

Photochemical Primary Processes of Xanthene Dyes. 7.[†] Xanthene Dyes as Probes for the Characterization of Anionic Micelles

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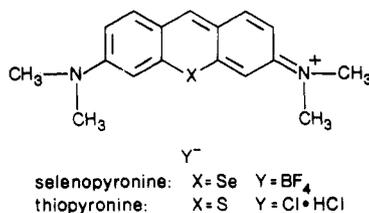
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The cationic xanthene dyes thiopyronine and selenopyronine are solubilized in the Stern regions of anionic micelles. Upon photoexcitation, the excited triplet states of the dyes are observed to decay via unimolecular processes ($k_1 \approx 2 \times 10^3 \text{ s}^{-1}$) for the case of one dye per micelle and via bimolecular processes ($k_2 \approx 5 \times 10^6 \text{ s}^{-1}$) for the case of more than one dye per micelle. If the number of dye triplet states that undergo slow decay is measured, the number of micelles can be obtained and thus the micellar aggregation numbers can be evaluated. The aggregation numbers of several surfactant alkanesulfonates, 2,5-dialkylbenzenesulfonates with a total of 14 carbon atoms in the alkyl chains, and other detergents, which are determined in this manner, are in agreement with corresponding values determined by using other photophysical methods and with literature values. The aggregation numbers of the dialkylbenzenesulfonate surfactants increase from 38 to 56 with increasing effective chain length. The fluorescence lifetime and fluorescence depolarization of thiopyronine solubilized in the dialkylbenzenesulfonate micelles are consistent with a low local polarity and high local viscosity for the interior of these micelles, compared to micelles of aliphatic detergents. Investigations using sodium 11-(3-hexyl-1-indolyl)undecyl sulfate (6-In-11) as a fluorescence probe suggest that the polarity of the interior of the dialkylbenzenesulfonate micelles is similar to that of liquid hydrocarbons. These results suggest a compact structure for the dialkylbenzenesulfonate micelles with low water penetration into the micelles.

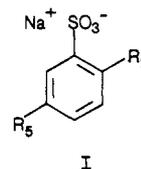
Introduction

Investigations into the primary photophysical properties of the cationic xanthene dyes thiopyronine (Tp^+) and selenopyronine (Sp^+) have shown that in aqueous anionic micellar solution the dyes are solubilized in the micellar Stern layers.¹⁻³ The decay processes of the dye triplet states depend upon the distribution of the dye ions among the micelles. The triplet states of dyes in which there is only one dye ion per micelle



decay via a slow unimolecular process ($k_1 \approx 2 \times 10^3 \text{ s}^{-1}$).² However, the triplet states of dyes in which there is more than one dye ion per micelle undergo fast bimolecular deactivation.² Because the difference in the decay rates of the dye triplet under these two conditions is large, it is possible to determine the concentration of micelles containing only one dye molecule using time-resolved techniques. Thus, the time-resolved triplet-state absorption of these dye molecules can be used as a probe for the aggregation numbers (n) of anionic micelles in a similar manner to the luminescence of fluorescent probes.⁴⁻⁶ In addition, fluorescence lifetime and depolarization measurements of solubilized xanthene dyes can provide information concerning the microenvironment of the dye ions which are located in the micellar Stern layer. In this work we have used selenopyronine ($\Phi_{\text{isc}} \approx 1.0$, $\Phi_f \approx 0.01$) in laser flash absorption experiments as a probe for micellar aggregation number and thiopyronine ($\Phi_f \approx 0.2$) in fluorescence experiments as a probe for micellar microenvironment. The results are compared to those obtained by using other fluorescence probes (pyrene, tris(bipyridine)ruthenium dichloride ($\text{Ru}(\text{bpy})_3\text{Cl}_2$) and sodium 11-(3-hexyl-1-indolyl)undecyl sulfate (6-In-11)), whose properties as probes were known from the lit-

erature.⁴⁻⁶ The properties of the micelles of a series of 2,5-dialkylbenzenesulfonates, each with 14 carbon atoms in the n -alkyl chains (I), and of several other detergents were investigated by using these photophysical methods.



