

pages). Ordering information is given on any current masthead page.

## References and Notes

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# Photochemical and Photophysical Studies of Organized Assemblies. Interaction of Oils, Long-Chain Alcohols, and Surfactants Forming Microemulsions

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**Abstract:** The conditions necessary for forming a microemulsion system with sodium lauryl sulfate, pentanol, dodecane, and water have been established. This system was then used to influence photophysical reactions of molecules solubilized in the microemulsion aggregates. The sizes of the microemulsion aggregates were also determined by a photophysical method and by utilizing a Poisson distribution of reactants in the aggregates. Comments on the nature of the aggregate were obtained from the fluorescence spectra of pyrene carboxaldehyde which resides in the surface and pyrene which resides in the microemulsion interior. It was concluded from studies with the latter probe that pyrene samples a large fraction of the microemulsion interior during the measurements. Photoinduced reactions of excited pyrene and pyrene butyrate with thalious ions bound to the microemulsions surface indicated that pyrene penetrates further into the aggregate than pyrene butyrate, unlike similar experiments in micelles. The local oxygen solubility in the microemulsion was much higher than that in water. The results are discussed in terms of the increased utility of microemulsions over micelles with regard to promotion of certain photochemical reactions.

## Introduction

There are many examples of catalysis of reactions by simple micellar systems, some 1000-fold increase in rate resulting in some systems,<sup>1-4</sup> and it is customary to compare these systems to enzymes. Although the precise nature of micellar catalysis is uncertain, it may be at least expected that micelles effectively crowd together reaction partners, by micelle-solute interaction. This is much akin to increasing the local concentration of reactants, but, although effective in practice, the rate enhancements obtained by sole consideration of this mechanism are not *always* sufficient to explain the observed catalytic efficiencies. Of consequence is the suggestion<sup>5</sup> that the ionic nature of the micellar surface influences the transition state

of the reaction either adversely or positively. By analogy with the above thermal systems it has been possible to design micellar systems that show significant effects on radiation-induced reactions, both photochemical and radiolytic.<sup>3,6</sup> These systems are understood in terms of electrostatic influence of the micellar surface on the ionic nature of the reactions.<sup>6,7</sup> Reactions are both promoted and inhibited by the correct choice of micellar structure. It is desirable at this stage to vary the parameters of the micelle as much as possible. In particular micellar size, which controls the separation of reactants, is of prime importance. One method of achieving this effect is via microemulsions.

Microemulsions are reminiscent of micelles but provide two additional unique features: (a) the possibility of using larger

structures (micelles have radii  $\approx 20 \text{ \AA}$  in comparison to  $>100 \text{ \AA}$  for microemulsions) allowing a greater variation in the separation of reactants, and (b) the provision of a large oil drop center for locating hydrophobic molecules. It may be noted that microemulsions are far better vehicles for solubilizing hydrophobic molecules than their smaller micellar counterparts. In some instances the dimension of a hydrophobic molecule of interest (e.g., chlorophyll) may be comparable to that of the micelle. This is rectified in the case of a microemulsion.

The classical picture of a microemulsion derives much of its justification from the early work of Schulman and co-workers,<sup>9</sup> in particular their electron-microscope pictures of large, spherical microemulsion droplets of radii 200–500  $\text{\AA}$ . There have recently been several authoritative reviews of the nature of microemulsions;<sup>10–12</sup> some work has also been published regarding the influence of these species on chemical and photochemical reactions.<sup>13,14</sup> It is suggested that the cosurfactant (long-chain alcohol) interacts with the charged head groups of the surfactant monomers, increasing their separation and leading to a larger aggregated structure. The oil provides the stability for the larger structure by decreasing the curvature of the assembly. Light-scattering data<sup>15</sup> and electron microscopy indicate large ( $>100 \text{ \AA}$ ) spherical microemulsion aggregates.

There has been some modification of such a simple picture. Shah and co-workers<sup>16</sup> suggest that the systems formed using pentanol as cosurfactant should be looked upon as molecular solutions where the components of the system are cosolubilized. However, with hexanol true microemulsions are formed. Friberg suggests that some microemulsion systems might be looked upon as reversed micelles,<sup>10</sup> and Adamson<sup>17</sup> suggests the usage of "swollen micelles" rather than microemulsions.

It is apparent that reliable experimental conditions for the formation of various microemulsion systems are available in the literature. The thermodynamic factors controlling the systems are also understood with some discussion still taking place. However, further microscopic details of the systems would be desirable: a second goal is to utilize microemulsions to control certain features of photochemical reactions that have already been studied in micellar systems. Experiments described in this paper reflect both on the nature and surroundings of probe molecules dissolved in microemulsions and on the effect of these systems on the photophysical properties of the probes.

