Fluorescence Quenching of Pyrene by Chromium Complexes in Sodium Dodecyl Sulfate Micelles

Mookandi Kanthimathi, Kannamvelly Deepa, Balachandran Unni Nair,* and Asit Baran Mandal*

Chemical Laboratory, Central Leather Research Institute, Adyar, Madras 600020, India

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The aggregation number of sodium dodecylsulfate (SDS) is known to vary with its concentration. Keeping the SDS concentration fixed at 15, 50, and 100 mM, the effect of various Cr(III) quenchers on the aggregation behavior of SDS was studied using pyrene as a probe during static and time-resolved fluorescence measurements. Cr(III) compounds, such as $[Cr(en)_3]Cl_3$, $[Cr(salprn)(H_2O)_2]^+$, $[Cr(phen)_3](ClO_4)_3$, and $[Cr(bpy)_3](ClO_4)_3$ were used as quenchers in this investigation. Cetylpyridinium chloride (CPC) was also used as a quencher to keep the Cr(III) complexes fixed at 0.05 and 0.1 mM in order to further confirm the aggregation behavior of SDS micelles in the presence of various ligands. The aggregation numbers of SDS are very low (2 to 32) when the ligand is aliphatic, whereas they are surprisingly high (75—860) in the presence of Schiff-base and aromatic ligand environments. The aliphatic ligand acts as a structure breaker, whereas Schiff-base and aromatic ligands act as structure makers for aggregated SDS micelles, which have been further substantiated by lower and higher counterion association values, respectively, obtained from conductivity experiments.

The study of the photophysical properties by fluorescence excitation and emission spectra and their shifts, the relative intensity of vibronic bands, the quantum yields and the lifetimes of the excited state of the probes, has provided significant information on micellar structure at the molecular level.[1,2] Among the various techniques recently used, fluorescence quenching is presently a valuable tool to measure micellar size as well as the dynamic properties of aggregates and solubilized species in a host structure.[3,4] Fluorescence quenching studies have provided a variety of information on the properties of micelles: cmc, the extent of counterion binding to the micellar surface, the aggregation number and the influences of additives on the permeability properties of the aggregate. The aggregation number of surfactants has been known to be influenced by the ionic strength and pH of the solution.[5,6] Recently, surfactants are being used to study solution chemistry and the electrochemistry of transition metal complexes.[7,8] Recently, we used pyrene and 8-anilino-1-naphthalenesulfonic acid (ANS) fluoroprobes with a cetylpyridinium chloride (CPC) qnencher to determine the quenching kinetics and aggregation numbers of various peptides and macromonomer micelles[9—14] in both the absence and presence of surfactant micelles. Recently, the aggregation numbers of hydrophobic microdomains formed from poly(dimethyl diallyl ammonium-co-methyldodecyl diallyl ammonium) salts in aqueous solutions using the fluorescence technique have been reported.[15] The aggregation numbers of sodium dodecyl sulfate (SDS) micelles and the fluorescence quenching constants of pyrene by Cu^{2+} have recently been measured[16] as a function of the SDS concentration; micelles are shown to grow from 57 to 89 molecules as the SDS concentration increases from 25 to 200 mM.[16] The variation of the aggregation number with the concentration of macromonomer micelles has been studied,[17,18] and the quenching of pyrene by other metal ions in SDS has also been reported.[19] However, the possible effect of the ligand structure on the aggregation number of the surfactant micelles has not yet been examined. In this paper we report on the effect of various ligand environments of Cr^{3+} complexes (which act as quenchers on the pyrene probe) on the aggregation number of SDS micelles and Stern–Volmer constant (k_{sv}) of the quenching process by using both static and time-resolved fluorescence spectroscopic measuremetns. The aggregation number for SDS micelles was also determined using pyrene as a probe and CPC as a quencher to keep the Cr(III) complex concentration fixed (0.05 and 0.1 mM). The results of the critical micelle concentration (cmc), counterion association of the SDS micelles in the absence and presence of various Cr(III) complexes obtained from conductivity experiments, and the transfer of the standard Gibbs' free-energy change of SDS micelles from aqueous to Cr(III) additive environments have also been highlighted briefly.