Experimental Section

Materials. Thiopyronine and selenopyronine were synthesized as described previously.⁷ Thiopyronine was purified as the salt ($\text{Tp}^+\text{Cl}^-\text{HCl}$) by recrystallization from hydrochloric acid. Selenopyronine was recrystallized from 10% HBF_4 and obtained as the salt (Sp^+BF_4^-). Pyrene (Merck-Schuchardt) was used without further purification. $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was used as received from Aldrich Chemical Co. 6-In-11 was available from previous studies.^{4b} 9-Methylanthracene was prepared according to ref 8 and was purified by recrystallization from ethanol. Sodium dodecyl sulfate (SDS) and sodium dodecyltris(oxyethylene) sulfate were prepared according to ref 9 and 10, and purified by extraction with n -hexane and recrystallization from water and ethanol. The preparation of the dialkylbenzenesulfonates has been previously described.¹¹ The alkanesulfonates were a gift from VEB Leuna-Werke (DDR). Doubly distilled water was used as the solvent.

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TABLE I: Surfactant Aggregation Numbers and Critical Micelle Concentrations Determined by Using Photophysical Techniques

surfactant	temp, °C	n				
		Sp ⁺	pyrene	Ru(bpy) ₃ Cl ₂	mean	cmc, 10 ⁻³ M
sodium dodecyl sulfate	25	60	63	67	63	8.2
sodium dodecyltris(oxyethylene) sulfate	25	81	74	78	78	2.0
ammonium dodecane-1-sulfonate	25	46	39	61	49	10.0
sodium pentadecane-1-sulfonate	45		67		67	1.5
sodium pentadecane-8-sulfonate	45		41		41	5.4
sodium pentadecane-8-sulfonate	25		63		63	6.6
E 30 (sodium salt)	25	87	90	90	94	2.6
E 30 (diethylammonium salt)	25	103	81	81	88	1.8
sodium 2,5-dialkylbenzenesulfonates						
R ₂ , R ₅ =						
C ₁₃ H ₂₇ , CH ₃	25		56		56	0.66
C ₂ H ₅ , C ₁₂ H ₂₅	25	49	58	54	54	0.52
C ₁₂ H ₂₅ , C ₇ H ₅	25	42	60	54	52	0.88
C ₃ H ₇ , C ₁₁ H ₂₃	25	43	42	50	45	0.72
C ₁₁ H ₂₃ , C ₃ H ₇	25	37	43	49	43	1.21
C ₇ H ₁₅ , C ₇ H ₁₅	25	35	34	44	38	2.02

Sample Preparation. The dye solutions were prepared by dissolving each dye in water and determining the concentrations by UV/vis spectroscopy (selenopyronine; $\lambda_{\max} = 574$ nm, $\epsilon_{\max} = 81\,000$ M⁻¹ cm⁻¹; thiopyronine: $\lambda_{\max} = 564$ nm, $\epsilon_{\max} = 78\,500$ M⁻¹ cm⁻¹). Typically the dye concentrations were $\approx 1 \times 10^{-5}$ M. The samples were prepared by dissolving weighed amounts of the dry detergents in the dye solutions. Pyrene and methylanthracene were dissolved in micellar solutions by stirring for several hours. The solutions were centrifuged and the concentrations of the probes determined by UV spectroscopy (pyrene: $\lambda_{\max} = 337$ nm, $\epsilon_{\max} = 45\,000$ M⁻¹ cm⁻¹; 9-methylanthracene: $\lambda_{\max} = 388$ nm, $\epsilon_{\max} = 7500$ M⁻¹ cm⁻¹).¹²

Apparatus. The micellar critical micelle concentrations (cmc) were determined by using a stalagmometer for surface tension measurements, and for some surfactants the variation of the fine structure of the fluorescence of pyrene was used. The flash photolysis apparatus has been described previously.¹³ The apparatus uses 20- μ s flash lamps for excitation and a steady-state xenon arc lamp as the monitoring source. The path length of the analyzing light in the irradiated volume of the sample was 5 cm. The samples were degassed by the freeze-pump-thaw technique. The experiments in the nanosecond time scale were performed using a Quanta Ray DCR-2A Nd-YAG laser (532 nm), ≈ 40 mJ, 8 ns). The analyzing light was a pulsed xenon arc lamp (Osram XBO 150 W). The transmitted light was analyzed by using an RCA 4840 photomultiplier tube, and the transient signals were digitized by using a Tektronix 7912AD transient digitizer interfaced to a DEC PDP-11/23 minicomputer. The samples were degassed by bubbling with argon. The fluorescence lifetime and depolarization measurements were performed using an LIF 200¹⁴ which was interfaced to a BCl 280 boxcar integrator and an MC 80 computer (VEB Elektronik Gera). Thiopyronine was excited with a dye laser at 573 nm. The fluorescence lifetimes (τ_f) and the orientation relaxation times (τ_{rot}) were determined by deconvolution of the fluorescence decay curves. Pyrene was excited by using a nitrogen laser for the determination of the micellar aggregation numbers. The scattered laser light and the excimer fluorescence were absorbed by using WG 9 and UG 5 filters from VEB Jenaer Glaswerk. The decay curves of the pyrene monomer fluorescence were analyzed by using a nonlinear least-squares method.¹⁵ The data analysis yields the fluorescence lifetime of the pyrene, the rate constant for the intramicellar excimer formation, and the quotient of the pyrene and the micelle concentrations.⁶