### Experimental Section

**Materials.** Sodium lauryl sulfate (NaLS) was BDH specially pure grade, and was used as supplied. The cmc was measured as 8 mM, in good agreement with the literature. Related experiments with this preparation and one that had been doubly recrystallized from ethanol/water showed essentially the same results. 1-Pentanol (99%, Aldrich) was redistilled after treatment with  $\text{H}_2\text{SO}_4$  and 2,4-dinitrophenylhydrazine. *n*-Dodecane was Phillips research grade, 99.7 mol %. Water was quadruply distilled. Pyrene and its derivatives were purified either by recrystallization from ethanol or by TLC.  $\text{TiNO}_3$  was Ventron ultrapure (99.9%).

Oxygen was removed from aqueous solutions by bubbling with oxygen-free nitrogen ( $<0.5 \text{ ppm O}_2$ ).

**Procedures and Experimental Equipment.** Pulsed laser photolysis experiments were conducted with a system that has been described in detail elsewhere.<sup>18</sup> The excitation source was the 347.1-nm line from a Q-switched frequency doubled ruby laser. Steady-state fluorescence measurements were taken on a Perkin-Elmer MPF-44 spectrophotometer. Pulse radiolysis experiments were made with the Notre Dame 7-MeV linear accelerator. A description of the analysis instrumentation is given by Kajiwara and Thomas.<sup>18</sup>

### Results and Discussion

**(i) The Microemulsion System.** The composition of the microemulsion which was used in the experiments to be described in this report consisted of (in wt %) 5.53 NaLS, 10.28 1-pen-

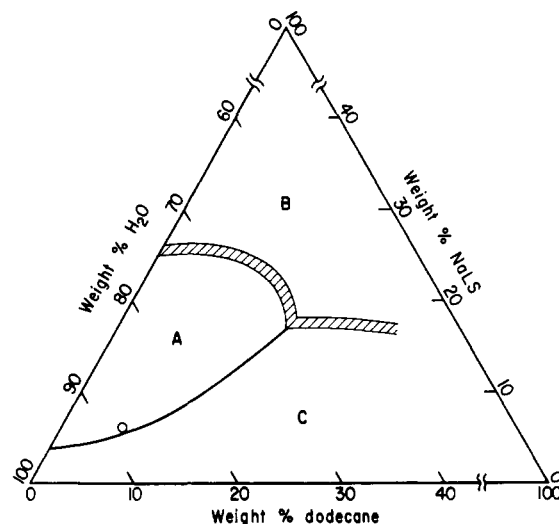


Figure 1. Phase diagram for the NaLS/pentanol/dodecane/water system. A is a clear, transparent solution. B is highly viscous and gel-like. It is transparent, and the division between A and B is not well defined. C represents a two-phase region, a turbid mixture that separates into two phases on standing. The transition between A and C is sharp. The point o in the region A gives the composition of the microemulsion used in the present study. The content of pentanol is 10.28% on an absolute scale.

tanol, 5.14 *n*-dodecane, and 79.05 water. The solution formed from these components was completely clear with no noticeable light scattering on visual inspection. Simple tests<sup>19</sup> indicated that the microemulsion was of the oil in water type, as may be expected from the relatively large proportion of water in the mixture. Stopped samples of the microemulsion which had been stored for periods up to 7 months were still clear with no separation of phases evident. The extension of the microemulsion region at a fixed proportion of pentanol, with varying amounts of the other constituents, is shown in Figure 1. The isotropic solution becomes increasingly more viscous as the water content decreases until it is transformed into a gel. Whether the gel region remains a one-phase area is unclear. The transition between the microemulsion region and the turbid two-phase solution is very sharp. A half-percent variation in the oil component along the transition line will cause the clear phase to become milky. The milky, turbid solution separates into two layers on standing.

Other compositions with varying proportion also of pentanol were made, but these were only briefly studied. Essentially all the results reported here are from the composition indicated in Figure 1.