Experimental

Materials and Methods. The characteristics of the pyrene, CPC and SDS used in this study were described earlier.[9—14,20—25] Pyrene, CPC, and SDS, purchased from Fluka, were recrystallized twice from ethanol. Doubly distilled water of sp. cond. 2—3 $\mu S\,cm^{-1}$ at 25 °C was used throughout the experiment. The tetradentate Schiff-base ligands, *N,N'*-propylenebis(salicylideneimine) (abbreviated as salprn) and their Cr(III) derivatives were prepared by previously known procedures.[26,27] IR and electronic spectra, and elemental analyses were carried out to confirm the formation of Cr(III) Schiff-base complexes. The compounds $[Cr(bpy)_3](ClO_4)_3$, $[Cr(phen)_3](ClO_4)_3$, and $[Cr(en)_3]Cl_3\cdot 3.5H_2O$ (where, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, and en = ethylenediamine, respectively) were prepared using published

methods.[28—30] The structures of $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$, $[Cr(salprn)(H_2O)_2]ClO_4$, $[Cr(phen)_3](ClO_4)_3$, and $[Cr(bpy)_3](ClO_4)_3$ are given below (Chart 1):

Typically, sample solutions of pyrene (1 μM, fixed, 1 M = 1 mol dm^{-3}), SDS (15, 50, and 100 mM, fixed), and Cr(III) complexes (0.05 and 0.1 mM, fixed) and varying concentrations of CPC quenchers [(0.01—0.3) mM] were prepared in 10 mL volumetric flasks in one set of experiments. In another set of experiments, Cr(III) complexes were varied (0.01—0.3 mM) in place of CPC keeping pyrene and SDS fixed at 1 μM and 15 mM (50 and 100 mM also), respectively, in order to understand the role of Cr(III) complexes as quenchers. All of the solutions were sonicated for 1 h at room temperature, stirred overnight in the dark, and finally transferred to cuvettes for fluorescence measurements. Thus, typically, spectral measurements were carried out about 2 days after the SDS was first prepared and 1 day after the metal complexes were added. UV-visible and fluorescence spectral measurements were made at 25±0.05 °C on a Shimadzu UV-160 spectrophotometer and a Hitachi Model No. 650-40 fluorimeter, respectively. The fluorescence decay curves and lifetime measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrofluorimeter (IBH, Model 5000U). The excitation source was a 5000f coaxial flash lamp operated at a frequency of 100 kHz; the pulse-width of the lamp under the operating conditions used was 1.2—1.5 ns full width half maximum (FWHM) using nitrogen at a pressure of 1 bar. The fluorescence emission was monitored at right angles to the excitation path, and photons were detected by a MCP-PMT (Hamamatsu, Model R3809U-50) detector. The lifetimes were estimated from the measured fluorescence decay curves, and were analyzed using a nonlinear least-squares iterative fitting procedure (software provided by IBH).

The fluorescence-quenching reaction between the pyrene probe in SDS micellar and the quenchers, viz. CPC, and Cr(III) at aliphatic, aromatic and Schiff-base ligand environments were studied fluorimetrically. The molar concentration ratio between pyrene to SDS was 1 : 15000, whereas the Cr(III) : SDS molar ratio varied from 1 : 1500 to 1 : 50. Very poor quality of emission spectra had been observed when the pyrene probe concentration was high (say 0.1 mM). Therefore, in our experiments, the probe concentration had been kept sufficiently low (1×10^{-6} M) to prevent excimer formation, as judged by static fluorescence emission measurements.

