Photophysics of Molecules in Micelle-forming Surfactant Solutions

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1 Introduction

Amphiphilic molecules containing both hydrophobic and hydrophilic moieties associate in water above a certain critical concentration to form aggregates of colloidal dimensions called 'micelles'. The architecture of a micelle is such that the interior contains the hydrophobic alkyl chain part of the amphiphiles and the charged headgroups are located at the surface forming a charged electrical double layer (interface) in contact with the bulk water. Detailed structural and dynamical aspects of these organised multimolecular assemblies have been the subject of intense research activity using various physical methods. Recent advances on the many facets of micellar chemistry have been reviewed in several places.[1] Though not a pre-requisite for this review, readers are well advised to consult a recent review[1c] in this series for an up-to-date account and for an explanation of the terminologies used in this field.

Among the various physical methods that have been used, photophysical methods stand unique for their simplicity, wide scope, and extreme sensitivity at very low solute (probe) concentrations. Also the time scales spanned by photophysics—from few picoseconds to several seconds—enables one to study both the fast and the slow dynamical processes associated with the aggregates. The advantages and potentialities of photophysical studies in aqueous micellar media are manifold. The peculiar make-up of the micelle enables one to organize the reactants on a molecular level. By comparison of the data in micelles with similar data in homogeneous solvent systems, one learns more about the molecular details of a given reaction, picks up conditions which favour one pathway over another, and at the same time is able to comment on the intricate details of micellar structure and dynamics. The random, statistical distribution of the solute amongst the micelles, coupled with the presence of a charged interface nearby, often lead to significant differences in the rates and efficiency of the reactions undergone by the solute. The methodology of the technique has

[1a] C. Tanford, 'The Hydrophobic Effect', Wiley, New York, 1973; J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems', Academic Press, New York, 1975; P. H. Elworthy, A. T. Florence, and C. B. Macfarlane, 'Solubilisation by Surface Active Agents', Chapman and Hall, London, 1968.

[1b] 'Micellisation, Solubilisation and Microemulsions', ed. K. L. Mittal, Plenum Press, New York, 1977, vols. 1 and 2.

[1c] L. R. Fisher and D. G. Oakenfull, *Chem. Soc. Rev.*, 1977, **6**, 25.

advanced to such a level in micelles that these applications can be easily carried over to studies of similar bioaggregates such as lipid vesicles, liposomes, polymers, and proteins.

The scope of this review is to outline some of the various photophysical processes that have been studied in aqueous micellar solutions and to indicate their applications in several areas. The field is still very much in its infancy and is experiencing a rapid growth. Except for those studies referred to in the section on 'reversed micelles', all references are to the micelles formed in water as the medium. For lack of space the various photophysical processes as such will not be discussed at any length, and readers are referred to the excellent monographs available.[2] Also, the review is more illustrative in nature than a comprehensive discussion of all the reported work.

In studies of photophysical processes in micelles there are a few cautionary notes worth mentioning. In multiphase heterogeneous systems such as micelles, the high local electric fields present near the surface fall off quite rapidly as one moves deeper into the inner core. So for any generalization of a set of results using different probes it is useful, and even mandatory, to talk about the exact solubilization or binding site of the probe in the aggregate. A probe can reside solely in the inner hydrocarbon phase, sandwich at the surface with the polar headgroups, or just adsorb at the surface by electrostatic interactions. Depending on the solubility characteristics, the reactants (the probe and the quenchers) can be dispersed primarily in the micellar pseudophase or in the bulk water, or partition between the two phases with an associated distribution coefficient. In the latter case, one has a situation in which a reaction can occur simultaneously in more than one phase with very different features in each phase.

When condensed aromatic hydrocarbons whose dimensions compare favourably with the overall dimensions of the micelle itself (radius 20—25 Å) are used, assignments to the dynamic solubilization sites are qualitative in nature. With large size probe molecules it is also likely that the solubilization perturbs the micellar structure creating water channels. To overcome some of the above problems it is advantageous to use a built-in chromophore, or even pick up the components of the surfactant themselves to be the reactants (functional surfactants) whose size is quite small. If a highly polar group is built into a hydrophobic alkyl chain, there may be a perturbation of the micellar structure by the intrinsic property of the probe to seek polar environments. Thus, to provide confidence in the usage of photochemical probes, it is advantageous to employ other complimentary physical methods to ascertain the average, dynamic solubilization sites and on the pertubations, if any, due to the introduction of the solutes.