The fluorescence spectra and the steady-state fluorescence measurements were performed on an apparatus constructed with

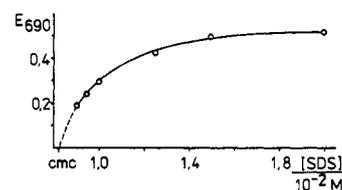


Figure 1. Absorbance of the selenopyronine triplet state at 690 nm (E_{690}) as a function of detergent concentration. Selenopyronine concentration = 1.0×10^{-5} M, path length = 5 cm.

high-intensity monochromators. For the determination of the average aggregation numbers according to ref 4, the 9-methylanthracene concentration was varied and the Ru(bpy)₃Cl₂ and detergent concentrations held constant. The UV/vis spectra were recorded with Specord M 40 UV (VEB Carl Zeiss Jena) and Perkin Elmer 559 spectrophotometers.

Results and Discussion

Average Aggregation Numbers of the Surfactants. In Figure 1 is shown the dependence of the absorption of the triplet state of selenopyronine in water, observed by microsecond flash photolysis, as a function of concentration of sodium dodecyl sulfate (SDS) at constant dye concentration. As the SDS concentration decreases the absorption due to the triplet state decreases because the number of micelles containing one dye molecule becomes smaller, multiple occupancy increases, and fast bimolecular decay processes become dominant. With microsecond flash photolysis, the fast decay of the triplet states in micelles containing more than one dye cannot be observed. With nanosecond laser flash photolysis this fast bimolecular decay of the triplet absorption was observed under the conditions of low surfactant concentration. A first-order decay constant of 5×10^6 s⁻¹ was observed under these conditions, which is in good agreement with previously reported data for other intramicellar bimolecular reactions.^{16,17}

Using microsecond flash photolysis it is possible to excite all of the selenopyronine dye molecules in solutions containing ca. 10^{-5} M dye. For the determination of the micellar aggregation numbers (n) a series of solutions with constant dye concentration and varying surfactant concentration were analyzed in order to determine the absorbance of the triplet state at 690 nm (E_{690}) after the fast bimolecular decay had taken place. The aggregation numbers were determined by using eq 1 and 2, which take into

$$[M] = \frac{[Sp^+]}{\ln(E_{690}/\epsilon_{690}d[Sp^+])} \quad (1)$$

$$n = \frac{[S] - cmc}{[M]} \quad (2)$$

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TABLE II: Photophysical Properties of Fluorescent Probes in Micellar Environments

surfactant	k_{exit} , 10^3 s^{-1}	$\tau_f(\text{Tp}^+)$, ns	$\tau_{\text{rot}}(\text{Tp}^+)$, ns	I_1/I_3	$\lambda_{\text{max}}(6\text{-ln}\cdot 11)$, nm
sodium dodecyl sulfate	2.4	2.63	0.55	1.15	357
sodium dodecyltris(oxyethylene) sulfate	8.2	2.40	1.02	1.24	
ammonium dodecane-1-sulfonate	6.2	2.47	0.52	1.16	
sodium pentadecane-1-sulfonate					
sodium pentadecane-8-sulfonate					
sodium pentadecane-8-sulfonate		2.66	0.48	0.95	
E 30 (sodium salt)	2.1	2.55	0.68	1.02	
E 30 (diethylammonium salt)	4.1	2.38	0.56	1.00	
sodium 2,5-dialkylbenzenesulfonates					
$R_2, R_5 =$					
$\text{C}_{13}\text{H}_{27}, \text{CH}_3$		2.98	1.32	1.16	
$\text{C}_2\text{H}_5, \text{C}_{12}\text{H}_{25}$		3.14	1.13	1.14	336
$\text{C}_{12}\text{H}_{25}, \text{C}_2\text{H}_5$	≈ 1.6	2.94	0.97	1.09	334
$\text{C}_3\text{H}_7, \text{C}_{11}\text{H}_{23}$		3.03	1.19	1.14	333
$\text{C}_{11}\text{H}_{23}, \text{C}_3\text{H}_7$		2.89	0.88	1.15	331
$\text{C}_7\text{H}_{15}, \text{C}_7\text{H}_{15}$	≈ 1.8	3.0	0.90	0.98	331

