

trostatic binding to the micellar surface.

The interaction of the methylviologen cation radical with the SdecS micelles stabilizes this species not only toward disproportionation but also toward dimerization. The experimental data available in the chemical literature on viologen chemistry suggest that this might result from an increased hydrophobicity of the cation radical's microenvironment. Indeed, this requires at least partial penetration of $MV^{•+}$ into the hydrophobic core of the micelles. The data presented here for solutions with surfactant concentrations slightly above the cmc indicate that the cation radical is also stabilized by interactions with the monomeric surfactant anions (or with the scarcely abundant micellar aggregates). This is in good agreement with Park and Nam's report¹⁶ of a strong interaction between the methylviologen cation radical and monomeric dodecyl sulfate anions. Most interestingly, the extensive micellization of the surfactant was found to depress the dimerization equilibrium while the opposite effect, an increase in the extent of dimerization, was observed for solutions containing a very low concentration of SdecS micelles. This constitutes an interesting example of the influence of the relative abundance of micellar aggregates on the dimerization equilibrium of a cation radical. The reasons for this effect are probably related to the statistical distribution of the cation radicals among the aggregates.

Finally, the interaction of the neutral species MV with the SdecS micelles, although not addressed in detail in this work, can be simply described as the solubilization of a hydrophobic molecule by micellar assemblies. This is evidenced by the diffusional shape of the peak associated

with MV oxidation to $MV^{•+}$. As discussed above, this peak appears frequently distorted in micelle-free aqueous solution owing to the insolubility of this uncharged molecule in water. Since these distortions are not observed in the presence of SdecS micelles, it seems reasonable to postulate that the neutral viologen species is solubilized by the micellar aggregates.

Conclusions

We have shown that the reductive electrochemistry of MV^{2+} in SdecS micellar solutions is quite similar to that previously reported in SDS micellar solutions. This is so despite small differences in surfactant chain length and large differences in the free surfactant concentration in equilibrium with the micelles, pointing to a predominance of substrate-micelle over substrate-surfactant interactions even in experimental conditions wherein the monomeric surfactant is present in concentrations 10-fold larger than those of the micelles and the electroactive substrate. The dimerization of the methylviologen cation radical was found to be enhanced by small concentrations of SdecS micelles and suppressed in the presence of micellar concentrations similar to that of the cation radical.

Acknowledgment. This work was partially supported by the University of Miami Research Council. We express our gratitude to Richard Reno for performing the surface tension measurements and to one of the reviewers for offering several helpful suggestions.

Registry No. SdecS, 142-87-0; MV^{2+} , 4685-14-7; $MV^{•+}$, 25239-55-8; MV, 25128-26-1.

Excimer Formation of a Water-Soluble Fluorescence Probe in Anionic Micelles and Nonionic Polymer Aggregates

Nicholas J. Turro* and Ping-Lin Kuo

Chemistry Department, Columbia University, New York, New York 10027

Received January 14, 1987. In Final Form: March 10, 1987

The excimer/monomer emission of the water-soluble fluorescence probe, sodium pyrene-3-sulfonate (Py-S), has been investigated in aqueous solutions containing anionic micelles of sodium dodecyl sulfate (SDS), nonionic micelles of a series of polyethylene glycol *n*-nonyl phenyl ethers (C_9PhE_n), and aggregates of poly(ethylene oxide-propylene oxide-ethylene oxide) copolymers (EPE). The influences of temperature, pressure, and added salt on the intensity of the excimer to monomer emission (I_e/I_m) in the various systems were investigated. Dramatic differences were observed in the intensity of the excimer to monomer emission (I_e/I_m) under the varying environmental conditions. The results are interpreted in terms of a dynamic equilibrium of Py-S between the aqueous phase and the aggregate phases in response to variations of aggregate structure that are induced by the experimental variations.

Introduction

Investigations of the solution behavior of molecules solubilized in micelles or in bilayer vesicles provide information and generate methods and concepts that can be transferred to experimental systems involving biological molecules such as enzymes.¹ Photophysical techniques have been developed which make photoluminescence probes a very convenient means for investigating the nature and structure of molecules solubilized in hydrophobic aggregates in aqueous solution.² For example, excimer

formation of pyrene has been employed to investigate the microscopic viscosity of micelles and to determine aggregation numbers of micelles.³ Since pyrene is a strongly hydrophobic molecule, it has low water solubility and tends

(2) (a) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic: New York, 1975. (b) Thomas, J. K. *Acc. Chem. Res.* 1977, 10, 133. (c) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 675.

