at mainly in gas–solid systems.[15] A much slower rate of oxygen uptake was also observed with EDTA and Pt–CdS. In addition, a dark oxygen uptake in methanol with Pt–CdS occurred.

Addition of the nitrone, DMPO at a concentration of $\sim 2 \times 10^{-2}$ M did not increase the rate of O_2 uptake in either the Pt–CdS or Pt–CdS–EDTA systems. This suggests that singlet oxygen is not generated upon photolysis of the platinized pigment.[16]

ESR Measurements. The reduced form of MV^{2+} is the cation radical (MV^+) which is readily detected by ESR. Upon illumination of a N_2 purged CdS–EDTA dispersion, a large ESR signal due to MV^+ is observed. This is consistent with the fact that no catalytic surface is available to convert MV^+ to H_2. Addition of Pt on Kaowool (1 mg/1 mg of solution) reduced the ESR signal intensity by a factor of 5. Doubling the Pt concentration reduced the intensity of the MV^+ ESR signal by an additional factor of 6. It should be noted that these ESR experiments were carried out in an aqueous ESR cell with no stirring which can be contrasted to both the O_2 uptake and H_2 production experiments where vigorous stirring of the dispersion occurred. Finally, with N_2 purged Pt–CdS–EDTA no MV^+ was detectable upon irradiation. This suggests that if MV^+ is being generated, it is efficiently being converted to H_2 and MV^{2+}.

When MV^{2+} is excluded and O_2 allowed in the CdS–EDTA system, the generation of O_2^- can be detected upon photolysis using the spin trap, DMPO.[17] Addition of Pt on Kaowool to this dispersion does not prevent the generation of O_2^-. However, with Pt–CdS–EDTA no O_2^- adduct was observed upon irradiation. In fact, no adducts were detected with this sytem (e.g., no H· adduct).[18]

These ESR results are consistent with the O_2 uptake and H_2 evolution data. In both the CdS–EDTA and CdS–EDTA–Pt on kaowool systems, O_2^- was detectable and H_2O_2 produced. Since O_2^- is an intermediate in the two electron reduction of O_2 to H_2O_2, these results are consistent. Similarly, O_2^- is not observed with Pt–CdS–EDTA and no H_2O_2 was detected. For the MV^{2+} system, addition of Pt on Kaowool reduced the MV^+ signal which is consistent with the observation of H_2 evolution.

Conclusions

Platinization of CdS results in the deposition of ultrafine particles (20 to 50 Å) of Pt onto the surface of the larger CdS particles. These Pt particles appear to be evenly distributed over the surface creating a checkered appearance. This checkering quality explains the marked light intensity dependence differences between Pt–CdS and CdS in the O_2 uptake experiments. The fact that Pt–CdS has a rate 12 times that of CdS at high light intensities is important in solar energy systems where solar concentrators may be employed.

H_2 evolution was accomplished under illumination of the Pt–CdS EDTA system with a Φ of 0.2%. Addition of MV^{2+} actually halves the efficiency. Addition of Pt on Kaowool to a CdS–EDTA system also resulted in the photoproduction of H_2. It is particularly significant that this latter system also works without MV^{2+}.

Acknowledgment. We thank Alexandra Perovic for carrying out the TEM analysis and Denis Brillon for measuring the intensity dependence of the O_2 uptake.

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Measurement of the Rates of Detergent Exchange between Micelles and the Aqueous Phase Using Phosphorescent Labeled Detergents

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Phosphorescence quenching is used to measure micelle-probe detergent dynamics. For phosphorescent detergent probes with varying hydrocarbon length the rate constants for escape (k_-) from cationic host micelles are measured using cobalt(III) hexamine as an aqueous soluble triplet quencher. For 10-(4-bromo-1-naphthoyl)decyltrimethylammonium bromide (BND-10), k_- is 3.2×10^3 s^{-1}, and k_+, the reentry rate constant, is 5.7×10^7 M^{-1} s^{-1} for hexadecyltrimethylammonium chloride (HDTCl) host micelles at 25 °C. The log of k_- is a linear function of the number of methylenes in the probe alkyl chain, in agreement with rates determined previously with relaxation methods. The apparent activation energy for escape of BND-10 from HDTCl micelles is 9 kcal/mol. Escape rates are measured for several host micelles and for micelles composed of probe detergents—self-micelles.