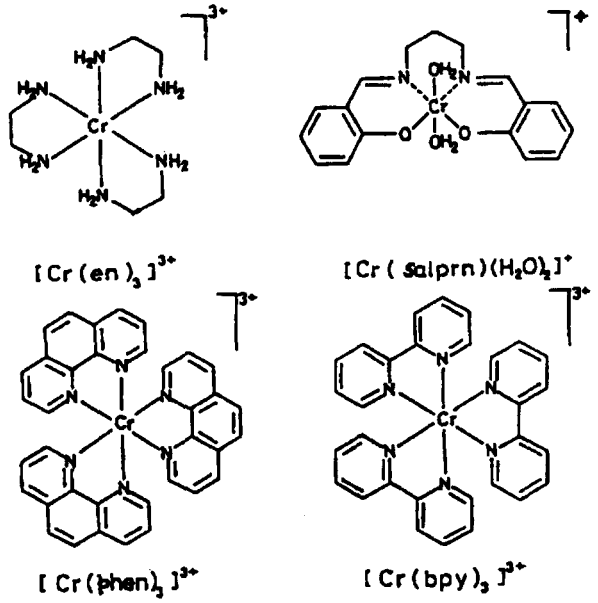

Chart 1.

Conductivity measurements were made using a Global digital (Model DCM 900, made in India) conductivity bridge with a dip-type cell having a cell constant of 1.0 cm^{-1} at 25 °C. A direct determination of the conductivity was carried out. Prior to the measurements, all of the solutions were thermostated for > 25 min at 25 °C. The temperature reproducibilities were within ±0.1 °C. In the determination of the cmc of SDS, a series of solutions were made at a particular concentration of the Cr(III) additives (in this case 0.05 and 0.1 mM, fixed) and varying concentration of SDS. The specific conductance of each solution was plotted as a function of the concentration of SDS. Any abrupt changes in the value of the initial slopes at a particular concentration were considered to indicate the cmc. In the absence of Cr(III) additives, the difference in the specific conductance was Δk = (specific conductance of the SDS solutions in water)−(specific conductance of water); however, in the presence of Cr(III) additives, Δk = (total specific conductance of the SDS solutions in water including Cr(III) additives)−(specific conductance of Cr(III) additives in water). Regarding the details concerning the determination of the cmc using various techniques, including conductivity, we refer to our earlier studies.[7—14,20—23]

Results and Discussion

Graphical representations of the plot of Δk vs. concentration of SDS to determine cmc of SDS in both the absence and presence of various Cr(III) additives are not shown here. However, the results of cmc, degree of dissociation α (ratio of post micellar slope to premicellar slope from specific conductance, k vs. concentration of SDS plots), and counterion association β (= $1-\alpha$) of SDS micelles in the presence of different Cr(III) complexes are given in Table 1.

Following Turro and Yekta,[31] the aggregation number was determined by measuring the quenching of a micelle-bound fluorescent probe by binding a quencher using the following expression:

$$\ln (I_0/I) = N[Q]/(C_s - \text{cmc}) \quad (1)$$

where I_0 and I are the emitted light intensities with a quencher concentrations of zero and $[Q]$, respectively. N is the mean aggregation number and C_s is the total concentration of the surfactant. Figure 1 shows typical $\ln (I_0/I)$ vs. $[Q]$ plots. The validity of the Turro and Yekta model was examined, and we found that the above model held good in our present investigations for Cr(III) concentrations upto 0.1 mM. In a time-resolved fluorescence spectroscopic technique, the general decay equation;

$$I(t) = I(0)\exp\{-A_2t - A_3[1 - \exp(-A_4t)]\} \quad (2)$$

was fitted to the decay curves using a weighted least-squares procedure. $I(t)$ and $I(0)$ are the fluorescence emission intensities at time t and zero, respectively. A_2, A_3, and A_4 are three constants, which are determined as adjustable parameters. The ratio between the molar concentrations of pyrene and SDS micelles was kept at $\ll 1$ so that the question of perturbation of the micellar structure by the probe would not arise at all.[7—14,24,25,32] The aggregation number was calculated using the following protocol as reported by Zana et al:[33]

Table 1. The cmc, α, β, and $(\Delta G_m^\circ)_{tr}$ of SDS Micelles in Aqueous Solutions Using Various Cr-Ligand Complexes (0.05 and 0.1 mM, fixed). The Stern–Volmer Constant k_{sv} of the Quenching Process at 25 °C in Various Concentrations of SDS Micelles The cmc, N, α, and β of SDS at 25 °C are 8 mM, 50, 0.58, and 0.42, respectively.

