

## **FLUORESCENCE PROBING OF MICROFLUIDITY OF SURFACTANT LAYERS AT THE SOLID-LIQUID INTERFACE**

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### **ABSTRACT**

Excimer formation of dinaphthylpropane (DNP) and pyrene fluorescence probes is used to monitor the microfluidity of dodecylsulfate hemimicelles formed on alumina particles. The efficiency of excimer formation of both probes indicate that the hemimicelle environment is considerably less fluid than that of SDS micelles suggesting a higher structural organization inside the hemimicellar aggregate.

### **INTRODUCTION**

Surfactant adsorption on particles in suspensions has been studied in the past by determining adsorption, zeta potential, particle wettability, etc. These studies have been helpful in formulating mechanisms that govern the formation of surfactant layers on solids. In particular, a major driving force for adsorption of long-chain surfactants arises from the self-aggregation of the surfactant molecules on the solid surface resulting in the formation of localized surfactant aggregates called hemimicelles [1]. Hemimicellization occurs at concentrations well below the critical micelle concentration (CMC) of the surfactant owing to favorable electrostatic surface-surfactant interactions.

Even though the mechanism of hemimicellization has been well discussed in the past, hemimicelle structural characteristics have not, however, yielded to investigations using the conventional techniques. Spectroscopic techniques capable of insitu probing of the adsorbed layer at a molecular level should, on the other hand, help to study these structures directly. Structural differences, if any, between hemimicelles and micelles could also be elucidated. The hemimicelle is often envisioned as existing on the surface as a two-dimensional, closely-packed aggregate [1]. If this structural representation is valid, significant differences in the microfluidity of the hemimicellar environment compared to that of the micellar environment can be expected. The microfluidity of micelles can be measured by fluorescence probing methods such as fluorescence polarization and excimer formation [2,3].

In this communication, we demonstrate that the excimer formation technique can be extended to obtain microfluidities of hemimicelles formed by dodecylsulfate (SDS) on alumina. We have chosen as the excimer forming probes, dinaphthylpropane and pyrene, which owing to their hydrophobic nature, are solubilized exclusively in the SDS micelles and

hemimicelles.<sup>1</sup> Excimer formation is known to occur *intermolecularly* in the case of pyrene or, *intramolecularly* in the case of the bichromophoric probe, dinaphthylpropane (DNP) [4].

## RESULTS AND DISCUSSION

### Intramolecular Excimer Formation of Dinaphthylpropane (DNP)

The excimer formation of DNP, depends upon the motion of the arene groups in order to achieve the excimer conformation as illustrated below [3]:

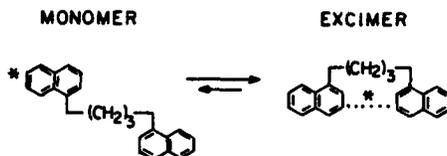


Figure 1: Schematic representation of intramolecular excimer formation of dinaphthylpropane (DNP)

Excimer formation at low probe concentrations, can be considered to be exclusively unimolecular (intramolecular) so that only the medium viscosity determines the extent of excimer formation [4]. Thus the monomer to excimer intensity ratios,  $I_m/I_e$  obtained from the steady-state emission spectrum of DNP can be used to estimate the effective fluidity of the microenvironment of the probe using values obtained in solvents of known viscosity [7]

The emission spectra obtained for the DNP solubilized in SDS micelles and SDS-alumina hemimicelles were identical except for the relative intensities of the monomer ( $\lambda_{\max} = 340\text{nm}$ ) and excimer ( $\lambda_{\max} = 420\text{nm}$ ). The  $I_m/I_e$  values obtained and the corresponding viscosities for the various systems studied are summarized in Table 1.

