that the $C_3H_5Cl^+$ skeleton is derived from the neutral reactant, perhaps by formal H_2^- abstraction; a complementary isotope-labeling study will clearly be useful.

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Luminescent Probes for Detergent Solutions. A Simple Procedure for Determination of the Mean Aggregation Number of Micelles

Sir:

One of the most fundamental and important structural parameters of micellar aggregates is the aggregation number, or the average number of detergent molecules in a micelle unit.[1] The measurement and establishment of aggregation numbers is therefore of great significance. We report here a simple procedure for measuring the mean aggregation numbers of detergent solutions. The method is based on the quenching of a luminescent probe by a hydrophobic quencher.

The mean aggregation number of micelles may be derived from luminescence quenching measurements if "static" or "active" sphere[2] quenching of a micellar donor by a micelle associated quencher is dominant. Suppose a solution contains a well-defined but unknown micelle concentration [M] and a macroscopic concentration of quencher [Q]. If Q is selected so that it resides exclusively in the micellar phase, then the molecules of Q will be distributed among the available micelles in some fashion. If a luminescent molecule D, which is also completely associated with micelles, is now added to the system, D will partition itself both among micelles containg Q and among "empty" micelles. We select Poisson statistics to describe the distribution of D and Q among micelles in the tertiary system D, Q, M. If D is luminescent only when it occupies an empty micelle (i.e., D* is completely quenched when it occupies a micelle containing at least one Q), then the *measured* ratio of luminescence intensities (I/I°) in the presence of Q to that in the absence of Q is related by the very simple expression

$$(I/I^\circ) = \exp\{-[Q]/[M]\} \qquad (1)$$

The simplicity of this expression derives from the assumption that only D* in micelles containing no Q emit.[3] This assumption can be tested experimentally since, as a function of increasing [Q], the luminescence lifetime should not change even though the luminescence intensity is decreased, i.e., "static" quenching occurs. [M] can be related to the measurable
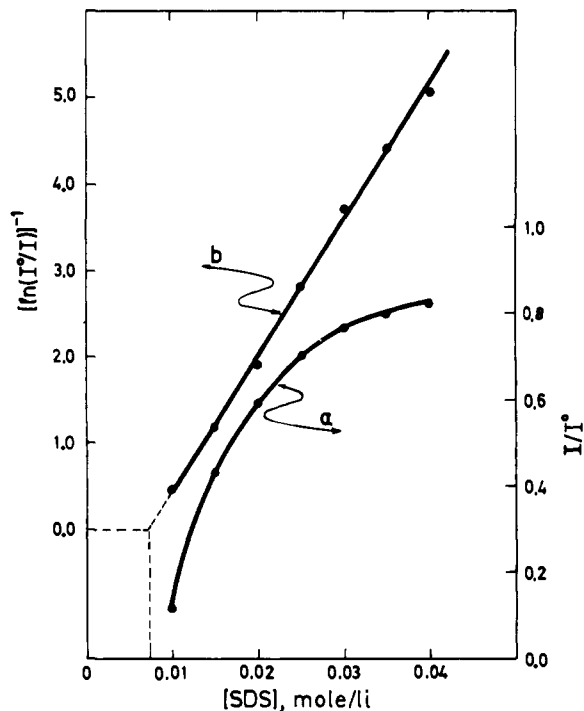

Figure 1. Detergent concentration dependence of 7.2×10^{-5} M, D = $Ru(bipy)_3^{2+}$ luminscence intensity. Q = 9-methlanthracene fixed at 1.05×10^{-4} M. Curve a: intensity normalized relative to that in the absence of Q. Curve b: analysis according to eq 3 of text. Excitation and emission wavelengths were at 450 and 630 nm, respectively (25 °C).

macroscopic concentration of detergent, [Det], and the mean aggregation number, $\bar{n}$, by the expression

$$[M] = \frac{[Det] - [\text{free monomer}]}{\bar{n}} \qquad (2)$$

where the free monomer concentration in equilibrium with the micellar aggregates is almost equal to the critical micelle concentration, cmc. The combination of expression 1 and 2 leads to

$$\ln(I^\circ/I) = \frac{[Q]\bar{n}}{[Det] - [\text{free monomer}]} \qquad (3)$$

We are in a position to evaluate both the aggregation number, $\bar{n}$, and the concentration of free monomer in equilibrium with micelles by measuring I°/I as a function of [Q] at fixed [Det] and by measuring I°/I as a function of [Det] at fixed [Q].

The experimental system of this report uses luminescent donor D = $Ru(bipy)_3^{2+}$, luminescence quencher Q = 9-methylanthracene, and detergent = sodium dodecyl sulfate (SDS). The system meets the requirement of a water-insoluble quencher and micelle-associated donor.[4] Furthermore, several evaluations of the aggregation number of SDS have been reported in the literature as a function of experimental variables.[5-8]

At [D] $\leq 7.2 \times 10^{-5}$ M, eq 1 is obeyed. Measurements of luminescence lifetime of D* yielded a constant value at 0.48 μs ($\pm 3\%$) *even under conditions where quenching had reduced the luminscence intensity by an order of magnitude*. Comparable quenching in a homogeneous solvent such as acetonitrile (no SDS) resulted in the expected (Stern-Volmer) decrease of both luminscence intensity and lifetime.[9]

