	110
Triton X 100	46.2	217,876	136