<sup>1</sup>A known volume of  $10^{-1}\text{M}$  a sodium dodecylsulfate (SDS, Fluka Chemicals) solution containing  $10^{-4}\text{M}$  or  $4 \times 10^{-5}\text{M}$  DNP (synthesized as in reference 4) or  $5 \times 10^{-5}$ ,  $8 \times 10^{-5}$ ,  $4 \times 10^{-5}\text{M}$  pyrene (Aldrich Chemicals, recrystallized from ethanol-water) was added to a final volume of 150ml, 0.1M NaCl solution containing 5 g of alumina (Linde A grade, Union Carbide Corp., 0.3 microns,  $15\text{m}^2/\text{g}$  surface area) at pH 6.5. After mixing the suspension for 12 hours, the supernatant was analyzed for the residual SDS concentration [5]. The steady-state emission spectrum of DNP in the slurry was measured in a 2ml cell with an excitation wavelength of 280nm. The emission spectrum (310nm to 500nm) of DNP in the slurry was obtained and corrected for scattered incident light by scanning a solid slurry without any DNP. Steady-state and fluorescence decay (single photon counting) methods [6] were used to monitor the fluorescence of pyrene. Comparative studies were performed with both DNP and pyrene in 0.1M SDS (0.1M NaCl) solutions. In addition, the centrifuged solutions from the adsorption tests were also examined; in all cases reported here, no probe was detected in solution.

TABLE 1  
Monomer to excimer ratio of DNP and corresponding viscosities  
in various systems

Test # 1) SDS MICELLE (0.1M NaCl)					
[SDS], M	CMC, M	SDS/PY*	Im/Ie	$\eta$ , cP	
$8.2 \times 10^{-2}$	$1.5 \times 10^{-3}$	785	1.7	8	
Test # 2) SDS-ALUMINA HEMIMICELLE (0.1M NaCl, pH 6.5)					
Adsorption Density, mol/cm <sup>2</sup>	Equilibrium SDS conc., M	SDS/PY**	Im/Ie	$\eta$ , cP	
a) $4.5 \times 10^{-10}$	$6.0 \times 10^{-4}$	672	3.3	90	
b) "	"	1680	3.3	90	
(note: no DNP in supernatant)					
Test # 3) SDS-SILICA (0.1M NaCl, pH 6)					
Adsorption Density, mol/cm <sup>2</sup>	Equilibrium SDS conc., M	SDS/PY*	Im/Ie		
0	$8.2 \times 10^{-2}$	785	1.8		
(note: Im/Ie in supernatant = 1.7)					

\* ratio of micellized SDS to added DNP

\*\* ratio of adsorbed SDS to added DNP

Viscosities based on Im/Ie in ethanol-glycerol mixtures

It is evident that the effective viscosity reported by the probe in the SDS-alumina hemimicelles (90 cP) is significantly greater than that in SDS micelles (8cP). It is to be noted from the results obtained in test 2 that varying the level of DNP had no effect on the Im/Ie value thus supporting the assumption that excimer formation occurs unimolecularly (intramolecular). Also, SDS-DNP micellar solution added to non-adsorbing silica particles (test 3) gave almost the same Im/Ie value as that of the supernatant as well as that of the SDS micellar solution (test 1) suggesting that the presence of solid particles does not interfere with the measurement; DNP is apparently present exclusively in micelles.

Based on the above data, DNP response in the alumina slurry can be considered to reflect its mobility in the adsorbed layer.<sup>2</sup> We thus interpret the higher viscosity (or lower probe mobility) in SDS-alumina system as being due to a higher structural order (rigidity) of the surfactant molecules in hemimicelles than in micelles.

#### Intermolecular Excimer Formation of Pyrene

The intermolecular excimer formation of pyrene occurs intramicellarly owing to the slow exit of pyrene from micelles compared to its fluorescence lifetime [3]. In micellar solutions, in

<sup>2</sup>There remains the question as to whether DNP interacts with the alumina surface directly even though the hydrophobic probe is not expected to interact with the hydrophilic alumina surface. The extremely low solubilities of DNP in water made it not possible to determine the extent of adsorption of DNP on to alumina in the absence of SDS so a control test was conducted in following manner as suggested by the reviewer: A constant reservoir of DNP crystals was maintained on the inside of a filter paper which in turn was immersed in an alumina-water suspension. After 4 days of stirring, weak fluorescence due to DNP was observed in the supernatant of this suspension showing that some DNP had indeed dissolved. However, no detectable fluorescence was observed when the solid slurry was excited suggesting that DNP does not have a high affinity for the alumina surface.