(3) (a) Hirayama, F. *J. Chem. Phys.* 1965, 42, 3163. (b) Klopffer, W.; Liptay, W. Z. *Naturforsch., A: Phys., Phys. Chem., Astrophys.* 1970, 25A, 1091. (c) Kordas, A. J.; El-Bayoumi, M. A. *Chem. Phys. Lett.* 1974, 26, 273. (d) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* 1979, 101, 771. (e) Ito, S.; Yamamoto, M.; Nishijima, Y. *Bull. Chem. Soc. Jpn.* 1981, 54, 35.

(1) (a) Barton, J. K.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc.* 1986, 108, 6391. (b) Fox, M. A. *Adv. Photochem.* 1986, 13, 237.

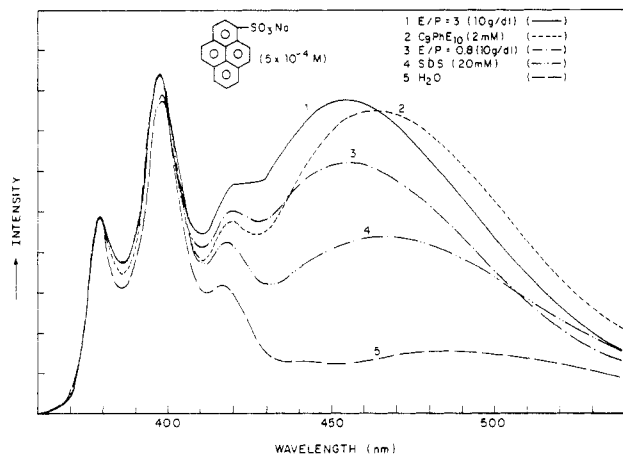


Figure 1. Fluorescence spectra of pyrene-3-sulfonate in aqueous solution containing various micellar aggregates. The spectra are normalized at 379 nm.

to be completely associated with hydrophobic aggregates in aqueous solution. Sodium pyrene-3-sulfonate (Py-S), on the other hand, has significant water solubility and therefore is capable of partitioning between the aqueous and hydrophobic aggregate phases. We decided, therefore, to investigate the formation of excimers of Py-S in aqueous systems containing three kinds of aggregate assemblies: (1) anionic micelles, (2) nonionic surfactant micelles, and (3) nonionic polymer micelles. The influences of pressure, temperature, and added salt on these systems were studied in order to determine the effect of these variables on excimer formation and to provide information that would be useful in elucidating the mechanism of partitioning of Py-S between the aqueous and aggregate phases.

Experimental Section

Materials. Sodium pyrene-3-sulfonate (Py-S, Pfaltz and Bauer Inc.) was purified by recrystallization 3 times from ethanol. Sodium dodecyl sulfate (SDS, Bio-Rad.), polyethylene glycol *n*-nonyl phenyl ether (C_9PhE_n , $n = 5, 7.5, 10, 15, 20$, Tokyo Kasei Co.), poly(ethylene oxide-propylene oxide-ethylene oxide) block copolymer with the ratio of 3 (EPE, MW 13 333, Polysciences), and sodium chloride (Alfa) were used as supplied. The synthesis of α, α' -1,3-dinaphthylpropane (DNP) is described in the literature.⁴

Measurements of Fluorescence Spectra and Lifetimes. All fluorescence spectra were taken on a Perkin-Elmer Hitachi spectrometer. A stainless steel high-pressure cell (Union Giken Engineering) was used for high-pressure measurements.⁵ The internal excimer formation of DNP (I_e/I_m' , the intensity ratio of monomer emission at 379 nm to excimer emission at 337 nm) is used to estimate the microviscosity of C_9PhE_n .^{4b}

Results

The excimer emission of Py-S has a broad maximum at ca. 460 nm, whereas the monomer emission of Py-S possesses a vibrational structure with a maximum at ca. 400 nm (Figure 1). The ratio of excimer emission to monomer emission (I_e/I_m) of Py-S (ca 5×10^{-4} M) was measured in pure water and in solutions containing SDS micelles, C_9PhE_{10} micelles, and EPE micelles (Figure 1). Compared to pure water, I_e/I_m increases significantly in the aggregate-containing solutions. The ratio I_e/I_m for SDS (0.6) is considerably larger than that for water (0.2) but is less than the value found in any of the nonionic aggregates (Figure 1 and Table I).