Sl No.	Cr complexes	cmc of SDS/mM [Cr(III)]/mM		α of SDS [Cr(III)]/mM		β of SDS [Cr(III)]/mM		$(\Delta G_m^\circ)_t$/kJ mol^{-1} [Cr(III)]/mM		$k_{sv}/10^4$ M^{-1} [SDS]/mM		
		0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1	15	50	100
1	$[Cr(en)_3]Cl_3$	11	13	0.78	0.84	0.22	0.16	+0.79	+1.20	0.05	0.23	0.26
2	$[Cr(salprn)(H_2O)_2]^+$	6.0	4.0	0.50	0.45	0.50	0.55	−0.71	−1.72	10.00	13.5	15.0
3	$[Cr(phen)_3](ClO_4)_3$	5.0	3.5	0.46	0.40	0.54	0.60	−1.16	−2.05	20.00	22.2	23.5
4	$[Cr(bpy)_3](ClO_4)_3$	3.5	1.5	0.38	0.30	0.62	0.70	−2.05	−4.15	36.00	37.5	30.0

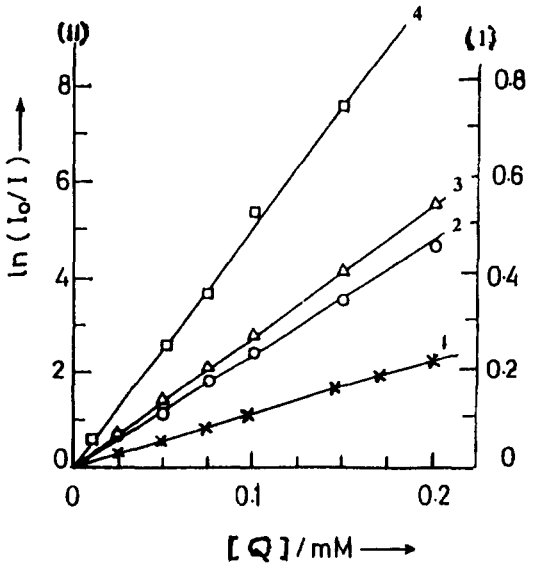

Fig. 1. Plot of $\ln(I_0/I)$ vs. [CPC] quencher for micellar solutions of the SDS at 25 °C. [SDS] = 15 mM (fixed), [pyrene] = 1 μM (fixed) and Cr(III) complexes (0.1 mM, fixed) in aqueous solutions. λ_{ex} = 300 nm and λ_{em} = 394 nm. Curve Nos. 1—4: $Cr(en)_3Cl_3$, $Cr(salprn)(H_2O)_2^+$, $Cr(phen)_3(ClO_4)_3$, and $Cr(bpy)_3(ClO_4)_3$, respectively. Ordinate scale number I corresponds to curve number 1, whereas ordinate scale number II corresponds to curve numbers 2, 3, and 4.

$$A_3 = [Q]/\{(C_s - \text{cmc})/N\} \quad (3)$$

The aggregation numbers obtained by the static fluorescence method are in good agreement with those of the time-resolved fluorescence methods (cf. Table 2). However, when the Cr(III) concentration is > 0.1 mM, the micelles may not be monodispersed; in that case, the Turro–Yekta model will not hold. The N value of 15 mM SDS in aqueous solution at 25 °C is 50, which is in good agreement with the literature[16] value. The N value of SDS is very low (2) when the ligand environment is aliphatic, whereas the N of SDS are surprisingly high (75 to 675) in the presence of Schiff-base and aromatic ligand environments (cf. Table 2); the k_{sv} value also increases with an increase of N (see Tables 1 and 2). The salts of trivalent metal ions and DS^- are insoluble, and there is a possibility of coacervate formation[21] when Cr-ligand complexes interact with SDS at equimolar concentrations. Spin-lattice relaxation-time measurements[8,10,18] show that almost certainly for Co and Cr salts cations are located on the surface of the micelles, and therefore the systems are soluble. Because the Cr(III) concentrations are very low (0.1 mM), compared to SDS, the micelles are able to solubilize the cations in the micelles to inrease in size. However, the situation is not as simple with the complexes; it has been found[25] that they are solubilized inside the micellar structure compared to the head-group surface. The reason for using a low concentration of SDS (15 mM) is justified due to premicellar aggregation in the presence of some Cr(III) complexes (sl. Nos. 2 to 4 in Table 1).