account the fact that the dye molecules are distributed among the micelles according to Poisson statistics. In the equations $[M]$ is the concentration of the micelles, $[Sp^+]$ the concentration of the dye, $[S]$ the concentration of the surfactant, E_{690} the absorbance of the dye triplet state after the fast bimolecular decay, ϵ_{690} ¹⁸ the extinction coefficient of the dye triplet state, d the path length, and cmc the surfactant critical micelle concentration.

The aggregation numbers which are determined with this method, for all of the surfactants included in the present study, are summarized in Table I. The aggregation numbers were also determined by using two other photophysical probe techniques, i.e., the pyrene fluorescence decay method,⁶ and the 9-methylanthracene/ $\text{Ru}(\text{bpy})_3\text{Cl}_2$ quenching method⁴ (Table I). Within experimental error the three methods all give the same value for the aggregation number for SDS, which agrees well with previously reported values.^{19,20} The three methods also give aggregation numbers which agree fairly well for the other detergents studied (Table I). The errors are estimated to be ca. $\pm 15\%$ for each of the methods.

The advantage of the flash photolysis method for determining aggregation numbers, over other photophysical methods, is due to the fact that the rates of the intramicellar bimolecular and unimolecular decays differ by 3 orders of magnitude. It is thus easy to distinguish micelles containing one dye molecule from those containing more than one molecule. It is unlikely that in larger aggregate systems the bimolecular process will become sufficiently slow that the rates of the two processes will become comparable, as might happen with the 9-methylanthracene/ $\text{Ru}(\text{bpy})_3\text{Cl}_2$ method. In addition, it is possible to prepare water stock solutions of the selenopyronine dye so that experiments can be performed using many detergents without time-consuming sample preparation. However, the necessity to remove dissolved oxygen is an inconvenience compared to other methods.

The aggregation numbers which are determined for sodium dodecyltrioxyethylene sulfate and ammonium dodecane-1-sulfonate are consistent with those previously reported for related detergents (sodium tetradecyltris(oxyethylene) sulfate: $n = 95$,²² $n = 65$;²³ sodium dodecane-1-sulfonate: $n = 54$,²⁴ $n = 45$ ²⁵ (40 °C)). The aggregation number obtained for pentadecane-8-sulfonate is

(18) The extinction coefficient was estimated under conditions of high surfactant concentration in which there was approximately one dye per micelle. The average aggregation numbers at lower surfactant concentrations were calculated by using this estimate. The concentration of the micelles containing only one dye at the higher surfactant concentrations could then be determined by using Poisson statistics. Thus a more accurate estimate for the extinction coefficient was obtained, and this value was used for the final calculations of the aggregation numbers.

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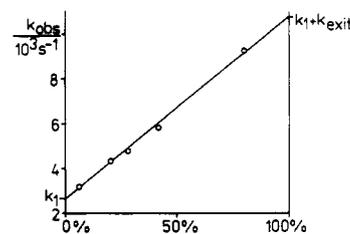


Figure 2. Decay constant of the selenopyronine triplet state as a function of the percentage of sodium tris(oxyethylene) sulfate micelles containing more than one dye ion.

smaller than the value for pentadecane-1-sulfonate. The aggregation numbers measured at 45 °C for sodium pentadecane-1-sulfonate and sodium pentadecane-8-sulfonate are slightly smaller than previously predicted values.²⁶ The value for pentadecane-8-sulfonate was also determined at 25 °C because of the high solubility of this detergent. The value at 25 °C is 1.5 times larger than that at 45 °C. Emulgator E 30²⁷ is a mixture of all of the isomers of the $n\text{-C}_{12}\text{-C}_{18}$ alkanesulfonates with an average formula $\text{C}_{15}\text{H}_{31}\text{SO}_3\text{-Na}^+$. The observed aggregation number for E 30 is slightly higher than the value for sodium pentadecane-8-sulfonate and is the same for both Na^+ and H_2NEt_2^+ counterions.