Introduction

Solutions of detergent molecules exist as a dynamic equilibrium between monomer detergents and micellar aggregates.[1] A stepwise equilibrium can be formulated to include entrance and exit rate constants, k_+ and k_-, for the detergent/micelle exchange

$$D_n \underset{k_+}{\overset{nk_-}{\rightleftharpoons}} D_{n-1} + D_1 \rightleftharpoons \ldots nD_1 \quad (1)$$

where D_n represents a micelle as an aggregate of n monomer detergents, D_1. Typical mean aggregation numbers, $\langle n \rangle$, are of the order of 50–100 for ionic micelles. For micelles of aggregation number close to $\langle n \rangle$ it is assumed

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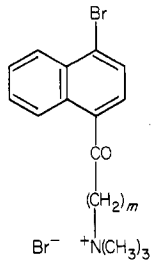
that k_- is approximately constant.

The equilibrium between micelles and detergent molecules has been investigated by relaxation methods, including T-jump, P-jump, stopped flow, and ultrasonic relaxation.[1,2] Application of a theory of stepwise association in analogy to reaction flow theory (i.e., conduction of diffusion) has led to a unified interpretation of the relaxation experiments.[1-4] The typical exit rates, k_-, are found to vary from 10^4 to 10^8 s^{-1}. For ionic detergents the log k_- varied linearly with the length of the detergent hydrocarbon chain, longer chains having slower rates. The exit rates were nearly independent of size and type, cationic or anionic, of the detergent head group.[4]

Because many of these exit rates are comparable to the rates of triplet decay in micelle solutions at room temperature,[5-8] we sought an experimental scheme for measuring k_+ and k_- using the phosphorescence of detergent molecules as a probe of the equilibrium dynamics. Previous investigations have reported entrance and exit rates of aromatic hydrocarbons into and out of micelles,[7,8] by the measurement of phosphorescent lifetimes in the presence of aqueously soluble quenchers. With excess quencher the phosphorescence decay was determined by a sum of the exit rate of the probe arene and the decay rate in the absence of quencher.[7] We have used phosphorescent labeled detergents[9] (BND-5, -8, -10, and -11) to measure the rates of exchange, k_- and k_+ of eq 1.



BND-5 (m = 5)
BND-8 (m = 8)
BND-10 (m = 10)
BND-11 (m = 11)

Experimental Section

Materials. Hexadecyltrimethylammonium chloride, HDTCl (Eastman), dodecyltrimethylammonium chloride, DDTCl (Eastman), and hexadecyltrimethylammonium bromide, HDTBr (Sigma) were washed exhaustively with ethyl ether and recrystallized from ethanol–ether mixtures. The probe detergents BND-5, -8, -10, and -11 were purified similarly.[9] Hexamine cobalt(III) chloride (Alfa) was recrystallized twice from water. NaCl (Alfa, ultrapure grade) and 1-butanol (Fischer) were used as supplied. Water was distilled twice.

Sample Preparation. All measurements were made on aqueous solutions at 25 °C unless otherwise specified. In host micelle experiments the probe concentrations were adjusted to keep the mean occupancy number less than 1. Typically, probe concentrations were 5×10^{-5} M. No changes in phosphorescent lifetimes were observed at tenfold higher concentrations. All samples were purged of oxygen by bubbling with nitrogen (Linde, oxygen free grade) for approximately 30 min.[6]

Phosphorescence Measurements. Total luminescence spectra were obtained using a Perkin-Elmer Hitachi MPF-3L fluorimeter. Phosphorescence lifetimes were measured as described previously using the photon counting–multichannel analyzer technique.[8] Excitation light from an airgap arc lamp, Xenon Corp. Model 437A nanopulser, was either unfiltered or passed through a Corning 7-54 bandpass filter. Phosphorescence emission was measured at 575 nm with 5 to 10 nm bandpass.