It is pertinent to mention here that the aggregation number for 15 mM SDS solutions, in the presence of 0.1 mM $[Cr(en)_3]Cl_3$, is reported to be as small as 2. Therefore, by decreasing the concentration of $[Cr(en)_3]Cl_3$ or increasing the concentration of SDS, the aggregation number must increase. However, in the presence of 0.1 mM $[Cr(phen)_3](ClO_4)_3$ and $[Cr(bpy)_3](ClO_4)_3$ the aggregation numbers are surprisingly large (see Table 2). Thus, if we decrease the concentration of the Cr(III) species or increase the SDS concentration, the aggregation number must decrease. Hence, in order to test the above hypothesis, we have been tempted to study them further, and, accordingly, we have also performed experiments to determine the aggregation number for SDS micelles as a function of their concentrations (15, 50, and 100 mM, fixed) using Cr(III) complexes (varying concentrations) as quenchers in one set; in the other set, we used CPC as quenchers (varying concentrations) while keeping the Cr(III) complex concentrations fixed (0.05 and 0.1 mM), by employing both steady-state and time-resolved fluorescence spectroscopic methods (cf. Table 2). A typical example of the fluorescence decay curves for pyrene (1 μM, fixed) in SDS (50 mM, fixed) micelles using various concentrations of $[Cr(salprn)(H_2O)_2]^+$ quencher is shown in Fig. 2. The graphical representations of the fluorescence decay curves in the presence of other Cr(III) complexes and CPC quenchers are not shown here. However, the aggregation numbers and lifetimes obtained by time-resolved fluorescence methods are given in Tables 2 and 3, respectively. It has been observed that the aggregation numbers obtained by both steady-state and time-resolved methods are in good agreement with each other irrespective of the concentrations of SDS micelles (see Table 2). It can also be seen from Table 2 that the aggregation number (N) increased along with an increase in the SDS concentrations in the presence of all Cr(III) complexes.

Table 2. The Aggregation Number for SDS Micelles as a Function of Its Concentrations Using Cr(III) Complexes (varying concentrations) as Quenchers in One Set[a] and in Other Set[b]
CPC as quenchers (varying concentrations) keeping Cr(III) complex concentrations fixed (0.05 and 0.1 mM). Temperature = 25 °C. [Pyrene] = 1 μM (fixed).

Complex	Aggregation number (N) in presence of Cr(III) (0.05 mM)		Aggregation number (N) in presence of Cr(III) (0.1 mM)	
	[SDS]/mM	N	[SDS]/mM	N
$[Cr(en)_3]Cl_3$	15	20,[a] 19[b] (15[a])	15	2,[a] 2[b] (1.5[a])
	50	42,[a] 40[b] (36[a])	50	28,[a] 26[b] (25,[a] 22[b])
	100	68,[a] 65[b] (60[a])	100	35,[a] 32[b] (30[a])
$[Cr(Salprn)(H_2O)_2]^+$	15	65,[a] 62[b] (58[a])	15	75,[a] 70[b] (72[a])
	50	305,[a] 296[b] (290,[a] 282[b])	50	470,[a] 445[b] (455,[a] 440[b])
	100	504,[a] 495[b] (470[a])	100	862,[a] 810[b] (800[a])
$[Cr(phen)_3](ClO_4)_3]$	15	190,[a] 185[b] (172[a])	15	315,[a] 290[b] (270[a])
	50	295,[a] 288[b] (280,[a] 272[b])	50	465,[a] 405[b] (382,[a] 362[b])
	100	415,[a] 401[b] (382[a])	100	675,[a] 650[b] (612[a])
$[Cr(bpy)_3](ClO_4)_3$	15	305,[a] 291[b] (276[a])	15	675,[a] 615[b] (592[a])
	50	394,[a] 382[b] (370,[a] 365[b])	50	788,[a] 705[b] (690,[a] 682[b])
	100	280,[a] 275[b] (265[a])	100	512,[a] 503[b] (492[a])

Aggregation Numbers determined by time-resolved fluorescence method are given in the parenthesis.