**(ii) Size Determination.** To determine the average size of the microemulsion droplets a technique recently described by Turro and Yekta was used.<sup>20</sup> The method is based on the assumption that, if a solute is added to a system consisting of dispersed aggregates, such as micelles or microemulsion droplets, the solute will distribute itself among the aggregates in the form of a Poisson distribution. Thus by adding a luminescent probe,  $P^*$ , and some quencher,  $Q$ , both of which are associated with the aggregates, the relative emission observed as a function of the quencher concentration is given by

$$\ln \left( \frac{I_0}{I} \right) = \frac{\bar{N}}{[\text{surfactant}] - \text{cmc}} [Q] \quad (1)$$

$I$  and  $I_0$  are the emission intensities with and without a quencher present, respectively.  $\bar{N}$  is the average number of surfactant monomers in the aggregate, and cmc is the critical micelle concentration.

The luminescent probe and quencher used in this study were the same as those used by Turro and Yekta, namely,  $\text{Ru}(\text{bpy})_3^{2+}$  and 9-methylanthracene, respectively. The former

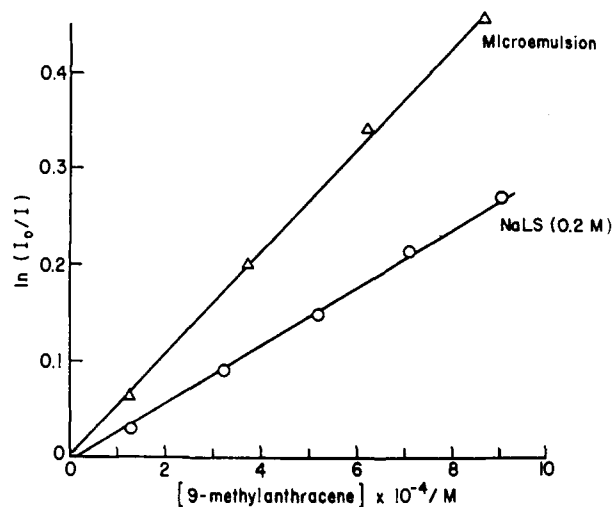


Figure 2. Luminescence quenching of Ru(bpy)<sub>3</sub><sup>2+</sup> by 9-methylanthracene in the microemulsion and in a micelle solution plotted according to eq 1.

component has been shown to bind strongly to negatively charged micelles,<sup>21</sup> and the latter is sufficiently hydrophobic to be almost exclusively dissolved in the microemulsion phase. A further condition which must be fulfilled for the application of eq 1 is that P\* must be completely quenched when the aggregate with which it is associated contains at least one Q. Therefore P\* is luminescent only when it resides with an empty micelle or microemulsion droplet. Time-resolved measurements of both the micelle and the microemulsion systems containing the probe and quencher showed that the luminescence lifetime remained constant over the whole range of quencher concentrations used. This observation justifies the use of eq 1.

The results obtained, plotted according to eq 1, are shown in Figure 2 for the microemulsion system and a high-concentration NaLS solution. The slope of these plots gives the average number of surfactant monomers in the microemulsion droplets as  $100 \pm 10$  and in NaLS micelles as  $70 \pm 5$ . The latter value can be compared to values of  $60 \pm 2$  and  $62$  obtained by this technique<sup>20</sup> and by light-scattering methods,<sup>22</sup> respectively. The slightly higher aggregation number of our results may be due to the relatively high surfactant concentration used (0.2 M). Lower concentrations of NaLS (<0.1 M) gave values around 60.<sup>23</sup>

The cmc values used to calculate the aggregation numbers were  $2 \times 10^{-3}$  and  $8 \times 10^{-3}$  M for the microemulsion and micelle solutions, respectively. The former value is not known precisely, but is the value of a NaLS solution saturated with pentanol.<sup>24</sup> In any case, because the surfactant concentration is quite large, the error introduced by this uncertainty of the cmc is not important.

Since the number of surfactant monomers that are part of a microemulsion droplet is now known, the average size of a droplet can be found if it is assumed that all the dodecane and pentanol is incorporated in the microemulsion phase. This is a reasonable assumption since both dodecane and pentanol are not very water soluble.<sup>25</sup> The molar volumes<sup>26</sup> of pentanol and dodecane are 0.1082 and 0.2275 M<sup>-1</sup>, respectively, and, taking the hydrocarbon part of the NaLS monomer to be the same as dodecane, the volume per droplet is  $2.1 \times 10^{-19}$  cm<sup>3</sup>. For a spherical droplet the core radius is then 37 Å.<sup>27</sup> This can be compared to an NaLS micelle, for which the core radius is about 16 Å.