2 Fluorescence

The basic idea behind the use of a fluorescence probe is that certain types of molecules display a selective affinity for a unique site on a macromolecule and the

[2] J. B. Birks, 'Photophysics of Aromatic Molecules', Wiley, New York, 1970; C. A. Parker, 'Photoluminescence of Solutions', Elsevier, New York, 1968; 'Organic Molecular Photophysics', ed. J. B. Birks, Wiley, New York, 1976, Vols. 1 and 2.

nature of the probe environment is reflected in their emission properties. The various fluorescence parameters that are used in this context are the fluorescence excitation and emission spectra, presence of vibrational fine structures and their intensities, shifts in the position of emission maxima, quantum yields, lifetimes, and the polarization of the fluorescence. The success and the ambiguities associated with the fluorescence probe analysis are very much dependent on to what extent the actual solubilization site can be specified and how well the medium effects on the above fluorescence parameters are characterized.

A. Solvent Effects on the Fluorescence Spectra.—One simple and seemingly rather straightforward application is that based on the solvent effects in the emission spectrum of a probe molecule. When excited states of a molecule are created in polar solvents like water or acetonitrile either by continuous or flash excitation, depending on their polarity, the excited states interact to a varying degree with the solvent molecules before the molecule returns to the ground state. Such solute–solvent interactions in the excited state are often reflected in the fluorescence spectral position, shape, and lifetimes. Milder interactions lead either to blurring or to variations in the relative intensities of the vibrational fine structures of the emission spectrum. In the case of stronger reactions, the Franck–Condon envelopes of the excited state themselves shift to give red or blue shifts in the emission maxima.

A case where the solvent interactions perturb mainly the relative intensities of the vibrational fine structures is the so-called 'Ham-effect'.[3] In aromatic molecules such as benzene or pyrene (with minimum D_{2h} symmetry) the absorption and fluorescence spectra show mixed polarizations owing to the vibronic coupling between the first (S_1) and the second (S_2) singlet excited states. The first singlet absorption ($S_0 \rightarrow S_1$) is symmetry forbidden and is weak. In the Ham effect, the forbidden vibronic bands in weak electronic transitions show marked intensity enhancements under the influence of solvent polarity. In pyrene, for example, if one numbers I to V the principal vibronic bands observed in the room temperature fluorescence in solution, peak III (0—737 cm^{-1} band) is strong (allowed) and shows minimal variations in intensity. Peak I (0—0 band) shows significant intensity enhancements in polar solvents. Thus the peak intensity ratio (III/I) in the normal fluorescence spectrum serves as a measure of the polarity of the medium. Quantitative studies[3,4] indicate that the solvent dipole moment as well as the dielectric constant contribute to these relative intensity enhancements. The peak ratio (III/I) has been used recently [5,6] as a probe in micelles to determine critical micelle concentrations (CMC) and the extent of water penetra-

[3] J. S. Ham, *J. Chem. Phys.*, 1953, **21**, 756; A. Nakajima, *Bull. Chem. Soc. Japan*, 1971, **44**, 3272; *Spectrochim. Acta*, 1974, **A30**, 860; *J. Mol. Spectroscopy*, 1976, **61**, 467.
[4] K. Kalyanasundaram and J. K. Thomas, *J. Amer. Chem. Soc.*, 1977, **99**, 2039.
[5] A. Nakajima, *Photochem. Photobiol.*, 1977, **25**, 593; *J. Luminescence*, 1977, **15**, 277.
[6] R. C. Dorrance and T. F. Hunter, *J. C. S. Faraday I*, 1977, **73**, 1891; D. A. N. Morris and J. K. Thomas, in ref. 1*b*; Th. Proske, Ch. H. Fisher, and M. Grätzel, *Ber. Bunsengesellschaft Phys. Chem.*, 1977, **81**, 816; W. Schencke, M. Grätzel, and A. Henglein, *ibid.*, 1977, **81**, 821.

tion in the micelles. In studies of lipid vesicles it has been used to monitor changes associated with lipid phase transitions and to determine the rather lower CMC values for the micelles formed by lysolecithins.