Table I. Relationship between I_e/I_m of Py-S and Microviscosity in Different Systems^a

	I_e/I_m of Py-S	I_e'/I_m' of DNP	microviscosity, cP
C_9PhE_5	0.51	0.17	67
$C_9PhE_{7.5}$	0.91	0.22	49
C_9PhE_{10}	1.01	0.24	43
C_9PhE_{15}	1.40	0.26	41
C_9PhE_{20}	0.92	0.19	58
EPE (3)	1.21	0.25	41
SDS	0.64	0.29	37
H ₂ O	0.20		1

^a [Py-S], 5×10^{-4} M; [DNP], 1.2×10^{-5} M.

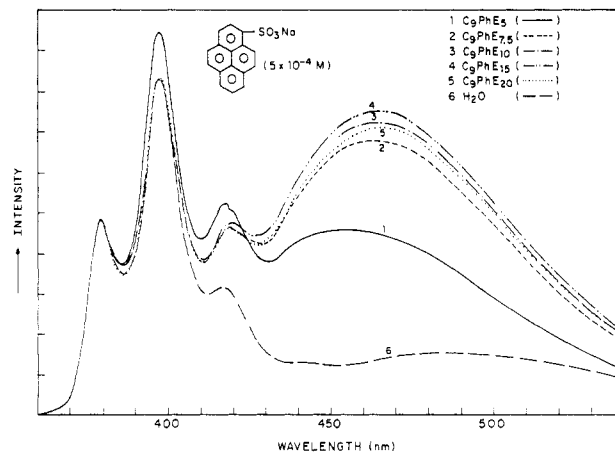


Figure 2. Fluorescence spectra of pyrene-3-sulfonate in aqueous solutions containing micellar aggregates of C_9PhE_n (2 mM, $n = 5, 7.5, 10, 15, 20$). The spectra are normalized at 379 nm.

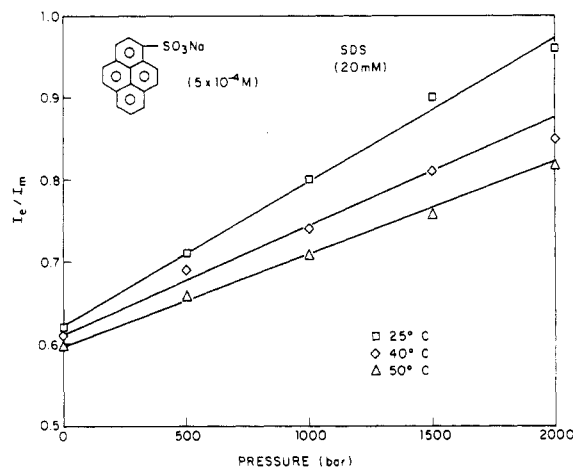


Figure 3. Variation of the relative excimer to monomer intensity (I_e/I_m) as a function of pressure at various temperatures for the SDS micellar system.

The excitation spectra at fixed emission of 460 nm (excimer) or at 400 nm (monomer) are experimentally indistinguishable, demonstrating that excitation of ground-state Py-S is responsible for the observed emission.

For the C_9PhE_n series, the ratio I_e/I_m was a function of n for a given fixed concentration of surfactant (Figure 2). Interestingly, I_e/I_m increases initially with increasing n but then decreases with $n = 20$.

For SDS and C_9PhE_{10} systems, the pressure and temperature cause significant variations in I_e/I_m (Figures 3 and 4). An increase in pressure (1–2000 bar) at fixed temperature causes a roughly linear increase in I_e/I_m , and an increase in temperature (25–50 °C) at fixed pressure causes a roughly linear decrease in I_e/I_m .