A simple calculation shows that about 620 pentanol molecules are present in a microemulsion droplet. If all the hydroxyl groups were oriented toward the water interface, with the surfactant head groups, each unit (surfactant and pentanol)

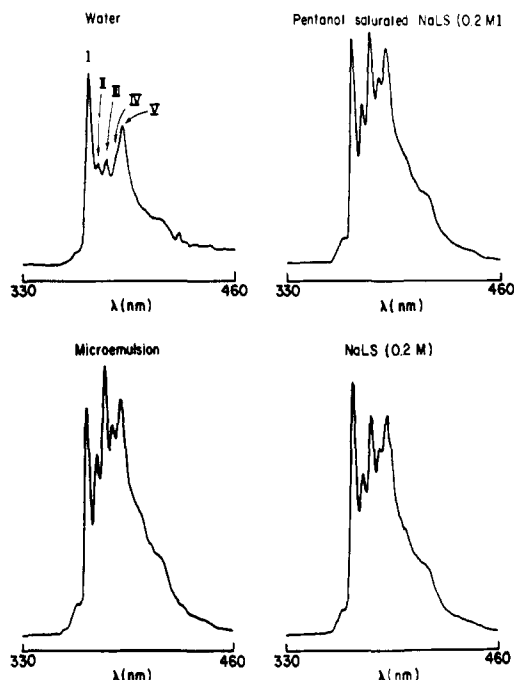


Figure 3. The fluorescence quenching of pyrene in four solutions, showing the variations of the vibronic band structure in various solvents. The concentration of pyrene in water was about  $10^{-6}$  M and in the other solutions  $10^{-5}$  M. The wavelength of excitation was 320 nm in all cases.

Table I. Ratio of the III/I Fluorescence Band Intensities of Pyrene in Various Solvents at  $21 \pm 1$  °C, and the Viscosity of the Solvents

solvent	III/I	viscosity, cP
water	0.55	0.98 <sup>c</sup>
NaLS, <sup>a</sup> 0.2 M	0.87	52 <sup>d</sup>
pentanol	0.95	1.36 <sup>c</sup>
dodecane	1.60	1.26 <sup>c</sup>
pentanol-dodecane <sup>b</sup>	1.13	5 <sup>d</sup>
microemulsion	1.18	4-5 <sup>d</sup>
0.2 M NaLS satd with pentanol	1.03	0-2 <sup>d</sup>

<sup>a</sup> The III/I ratio is independent of the NaLS concentration above the cmc. <sup>b</sup> 2:1 weight ratio, the same proportion as in the microemulsion. <sup>c</sup> Reference 25b. <sup>d</sup> Reference 33.

has an average surface area of about 24 Å<sup>2</sup>. This number is feasible, based on area measurements of monolayers<sup>28</sup> and micelle packing studies.<sup>29</sup>

**(iii) Structure of the Microemulsion Droplet and the Site of Solubilization of Pyrene.** Generally, the microemulsion is presented as a spherical, or near-spherical, aggregate with the head groups of the surfactant and the -OH of the alcohols ringing the core which is composed of the tail parts of these two constituents and an oil component. The oil component is often considered to have the same properties as the "bulk" oil, implying that the core volume is similar to that of a small drop of oil.

A method of obtaining more detailed information on the structure of the microemulsion droplets is by using the fluorescent probes pyrene and its derivatives. The application of these compounds to micellar systems<sup>30,31</sup> has shown their usefulness as probes for the properties of both water/lipid interfaces and micelle cores.

The pyrene fluorescence spectrum is extremely sensitive to the local environment.<sup>31</sup> Figure 3 shows the emission spectrum of pyrene in four solvents: water, NaLS solution, the microemulsion, and a pentanol-dodecane mixture (volume ratio 2:1). Table I shows the variation of the ratio of two of the band intensities, indicated in Figure 3, with solvent composition. As

can be seen from the value in Table I, the III/I ratio of pyrene in the microemulsion is close to that in the mixture of pentanol and dodecane. If the proportion of pentanol to dodecane is changed slightly in the microemulsion, the III/I ratio follows the same course as in a mixture of just pentanol and dodecane of the same proportions.