A more familiar example of solvent effects is the solvent-induced red shifts in the fluorescence maximum of molecules of the type arylaminonaphthalenes[7,8] [*e.g.* 1-anilino-8-naphthalene sulphonate (ANS), *N*-phenylnaphthylamine (NPN)], indoles,[9] and aromatic aldehydes[10] (*e.g.* pyrene-3-carboxaldehyde). In this class of compounds fluorescence lifetimes, emission maxima, and the quantum yields vary markedly with the solvent polarity. Though the exact photophysical processes involved in these intense solvent effects are not well understood and are still under active investigation,[11] several useful linear correlations of the emission maxima with the bulk solvent dielectric constant have been demonstrated and these correlations find increasing use as a rough measure of the polarity of the probe binding sites. Except with the non-ionic micelles, studies with charged molecules of ANS type have not been satisfactory. It is not clear whether these negatively charged probes bind to anionic micelles. In cationic micelles there is frequent interaction of probes with monomeric surfactants at surfactant concentrations well below the CMC. Nevertheless, estimates for polarity of probe binding sites in various micelles using these probes are available. In very early fluorescence probe studies,[12] changes in the quantum yields and lifetimes at a given wavelength were used to probe micellar structure.

For studies of this type, ideal probes are those which do not carry appreciable charge either in the ground or in the excited state. A probe under this category is pyrene-3-carboxaldehyde (PyCHO), which shows large red shifts due to the solvent-induced mixing of (n, π^*) and (π, π^*) excited states. With PyCHO near the micelle–water interface, the fluorescence spectral shifts have been used to estimate polarity at this water interface. The polarity estimates are in good agreement with similar estimates from electrophoretic measurements. Among the heterocyclics, indole fluorescence shows solvent-induced spectral shifts and several 1,3-dialkyl indoles with the indole moiety built into the alkyl chain have been examined.[9] Time-correlated single photon counting allows resolution of the indole fluorescence into those from aqueous and micellar components in the vicinity of CMC. The relative intensity of the 'normal' to the 'anomalous' long wavelength fluorescence of dimethylaminobenzonitrile[13a] has

[7] M. T. Flanagan and S. Ainsworth, *Biochim. Biophys. Acta*, 1968, **168**, 16; H-C. Chiang and A. Lukton, *J. Phys. Chem.*, 1975, **79**, 1935; R. C. Mast and L. V. Haynes, *J. Colloid Interface Sci.*, 1975, **53**, 35.

[8] G. A. Davis, *J. Amer. Chem. Soc.*, 1972, **94**, 5089.

[9] N. E. Schore and N. J. Turro, *J. Amer. Chem. Soc.*, 1974, **96**, 306; *ibid.*, 1975, **97**, 2488.

[10] K. Bredereck, Th. Förster, and H. G. Oeirstein, in 'Luminescence of Organic and Inorganic Materials', ed. H. P. Kallman and G. M. Spruch, Wiley, New York, 1960; K. Kalyanasundaram and J. K. Thomas, *J. Phys. Chem.*, 1977, **81**, 2176.

[11] E. M. Kosower, H. Dodiuk, K. Tanizawa, M. Ottolenghi, and N. Orbach, *J. Amer. Chem. Soc.*, 1975, **97**, 2167; G. R. Fleming, G. Porter, R. J. Robbins, and J. A. Synowiec, *Chem. Phys. Letters*, 1977, **52**, 228.

[12] For a review see, M. Grätzel and J. K. Thomas, in 'Modern Fluorescence Spectroscopy', ed. E. L. Wehry, Plenum Press, New York, 1976, Vol. 2, p. 169.

[13a] O. S. Khalil and A. J. Sonnessa, *Mol. Photochem.*, 1977, **8**, 399.

been used as a probe. Solvent effects on the relative ratio of cyclization to cleavage in Norrish Type II photoreactions[13b] also serve to monitor the local solvent properties of micelles.