The aggregation numbers of the 2,5-dialkylbenzenesulfonates depend upon the length of the alkyl chains. If the effective chain length is defined as the number of carbon atoms between the sulfonate group and the end of the longer alkyl chain, then the 2,5-diheptylbenzenesulfonate has the shortest effective chain length and also the smallest aggregation number (Table I). The aggregation numbers increase with the effective chain length. No significant differences are observed between the two isomers of the propylundecylbenzenesulfonate and the ethyldodecylbenzenesulfonate. In addition to the aggregation numbers, the critical micelle concentrations (cmc) of these detergents also show a strong dependence upon the effective chain length (Table I and ref 28). The 2,5-diheptylbenzenesulfonate possesses the highest cmc , and the cmc values decrease with increasing effective chain length.

Probe Exchange between Micelles. The decay processes of the triplet states of the dyes which are in micelles with no other dye molecules depend upon the micelle concentration. The observed first-order decay constant for the triplet decay (k_{obs}) increases with decreasing micelle concentration. This can be explained by exchange of the dye molecules among the micelles within the dye triplet lifetime. The observed decay constants depend linearly upon the percentage of the micelles containing more than one dye ion (Figure 2). Extrapolation of the straight line to the 0% and 100% values yields the rates of unimolecular triplet-state decay

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TABLE III: Photophysical Properties of Fluorescent Probes in Homogeneous Solution

solvent	viscosity, cP	$\tau_f(\text{Tp}^+)$, ns	$\tau_{\text{rot}}(\text{Tp}^+)$, ns	I_1/I_3	$\lambda_{\text{max}}(6\text{-ln-11})$, nm
water	1.005	2.00		1.87	370
methanol	0.591	2.17		1.35	
ethanol	1.192	2.18		1.18	
1-butanol	2.947	2.66		1.06	351
glycol	19.9	2.77	1.26	1.64	
glycerin	1499	3.14	7.7	1.60	
n-hexane				0.58	
dodecane				0.59	333

(k_1) and the sum of this rate and the dye ion exit rate (k_{exit}), respectively. The values of k_1 , which are determined ($(2.1 \pm 0.5) \times 10^3 \text{ s}^{-1}$) are found to be same for all of the detergents studied. However, the values of k_{exit} are found to vary with the surfactant structure (Table II). The exit rates of selenopyronine from the micelles of sodium dodecyltris(oxyethylene) sulfate, ammonium dodecane-1-sulfate, and the ammonium salt of E 30 are higher than that from SDS micelles, which suggests that the interactions between the dye ions and these micelles are weaker than those between selenopyronine and SDS. The exit rates of selenopyronine from the alkylbenzenesulfonate micelles are so small that the values of k_{obsd} do not change sufficiently as a function of surfactant concentration to accurately determine k_{exit} for these micelles. This is consistent with strong interactions between the dye ions and the dialkylbenzenesulfonate micelles.

Polarity and Viscosity of the Microenvironment of the Probes. The fluorescence lifetime and fluorescence depolarization of thiopyronine ions solubilized in the micellar aggregates were studied in order to investigate the viscosity and polarity of the microenvironment of this probe. The results obtained in homogeneous solution show that the fluorescence lifetime depends upon the polarity of the medium (i.e., the ability to form hydrogen bonds) and also upon the medium viscosity (Table III and ref 29). The orientation relaxation times (τ_{rot}), measured from the fluorescence depolarization, also depend upon the solvent viscosity.^{29,30} In water or in monoalcohols, τ_{rot} was too large to be determined by using the present apparatus.

The thiopyronine fluorescence lifetime is higher in the presence of anionic micelles than in water, and the values of τ_{rot} could be measured (Table II). The thiopyronine ions are presumably localized in the micellar Stern region, where the microenvironment is less polar and more viscous than water.^{31,32} The smallest fluorescence lifetimes are found in the presence of those detergents for which selenopyronine was found to have the largest exit rates. This indicates a more waterlike microenvironment for these micelles in which the interactions between the dye and the surfactants are weaker.

In the presence of micelles of sodium dodecyltris(oxyethylene) sulfate a higher exit rate, a lower fluorescence lifetime, and a higher value of τ_{rot} are observed compared to the other aliphatic detergents studied (Table II). This can be explained if the thiopyronine ions are localized in the water-filled pockets in the Stern layer.³¹ Such pockets could be easily formed in these micelles because of the hydrophilic properties of the tris(oxyethylene) group. Thus the thiopyronine ions "see" a microenvironment with high viscosity and a high water content and also have a high exit rate.