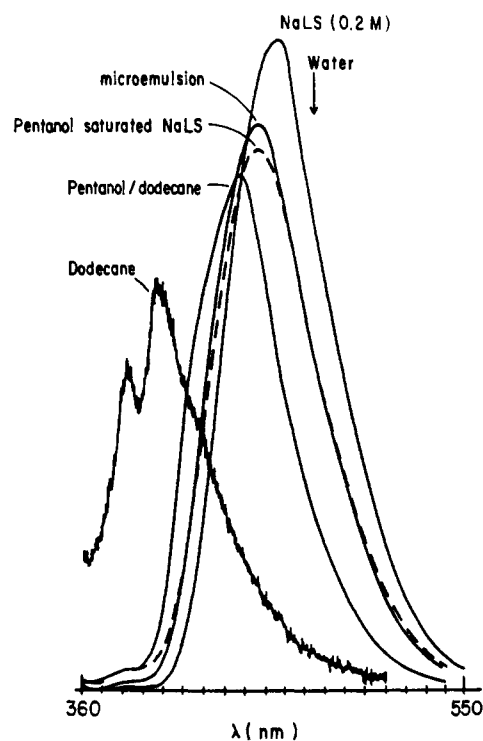
In interpreting these results it should be stressed that the observed spectrum is from pyrene in an average position: not only are the emitting molecules distributed throughout the volume of the microemulsion droplet, but the lifetime of the excited pyrene molecule is so long ( $\tau \approx 400$  ns in deoxygenated solution) that each excited molecule probably senses an average environment. The comparison between pyrene in NaLS and in the microemulsion clearly shows that pyrene spends more time away from the interface in the latter; this conclusion is further borne out by the results of quenching experiments to be discussed later. It is also seen in the case of the pentanol-saturated NaLS solution, where the pyrene III/I ratio is clearly bigger than in a pure pentanol, or pure surfactant solution, suggesting that the pyrene is on the average in a more hydrocarbon-like environment.

The significance of the observation that the III/I ratio in the microemulsion with a certain pentanol/dodecane ratio is close to the value in a mixture of these two solvents at the same ratio is less clear. It would be tempting to assume that pyrene experiences an environment in the interior of the droplets that closely resembles that of a mixture of the constituents pentanol and dodecane; however, as discussed in the previous section, it seems rather to be expected that a majority of the pentanol is at the surface, with the hydroxy groups hydrated. If pyrene were entirely within the droplet, a III/I ratio much closer to the hydrocarbon value would have been expected.

It therefore seems to be fortuitous that the III/I ratios in the microemulsions and the pentanol-dodecane mixtures agree so well. The observed III/I ratios in the microemulsions probably mean that pyrene to some extent is in contact with the interface, but to a much lesser extent than in the micelle. Whether the interior of the droplet contains a considerable amount of pentanol cannot be ascertained from these findings alone.

We have shown in another paper<sup>32</sup> that pyrene, to some extent, prefers the surface region in micelles. To examine this further two other probes were used, both of which are solubilized at the water/lipid interface.<sup>30,34</sup> These are pyrene-3-carboxaldehyde and the sodium salt of pyrenebutyric acid (since it is essentially completely ionized in aqueous solution it will be referred to as  $\text{PBA}^-$ ). The former compound is sensitive to the dielectric constant of the medium and therefore a monitor of the local environment. Figure 4 shows the spectrum of pyrene-3-carboxaldehyde in NaLS micelles, the microemulsion, pentanol-saturated NaLS micelles,<sup>35</sup> and in a 2:1 weight ratio of pentanol and dodecane. As can be seen, the spectrum of the probe in the microemulsion closely matches that of the pentanol-saturated NaLS solution. This result is consistent with the idea of the microemulsion surface region being composed of  $-\text{OH}$  groups from pentanol and surfactant head groups.

Other evidence that the alcohol molecules are oriented among the surfactant head groups is obtained from conductivity data. It was found that for both the pentanol-saturated micelles and the microemulsion system the conductivity was about 30% greater than in a pure micellar solution with the same concentration of surfactant. This increase in conductivity of micellar solutions on addition of alcohols has been observed previously.<sup>36</sup> It has been explained as an intervention of  $-\text{OH}$  groups between the charged surfactant head groups, which lowers the surface charge density and results in a concomitant increase of the ionization of the surfactant and a lowering of the cmc.



**Figure 4.** The fluorescence band of pyrene-3-carboxaldehyde in various solvents. The emission intensity is in arbitrary units, and the various bands have been shifted in height to facilitate the identification of the maxima. The emission in dodecane is at least a factor of 10 less intense than in the other solvents. The arrow indicates the position of the maximum in water. The excitation wavelength was 365 nm and the concentration of pyrene-3-carboxaldehyde was  $5 \times 10^{-5}$  in all solutions.

Although these results indicate that the water/microemulsion interface is of the composition usually ascribed to an oil-in-water microemulsion system, it does not tell us much about the core composition.