A substantially different behavior was found for the EPE systems (Figure 5). In this case an increase in pressure

(4) (a) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586. (b) Avouris, P.; Kordas, J.; El-Bayoumi, M. A. *Chem. Phys. Lett.* **1974**, *26*, 373.

(5) (a) Turro, N. J.; Okubo, T. *J. Am. Chem. Soc.* **1981**, *103*, 7224.

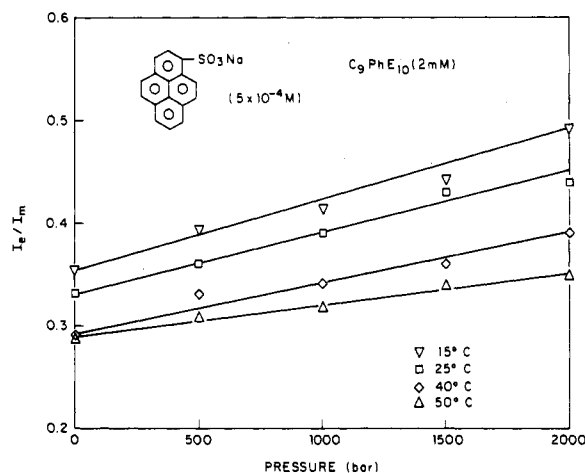


Figure 4. Variation of the relative excimer to monomer intensity (I_e/I_m) as a function of pressure at various temperatures for the C_9PhE_{10} micellar system.

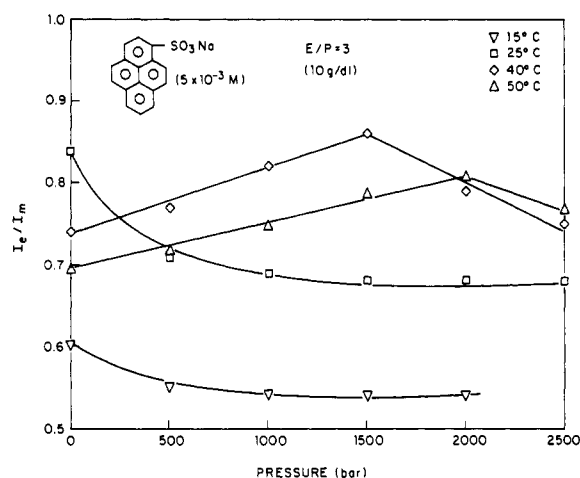


Figure 5. Variation of the relative excimer to monomer intensity (I_e/I_m) as a function of pressure at various temperatures for the EPE (3) polymer aggregates. The data points at the extreme left correspond to a pressure of 1 bar.

causes an initial decrease in I_e/I_m at 15 or 25 °C and an initial increase in I_e/I_m at 40 or 50 °C. As the pressure is increased, maxima in I_e/I_m are observed at the higher temperatures and a pressure-independent regime is observed at the lower temperatures.

Addition of NaCl (0.4 M) to aqueous solutions of Py-S causes an increase in I_e/I_m for the SDS and C_9PhE_n systems, whereas there is little effect of added salt for the EPE system. The sensitivity of I_e/I_m to pressure persists for the SDS and C_9PhE_n systems upon addition of NaCl but is suppressed for the EPE system when NaCl is added (Table II).

Discussion

The relatively long lifetime of the excited singlet state enhances its ability to form excimers, since excimer formation requires diffusion of the excited state until it can encounter a ground-state molecule to form the excimer (Scheme I). The intensity of I_e and I_m is dependent on several factors including the effective concentration of Py-S in the vicinity of $*Py-S$, the quenching of $*Py-S$ and $[Py-S \cdot Py-S]^*$, and the reversibility of excimer formation. These factors must be taken into account when interpreting I_e/I_m data.

