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Kinetic Studies in Bile Acid Micelles

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Abstract: Pyrene is solubilized in aqueous solutions of sodium taurocholate (NaTC) micelles and excited by a frequency doubled ruby laser pulse. The kinetics of the pyrene fluorescence decay are studied in the presence of nonionic and ionic quenchers. These data yield information about the permeability of the NaTC micelles with respect to various quenching solute molecules. While a neutral molecule such as oxygen readily penetrates into the micelle, the entry of iodide ions is inhibited by the negative micellar surface charge. Positively charged quenchers such as Cu^{2+} and Tl^+ are strongly absorbed at the surface of NaTC micelles. This allows for an investigation of the motion of pyrene within a NaTC micelle. The effect of additives such as cholesterol, benzyl alcohol, and Mg^{2+} ions on the permeability of NaTC micelles is also studied. The local viscosity in the interior of NaTC micelles is investigated by fluorescence depolarization measurement using 2-methylanthracene as the photoactive probe. The rotation of this probe within a NaTC micelle is strongly restricted and a microviscosity of 670 cP is derived from the degree of polarization of the emitted light. Mg^{2+} ions, benzyl alcohol, and sodium lauryl sulfate (NaLS) decrease the microviscosity. NaLS exhibits the strongest effect due to efficient comicellization with NaTC. The 347.1 nm laser photolysis of pyrene also produces significant amounts of positive ions and hydrated electrons. While the photoionization cross section in NaTC and NaLS micelles is similar, the lifetime of pyrene cations is much shorter in the former than in the latter type of micelles. This effect may be explained with the destruction of the smaller NaTC micelle by the positive charge. In comicelles of NaLS and NaTC the lifetime of pyrene cations increases rapidly with increasing NaLS content of the micelle. The electrons which are photoejected from the pyrene in the interior of the micelle become hydrated in the surrounding aqueous phase. Hydrated electrons have a low reactivity toward monomer NaTC ($k = 10^8\ M^{-1}\ \text{sec}^{-1}$). The reactivity decreases further upon micellization.

Bile acids participate in many important physiological processes. For example, the salts of these acids are involved in intestinal hydrolysis, and also act as emulsifying and solubilizing agents for neutral fats. The term bile acid covers the several derivatives of cholic acid which differ in the number and position of α-hydroxyl substituents. The acids have a rigid "cholesterol like" ring structure which is solubilized in water by glycine or taurine residues. The latter acids are linked to the ring structure by a peptide bond. The bile acids form aggregates called micelles, when dissolved in water above a certain critical concentration. This parallels the behavior of many other surface active molecules.[2,3] However, the bile acid micelles differ from conventional micelles in the fact that only a few molecules are associated in the micellar assembly. For example, trihydroxycholic acid and its derivatives form micelles with an aggregation number of four to ten.[4] In a conventional micelle formed by surfactant molecules such as sodium lauryl sulfate (NaLS) or cetyltrimethylammonium bromide (CTAB) the aggregation number lies between 50 and 100. The architecture of these micelles has already been discussed,[4] and the effect of micellization on the rate of hydrolysis of fatty acid esters has been studied.[5]

In earlier work[6-8] we have investigated the dynamic and kinetic properties of several micelles by laser photolysis and pulse radiolysis techniques. The laser photolysis method has also been successful in describing various permeability properties of *E. Coli* membranes.[9] The degree of rigidity and the rate of entry and exit of various molecules into and out of the micelle are readily measured by the techniques. Initial work with micelles of the bile acid, sodium taurocholate,[10] showed that the laser photolysis technique can be conveniently applied to a study of these micelles also. The present work is an enlarged and more rigorous study of kinetic processes in sodium taurocholate micelles. Pulse radiolysis is used to investigate the effect of micellization on the rate of reaction of e_{aq}^- with the peptide group. Laser photolysis is used to investigate the permeability of the micelles to various small molecules such as oxygen, iodide ion, etc. The effect of additives such as benzyl alcohol and sodium chloride on the permeability is also studied. Wherever possible fluorescence polarization techniques are used to complement the pulsed data.

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Experimental Section

The pulse radiolysis[11] and the laser photolysis[12] equipment have been described previously. In the pulse radiolysis experiments 10-nsec pulses of 2-MeV electrons were used. The dose in each pulse was approximately 10^{18} eV/g. A Korad KlQP ruby laser was used in the photolysis experiments. Approximately 15-nsec pulses of light of wavelength 694.2 nm or 347.1 nm were used. The outputs at these wavelengths were 2 J and 200 mJ, respectively. The short-lived species produced by the above pulses were monitored by fast absorption or emission spectroscopy.