To understand the significance of the pyrene III/I ratios better, we measured the fluorescence quenching rate constants of pyrene and a surface probe,  $\text{PBA}^-$ , using  $\text{Tl}^+$  as the quencher. The results are shown in Tables I and III. The values are the averages of three measurements at different  $\text{TlNO}_3$  concentrations, corrected for the fluorescence lifetime of the probe in the various systems. The errors quoted include the range of the individual measurements. All measurements were taken in nitrogen-bubbled solutions.

There are a number of points to be discussed regarding these two tables, but for the moment we shall restrict the discussion primarily to the results of the microemulsion and the two micellar systems. It can be seen from the tables that, although there is *not* a great deal of difference in the quenching constants of  $\text{PBA}^-$  in the microemulsion and the micellar systems, there is almost a factor of 10 difference in the rate constants for the quenching of pyrene in the microemulsion compared to the two micellar solutions. Since the  $-\text{COO}^-$  moiety of the  $\text{PBA}^-$  molecule would restrict the average position of this probe largely to the surface of both the microemulsion droplet and the micelle, it implies that the site of solubilization of pyrene in the microemulsion droplet and in the pentanol-saturated micelle solution is away from the water/core interface. This conclusion supports the interpretation of the previous III/I results. On the other hand, the similarity of the quenching constants of pyrene and  $\text{PBA}^-$  in NaLS micelles suggests that pyrene is also "surface" solubilized in NaLS micelles. This has already been implied from previous solubilization studies.<sup>32</sup>

Thus the overall picture of the microemulsion system generated by these data is one which is basically consistent with the usually proposed model. The surface of the microemulsion

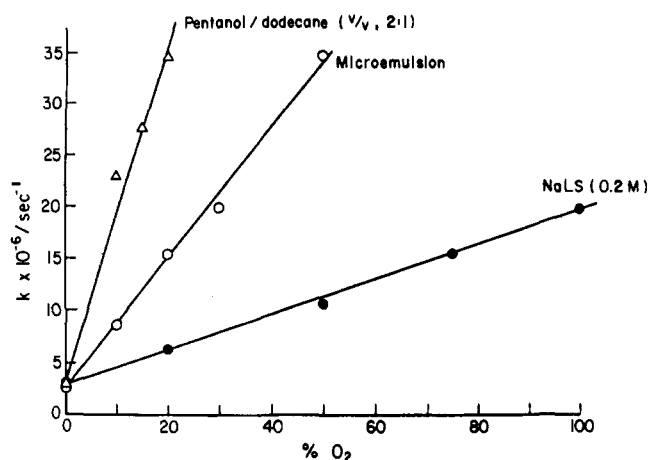


Figure 5. The effect of the oxygen concentration on the decay rate of the pyrene fluorescence in NaLS, the microemulsion, and in a mixture of pentanol and dodecane. Pyrene concentration is  $5 \times 10^{-5}$  M.

droplets is composed of the hydroxyl groups of the alcohol and the surfactant head groups, and the core is a fluid, hydrocarbon-like region, as indicated by the microviscosity data given in Table I. In such an environment pyrene is solubilized in the core region; however, because of dynamic motion of pyrene in the core, its vibronic spectrum is not truly hydrophobic, but reflects a distribution of pyrene between the surface and the core which must be environmentally different.

Since pentanol and dodecane are completely miscible it is possible that some pentanol is also solubilized in the interior instead of being stabilized through hydrogen bonding of the hydroxyl group by water at the surface. If this were true, the pentanol would probably not be randomly distributed in the core but rather exist as clusters with hydrogen bonding between the alcohol units. The present results do not indicate whether this occurs, but if it does it must be to a relatively small extent.

It is also worthwhile to comment briefly on the values of the quenching rate constants given in Tables I and II. The measurements in the bulk solvents were primarily taken to judge the effects of variations in the solvent composition on the effectiveness of the  $\text{Ti}^+$  quenching rate and to give a comparative basis for the values of the aggregate systems. A comparison of the  $\text{Ti}^+$  quenching of pyrene and  $\text{PBA}^-$  in the bulk solvents listed in Tables I and II shows that the fluorescence quenching rate constants are all greater for  $\text{PBA}^-$  than for pyrene in the same solvents. This is probably due to opposite charge attraction of  $\text{Ti}^+$  and  $\text{PBA}^-$ . In mixed solvents of alcohol and water, both probes have quenching rate constants about two times lower than in either of the pure solvents. Comparison of the viscosity of the mixed solvents with that of ethanol or water shows that for mixtures in the composition range 40–50 vol % ethanol the viscosity of the mixture is higher by about a factor of 2.5 than that of the pure solvents.<sup>25b,37</sup> Thus the decreased quenching rate constants in the mixed solvents may simply be ascribed to the viscosity effects.