The thiopyronine ions have higher fluorescence lifetimes and τ_{rot} values in the dialkylbenzenesulfonate micelles than in any of the aliphatic surfactants. This indicates a less polar and more viscous environment and thus a stronger interaction between the dye ions and the micelles. It is possible that interactions between the aromatic π electrons of the surfactant and the dye ions play an important role.

The measurements of the pyrene fluorescence in the micelles yield the lifetime of the pyrene excited singlet state and the rate of intramicellar excimer formation in addition to the micelle aggregation number. These rates are almost the same within experimental error for all of the detergents studied.³⁴ The excited singlet-state lifetime ($179 \pm 20 \text{ ns}$) agrees well with literature values. The rate of intramicellar excimer formation ($(3.4 \pm 1.0) \times 10^7 \text{ s}^{-1}$) is slightly higher than previously reported values.^{6,33} The fine structure of the pyrene monomer fluorescence can also be used to provide information concerning the polarity of the pyrene microenvironment.³⁵ The ratios of the intensities of the first to the third vibrational band of the pyrene monomer fluorescence (I_1/I_3) given in Tables II and III show that for this probe the polarity of the microenvironment is similar to an alcohol in each of the surfactants studied. Presumably the pyrene molecules are located in the Stern regions of each micelle where water contact is possible. Very similar results are obtained for each surfactant when this probe is used. The microenvironment of pyrene solubilized in micelles of sodium dodecyltris(oxyethylene) sulfate is slightly more polar than that of pyrene in SDS micelles because the hydrophilic nature of the tris(oxyethylene) group allows more extensive water penetration in these micelles. Compared to SDS a slightly lower micropolarity is observed for E 30, sodium pentadecane-8-sulfonate, and sodium 2,5-diheptylbenzenesulfonate. This can be explained if the hydrocarbon core of micelles of these surfactants are more rigid and do not allow water to penetrate so easily.

6-ln-11 was used as a fluorescence probe for the interior of the micelle structures.³⁶ The fluorescence maxima ($\lambda_{\text{max}}(6\text{-ln-11})$, Tables II and III) indicate a much smaller polarity for the interiors of the dialkylbenzenesulfonate micelles compared to SDS. The fluorescence data indicate a micropolarity which is similar to that of liquid hydrocarbons. These results demonstrate that the micelles of the dialkylbenzenesulfonates have a compact structure which is similar, for example, to that of the nonionic Triton micelles,³⁷ and that water penetration does not occur to a significant extent.

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Registry No. I ($R_2 = \text{C}_{11}\text{H}_{27}$, $R_5 = \text{CH}_3$), 106439-01-4; I ($R_2 = \text{C}_2\text{H}_5$, $R_5 = \text{C}_{12}\text{H}_{25}$), 106438-99-7; nI ($R_2 = \text{C}_{12}\text{H}_{25}$, $R_5 = \text{C}_2\text{H}_5$), 98282-45-2; I ($R_2 = \text{C}_3\text{H}_7$, $R_5 = \text{C}_{11}\text{H}_{23}$), 98282-26-9; I ($R_2 = \text{C}_{11}\text{H}_{23}$, $R_5 = \text{C}_3\text{H}_7$), 98306-26-4; I ($R_2 = \text{C}_7\text{H}_{15}$, $R_5 = \text{C}_7\text{H}_{15}$), 72601-88-8; SDS, 151-21-3; E₃₀ (sodium salt), 5896-54-8; E₃₀ (diethylammonium salt), 108036-06-2; Tp⁺Cl⁻HCl, 68406-98-4; Sp⁺BF₄⁻, 84835-12-1; sodium dodecyl trioxyethylene sulfate, 103800-09-5; ammonium dodecan-1-sulfonate, 2149-63-5; sodium pentadecan-8-sulfonate, 102867-78-7.

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(34) Upon excitation of the dialkylbenzenesulfonates at ca. 280 nm, fluorescence is observed with a maximum of 305–310 nm. The lifetime of this fluorescence (40–50 ns) does not depend upon the surfactant concentration since only those surfactants which are not aggregated in solution emit. In all of the experiments pyrene was excited at 337 nm. Under these conditions no fluorescence from the surfactants can be detected.

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