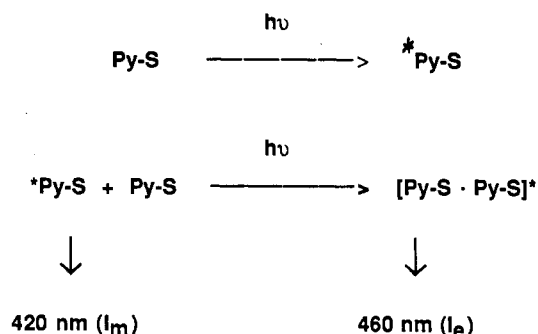
In homogeneous solution, the efficiency of formation of excimers is a function of excited monomer lifetime, diffusional motion of the excited monomer, and ground-state

Table II. Salt Effects on I_e/I_m of Py-S in Different Micellar Systems^a

micelles	NaCl, M	P, bar				
		1	500	1000	1500	2000
C_9PhE_{10}	0	0.76	0.83	0.90	1.00	1.09
	0.4	1.59	1.74	1.92	2.02	2.20
SDS	0	0.62	0.71	0.80	0.90	0.96
	0.4	1.74	1.83	1.95	2.04	1.99
EPE (0.3)	0	0.84	0.72	0.69	0.68	0.68
	0.4	0.72	0.77	0.69	0.61	0.59

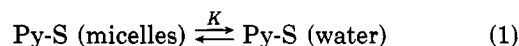
^a Measured at 25 °C

Scheme I. Mechanism of Monomer and Excimer Emission of Py-S



monomer concentration.⁶ In microscopic assemblies such as the micelles investigated in this study, exchange of hydrophobic probes (such as pyrene) from a given aggregate is generally slow relative to the excited monomer lifetime, so that only doubly (or multiply) occupied micelles contribute to excimer emission. However, the ground-state distribution of Py-S molecules in the micellar and aqueous phases should be an important factor in determining the efficiency of excimer formation. This distribution has been utilized in determining a method for evaluating aggregation numbers of micelles.⁷

Consider an aqueous solution containing micellar aggregates and Py-S, which exists in an equilibrium between the bulk aqueous phase and the micellar phase (eq 1). The



equilibrium constant, K , for partitioning of Py-S between the two phases will be a function of internal micellar structural properties and other variables such as pressure, temperature, and added salt. We will analyze our results in terms of the influence of the structural and other variables implied by the equilibrium of eq 1. The three classes of surfactants (SDS, C_9PhE_n , and EPE) form three different types of micelles in aqueous solution; i.e., SDS forms anionic micelles, C_9PhE_n forms nonionic surfactant micelles, and EPE forms nonionic polymeric micelles. These different aggregates possess significantly different interfacial properties and consequently should influence the equilibrium constant K differently. Since a change in K should in turn influence the local probe concentration in an aggregate and the distribution of probes in aggregates, the quantity I_e/I_m should be sensitive to variations in K and should serve as a qualitative parameter for variation in K unless the microviscosity of micellar aggregates be-

(6) For a general discussion, see: Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970. See also: (a) Turro, N. J.; Aikawa, M.; Yekta, A. *J. Am. Chem. Soc.* 1979, 101, 772. (b) Forster, T.; Selinger, B. K. *Z. Naturforsch., A: Phys., Phys. Chem., Astrophys.* 1964, 19, 38. (c) Hauser, M.; Klein, U. *Z. Phys. Chem.* 1972, 78, 32. (d) Pownall, H. J.; Smith, L. C. *J. Am. Chem. Soc.* 1973, 95, 3136. (7) Atik, S. S.; Nam, M.; Singler, L. A. *Chem. Phys. Lett.* 1979, 67, 75.

comes a significant feature in determining the extent of excimer formation. In order to test for this possibility, α, α' -1,3-dinaphthylpropane was employed as a probe of micellar microviscosity. The ratio of intramolecular excimer to monomer emission intensity has been shown to be a guide to micellar microviscosity by employing a series of homogeneous solutions of known viscosities as standard.^{4b} Values of I_e'/I_m' are translated into microviscosities in Table I along with values of I_e/I_m . If microviscosity were significant in determining the extent of excimer formation, a lower microviscosity would correspond to a greater value of I_e/I_m . Since no such trend is evident from Table I, we conclude that microviscosity is not generally significant in determining the magnitude of I_e/I_m .

The probability of finding multiply occupied micelles is given by the Poisson expression (eq 2), where S is [Py-

$$P(n) = S^n e^{-S} / n! \quad (2)$$

S]/[micelles] and n is the number of Py-S molecules per micelle.⁸ The concentration of micelles ([micelles]) is given by (eq 3), where cmc is the critical micelle concen-

$$[\text{micelles}] = (C - \text{cmc})/N \quad (3)$$

tration, C the concentration of surfactant, and N the aggregation number. At a given Py-S concentration, the increase of concentration of micelles decreases S and hence decreases the probability for Py-S to form excimer.