An Aminco-Bowman spectrofluorimeter was used for the fluorescence polarization measurements. Suitable cut-off filters were used in the excitation and emission channels of the instrument to minimize scattered light. Polacoat 105 polarizers, with a spectral range of 200 to 800 nm, were used both to produce polarized exciting light and to investigate the degree of polarization of the emitted light. All solutions for the fluorescence polarization experiments were centrifuged at 18,000 rpm for 30 min, to remove large particles. The supernatant solution was filtered though a millipore-membrane filter under an excess pressure of nitrogen, and transferred directly to the fluorescence cell.

Sodium taurocholate was purchased as pure grade from the Schwarz/Mann Co. and was used without further purification. Sodium lauryl sulfate was USP grade from the Matheson Coleman and Bell Co. This was recrystallized from methanol. Pyrene was purified chromatographically by washing it from a silica gel column using cyclohexane as solvent. Water was distilled from a Barnsted still, followed by a second distillation from potassium permanganate.

Pyrene is insoluble in water. However, it was solubilized in the micellar solutions by stirring the solution and pyrene for 8 hr at 70°. The final pyrene concentration was measured spectroscopically on a Cary spectrophotometer. All samples were deoxygenated by bubbling with nitrogen gas for 30 min. Oxygen concentrations were measured on a Van-Seyke apparatus.[11a]

Results and Discussion

Reactions of Hydrated Electrons. Reactions of hydrated electrons e_{aq}^-, with micelles and solutes solubilized in micelles have been reported.[6,13] The type of micelle, *i.e.*, anionic or cationic, has a profound effect on the rate of reaction of e_{aq}^- with solutes in the micelle. In the present work e_{aq}^- were readily produced and studied in solutions of taurocholic acid by pulse radiolysis. The variation in the concentration of e_{aq}^- with time was observed spectroscopically at 600 nm. Both OH radicals and hydrated protons are produced as well as e_{aq}^- in the radiolysis of water. These species are reactive with e_{aq}^- and increase its rate of decay.

$$e_{aq}^- + OH \longrightarrow OH^- \tag{1}$$

$$e_{aq}^- + H^+ \longrightarrow H \tag{2}$$

In order to eliminate reactions 1 and 2, [NaTC] $< 2 \times 10^{-4}$ *M*, the micellar solutions contained 10^{-2} *M* ethanol to remove the OH.

$$OH + C_2H_5OH \longrightarrow \dot{C}_2H_4OH + H_2O \tag{3}$$

The radical $\dot{C}_2H_4OH$ is relatively unreactive with e_{aq}^-. At higher bile acid concentrations the OH radicals are removed by the bile acid itself. Sodium hydroxide at 10^{-3} *N* was added to remove H^+. The sodium hydroxide may reduce the CMC of the bile acid. This may account for the lower CMC observed in this work compared to that given in the literature. The rate of decay of e_{aq}^- in any system is measured by the pulse radiolysis technique. The inverse of the half-lifetime for decay of e_{aq}^-, τ, is plotted versus sodium taurocholic acid (NaTC) concentration in Figure 1. Initially the parameter $1/\tau$ increases linearly with NaTC concentration. The rate constant *k*, for reaction of e_{aq}^- with NaTC, is given by

$$k = (0.7/[\text{NaTC}])(1/\tau - 1/\tau_0)$$

This gives a $k = 1.25 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ for the initial linear portion of the curve. Above 1.2×10^{-3} *M* NaTC the parameter $1/\tau$ fall off with increasing [NaTC]. This indicates a slower rate of reaction of e_{aq}^- with NaTC. Figure 3 would indicate that the break in the kinetics occurs at 1.2×10^{-3} *M* NaTC, which is close to the critical micelle concentration of 3×10^{-3} *M*.[14]

The data show that e_{aq}^- reacts with NaTC, and that the site of reactivity becomes "buried" when micelles are formed. The reactive site is situated within the surface region of the micelle and is screened from reaction with e_{aq}^- by the negatively charged sulfate groups. Below the critical micelle concentration, e_{aq}^- reacts with monomeric NaTC. The measured rate constant *k* suggests that e_{aq}^- reacts with the peptide group. The measured rate constant of $1.25 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ is close to that observed for the reaction of e_{aq}^- with other simple amides.[15]