B. Fluorescence Quenching.—The diffusion-controlled process of fluorescence quenching has been used to study various dynamical properties of aggregated systems of micelles and lipid vesicles. A fluorescence probe such as pyrene solubilized in the micellar interior is excited by a short nanosecond light pulse. In the presence of substances which act as quenchers the decay of fluorescence is enhanced. The rate at which the quenchers enter the micelle and/or the probe diffuses in the micellar interior determines the kinetics of the quenching process. Consequently, a kinetic analysis of the fluorescence decay curves and yields provides information on the permeability of the micelle or the vesicle to the quenchers and on the movement of the probe inside the aggregate. Several studies[14] based on this concept of fluorescence quenching have led to a variety of information on the properties of micelles: the CMC, distribution coefficients for the case of partitioning of the probe or the quenchers between the micellar phase and the bulk water, extent of counterion binding to the micellar surface, oxygen penetration, and the influences of additives on the permeability properties of the aggregate.

In cases where there is a single quenching process involved, *e.g.* probe dispersed primarily amongst the micelles and the quenchers restricted to the bulk aqueous phase, or *vice versa*, the fluorescence decay is exponential and the quenching process adequately described[14] by the well known Stern–Volmer kinetics scheme. Deviations from a single exponential decay are observed when there is a significant partitioning of the probe, *e.g.* naphthalene,[15] or the quencher, *e.g.* methylene iodide,[16a] between the bulk water and the micellar phase. If the overlapping quenching processes have very different rates and/or the partitioning coefficients are fairly large, the fluorescence decay can be approximated by the sum of two exponentials. Several kinetic models[16,17] for the analysis of such types of complex decays have been proposed. Complications also arise in cases where one uses electrically charged water-soluble probes and/or quenchers. For example, the charged probe can distribute itself in the two phases or more than one charged quencher molecule preferentially bind to the micellar surface. The latter case leads to quasi-static distributions in which there is locally high concentrations of the quencher on the micellar surface. Cu^{2+} quenching of pyrene

[13b] N. J. Turro, K. C. Liu, and M. F. Chow, *Photochem. Photobiol.*, 1977, **26**, 413.
[14a] M. Grätzel, K. Kalyanasundaram, and J. K. Thomas, *J. Amer. Chem. Soc.*, 1974, **96**, 7869.
[14b] M. Grätzel and J. K. Thomas, *J. Amer. Chem. Soc.*, 1973, **95**, 6885.
[14c] S. C. Wallace and J. K. Thomas, *Rad. Res.*, 1973, **54**, 49; H. J. Pownall and L. C. Smith, *Biochemistry*, 1974, **13**, 2594; L. K. Patterson and E. Vieil, *J. Phys. Chem.*, 1974, **96**, 306.
[15] R. R. Hautala and N. J. Turro, *Mol. Photochem.*, 1972, **4**, 545; R. R. Hautala, N. E. Schore, and N. J. Turro, *J. Amer. Chem. Soc.*, 1973, **95**, 5508.
[16a] P. P. Infelta, M. Grätzel, and J. K. Thomas, *J. Phys. Chem.*, 1974, **78**, 190.
[16b] P. P. Infelta and M. Grätzel, *J. Chem. Phys.*, 1978, in the press; M. Tachiya, *Chem. Phys. Letters*, 1975, **33**, 289.
[17] M. A. J. Rodgers and M. F. de Silva e Wheeler, *Chem. Phys. Letters*, 1978, **53**, 168.

fluorescence[17] and I^- quenching or pyrene-1-butyrate fluorescence,[18] both in anionic micelles, illustrate these cases. Detailed kinetic analysis assuming a two-phase model, in favourable cases, has led to the determination of the distribution coefficients.