For SDS micelles, increasing pressure causes the value of I_e/I_m to increase significantly (0.64–0.96 upon going from 1 to 2000 bar at 25 °C), whereas increasing temperature has a smaller effect (0.64–0.60 on going from 25 to 60 °C at 1 bar). The addition of NaCl causes an increase in I_e/I_m at all pressures. An increase in pressure is expected to cause a decrease in the solubility of Py-S in the aqueous phase⁹ and a decrease in the aggregation number¹⁰ of SDS micelles (and consequent increase in concentration of micelles). Since the net effect of increasing pressure is to increase I_e/I_m , we conclude that pressure is increasing the local concentration of probes in the aggregate. The increased local concentration, in turn, is evidently governed by an increase in the solubility of Py-S in the micellar phase. An increasing temperature causes an increase in Py-S solubility in water and a decrease in the aggregation number of SDS.¹¹ Both factors decrease the probability of Py-S to form excimers. The increase of I_e/I_m with added salt is ascribed to "salting out" of the Py-S and SDS from the aqueous phase, which increases the solubility of Py-S in the micellar phase and the aggregation number of SDS.^{11b}

For $C_9\text{PhE}_n$ micelles, the values of I_e/I_m are a function of n (Figure 2), and each system displayed a higher value than SDS micelles. Increasing the chain length of the $C_9\text{PhE}_n$ system is expected to increase the solubility of Py-S in the micellar phase and consequently to increase the value of I_e/I_m .¹² However, increasing the polyoxyethylene chain length causes a decrease in the aggregation number of these nonionic micelles.¹³ For example, $N =$

276 for $n = 10$ and $N = 64$ for $n = 20$. A decrease in N at fixed surfactant concentration implies an increase in the concentration of micelles. The observation of a maximum in I_e/I_m for $C_9\text{PhE}_{15}$ is attributed to a competition between the increasing solubility of Py-S in the micellar phase as the value of n increases and the decreasing probability of finding doubly occupied micelles as the value of n increases. The latter effect is postulated to become dominant in going from $n = 15$ to $n = 20$ and thereby causes a reversal of the trend for smaller values of n .

The effect of pressure is expected not only to decrease the aggregation number of nonionic surfactants¹⁰ but also to increase the hydration of the polyethylene chain,¹⁰ causing a decrease in the solubility of Py-S in $C_9\text{PhE}_n$ micelles. In opposition to this effect is the expected decrease in the solubility of Py-S in the bulk aqueous phase⁹ with increasing pressure. As a result, because of these competing and cancelling effects, the sensitivity of I_e/I_m to pressure is smaller for $C_9\text{PhE}_{10}$ micelles than for SDS micelles (compare Figures 4 and 5). The sensitivity of I_e/I_m to pressure is higher at lower temperature for both SDS and $C_9\text{PhE}_{10}$ micelles. This may be due to restructuring of water, which decreases the solubility of Py-S and is promoted by pressure.^{9b}

Increasing temperature not only increases the solubility of Py-S in the aqueous phase but also increases the aggregation number of $C_9\text{PhE}_{10}$ ¹⁴ (and consequently decreases the concentration of micelles). The former decreases but the latter increase the I_e/I_m values. Therefore, the effect of increasing temperature on I_e/I_m for $C_9\text{PhE}_{10}$ is smaller than that for SDS. The effect of added NaCl for $C_9\text{PhE}_{10}$ is also similar to that observed for SDS (i.e., I_e/I_m increases with added salt, Table II) and may be attributed to the increase in Py-S concentration in the micellar phase and, as in the case of SDS micelles, can be attributed to the increase of the aggregation number^{11b} of $C_9\text{PhE}_{10}$ as a result of the salting out effect.

EPE is a graft and block copolymer¹⁵ which forms polymeric aggregates at concentrations as high as 10%.¹⁶ The largest values of I_e/I_m were quite different for this system of aggregates (Figure 5). Indeed, the shape of the profile of I_e/I_m with pressure depends dramatically on temperature. At 40 and 50 °C, the value of I_e/I_m initially increases as it did with the SDS and $C_9\text{PhE}_n$ systems, but a maximum is observed at very high pressures. At 15 and 25 °C, an initial decrease in I_e/I_m with pressure is followed by a pressure-insensitive region.