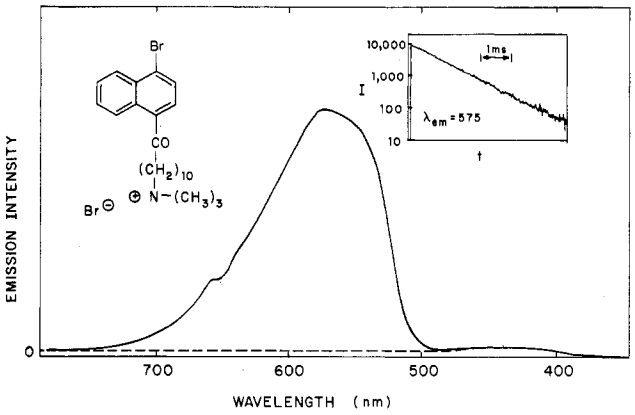


Figure 1. Luminescence spectrum of a 2.3×10^{-5} M solution of BND-10 in water. Solid line, N_2 purged; dashed line, aerated. Inset: semilog plot of the phosphorescence decay.

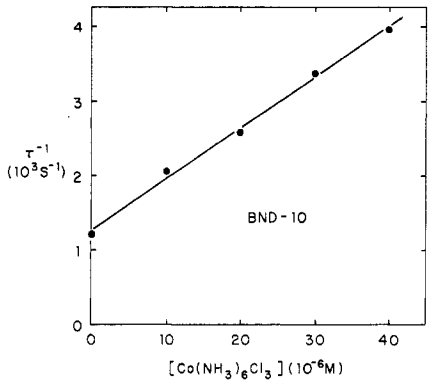


Figure 2. Co^{3+} quenching of phosphorescence of BND-10, 5×10^{-5} M in water. Decay rate (τ^{-1}) vs. quencher concentration.

Results

The luminescence spectrum of BND-10 in water, which is typical of the other probes employed in this study, is shown in Figure 1. In micelle solutions the spectrum shape and position are essentially unchanged. A semilog plot of the decay is also shown with a phosphorescence lifetime of 0.91 ms. At 25 °C in water the phosphorescence quantum yield of BND-10 is 0.023.[9] The spectroscopic properties of the BND probes are discussed in more detail elsewhere.[9]

Escape Rates from Host Micelles. The phosphorescence of BND's is readily quenched by oxygen, (e.g., Figure 1). A variety of other quenchers, including NO_2^-, $Fe(CN)_6^{3-}$, perylene (in CH_3CN), and Co^{3+}, are also effective quenchers of BND phosphorescence. For example, in the presence of Co^{3+} in aqueous solution, Stern–Volmer dynamic quenching of BND-10 is observed with k_q = (7.1 ±

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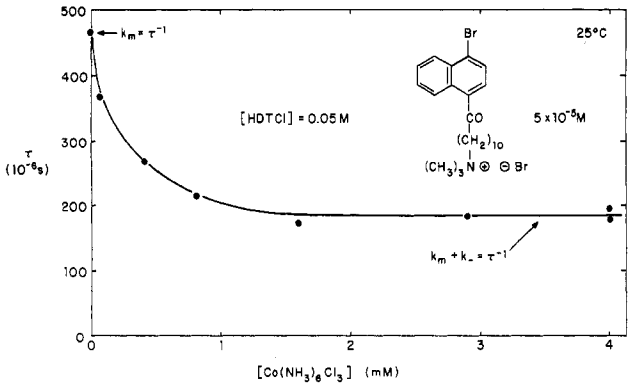

Figure 3. Phosphorescence lifetime of BND-10 in HDTCl micelles as a function of Co^{3+} as an aqueous quencher. Uncertainty is ±15 μs.

TABLE I: Escape and Entrance Rate Parameters for Phosphorescent Probe Association with HDTCl Micelles at 25 °C, HDTCl = 0.05 M[a]

probe	K_-[b]	$E_a^{k_-}$[c]	log A[c]	k_+[d]	K_{eq}[e]	k_q[f]
BND-11	0.68	10.2	10.5			6.9
BND-10	3.2	9.0	10.3	5.7	1.8	7.1
BND-8	15	6.7	9.0	17	1.1	6.6
BND-5	>50[g]				0.26	5.3

[a] All values are ±10% unless specified. [b] 10^3 s^{-1}. [c] $k_- = Ae^{-E_a/RT}$, E_a in kcal/mol; A in units of s^{-1}. [d] 10^7 M^{-1} s^{-1} (±30%). [e] 10^4 M^{-1}. [f] Stern-Volmer quenching in H_2O by Co^{3+}; 10^7 M^{-1} s^{-1} (±0.3). [g] The shortest measurable lifetime by our technique is 20×10^{-6} s.