An interesting and instructive situation arises in the photoionization of a probe molecule that is solubilized in a NaTC micelle. Previous ^{13}C NMR experiments show that pyrene affects the chemical shifts of C atoms in a NaTC

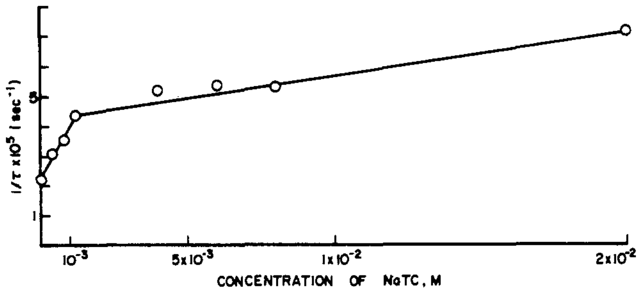
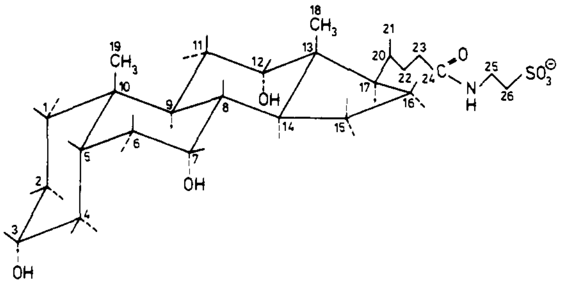


Figure 1. The inverse half-lifetime of e_{aq}^- as a function of NaTC concentration in pulse radiolysis investigations.



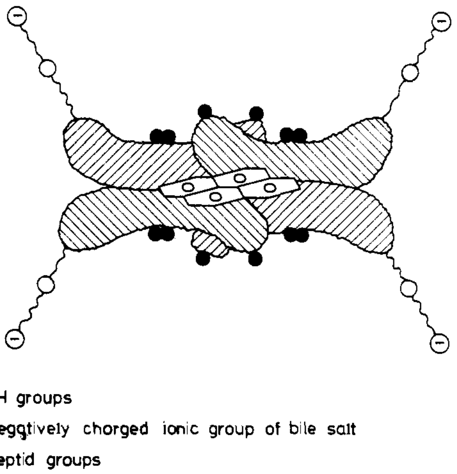


Figure 2. Schematic representation of a NaTC micelle occupied by a pyrene probe.

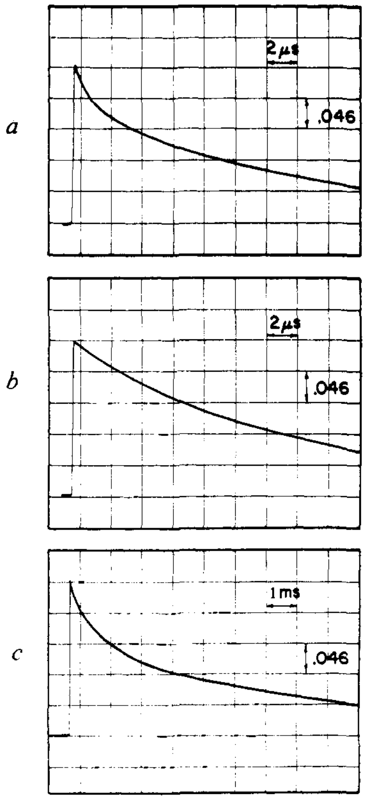


Figure 3. Laser photoionization of 10^{-4} *M* pyrene in NaTC micelles solutions, transient absorption of pyrene cations at $\lambda = 453$ nm: (a) in 0.1 *M* NaTC, N_2 saturated; (b) in 0.1 *M* NaTC, N_2O saturated, (c) mixed micelles of NaLS and NaTC, N_2O saturated, [NaLS] = 0.075 *M*, NaTC = 0.025 *M*.

micelle. The carbon atoms most affected are the C_{10} and C_{13}, and it is concluded that pyrene residues at this situation in the micelle.[16] A schematic representation of the solubilization site of pyrene in NaTC micelles is shown in Figure 2. Laser photolysis with light of wavelength 347.1 nm leads to photoionization of pyrene in the micelle and ejection of the photoelectron into the aqueous phase.

$$\text{(pyrene)} \xrightarrow{h\nu} \text{(pyrene)}^+ + e_{aq}^-$$

This effect has been observed previously for pyrene in other micelles.[17] The cation of pyrene and the hydrated electron are both identified spectroscopically. The pyrene cation is located in the micelle and the e_{aq}^- is outside the micelle in the aqueous phase. The relative yields of pyrene cations and e_{aq}^- are quite similar in NaLS and NaTC micelles. However, the subsequent kinetics of the ions are quite different.