addition to local fluidity, the nature of the distribution of the probe among micelles affects the efficiency and extent of excimer formation; excimer formation occurs in only those micelles with probe occupancies greater than one [8]. This distribution complicates analysis of the extent of excimer formation so that the monomer to excimer ratios cannot be readily related to local fluidity as in the case of intramolecular excimer formation [9].

The fluidity of the hemimicellar and micellar environments as reported by pyrene, can however, be compared on the basis of the excimer formation rates obtained through fluorescence decay measurements [10]. Kinetic models based on Poisson statistics for the probe distribution among aggregates, have been developed to account for the decay profiles obtained in micelles and hemimicelles and the equation describing the time dependence of monomer fluorescence is given below [11,12]:

$$I_m(t) = I_m(0)\exp[-k_0t + \bar{n}(\exp(-k_e t)-1)] \quad -1$$

where  $k_0$  is the reciprocal fluorescence lifetime of the excited monomer,  $k_e$  is the 1st order excimer formation rate constant, and  $\bar{n}$  is the Poisson average occupation number.

Figures 2a and 3a show the emission spectra for varying levels of pyrene in SDS micelles and SDS-alumina hemimicelles respectively. It is noted from the emission spectra, that values of the I3/I1 fluorescence parameter, which has been used as a monitor of environment polarity [10,13], are the same for both systems; pyrene thus reports a micelle-like polarity in the hemimicelle which is consistent with the formation of hydrocarbon chain aggregates at the surface.

The corresponding monomer (383nm) decay profiles obtained in micelles and hemimicelles are given in Figures 2b and 3b respectively. In the absence of excimer formation the profiles (Curves A) are single exponentials as expected. The decay profiles under excimeric conditions (curve B in Figure 2b and curves B and C in Figure 3b) which are multiexponential due to the formation of excimer in some of the aggregates (micelles or hemimicelles with occupancy > 1) were fitted to equation 1.<sup>3</sup> These results are summarized in Table 2.

TABLE 2  
Summary of Kinetic Analysis of Pyrene Excimer Formation

Test# 1) SDS MICELLE (0.1M NaCl)						
[SDS], M	CMC, M	SDS/PY*	1/k <sub>0</sub> , ns	k <sub>e</sub> , sec <sup>-1</sup>	$\bar{n}$	
8.2 x 10 <sup>-2</sup>	1.5 x 10 <sup>-3</sup>	108	175	1.4x10 <sup>7</sup>	1.1	
Test# 2) SDS-ALUMINA HEMIMICELLE (0.1M NaCl, pH 6.5)						
Adsorption Density, m/cm <sup>2</sup>	Equilibrium [SDS], M	SDS/PY**	1/k <sub>0</sub> , ns	k <sub>e</sub> , sec <sup>-1</sup>	$\bar{n}$	
a) 4.5 x 10 <sup>-10</sup>	6.0x10 <sup>-4</sup>	336	169	2.4x10 <sup>6</sup>	0.57	
b) "	"	139	169	2.8x10 <sup>6</sup>	1.55	

\* ratio of micellized SDS to added pyrene  
\*\* ratio of adsorbed SDS to added pyrene

<sup>3</sup> A non-linear regression analysis involving minimization of weighted sum of squares was used.  $k_0$  obtained from curves A was used as a known parameter to fit curves B and/or C. Fitting was begun from 50 ns without deconvolution. A background noise (< 1% of maximum intensity) obtained from the last 25 channels was subtracted from the actual data.