By comparison of the fluorescence lifetimes of a probe such as pyrene-1-sulphonate (PSA) (which binds on the micellar surface) in cationic micelles of cetyltrimethylammonium halides with different halide counterions, it is possible to estimate[14a] the local concentration of bound halide ions. Studies with the quencher bromide and non-quencher chloride as counterions give local bromide concentration of $\simeq$ 3M. A very rapid drop in this high local concentration with increase in distance into the inner core is inferred from comparative analysis of lifetimes of probes, PSA, pyrenebutyric acid (PBA), and pyrene, which penetrate the micelle to varying degrees. Similarly, the different fluorescence lifetimes for a given probe[19] under aerated, de-aerated, and oxygenated conditions, give a measure of oxygen penetration in micelles. The quenching rate constant for a given probe–quencher–micelle system has been used as a probe to monitor changes in the permeability properties of the aggregates when other non-quencher additives such as Mg^{2+} and benzyl alcohol are present,[14b] and also to study[20] processes such as electrolyte-induced phase transitions from spherical micelles to larger rod-shaped aggregates. Quenching of indole fluorescence, which occurs *via* both static and dynamical quenching processes in homogeneous solvents, has been examined[21] in anionic micelles in an attempt to gain further insight into the mechanisms involved in the quenching process. Dynamics of fluorescence quenching has also been used extensively in studies of bile acid micelles[22] and in lipid vesicles[23] to monitor lipid phase transitions.

Recently there has been some discussion in the literature[24] as to the exact region where the fluorescence quenching occurs; in the non-polar interiors with water-insoluble quenchers entering through water channels created by the introduction of the probe, or the excited probe diffuses out into the bulk aqueous phase. For water-insoluble probes, such as pyrene solubilized in ionic micelles, preferred mechanisms[25] require the quenchers to enter the micelle rather than the excited pyrene exit into the aqueous phase. With regard to the polarity of the average quenching site, it appears to be non-polar. Arguments based on the emission maxima of exciplexes have been advanced. Processes such as micelle–monomer exchange, micelle complete dissolution, and exit rates for aromatic

[17] F. H. Quina and V. G. Toscano, *J. Phys. Chem.*, 1977, **81**, 1750.
[18] M. W. Geiger and N. J. Turro, *Photochem. Photobiol.*, 1975, **22**, 273.
[20] K. Kalyanasundaram, M. Grätzel, and J. K. Thomas, *J. Amer. Chem. Soc.*, 1975, **97**, 3915.
[21] M. R. Eftink and C. A. Ghiron, *J. Phys. Chem.*, 1976, **80**, 486.
[22] M. Chen, M. Grätzel, and J. K. Thomas, *Chem. Phys. Letters*, 1974, **24**, 65; *J. Amer. Chem. Soc.*, 1975, **97**, 2052.
[23] S. Cheng and J. K. Thomas, *Rad. Res.*, 1974, **60**, 268; S. Cheng, J. K. Thomas, and C. F. Kulpa, *Biochemistry*, 1974, **13**, 1135; M. Wong, J. K. Thomas, and C. F. Kulpa, *Biochim. Biophys. Acta*, 1976, **426**, 711.
[24] M. A. J. Rodgers and M. F. de Silva e Wheeler, *Chem. Phys. Letters*, 1976, **43**, 587; B. B. Craig, J. Kirk, and M. A. J. Rodgers, *ibid.*, 1977, **49**, 437.
[25] J. K. Thomas, *Accounts Chem. Res.*, 1977, **10**, 133.

solubilizates all occur at very slow rates (microseconds, or longer) and so on nanosecond time-scales of fluorescence quenching, micelles with solubilized probes can be considered a rigid system.

C. Excimer Kinetics.—Another diffusion-controlled photo-physical process, which has received wide attention and application in micelles and lipid vesicles, is the formation of intermolecular excited dimers, often abbreviated as 'excimer'. In micelles, time-resolved fluorescence studies of excimer formation kinetics have provided a clear cut demonstration of the random (statistical) manner in which water-insoluble molecules distribute themselves amongst the micelles. In lipid vesicles similar analysis provides a means of monitoring lateral diffusion of probes in the lipid bilayer of membranes and also follow changes occurring during the lipid phase transitions.

Following the initial work of Förster and Selinger,[26] the formation of excimers of pyrene and other molecules in micellar media has been investigated by several groups.[20,27–29] In homogeneous solvents like cyclohexane, the yields and the rate of formation of excimers are dependent on the probe concentration, the temperature and the viscosity of the medium, and the process is adequately described by the familiar Förster–Kasper Scheme. In micellar media, for water-insoluble solutes such as pyrene, the probability of the excited singlet state leaving one micelle and finding another ground state pyrene (from another micelle) within its excited state lifetime is very low (estimates for the exit rate of probes from micelles, based on triplet state studies discussed later, are of the order of milliseconds) and hence the intermolecular formation of excimers is essentially an intramicellar process. Only those micelles which have more than one pyrene molecule incorporated at the instant of flash excitation alone give rise to excimers.