For EPE aggregates, similarly, the increasing pressure (1) decreases the solubility of Py-S in water (and consequently increases I_e/I_m), (2) decreases the aggregation number of EPE aggregates (and consequently decreases I_e/I_m), and (3) increases the hydration of EPE aggregates (and consequently decreases I_e/I_m).¹⁷ The EPE polymer aggregates are less compact than $C_9\text{PhE}_{10}$ micelles.¹⁷ At the higher temperature, EPE aggregates become more contracted¹⁷ and behave more similarly to $C_9\text{PhE}_{10}$. Thus factor 1 above can only be observed at higher temperature (40 and 50 °C) for EPE aggregates, but factors 2 and 3 become more obvious as the pressure is raised above 1500 bar. At low temperature, factors 2 and 3 become dominant; thus the initial increasing pressure decreases I_e/I_m .

(8) Thomas, J. K. *Chem. Rev.* **1980**, 283.

(9) (a) Nakahara, M.; Osugi, J. *Rev. Phys. Chem. Jpn.* **1975**, 45, 69. (b) Ueno, M.; Nakahara, M.; Osugi, M. *J. Solution Chem.* **1979**, 8, 881. (c) Neilson, G. W. *Chem. Phys. Lett.* **1979**, 68, 247.

(10) Nishikido, N.; Shinozaki, M.; Sugihara, G.; Tanaka, M.; Kaneshimka, S. *J. Colloid. Interface Sci.* **1980**, 74, 474.

(11) (a) Chen, J.-M.; Su, T.-M.; Mou, C.-Y. *J. Phys. Chem.* **1986**, 90, 2418. (b) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1978.

(12) Tokiwa, F. *J. Phys. Chem.* **1968**, 72, 1214.

(13) Schick, M. J.; Athas, S. M.; Eirich, F. R. *J. Phys. Chem.* **1962**, 66, 1326.

(14) (a) Nakagawa, T. *Nonionic Surfactants*; Schick, M. J., Ed.; Marcel Dekker: New York, 1967; p 558. (b) Mankowick, A. M. *J. Am. Oil Chem. Soc.* **1965**, 42, 185.

(15) Ceresa, R. J. *Block and Graft Copolymerization*; Wiley-Interscience: New York, 1976; Vol. 2.

(16) Prasad, K. N.; Luong, T. T.; Florence, A. T.; Paris, J.; Vaution, C.; Puisieux, F. *J. Colloid Interface Sci.* **1979**, 69, 225.

(17) Turro, N. J.; Kuo, P.-L. *J. Phys. Chem.* **1986**, 90, 1016.

The effect of added NaCl on I_e/I_m in the EPE system is small compared to the effects observed in the SDS and C_9PhE_n systems and is consistent with a higher solubility of Py-S in the EPE micelles.

Conclusions

The effects of pressure, temperature, and added salt on the micellar solubilization of the Py-S probe are dependent on micelle type. In anionic micelles such as SDS, pressure and added salt cause an increase in probe solubility in the micellar phase, whereas temperature has a weaker and opposite effect. In nonionic micelles of the C_9PhE_n systems, solubilization depends on n , and two effects occur: an increase in micelle hydrophilicity and solubility of Py-S with increasing n and a decrease in aggregation numbers with increasing n . For a typical member of the C_9PhE_n

family, increased pressure and added salt causes an increase in probe solubility in the micellar phase whereas increased temperature causes the opposite effect. For the EPE micelles, the probe solubility is not sensitive to added salt but exhibits unusual pressure and temperature behavior, compared to SDS and C_9PhE_n micelles. The latter behavior suggests a significant change in micellar structure with pressure and temperature for the EPE micellar systems.

Acknowledgment. We thank the Army Office of Research and the 3M Corp. for their generous support of this research.

Registry No. Py-S, 59323-54-5; SDS, 151-21-3; EPE, 106392-12-5; C_9PhE_n , 9016-45-9; C_9PhE_5 , 26264-02-8; NaCl, 7647-14-5.