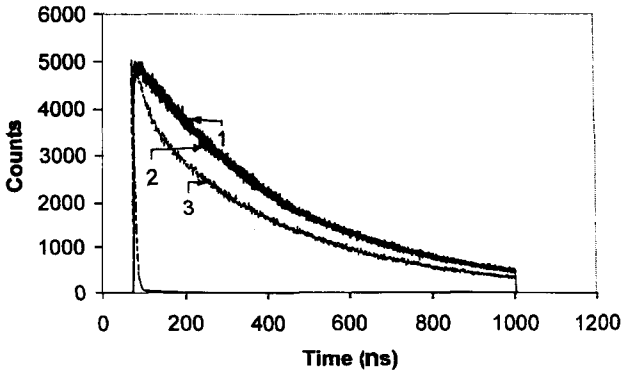

Fig. 2. Fluorescence decay curves for pyrene in presence of SDS micelles as a function of $[Cr(salprn)(H_2O)_2]^+$ at 25 °C. [Pyrene] = 1 μM (fixed); [SDS] = 50 mM (fixed). Curve numbers 1—3: $[Cr(salprn)(H_2O)_2]^+ = 1\times10^{-6}$ M, 1×10^{-5} M, and 1×10^{-3} M, respectively.

However, in the presence of $[Cr(bpy)_3](ClO_4)_3$, the N value of SDS increased with an increase in the SDS concentrations (surprisingly large upto 50 mM); above 50 mM, the N value started decreasing. It has also been observed that the N values of SDS increased, along with an increase in the Cr(III) complex concentrations, irrespective of the SDS concentrations (15, 50, and 100 mM in the present investigation). However, the N values of SDS decreased drastically with an increase in the $[Cr(en)_3]Cl_3$ concentrations, and always very much lower values were obtained than for the SDS alone. Therefore, $[Cr(en)_3]Cl_3$ acts as a structure breaker for the aggregated SDS micelles.

To determine the aggregation number (N) of the micelles, we have used Eqs. 1 and 3, where the exact cmc values used as the cmc are sensitive to additives[20,34] (see Tables 1 and 2), even in mixed micellar systems.[21] The cmc value of SDS increased from 8 to 13 mM at 25 °C in the presence of 0.1 mM $Cr(en)_3Cl_3$ (cf. Table 1). The extremely low values of N for SDS micelles in the presence of $Cr(en)_3Cl_3$ may be due to a displacement of water molecules from the micellar interface, like urea; the consequent desolvation[34,35] leads to the removal of fluoroprobe molecules from the interfacial region. However, we have not determined the hydration extent of the micelles in the presence of Cr(III). Further work in this direction may be worthwhile. Mazer et al.[36] had used a quasi-elastic light-scattering (QELS) spectroscopic technique to study the effect of NaCl on the aggregation properties of SDS micelles. They found that, for an aqueous solution of SDS (69 mM, fixed) at 25 °C, an increase of the ionic strength with NaCl in the concentration range C_{NaCl} = 0—0.6 M resulted in an increase of the surfactant aggregation number (N) from 80 to 1000. However, Lianos

Table 3. a) Fluorescence Lifetimes, τ for Pyrene in SDS Micelles as a Function of Cr(III) Quenchers Concentrations at 25 °C
[Pyrene] = 1 μM (fixed); [SDS] = 50 mM (fixed). Lifetime of pyrene in absence of quencher is 190 ns.