Given the bulk concentration of the probe (pyrene) and the concentration of the micelles, the probability of finding one, two, or more probe molecules in a given micelle can be computed assuming a random distribution of solute amongst the micelles present. The simplest, and also a fairly reasonable model, is that based on Poisson–Boltzmann statistics (P–B). According to the Poisson distribution, the probability P_n of finding n solute molecules in a given micelle is given by

$$P_n = \frac{m^n e^{-m}}{n!} \tag{1}$$

where m is the mean (average) number of solute molecules per micelle. The micelle concentration at various bulk surfactant concentrations (surf.) can be computed from the aggregation number and the CMC

$$\text{(Micelle)} = [\text{(surf.)} - \text{(CMC)}]/\text{Agg. No.} \tag{2}$$

Since micelle-monomer exchange and solute exit rates from the micelle are quite

[26] Th. Förster and B. K. Selinger, *Z. Naturforsch.*, 1964, **19**, 38.
[27] R. C. Dorrance and T. F. Hunter, *J.C.S. Faraday I*, 1972, **68**, 1312; *ibid.*, 1974, **70**, 1572.
[28] M. Hauser and U. Klein, *Z. Phys. Chem.* (*NF.*), 1972, **78**, 32; *Acta Phys. Chem.*, 1973, **19**, 363.
[29a] U. Khuanga, B. K. Selinger, and R. McDonald, *Austral. J. Chem.*, 1976, **29**, 1.
[29b] U. Khuanga, B. K. Selinger, and R. McDonald, *Z. Phys. Chem.* (*NF.*), 1976, **101**, 209.

slow, in the Poisson–Boltzmann distribution micelles are considered as rigid boxes in which the solutes are dispersed. Dorrance and Hunter,[27] however, prefer to treat the micelles as an open system (with a finite probability of micellar collapse) and use a slightly modified distribution

$$P_n = m^n/(1 + m)^{1+n} \quad (3)$$

which reduces to P–B statistics when n is large. Hauser and Klein[28] propose that the distribution is more like that of Bose–Einstein (B–E). However, when $m \leqslant 1$, both B–E and P–B statistics predict roughly the same type of distribution.

Experimental verifications[20,27-29] for a random distribution hypothesis come from time-resolved fluorescence studies on the monomer, excimer growth and decay, and from their relative yields for various probe-to-micelle ratios. Using a Poisson distribution of pyrene amongst the micelles, micellar aggregation numbers and diffusion rates have been determined. In studies of microviscosities of micellar core using the relative monomer-to-excimer yields,[30] failure to take this random distribution effects into account has resulted in abnormally high 'η' values for the inner core. The dynamics of excimer kinetics coupled to the monomer fluorescence quenching has been used to distinguish the lateral diffusion of the probe as against the vertical diffusion in larger rod-shaped micellar aggregates. For solutes such as 2-methylnaphthalene or 1-cyanonaphthalene, which form excimers at relatively high concentrations owing to low enthalpy changes, the statistical restrictions on the excimer formation are much less severe. With these solutes solubilized at high occupation numbers, one is dealing virtually with a dispersed lipophilic 'normal' solution.

In larger unilamellar bilayer vesicles formed by the lecithins, the hydrophobic volume over which the pyrene molecules are dispersed is considerably large and in these systems excimer formation can be described by the normal diffusion-controlled kinetics.[31-34] At temperatures well below the lipid phase transitions, the local viscosity is fairly high and the probe diffusion is very much lateral. Attempts have been made to describe this lateral diffusion of probes [32b,34] as well as the reactions between two reactants, both adsorbed on the micellar surface[35] as reactions occurring topologically in two-dimensional surfaces, as against the normal three-dimensional diffusional processes in bulk solvent systems. There have been several studies of lipid phase-transitions using pyrene excimers.