Interpretation of SERS Intensity-Lead Coverage Profiles for Pyridine and Chloride Ion in Terms of Electromagnetic Enhancement and Charge-Transfer Excitation

Anita L. Guy and Jeanne E. Pemberton*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received August 8, 1986. In Final Form: April 7, 1987

The excitation behavior of the quenching of SERS for pyridine and Cl^- at Ag electrodes in the presence of monolayer and submonolayer amounts of underpotentially deposited Pb is presented in this report. Intensity-coverage profiles are presented for the ring-breathing mode of pyridine at 1013 cm^{-1} and $\nu(\text{Ag-Cl})$ at 235 cm^{-1} with laser excitation at 4579, 4880, 5145, and 6226 Å. Electromagnetic contributions to the quenching behavior are evaluated by comparison of the experimental quenching profiles with theoretical profiles. Theoretical profiles are calculated from a model described by Murray which predicts electromagnetic enhancement at overlayer-covered metal ellipsoids. The experimental and theoretical profiles are in poor agreement, especially for excitation in the red-wavelength region. A chemical model based on photoassisted charge transfer is proposed to account for the experimental behavior at other excitation wavelengths.

Introduction

Recent experimental investigations into the phenomenon of surface-enhanced Raman scattering (SERS) have been directed toward unraveling the complex contributions to the overall surface enhancement made by classical electromagnetic (EM) and so-called chemical mechanisms. Elucidating the relative contribution of each has proven to be a difficult task. This is due, in part, to the difficulty in varying only one experimental parameter of the system in a systematic fashion while leaving others unchanged. One approach to the systematic variation of surface properties that has received considerable attention is the use of ultrathin metal films deposited onto foreign metal substrates. In electrochemical environments, this is readily accomplished through the use of underpotential metal deposition (UPD). This technique allows submonolayer amounts of the film metal to be deposited in a highly reproducible and quantifiable fashion. The electronic properties of the surface are known to be altered by small amounts with each submonolayer increment of the film deposited. When this metal deposition process is carried out in the presence of SERS-active adsorbates, the relative change in SERS intensity of the probed species can be

readily followed as a function of surface coverage.

This approach has been successfully applied to the investigation of many systems.¹⁻¹² In all of the studies involving the deposition of a nonenhancing metal onto an enhancing metal, the SERS intensities of the probe adsorbate are quenched to undetectable levels upon deposition of monolayer amounts of the nonenhancing metal. Moreover, the quenching of SERS for some adsorbates at Ag has been shown to qualitatively correlate with an increase in the imaginary part of the surface dielectric function or surface absorptivity for fractional Pb coverages between 0% and ca. 40% of a monolayer.⁷ This has been

- (1) Loo, B. H.; Furtak, T. E. *Chem. Phys. Lett.* **1980**, *71*, 68.
- (2) Pettinger, B.; Moerl, L. *J. Electron. Spectrosc. Relat. Phenom.* **1983**, *29*, 383.
- (3) Moerl, L.; Pettinger, B. *Solid State Commun.* **1982**, *43*, 315.
- (4) Watanabe, T.; Yanagihara, H.; Honda, K.; Pettinger, B.; Moerl, L. *Chem. Phys. Lett.* **1983**, *78*, 7466.
- (5) Kester, J. J. *J. Chem. Phys.* **1983**, *78*, 7466.
- (6) Pemberton, J. E. *J. Electroanal. Chem.* **1984**, *167*, 317.
- (7) Guy, A. L.; Bergami, B.; Pemberton, J. E. *Surf. Sci.* **1985**, *150*, 226.
- (8) Guy, A. L.; Pemberton, J. E. *Langmuir* **1985**, *1*, 518.
- (9) Guy, A. L.; Pemberton, J. E. *Langmuir* **1987**, *3*, 125.
- (10) Kellogg, D. S.; Pemberton, J. E. *J. Phys. Chem.* **1987**, *91*, 1127.
- (11) Coria-Garcia, J.; Pemberton, J. E.; Sobocinski, R. L. *J. Electroanal. Chem.* **1987**, *219*, 291.
- (12) Pemberton, J. E.; Coria-Garcia, J.; Hoff, R. L. *Langmuir* **1987**, *3*, 150.

* Author to whom correspondence should be addressed.