0.4) × 10^7 M^{-1} s^{-1} (Figure 2). In the presence of HDTCl micelles the phosphorescence quenching by Co^{3+} is greatly inhibited (Figure 3). The phosphorescent lifetime decreases with increasing [Co^{3+}] until a plateau level is reached. Almgren et al.[7] have presented a kinetic analysis for quenching of a micelle solubilized triplet in the presence of an aqueous soluble quencher. The observed decay constant, k_0, is given by

$$k_0 = \frac{1}{\tau_0} = k_m + k_- - \frac{k_+k_-[M]}{k_+[M] + k_w + k_q[Q]} \quad (2)$$

where τ_0 is the observed lifetime, k_- and k_+ are defined by eq 1 as the escape and entrance rate constants of the probe, k_m and k_w are the triplet decay constants in the micelle and in the aqueous phase, respectively, k_q is the Stern–Volmer quenching constant in the aqueous phase for the quenching by Q, and [M] is the micelle concentration given by

$$[M] = ([\text{detergent}] - \text{cmc})/\langle n \rangle \quad (3)$$

In the *absence* of Q, the third term in eq 2 reduces to k_- if k_+ [M] ≫ k_w, so that $k_0 = k_m$. In the *presence of sufficiently large concentrations* of Q the third term becomes small relative to the first two, so that $k_0 = k_m + k_-$. Figure 3 shows that our data fit eq 2 very well. The observed lifetime decreases with increasing [Co^{3+}] until $\tau_0 = (k_m + k_-)^{-1}$ in the plateau region. From Figure 3 it is found that $k_m = 2.2 \times 10^3$ s^{-1} and $k_- = 3.2 \times 10^3$ s^{-1} for BND-10. The values of k_-, the escape rate of the BND probes from HDTCl micelles, are listed in Table I. As the size of the probe hydrocarbon chain decreases, k_- increases dramatically. For BND-5, with five methylenes, k_- was too large to measure the phosphorescence technique; i.e., the escape rate could not be made to be rate limiting.

BND-10 escapes from HDTBr micelles with $k_- = (3.4 \pm 0.5) \times 10^3$ s^{-1}, a similar value to k_- from HDTCl micelles.

TABLE II: Escape Rates of Anionic Phosphorescent Detergent from Sodium Alkyl Sulfate Host Micelles[a]

host	$k_-(10^3\ s^{-1})$[b] 20 °C	30 °C
sodium decyl sulfate	5.7	9.8
sodium dodecyl sulfate	1.4	2.5
sodium tetradecyl sulfate	0.7	0.8

[a] The probe detergent is sodium 10-(4-bromo-1-naphthoyl)decyl sulfate. The aqueous quencher is ferric cyanide. [b] ±10%.

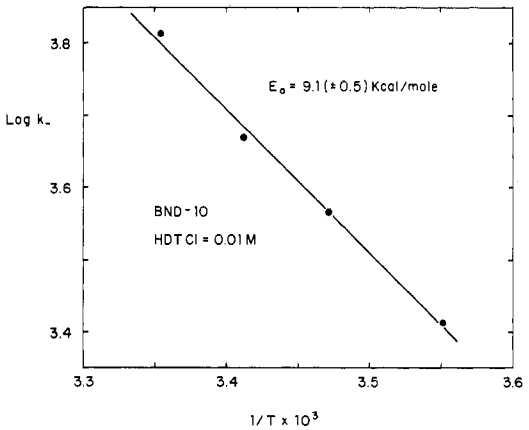

Figure 4. Plot of log k_- (escape rate) vs. $1/T$ for BND-10 in HDTCl.

In DDTCl micelle solutions where the host detergent hydrocarbon chain is decreased by four methylenes, the escape rates of BND-10 and -8 are increased fivefold and twofold, respectively (see Table II).

The temperature dependence of k_- was determined for the BND probes in the temperature range 5–45 °C. For BND-10 escape from HDTCl micelles, an Arrhenius plot gives an apparent activation energy, $E_a^{k_-}$ of 9.0 ± 0.7 kcal/mol (Figure 4). The values for BND-8, -10, and -11 are included in Table I. Again, the larger probes give larger apparent activation energies. $E_a^{k_-}$ values for other micelle/probe systems investigated are given in Table II.