Cr(III) complex	$[Cr]^{3+}$/M	Lifetimes τ/ns	Relative amplitudes (%)
$[Cr(salprn)(H_2O)_2]^+$	1×10^{-6}	185.0	100
	1×10^{-5}	182.0	100
	1×10^{-3}	170.6	97.62
		11.0	2.38
$[Cr(phen)_3](ClO_4)_3$	1×10^{-6}	187.2	100
	1×10^{-5}	185.0	100
	1×10^{-3}	177.0	98.28
		12.0	1.72
$[Cr(en)_3]Cl_3$	1×10^{-6}	179.2	78.95
		13.9	21.05
	1×10^{-5}	151.3	80.05
		35.7	19.95
	1×10^{-3}	184.0	27.13
		69.4	2.87

b) Fluorescence Lifetimes, τ for Pyrene in SDS Micelles as a Function of CPC Quencher Concentrations at a Fixed Concentration of $[Cr(Salprn)]^+$ (0.1 mM, fixed) at 25 °C
[Pyrene] = 1 μM (fixed); [SDS] = 50 mM (fixed).

Cr(III) complex	[CPC]/M	Lifetimes τ/ns	Relative amplitudes (%)
$[Cr(salprn)(H_2O)_2]^+$	1×10^{-6}	178.7	94.32
		21.1	5.68
	1×10^{-5}	170.0	98.74
		19.4	1.26
	1×10^{-3}	153.0	81.81
		16.3	18.19

and Zana[37] had mentioned earlier the inaccuracy of the N values obtained by the time-resolved fluorescence method; also, the upper limit of N was reported to be 200 when pyrene was employed as the probe. To our surprise, we obtained an N value as large as 800 using the exact cmc values of SDS in the presence of small concentrations of Cr(III) additives viz. 0.1 mM $[Cr(salprn)(H_2O)_2]^+$. The extremely high N values of SDS in the presence of a higher concentration of NaCl ($C_{NaCl} > 0.4$ M) had accounted for the spheroid-rod transition.[36,38] There may be some possibilities for shape and polydispersity changes of the SDS micelles at its higher concentrations, even in the presence of small concentrations of Cr(III) additives, especially when the aggregation number is quite large. However, we cannot predict these changes at present until further work can be done in this direction.

It is interesting to note that the fluorescence decay curves for pyrene are monoexponential in nature in the presence of low concentrations of Cr(III) complexes, whereas they are biexponential in the presence of high concentrations of Cr(III) complexes (1 mM). However, in the presence of $[Cr(en)_3]Cl_3$, the fluorescence decay curves for pyrene are always biexponential even at the low concentrations of $[Cr(en)_3]Cl_3$ (1 μM). The lifetimes were obtained from the following reconvolution fit and depicted in Table 3:

$$\text{for monoexponential, } A + B^* \exp(-t/\tau);$$
$$\text{biexponential, } A + B_1^* \exp(-t/\tau_1) + B_2^* \exp(-t/\tau_2). \quad (4)$$

The fluorescence lifetimes for both components (major and minor) of pyrene were decreased along with an increase in the concentration of the quenchers (see Table 3). Although in the presence of $[Cr(en)_3]Cl_3$ quencher, the lifetime of major component of pyrene decreased with an increase in the concentration of $[Cr(en)_3]Cl_3$ upto 1×10^{-5} M, above 1×10^{-5} M, the lifetime for the major component increased along with a remarkable increase of the lifetime for the minor component. On the other hand, the lifetime for the minor component of the pyrene increased with an increase in the concentration of $[Cr(en)_3]Cl_3$ This further indicates that $[Cr(en)_3]Cl_3$ acts as a structure breaker for the aggregated SDS micelles. Using a biphasic model,[20] the transfer of the standard free-energy change $(\Delta G_m^\circ)_{tr}$ of SDS micelles from aqueous to Cr-ligand environments has also been presented (Table 1). The positive value of $(\Delta G_m^\circ)_{tr}$ indicates that transfer is possible, whereas the reverse situation exists for negative values.