In NaLS micelles, the pyrene cation has a long lifetime (>5 msec). This is attributed to the fact that the cation resides in the micelle and is protected from reaction with water and impurities. The electron lifetime is much shorter (μsec). A typical trace of the variation of the cations with time is shown in Figure 3, top. The addition of e_{aq}^- scavengers such as N_2O to the system increases the lifetime of the cation, Figure 3, middle. The lifetime of the positive ion in a mixed micelle of NaLS and NaTC is dramatically increased. The formation of mixed micelles of NaLS and NaTC leads progressively to longer lifetimes for the pyrene cation, Figure 4.

The explanation of the data is as follows. NaTC forms small micelles compared to NaLS. The formation of a positive charge such as a pyrene cation in the NaTC micelle may be sufficient to overcome the hydrophobic bonding of the micelle. The micelle breaks up and releases the cation to the aqueous environment. A mixed micelle of NaLS and NaTC will be larger than the simple NaTC micelle, and the tendency for self-destruction of the micelle due to pyrene cation will be diminished. Hence the longer lifetime of the cation.

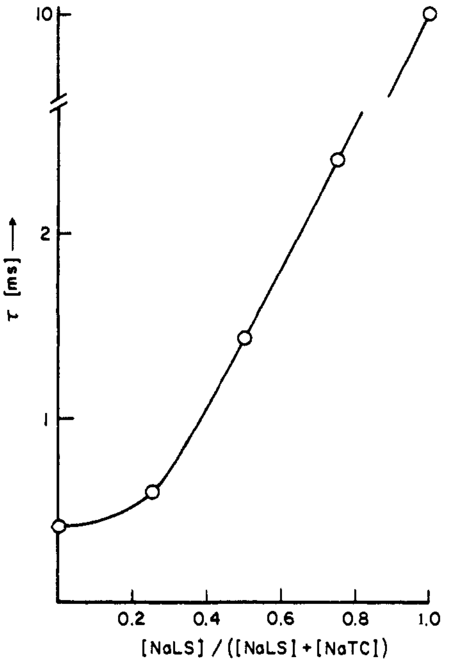


Figure 4. Effect of NaLS on the lifetime of pyrene cations in mixed micellar solution of NaLS and NaTC. [NaTC] + [NaLS] = 0.1 *M*.

On release from the NaTC micelle the pyrene cation will react with anions. Typical anions may be e_{aq}^- or NaTC anions formed by reaction of e_{aq}^- via the initial rapid decay in the top part of Figure 3. A concomitant reaction of e_{aq}^- with NaTC gives the anion NaTC^- which will react more slowly with the cation. The degree of reactivity in the neutralization process is presumably controlled by the mobility of the anion, and is larger for e_{aq}^-. The removal of e_{aq}^- by N_2O leads to the formation of OH^- which has a lower reactivity than e_{aq}^-, and hence the cation decay via neutralization is slower in the middle part of Figure 3.

Quenching of Pyrene Excited States. The pyrene (p) situated inside the micelle may be excited with the laser pulse of 15 nsec and wavelength 347.1 nm light, to the first excited singlet state p_1.

$$p \xrightarrow{h\nu} p_1 \qquad (4)$$

The first excited state fluoresces with a lifetime of several hundred nsec.[7] Other processes also contribute to the decay of p_1, but the overall rate of decay may be monitored by observing the fluorescence. The excited state may be quenched by a solute with rate constant *k*, thereby leading to an increased rate of decay of the p_1. The observed rate constant *k'* for decay of p_1 via all processes is given by

$$k' = \alpha + k[Q] \qquad (5)$$

where α is the decay of p_1 in the absence of quencher Q.

Pyrene was excited to the first excited state p_1 and the subsequent decay of this state with and without added quenchers observed via the characteristic fluorescence of p_1. Two representative oscilloscope traces showing the pyrene fluorescence decay in NaTC micellar solution with and without added quenchers are shown in Figure 5. The rate constants *k* for reaction of Q with p_1 were measured in this way and are shown in Table I. For the convenience of comparison similar data are also shown for pyrene in other micelles and in liquid CH_3OH.