The effects of two additives in the HDTCl/BND-10 system were studied. 1-Butanol increased k_- with a decrease in both $E_a^{k_-}$ and the preexponential A factor. Sodium chloride had little effect on k_- at 25 °C. However, the apparent activation energy decreased, but was accompanied by a decrease in A.

The escape rates of an anionic detergent probe, sodium 10-(4-bromo-1-naphthoyl)decyl sulfate, from sodium alkyl sulfate host micelles were determined (Table II). As with the cationic micelles, decreasing host detergent size increases the escape rate. Again it is possible that the τ_2 process influences the observed rate for the shorter chain hosts. In fact, for the lower temperature (Table I) and for the longer chain detergents (C_{12} to C_{14}) the difference in k_- is smallest. These are conditions which suppress the τ_2 process.[1-4] Overall, our results for anionic detergents parallel those for the cationic detergents.

Probe Micelles as Hosts. The escape rates in Table I represent the escape of probes from HDTCl micelles. We obtain qualitatively similar results when the lifetime of the probes were measured as a function of Co^{3+} above the probe cmc's and in the absence of other detergents. The results are included in Table III.

Entrance Rates. Equation 2 may be rearranged at low quencher concentrations[7] to give

$$k_0 = \frac{(k_- + k_m)k_q[Q]}{k_+[M]} + k_m \quad (4)$$

TABLE III: Escape Rate Host Micelle Dependence

probe	host	k_-[a]	k_m[a]	temperature dependence[b] E_a	k_- log A
BND-10	HDTCl				
	0.065 M	3.9	1.5		
	0.052 M	3.2	2.2	9.0	10.3
	0.034 M	4.2	2.3		
	0.015 M	6.5	2.0	9.1	10.6
	0.005 M	8.6	2.6		
	0.05 M + 0.1 M NaCl	3.0	2.0	5.4	7.5
	0.05 M + 0.2 M 1-butanol	5.9	1.3	6.3	8.4
	HDTBr				
	0.05 M	3.4	2.4		
	DDTCl				
	0.05 M	15	2.5	5.0	7.8
	BND-10				
	0.01 M (self-micelles)	3.4	4.7		
BND-8	HDTCl				
	0.05 M	15	2.0	6.7	9.0
	DDTCl				
	0.05 M	29	3.7	5.0	8.2
	BND-8				
	0.01 M (self-micelles)	19	6.2		

[a] 25 °C. Units, 10^3 s^{-1}. Error limits as in Table I. [b] $k_- = Ae^{-E_a/RT}$. Units of E_a, kcal/mol. Units of A, s^{-1}.

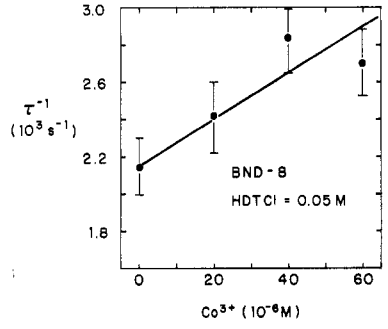

Figure 5. The measured phosphorescence decay rate (τ^{-1}) of BND-8 in the presence of HDTCl at low quencher concentrations.

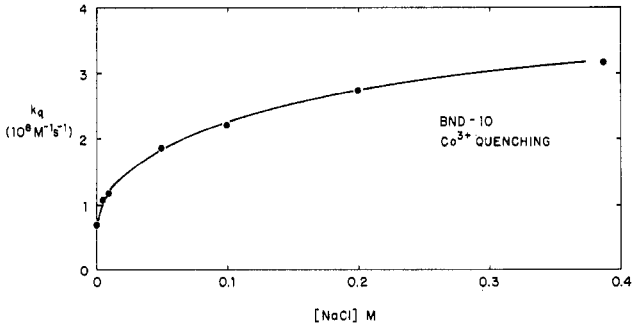

Figure 6. The effect of salt on aqueous quenching rate constant, k_q for Co^{3+} quenching of BND-10 at 25 °C.