It is well known that the average polarity[39—41] sensed by a hydrophobic probe molecule decreased with increasing micelle size. However, a detailed model has not been offered, and no other data are yet available. Figure 3 shows the fluorescence emission intensity ratio of the first vibronic band to the third as a function of the concentrations of Cr(III) complexes for fixed concentration of pyrene (1 μM) and SDS (15 mM). The I_1/I_3 value decreases with an increase of the Cr(III) complex concentration for $[Cr(salprn)(H_2O)_2]^+$, $[Cr(phen)_3](ClO_4)_3$, and $[Cr(bpy)_3](ClO_4)_3$ complexes, whereas for other complex (when ligand is aliphatic) the above I_1/I_3 value increased with an increase of the Cr(III) concentration (cf. Fig. 3). The decrease in I_1/I_3 value is interpreted as being a decrease in the average polarity sensed by the pyrene as the SDS micelles grow due to presence of Cr(III) complexes, particularly when the ligand environments are Schiff-base and aromatic in nature. The I_1/I_3 values of 1.01 and 1.03 have been reported for SDS[16,42] at a concentration near 100 mM. It is well established that the above ratio of I_1/I_3 correlates with the polarity of the immediate environment of the pyrene molecules.[43] It is equal to 1.8—1.9 in water, and reaches 0.9 in nonpolar solvents. It has also been found that the I_1/I_3 value for the SDS at its cmc[44] in aqueous solution was 1.14. The I_1/I_3 ratio varies from 1.2 to 1.01 in presence of Cr(III) complexes, depending on the nature of ligands. Therefore, our results agree with the above studies.[16,42,44] Hence, we conclude that the ligand plays a vital role in the aggregation of surfactant micelles. The same phenomena have also been observed in the case of cobalt-ligand complexes.[45] It

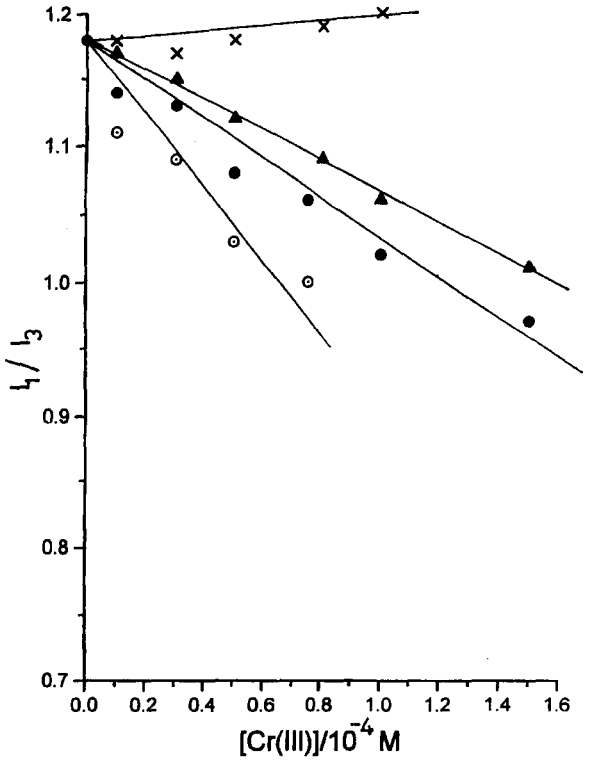

Fig. 3. Fluorescence emission intensity ratio of the first vibronic band to the third (i.e., I_1/I_3) for pyrene (1 μM, fixed) in presence of SDS (15 mM, fixed) micelles as a function of [Cr(III)]. Symbols: ×, $[Cr(en)_3]^{3+}$; ▲, $[Cr(salprn)(H_2O)_2]^{+}$; ●, $[Cr(phen)_3]^{3+}$, and ○, $[Cr(bpy)_3]^{3+}$, respectively. Temperature = 25 °C.

can be seen from Table 2 that the N value for 15 mM SDS in the presence of 0.1 mM $Cr(en)_3Cl_3$ is very low (2). It may indicate that there are no micellar aggregates of SDS at all within some experimental errors, but simply ion-pairs or premicellar clusters, when the concentration of SDS is 15 mM. The overall aggregation number and lifetime measurements suggest that the aliphatic ligand acts as a structure breaker, whereas Schiff-base and aromatic ligands act as structure makers for surfactant micelles.

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