Table I. Rate Constants k_q for the Quenching of Pyrene Monomer Fluorescence in Different Types of Micelles and in MeOH[a]

	Micelles				
Quencher	NaTC	NaLS	CH_3OH	CTAB[c]	NaTC + cholesterol
O_2	4.6×10^9	9.2×10^9	2.0×10^{10}	8.3×10^9	7.3×10^9
Triethylamine	1.4×10^7	2.5×10^8	2.3×10^8		4.2×10^7
Triethylamine[b]	1.6×10^8				
CH_3NO_2	1.2×10^8	3.0×10^9	3.6×10^9	1.8×10^9	
I^-	3.6×10^7	2.6×10^6	3.04×10^9[e]	6.5×10^9	5.4×10^7
I^-[b]	3.8×10^8				
I^-[d]	7.3×10^7	1.9×10^7			
MgI_2	2.2×10^7				

[a] Solution [NaTC] = 10^{-2} *M*, [Py] = 2×10^{-5} *M*, [NaI] = 0.2 *M*, [CH_3NO_2] = 1.9×10^{-3} *M*, [MgI_2] = 0.2 *M*, [NaTC] = 7.2×10^{-3} *M*, [cholesterol] = 2.5×10^{-4} *M*. [b] In the presence of 0.2 *M* BzOH. [c] Data from S. C. Wallace and J. K. Thomas, *Radiat. Res.*, 54, 49 (1973). [d] In the presence of 0.1 *M* NaCl. [e] Measured in 2×10^{-5} *M* pyrenesulfonic acid aqueous solution.

The data in methanol are taken to represent the condition where p_1 reacts with the quencher without the inhibiting effect of a micelle. This is taken as a standard condition for each quenching reaction. In each micelle the quenching reaction for oxygen is lower than in methanol, the micelle presenting the greatest impedance to reaction being NaTC. The same trend is also seen for the quenching reaction with nitromethane and triethylamine. The smaller rate constants in micellar solutions imply that the micelles inhibit the approach of p_1 and quencher indicating a greater obstruction of the micelles to the reaction. In previous work it was shown that the inhibiting effect of the micelle on the kinetics is due to the rigidity of the micelle.[7] The implication in the present data is that NaTC micelles are more rigid than either NaLS or CTAB. A direct linear correlation of the internal viscosity of the micelle, with the rate constants for the quenching reactions, is not possible. The internal viscosity is measured by noting the rotational movement of a large chromophore such as methylanthracene. A small molecule such as oxygen can move more easily in the micelle interior. However, a qualitative trend can readily be observed.

In the above quenching experiments it is suggested that the quencher enters the micelle and there quenches the p_1 state of pyrene. The triethylamine data give support to this suggestion since the reaction product is the excited complex of p_1 and the amine. The fluorescence of the p_1-triethylamine excimer is observed. This fluorescence is identical to that observed in the excitation of solution of pyrene and triethylamine in cyclohexane. No fluorescence is observed in polar media such as water.[18] It is concluded that the quenching reaction that yields the excimer occurs inside the micelle and away from the aqueous phase.

The quenching of p_1 by iodide ion is a special case as the anion is repelled by the negative charge of the micelle. The rate constant for quenching in NaTC is much lower than in CTAB or in CH_3OH. However, it is larger than in NaLS which is also an anionic micelle. The micelles of NaLS have a much larger negative charge than those of NaTC, which accounts for the smaller I^- quenching rate constant in the former micelles.

The effect of additives on the rate of entry of quenchers into NaTC micelles is also portrayed in the rate constant for quenching. Benzyl alcohol increases the quenching rate constant for triethylamine and iodide I^- by a factor of 10. Several polar aromatic molecules such as benzyl alcohol are absorbed at the head groups of micellar systems.[2] This interaction tends to displace the head group and makes the micelles more permeable to small molecules. This effect has been observed for NaLS and CTAB micelles.[7]

Magnesium ions tend to decrease the permeability of anionic micelles to small molecules.[7] In NaTC micelles a reduction of a factor of 2× is observed for the I^- quenching rate constant on addition of Mg^{2+}. This may be interpreted as a reverse of the benzyl alcohol effect. The Mg^{2+} ions tend to pull the negatively charged head groups together and hence decrease the permeability of the micelle. The adsorption of Mg^{2+} ions on the micelle will also reduce the net negative charge of the micelle. This type of effect is clearly illustrated by the addition of NaCl to NaTC micelles. The rate constant for I^- quenching increases by a factor of 2×. The sodium ions are adsorbed on the NaTC micelle thereby reducing the net negative charge, and increasing the permeability of the micelle to I^- ions.