Thus, a plot of k_0 vs. [Q] allows calculation of k_+ (see Figure 5, for example). For BND-8 and -10, k_+ was determined for Co^{3+} concentrations from 0 to 6×10^{-5} M as given in Table I. From this analysis, the reentry rate constant for BND-10 is found to be 5.7×10^7 M^{-1} s^{-1}. For BND-8, k_+ increases to 1.7×10^8 M^{-1} s^{-1}. However, the overall equilibrium ($K_{eq} = k_+/k_-$) decreased with increasing hydrocarbon chain length as expected for a less hydrophobic molecule. In eq 4, if $k_- >> k_m$ as is the case for BND-5, K_{eq} may be obtained without knowledge of k_-. For BND-5, $K_{eq} = 0.26 \times 10^4$ M^{-1}. From the K_{eq}'s, the $\Delta G°$'s, for BND-10, -8, and -5 association with HDTCl are calculated as −5.8, −5.5, and −4.7 kcal/mol, respectively.

Effects of Salt and Charge on k_q. The quenching of BND's by Co^{3+} requires the approach of two positively charged species. The partial shielding of charges by salt is demonstrated in Figure 6, where k_q is measured for BND-10 as a function of NaCl concentration. k_q increases from 7.1×10^7 to 3.2×10^8 M^{-1} s^{-1} as NaCl increases to 0.4 M.

The calculation of k_+ required knowledge of the value of k_q as in eq 4. Since HDTCl micelle solutions are also salt solutions we expect that k_q may be increased relative to the low ionic strength conditions under which k_q was measured (Table I). The concentration of Cl^- ions available to shield positive charges of BND's and Co^{3+} will be determined by the cmc and the relative ionization (fractional charge) of the micelles. The fractional charges of similar micelles are estimated to be 0.1 to 0.2.[10] A rough calculation gives a free chloride concentration of 0.006 to 0.012 M. (In fact, the conductivity of 0.05 M HDTCl is approximately equal to that of 0.012 M NaCl). Then from Figure 6 we estimate as much as a 70% increase in k_q due to the salt effect. Although this is a crude approximation we may expect that the k_+ and K_{eq} values of Table I are proportionately larger. Nevertheless, the relative values of k_q, k_+, and K_{eq} for the different probes remain unchanged.

The effect of the proximity of the positive charge to the chromophore is shown by comparison of k_q for BND-5 through -11 in Table I. As the distance between the chromophore and the tetraalkyl group decreases, k_q also decreases.

Discussion

The assumptions on which eq 2 is based are: (1) the probes are preferentially solubilized in the micellar subphase, and (2) the probes are in dynamic equilibrium between the aqueous and micellar regions. For the latter, the exit and entrance rates must be rapid compared to the decay rate in micelles, k_m, and in water, k_w. At 0.05 M HDTCl, [M] = 5.1×10^{-4} M and K_{eq} for BND-10 is 1.8×10^4 M^{-1}. Thus, the probe is preferentially partitioned in micelles ($BND\text{-}10_{micelles}/BND\text{-}10_{H_2O} > 9$). From the calculated reentry rate constant, $k_+[M] = 2.9 \times 10^4$ s^{-1} >>

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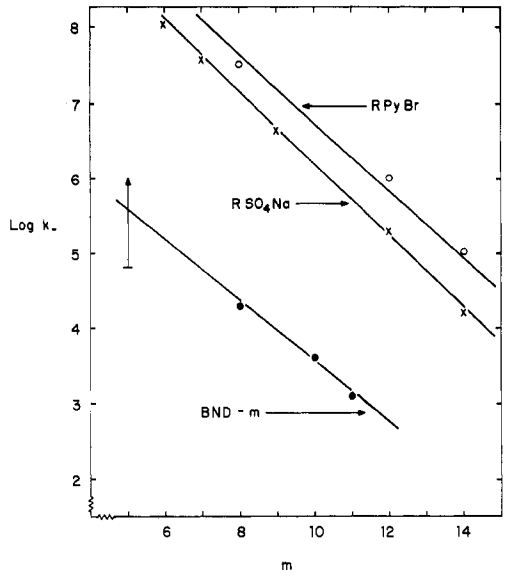

Figure 7. The dependence of escape rate of detergents from micelles as a function of number of aliphatic carbons in hydrocarbon tail. Literature data from ref 11 for sodium alkylsulfates (X) and *N*-alkylpyridinium bromides (O). Present work for escape of BND-*m* probes from HDTCl (0.05 M) at 35 °C. The displacement of the present data from the literature data is due to the hydrophobic contribution of the probe chromophore.

k_w or k_m, 1.1×10^3 and 2.2×10^3 s^{-1}, respectively. Thus, the assumptions leading to exit rates listed in Table I are valid. The correction due to salt enhancement of k_q discussed above (Results section) would increase k_+, lending even better agreement with those assumptions.