The comparison of the quenching rate constants in the micelle and microemulsion systems to the bulk solvent rate constants is, however, not a simple matter. Since the micelle is negatively charged it can be expected that there is a concentration gradient of  $\text{Ti}^+$  ions in favor of the micelle surface. In this respect it may be anticipated that the observed quenching rate constant of the fluorescent probe would be greater than the free solution value. However, factors such as steric hindrance by the surfactant head groups, viscosity of the microenvironments, and site of solubilization may all contribute to a varying and unknown extent in decreasing the  $\text{Ti}^+$ -probe interaction rate. Thus it is only valid, on a quantitative basis,

Table II. Pyrene Fluorescence Quenching Rate Constants in Various Solvents, Using  $\text{TiNO}_3$  as Quencher, at  $21 \pm 1$  °C

solvent <sup>a,b</sup>	$k_q \times 10^{-9} / \text{M}^{-1} \text{s}^{-1}$
ethanol	$2.2 \pm 0.2$
methanol	$3.6 \pm 0.3$
water	$5.0 \pm 0.3$
0.2 M NaLS	$7.0 \pm 0.3$
0.2 M NaLS satd with pentanol	$9.7 \pm 0.3$
microemulsion	$0.80 \pm 0.03$
50% ethanol-water (v/v)	$1.0 \pm 0.2$
50% methanol-water (v/v)	$2.8 \pm 0.1$

<sup>a</sup> All solutions nitrogen bubbled. <sup>b</sup> The concentration of pyrene was  $10^{-5}$  M in all solutions except water. Measurements in water were with a saturated solution ( $\sim 10^{-6}$  M).

Table III. Pyrenebutyric Acid (Sodium Salt) Fluorescence Quenching Rate Constants in Various Solvents at  $21 \pm 1$  °C, Using  $\text{TiNO}_3$  as Quencher

solvent <sup>a,b</sup>	$k_q \times 10^{-9} / \text{M}^{-1} \text{s}^{-1}$
ethanol	$8.8 \pm 0.4$
methanol	$14.0 \pm 1.5$
water	$7.9 \pm 0.2$
0.2 M NaLS	$5.0 \pm 0.7$
0.2 M NaLS satd with pentanol	$2.6 \pm 0.2$
microemulsion	$3.0 \pm 0.5$
50% ethanol-water (v/v)	$3.5 \pm 0.1$
50% methanol-water (v/v)	$5.7 \pm 0.2$

<sup>a</sup> All solutions were nitrogen bubbled. <sup>b</sup> Concentration of PBA was about  $10^{-5}$  M. The pH of the solutions was adjusted to about 9 to ensure that all PBA was ionized.

Table IV. O<sub>2</sub> Concentrations Measured by van Slyke Apparatus<sup>a</sup> at  $21 \pm 1$  °C

solvent	$[\text{O}_2]_{\text{sat}} / \text{M}$
water	$1.3 \pm 0.1 \times 10^{-3}$
microemulsion	$2.5 \pm 0.1 \times 10^{-3}$
pentanol-dodecane (2:1)	$8.0 \pm 0.1 \times 10^{-3}$
0.2 M NaLS	$1.4 \pm 0.1 \times 10^{-3}$

<sup>a</sup> Reference 42.

to compare the quenching rate constant of pyrene and  $\text{PBA}^-$  in the micelle and microemulsion system with each other and not against the bulk solvent rate constants.

It should also be mentioned that the quenching curves observed in the micelle and microemulsion systems were all first-order decays, and no slow component was noticed.  $\text{Ti}^+$  apparently, unlike  $\text{Ru}(\text{bpy})_3^{2+}$ , is not strongly bonded, and must exchange rapidly among the aggregates to give a relatively uniform concentration in solution during the fluorescence lifetime. If this were not the case, results similar to those from the quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  would have been obtained.

(iv) **O<sub>2</sub> Solubility in the Microemulsion.** The solubility of oxygen in the microemulsion system and the micelle solution was investigated in order to understand the dynamics of its partitioning between the bulk water and the dispersed droplets.