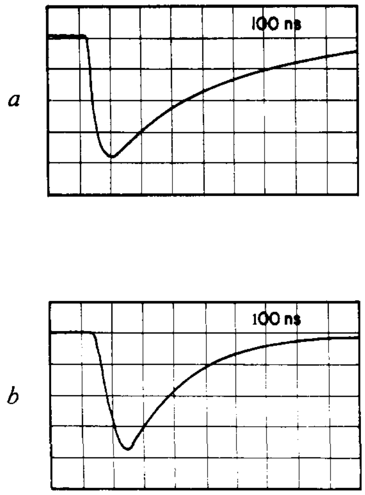


Figure 5. Oscilloscope traces of pyrene fluorescence decay at 400 nm: (a) 10^{-5} *M* pyrene, 10^{-3} *M* NaTC; (b) added 0.04 *M* NaI.

Cholesterol tends to increase the rigidity of micelles.[19] Table I shows that the addition of cholesterol to NaTC micelles increases the quenching rate constant for O_2, triethylamine, and iodide ions. The interpretation of these data suggests that cholesterol increases the permeability of NaTC micelles. Possibly the addition of cholesterol to the small NaTC micelles causes a disruption of the micelle structure and increased disorder. It has been suggested for membrane systems[19a] that cholesterol acts as a plasticizer and makes these systems more fluid. The presence of cholesterol in fatty acid monolayers increases the rate of evaporation through the monolayers.[20] The cholesterol disrupts the hydrophobic bonding forces between the lipid chains and increases the fluidity of the structure.

The excited state of pyrene is quenched efficiently in methanol solution, by cupric and thallous ions; the rate constants being 1.2×10^{10} M^{-1} sec^{-1} and 5×10^9 M^{-1} sec^{-1}, respectively. These ions also quench the excited state of pyrene when it is inside a NaTC micelle. The variation in the inverse of the half-lifetime $1/\tau$, for the excited state with Cu^{2+} and Tl^+ concentrations, is shown in Figure 6. The rate of quenching which is proportional to $1/\tau$ increases with cation concentration up to about 3×10^{-3} *M* and then remains constant to at least 2×10^{-2} *M*. It is suggested

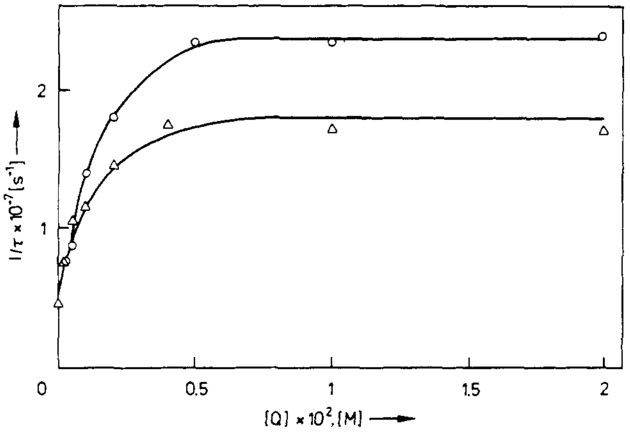


Figure 6. Effect of Cu^{2+} (○) and TL^+ (△) on the half-lifetime of pyrene fluorescence decay at λ = 400 nm, solution 10^{-5} *M* pyrene, 10^{-2} *M* NaTC.

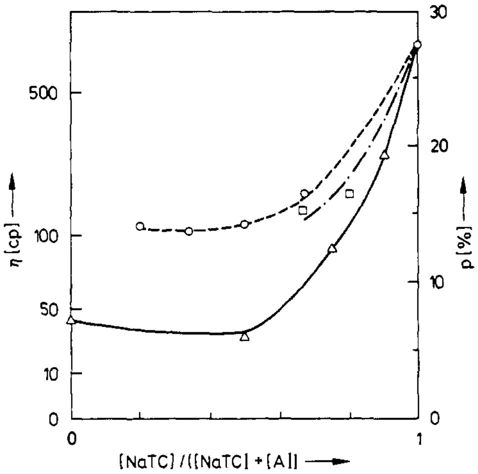


Figure 7. Effect of additives on the degree of polarization of 2-methylanthracene (4×10^{-6} *M*) in NaTC solutions. (△) NaLS, [NaTC] + [NaLS] = 0.1 *M*; (○) MgI_2, [NaTC] = 0.01 *M*; (□) benzyl alcohol [NaTC] = 0.01 *M*.