The dynamics of BND probe association with host micelles are clearly dependent on probe hydrocarbon chain length. A comparison between the probe exit rates and those rates determined by relaxation measurements is informative. A plot of log k_- vs. number of aliphatic carbons in the detergent tail is given in Figure 7. (Note that our value of k_- from eq 1 is equivalent to k^-/n of ref 2–4 and 11). There is excellent agreement between the slopes of our data and those of previous techniques.[11] The data are essentially coincident if the hydrophobic contribution of the chromophore is taken as equivalent to 6 or 7 methylenes. In support of this suggestion, the critical micelle concentrations and the mean aggregation numbers of the phosphorescent probes are nearly equal to alkyltrimethylammonium bromide detergents containing 6 or 7 additional aliphatic carbons.[9]

Furthermore, the entrance rate constants for BND-8 and -10 (Table I) are the same order of magnitude as found for k_+ from relaxation measurements of the longer chain (C_{16}) alkyl sulfates.[2] Aniansson et al. found that k_+ for shorter chain (C_6) alkyl sulfates was greater than 10^9 M^{-1} s^{-1}.[2] They discuss the factors which reduce k_+ for longer chain detergents from diffusion controlled values.

The phosphorescent probe escape rates are from a single host micelle, composed of HDTCl, while the relaxation measurements give excape rates of detergents from hosts composed of the varying chain length detergents themselves. Our results are consistent with the postulate that the hydrophobic size of monomer detergent which exits determines the escape parameter. The slight difference in slopes of Figure 7 may reflect the host micelle influence on k_-. Comparison of k_- from DDTCl and HDTCl for BND-8 and -10 as shown in Table III demonstrates an increase in the escape rate with decrease in host hydrocarbon. However, the effect is not as great as for an equivalent change in probe hydrocarbon. It is also possible that the "slow" relaxation process, τ_2 of ref 2–4, is significant for DDTCl micelles. The τ_2 process corresponds to complete dissolution of a micelle, eq 1.[1] We are currently testing these suggestions by measuring the escape rates of anionic phosphorescent detergents from a homologous series of alkyl sulfates.

The trend in apparent activation energy for escape is a decrease with decreasing probe length as might be expected. Again, agreement is found with the relaxation measurements.[12] However, the decrease in the preexponential factor, log A in Table I, suggests a greater decrease in entropy, i.e., more reordering in reaching a "transition state" for the smaller probes. We expect that escape requires a multistep process. Perhaps the transition state for escape is reached earlier for the shorter probes. Thus, experimental factors which increase k_- may affect either the energy barrier(s) or the number of steps involved. The effects of additives, NaCl and 1-butanol (Table III) are most apparent in their decrease of E_a^{k-} and A. The trends are similar despite the opposite effects of salt and low molecular weight alcohols on micelle mean aggregation number and microviscosity.[13,14]

Further comparisons can be made from the data in Table III. The relative independence of escape rate of BND-10 from HDTCl, HDTBr, or self-micelles suggests similar structures and/or other factors which influence k_- among the three micelles. The overall agreement is excellent. The increase in k_m for self-micelles may reflect either self-quenching or trace impurities in the detergent preparation.

We observe a slight decrease in k_- as host detergent concentration is increased above the cmc, as shown in Table III. The change in k_- may reflect a subtle change in micelle structure which occurs above the cmc, but below concentrations which produce gross micelle structural changes observable by light scattering and viscosity. In fact, Ban-Naim and Stillinger predict changes in micelle size distribution as the detergent concentration is increased above the cmc.[15] However, no change in apparent escape activation energy is observed. The decay rate in the absence of quencher, k_m, is relatively insensitive to detergent concentration. The slight decrease in k_m with HDTCl concentration may reflect shielding from trace impurities which act as quenchers (see Table III).

The technique described here allows measurement of k_- under a wide variety of experimental conditions. The need to extrapolate to the cmc inherent in relaxation measurements is absent. We emphasize that the luminescence quenching technique allows measurement of the probe exchange dynamics on the molecular level. We also note that our results apply (strictly speaking) to triplet molecules and not to ground-state molecules. The analysis scheme is straightforward and applicable to many systems. Overall, there is excellent agreement between these results and those obtained by the relaxation measurements.

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