To verify the functional form of eq 3, two sets of experiments were run, in each keeping one of the variables constant. Figure 1a shows the dependence of luminescence intensity keeping [Q] fixed at 1.05×10^{-4} M. The luminescence intensity *increases* as [SDS] is *increased*. This observation is readily explained by our model. Increased micelle concentration plays a protective role by keeping the donor and quencher molecules
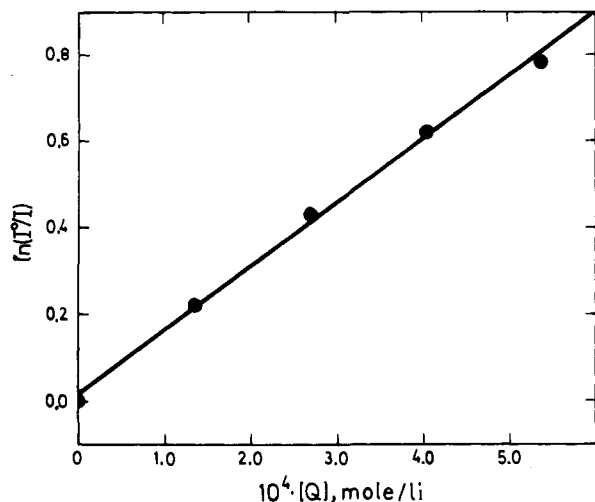
Figure 2. 9-Methylanthracene quencher concentration dependence of 7.2 × 10^{-5} M, D = Ru(bipy)$_3^{2+}$ luminescence intensity. Detergent SDS fixed at 0.045 M. Other conditions as given in caption to Figure 1.

Figure 3. Dependence of the mean aggregation number of 0.070 M SDS solution on sodium chloride concentration. Calculation of $\bar{n}$ based on eq 3 of text. D = Ru(bipy)$_3^{2+}$ fixed at 7.2 × 10^{-5} M; Q = 9-methylanthracene fixed at 8.25 × 10^{-4} M. Other conditions as given in caption to Figure 1.

separated. Figure 1b shows the analysis of data according to eq 3, which identifies the slope of the line as $\{\bar{n}[Q]\}^{-1} = 157$ M^{-1}. We thus calculate a mean aggregation number $\bar{n} = 60$ ± 2 at 25 °C. This value agrees well with the mean aggregation number, 63, for SDS obtained[7] from membrane osmometry studies and the weight averaged aggregation number, $\bar{n}_W = 62$ obtained[5] from classical light scattering studies. The observation that $\bar{n}_W \simeq \bar{n}$ implies that the size distribution of SDS micelles is narrow.[10] The intercept at the limit of total quenching gives a free monomer concentration equal to 7.5 × 10^{-3} M. Comparison with the "best" reported value[11] of cmc for SDS, 8.2 × 10^{-3} M, shows that the usual[12] conjecture that the free monomer concentration remains relatively constant above the cmc is a valid one for SDS. The general agreement of results with other methods of measurement and the excellent fit of eq 3 to the data serve as strong support that the physical assumptions made in the derivation of eq 3 are essentially correct. Further experimental support is derived from the set of experiments where the detergent concentration is fixed at 0.045 M and [Q] is varied. Figure 2 shows the fit of such data to eq 1 with the slope yielding a micelle concentration 6.7 × 10^{-4} M. Using eq 2 we calculate $\bar{n} = 55 ± 5$ again in agreement with the literature values quoted above.

The addition of electrolyte to detergent solutions causes an increase in the size of micellar aggregates. However, there are large variations among reported[5-8] values of SDS aggregation numbers in strong electrolyte solutions. For example it is reported $\bar{n} = 63$ and 115 at 0.03 and 0.34 M NaCl, respectively, when $\bar{n}$ is measured by membrane osmometry.[7] Similar values of $\bar{n}$ for SDS are found for comparable electrolyte concentration via sedimentation velocity[5] and classical light scattering measurements.[6] A recent report[8] conflicts with the three above evaluations of $\bar{n}$. Measurements of micellar mean diffusion coefficients and application a series of assumptions resulted in derivation of $\bar{n} \sim 1000$ for NaCl concentrations of $\sim$0.6 M. We have measured $\bar{n}$ as a function of NaCl concentration (Figure 3). Our data are in good agreement with the values reported earlier and not with the most recent evaluation of $\bar{n}$.

In summary, we think the luminescence quenching method of obtaining mean aggregation numbers of micelles offers the possibility of a simple method so necessary for studies of the theories of micelle formation[10,12-19] where the mean aggregation number must be measured as a function of such parameters as temperature, pressure, and various concentrations. In contrast[8] to other methods, luminescence quenching also
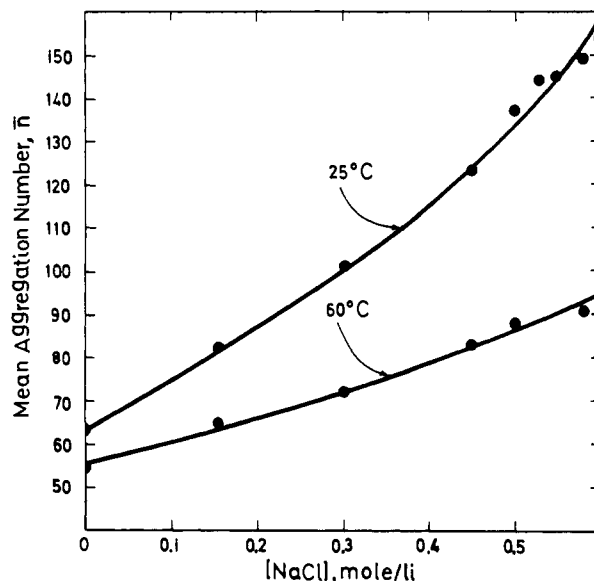
offers the advantage that the measurement of $\bar{n}$ is not restricted to detergent concentrations near the cmc.

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