that the cations Tl^+ and Cu^{2+} are adsorbed at the surface of the NaTC micelles. The quenching reaction then occurs by the migration of the excited state p_1 to the micellar surface where it interacts with the cations. At low cation concentrations all the micelles are not associated with cations. This situation changes with increasing cation concentration, until saturation is reached. This theory indicates that at high [Cu^{2+}] and [Tl^+], the $1/\tau$ for p_1 should be constant. A difference is observed, however, which may reflect a change in the structure of the micelle with the two different cations. The average time taken for p_1 to diffuse to the surface is 57 nsec and 42 nsec for the Tl^+ and Cu^{2+} systems, respectively. Similar behavior has been reported for CTAB micelles.[7]

Polarization Studies. The degree of rigidity of a micelle or membrane system may also be measured by the technique of polarized fluorescence. Reference 21 is a review containing the theory and the pertinent details of this technique, and it suffices here to outline the procedure. A fluorescence probe such as methylanthracene is located in the micelle or membrane. It is subsequently excited by polarized light, and the degree of polarization p_1 of the fluorescence is measured. The degree of polarization may be related to the microscopic viscosity of environment of the probe by the Perrin expression

$$(1/p - 1/3)/(1/p_0 - 1/3) = 1 + kT\tau/\eta V_0$$

The symbols are defined as follows: p_0 is the degree of fluorescence polarization in a solvent of extremely high viscosity; τ is the fluorescent lifetime of the excited state; η is the microscopic viscosity; T is the temperature in degrees Kelvin; k is the Boltzmann constant; V_0 is the effective volume of the fluorescent molecule = 105 Å^3. The microscopic viscosities of NaTC and mixed NaTC-NaLS micelles under various conditions are shown in Figure 7. The very high viscosity 675 cP in a pure NaTC micelle is an indication of the rigid nature of these micelles. The viscosity is much larger than that of a NaLS micelle. The quenching data in Table I also indicate the same trend. The gradual addition of NaLS to form large mixed micelles with NaTC gives rise to a much less rigid micelle. Benzyl alcohol and magnesium chloride make the micelle less rigid. For benzyl alcohol the decreased rigidity is also reflected in the quenching data and has been discussed. However, the trend is reversed for Mg^{2+} ions. The quenching data show that Mg^{2+} ions make the entry of a molecule into the micelle more difficult. However, interior of the micelle is less rigid as the Mg^{2+} ions displace the head groups and impair the internal structure of the micelle.

Exit Rate from the Micelle. In a previous paper[8] the rate of exit of the triplet excited state of anthracene from a CTAB micelle was measured. The exit rate was slow and the long-lived triplet state of the probe had to be used in these observations. In the present work an estimate of the rate of exit of the anthracene triplet state from NaTC was obtained in the following way. Anthracene in NaTC micelles was excited by the pulsed laser system to the excited singlet state, which in turn converts rapidly to the triplet state. The triplet state subsequently leaves the micelle and is destroyed by reaction with another triplet state. The rate constant for this reaction is $\sim 2 \times 10^{10}$ M^{-1} sec^{-1}.[22] The concentration of the triplets is measured spectroscopically. The triplet-triplet annihilation can only occur if the triplet states diffuse from the micelles into the bulk of the solution where reaction occurs. The rate-determining step is then the rate of exit of the triplet state from the micelle. The observed half-lifetime for triplet decay is 360 μsec at a triplet concentration of 10^{-5} *M*. The half-lifetime of the triplet-triplet annihilation reaction is $\frac{1}{2} \times 10^{10} \times 10^{-5} = 5$ μsec. Hence a lower limit for the exit time of a triplet from the micelle is $\sim$360 μsec.