The concentration of oxygen in saturated solutions at  $21 \pm 1$  °C is given in Table IV. These values were used in determining the pyrene fluorescence quenching rate constants in the various solutions shown in Figure 5. The O<sub>2</sub> concentration in the microemulsion system is consistent with the sum of the O<sub>2</sub> concentrations normally in water and the amount proportional to the volume of the pentanol and dodecane constituents. Thus the quenching rate of pyrene in the microemulsion droplets is the same as in the bulk solvent of pentanol and do-

decane. The quenching rate constant of pyrene in the micelle system is the same as if pyrene were in the water only. Since there is on the average less than one O<sub>2</sub> molecule even in the microemulsion droplets, both these observations indicate that O<sub>2</sub> must be rapidly exiting and entering the aggregated units, and there is no large free-energy barrier for either direction of motion. An example of pyrene fluorescence quenching by a molecule that is relatively hydrophobic is given by iodoheptane. The kinetic decay of the pyrene fluorescence with addition of iodoheptane is no longer first order in either the micelle or the microemulsion system. Both a fast (dependent on the iodoheptane) and slow component (with the same decay rate as without quencher) in the fluorescence decay is observed. This can be interpreted as due to the presence of aggregates both with and without iodoheptane, in the same way as described by Turro and Yekta<sup>20</sup> for the Ru(bpy)<sub>3</sub><sup>2+</sup> case. In these experiments the movement of the quencher molecules between the micelles is much slower than the lifetime of the excited probe. This is obviously not the case with O<sub>2</sub>.

To check the O<sub>2</sub> content of the water phase in the microemulsion system the rate of reaction of the hydrated electron was measured in an air-saturated solution. Taking the e<sup>-</sup><sub>aq</sub> + O<sub>2</sub> rate constant as 1.9 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>,<sup>38</sup> the concentration of O<sub>2</sub> was measured as (2.4 ± 0.2) × 10<sup>-4</sup> M (cf. 2.6 × 10<sup>-4</sup> M in air-saturated water). Since there is probably some pentanol in the water phase, the reliability of the e<sup>-</sup><sub>aq</sub> + O<sub>2</sub> rate constant was checked, by measuring the reaction of e<sup>-</sup><sub>aq</sub> + NO<sub>3</sub><sup>-</sup>. The rate constant (as the average of three determinations at different concentrations of NaNO<sub>3</sub>, and allowing for the background electron rate) was (1.1 ± 0.1) × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>, in excellent agreement with the literature value for this reaction.<sup>38</sup>

Thus this confirms that the solubility of O<sub>2</sub> in the microemulsion droplet is much the same as in a bulk pentanol-dodecane mixture. The results allow an equilibrium constant to be established:

$$K_D = [\text{micro-O}_2]/[\text{micro}][\text{O}_2] = k_+/k_- = 500 \text{ M}^{-1} \quad (2)$$

$k_+$  is the entrance rate constant of O<sub>2</sub> into a microemulsion droplet and  $k_-$  is the exit rate constant. The values used in eq 2 are taken from Table III and section (i). Assuming that the entrance rate of oxygen is diffusion controlled, the exit rate can be calculated from the relationship above. The diffusion constant of O<sub>2</sub> in water is  $D = 2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .<sup>39</sup> With

$$k_+ = 4\pi R_0 D N \quad (3)$$

where  $R_0$  is the encounter radius, taken as 40 Å, and  $N$  is Avogadro's constant,  $k_+ = 6.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  is obtained. Thus  $k_- = 1.5 \times 10^8 \text{ s}^{-1}$ , i.e., a residence time of about 7 ns. This value also supports the observation of a uniform decay rate in the pyrene fluorescence quenching by O<sub>2</sub>.

The same calculation can be made for the micelle systems; however, in this case the accuracy of the O<sub>2</sub> concentration measurement does not allow a definite value to be obtained. At best it can be calculated that the O<sub>2</sub> molecule exits a NaLS micelle within less than 2 ns.

(v) **Photoionization in the Microemulsion System.** The results presented in the earlier sections show that pyrene is solubilized in the microemulsion droplet in an environment quite different than in a micelle. We have studied the photoionization of pyrene using 347.1 nm as excitation wavelength from a pulsed ruby laser. The photoionization was a two-photon process, very similar to the results of pyrene in NaLS micelles.<sup>40</sup> Tetramethylbenzidine was also measured and gave, again similar to the micelle results,<sup>41</sup> photoionization by a one-photon process.

These preliminary results do not indicate any marked difference in the photoionization process of molecules dissolved

in a microemulsion as compared to a micelle solution. This does not rule out the possibility of some molecules being more susceptible to their local environment, and consequently manifesting different behavior in the two systems. More work in this area is needed before definite statements can be made regarding the photoionization process in a microemulsion droplet.

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