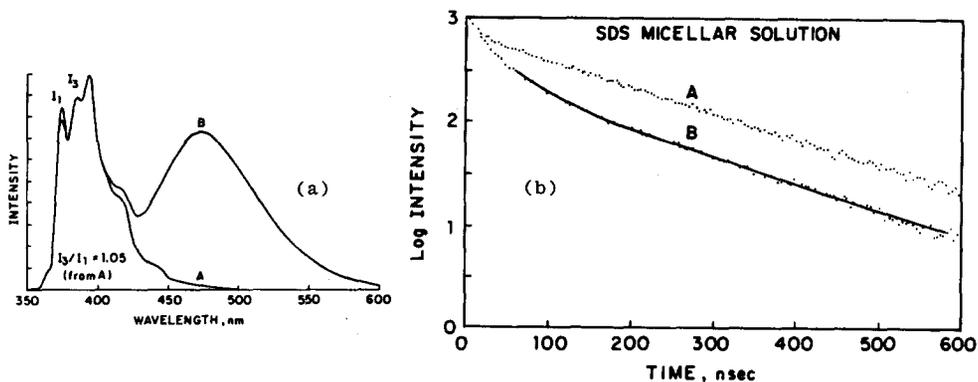


Figure 2: (a) Pyrene emission spectra in SDS micelles (0.1 M NaCl); ratio of micellized SDS to added pyrene, 2160 (A), 108 (B); excitation at 332nm.  
 (b) Monomer decay profiles under conditions corresponding to 2a; excitation at 320nm, emission at 383nm.

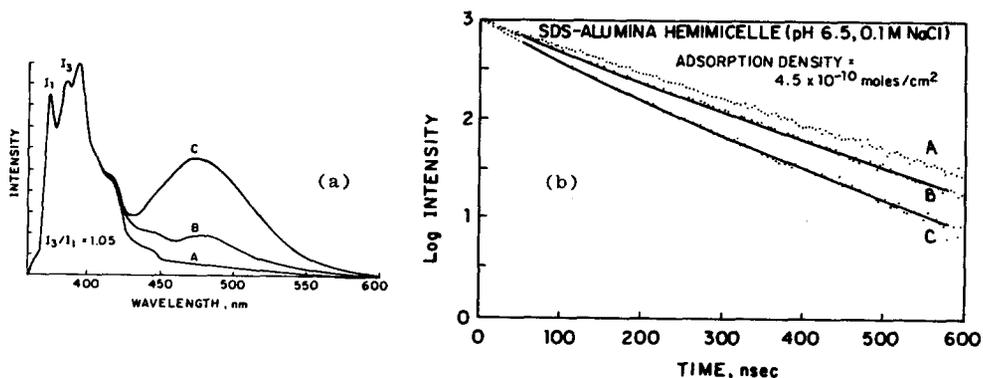


Figure 3: (a) Pyrene emission spectra in SDS-alumina hemimicellar system; ratio of adsorbed SDS to added pyrene, 1390 (A), 336 (B) 139 (C); excitation at 332nm.  
 (b) Monomer decay profiles under conditions corresponding to 3a; excitation at 320nm, emission at 383nm.

The parameter that is of interest with respect to the fluidity of the microenvironment is the excimer formation rate constant,  $k_e$ . The value of this constant is independent of pyrene concentration (tests 2a and 2b) in accordance with the predictions of the kinetic model used here. Importantly, the rate of excimer formation is 5-6 times less in the hemimicelle than in the micelle. These results support the conclusion that the hemimicelle environment is considerably less fluid than that of the micelle.

## CONCLUDING REMARKS

This study illustrates the application of fluorescence techniques using dinaphthylpropane and pyrene as probes for investigating the structure of surfactant aggregates formed on solid surfaces. Both the extent of excimer formation of DNP and the rate of excimer formation of pyrene show the hemimicelle to be considerably less fluid than the micelle suggesting a higher degree of structural organization in the hemimicelle. The use of pyrene as a probe, can also yield information on the micropolarity and surfactant aggregation numbers for the hemimicelles. This latter aspect will be discussed separately where the evolution of the adsorbed layer will be examined as a function of adsorption density [14].

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