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The Use of Spin–Orbit Coupling in the Interpretation of Photoelectron Spectra. I. Application to Substituted Rhenium Pentacarbonyls

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Abstract: The uv photoelectron spectra of the substituted rhenium pentacarbonyls, $LRe(CO)_5$ (L = H, CH_3, $COCF_3$, $Re(CO)_5$, Cl, Br, and I), have been measured. We have developed the spin-orbit coupling matrices appropriate for this symmetry and have used these to analyze the spectra. The results provide a definitive assignment for the spectra of $HRe(CO)_5$, $CH_3Re(CO)_5$, $COCF_3Re(CO)_5$, and the analogous manganese complexes. The analysis of the spin-orbit coupling in the rhenium halides, where both the rhenium and halogen spin-orbit coupling were taken into account, shows that, contrary to expectations, the first band of $ClRe(CO)_5$ is mainly rhenium in character, while the corresponding band of $IRe(CO)_5$ is mainly iodide in character. Our success with these systems suggests that our type of analysis for the spin-orbit coupling may be a valuable tool in the assignment and interpretation of the photoelectron spectra of other transition metal systems.

Photoelectron spectroscopy (PES) has proven to be a valuable tool in the elucidation of the electronic structure of molecules.[1] One of the first applications of this technique to transition metal complexes was to a series of $Mn(CO)_5X$ compounds.[2] While many of the conclusions of this work were supported by approximate molecular orbital calculations,[3,4] the calculations did suggest that some important features of the spectra were not observed in this early work. Subsequent investigations of the spectra under higher resolution revealed many of these features.[5-7] Recently, ab initio calculations have been made on several of these complexes.[8] These calculations agree with the earlier approximate calculations in predicting additional bands in the upper valence region of the spectra. However, they provided a different assignment for the hydride and methyl spectra. Recent theoretical work on other transition metal systems suggests that Koopmans' theorem,[9] which was used to assign the spectra from the ab initio calculations, may not reproduce the correct order for the ionization potentials (IP).[10] Thus, there remains considerable doubt as to the correct assignments.

A study of the $Re(CO)_5X$ analogs was undertaken in order to resolve some of the ambiguities surrounding the assignments in these systems. A correct assignment for these systems is important since, as the simplest of the substituted carbonyl complexes, their interpretation will form the basis for the interpretation of the PES of more complex systems. The spin-orbit coupling of the rhenium should facilitate the identification of those bands which are mainly metal in character. A complete analysis of the effects of spin-orbit coupling will provide additional information about the delocalization of the metal electrons and the degree of mixing between metal orbitals and ligand orbitals. Although some work has been done on the analysis of spin-orbit coupling in PES,[11] the theory has not been extended to transition metal systems. We should also be able to observe some general trends in the spectra due to the change from manganese to rhenium, which could aid our interpretation of these molecules. Evidence that the spectra of manganese and rhenium should parallel each other comes from work on $Cr(CO)_6$, $W(CO)_6$[1] and $Cr(CO)_5NH_3$, $W(CO)_5NH_3$.[12] In addition to the assignment of the spectra, the study of the spin-orbit coupling in these complexes should provide some insight into the bonding and electronic structure of both the manganese and rhenium pentacarbonyls.

Experimental Section

A sample of $HRe(CO)_5$ was kindly supplied by Professor D. F. Gaines of this Department and was distilled under vacuum before use. $Re_2(CO)_{10}$ and $Re(CO)_5Cl$ were purchased from Pressure Chemical Co., Pittsburgh, Pa. 15201 and were sublimed under vacuum. Other samples were prepared by forming the $NaM(CO)_5$ salt in tetrahydrofuran (THF) from the reaction of $M_2(CO)_{10}$ with Na-Hg amalgam. This salt was then allowed to react with H_3PO_4, ICH_3, $(CF_3)_2CO$, and I_2 to form $HMn(CO)_5$, $CH_3Re(CO)_5$, $CF_3CORe(CO)_5$, and $IRe(CO)_5$, respectively. The bromide, $BrRe(CO)_5$, was prepared by direct reaction of Br_2 and $Re_2(CO)_{10}$ in THF. These preparations are analogous to the standard methods of preparation for the manganese compounds.[13] The samples were all sublimed or distilled under vacuum and their purity was checked by mass or infrared spectroscopy.

The PES spectra were measured using a Varian IEE-15 electron spectrometer in the uv configuration. The argon line at 15.76 eV was used as a single internal standard. The resolution of the instrument (FW Hm) was 22–23 mV for the argon $^2P_{3/2}$ state. The spectra, taken from multiple 1000-channel, 10-eV scans, were then fit by asymmetric Gaussian peaks to obtain the peak positions and integrated intensities. This fitting procedure[6] yields more accurate positions and intensities then can be obtained from considering only the band maxima, especially for strongly overlapping bands.

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