Intramicellar, intermolecular formation of phenyl excimers between built-in

[30] H. J. Pownall and L. C. Smith, *J. Amer. Chem. Soc.*, 1973, **95**, 3136.
[31] H. J. Galla and E. Sackmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **98**, 949; *Biochim. Biophys. Acta*, 1974, **339**, 103; P. Sengupta, E. Sackmann, W. Kuhlne, and H. P. Scholtz, *ibid.*, 1976, **436**, 839.
[32a] J. M. Vanderkooi and J. B. Callis, *Biochemistry*, 1974, **13**, 400; J. M. Vanderkooi, S. Fischoff, B. Chance, and R. Cooper, *ibid.*, 1974, **13**, 1589.
[32b] J. M. Vanderkooi, S. Fischoff, M. Andrich, F. Podo, and C. S. Owen, *J. Chem. Phys.*, 1975, **63**, 3661.
[33] A. K. Soutar, H. J. Pownall, A. S. Hu, and L. C. Smith, *Biochemistry*, 1974, **13**, 2828.
[34] D. A. N. Morris, Doctoral dissertation, University of Notre Dame, 1977.
[35] A. J. Frank, M. Grätzel, and J. J. Kozak, *J. Amer. Chem. Soc.*, 1976, **98**, 3317; A. J. Frank, M. Grätzel, A. Henglein, and E. Janata, *Internat. J. Chem. Kinetics*, 1976, **8**, 817.

phenyl (or phenoxyl) groups has been reported.[36] Studies of intramolecular phenyl excimers in compounds such as biphenyl alkanes, dibenzylether and dibenzylamines in micelles[37] provide another elegant way of probing dynamics of intramolecular excimer-forming systems.

D. Excited State Charge-Transfer Complexes (Exciplexes).—Formation of charge-transfer complexes (exciplexes) in the fluorescence quenching of aromatic molecules by quenchers such as amines have been observed in the laser photolysis studies in homogeneous solvents. In non-polar solvents the exciplex is quite stable, luminesces and, in polar solvents, rapidly dissociates into molecular ions. Studies of the exciplex formation kinetics in micellar aggregates,[38,39] with either one or both the donor–acceptor pair solubilized in the micelle, provide an elegant method of probing heterogeneities in the micellar structure and their effect on the dissociation of the exciplex.

Features of intermolecular exciplex of pyrene-dimethylaniline (Py/DMA) with pyrene and several of its derivatives and of the intramolecular exciplex Py-$(CH_2)_3$-DMA have been investigated recently in various ionic and non-ionic micellar systems. Singlet excited states of pyrene are efficiently quenched by DMA by a charge-transfer process to form the ionic exciplex $(Py^- \cdots DMA^+)^*$ whose fate depends critically on the nature of the micelle. Stern–Volmer plots for the pyrene fluorescence quenching are non-linear due to multiple binding of DMA to the ionic micelles.

In cationic micelles, following the quenching, the $DMA^{+\cdot}$ cation is expelled from the micellar surface while $Py^{-\cdot}$ is retained (stabilized) leading to a long lifetime for $Py^{-\cdot}$. (Similar solute ejection mechanisms have been proposed[40] earlier for the ejection of duroquinone anion ($DQ^{-\cdot}$) from anionic micelles following its electron-transfer quenching of the chlorophyll *a* singlets.) In anionic micelles, on the contrary, the micellar surface traps $DMA^{+\cdot}$ ions leading to an enhanced geminate ion-combination. Because of the trapping of $DMA^{+\cdot}$ at the surface some of the $Py^{-\cdot}$ ions escape the recombination and decay with lifetimes much longer than those observed in homogeneous solvents. Earlier transient absorptions due to the exciplex have been reported[14b] in the pyrene fluorescence quenching in the mixed micelles of laurylamine and sodium lauryl sulphate. However, this has been questioned[41] as this report implies the presence of free base at pH of the solutions of well below the pK_a of the amine. In the case of Py-$(CH_2)_3$-DMA, the emission from the intramolecular exciplex as well as formation of $Py^{-\cdot}$ have been observed to varying degree in various micelles. The exciplex yield and lifetime decrease as one goes through the series: hexane, neutral micelle

[36a] S. J. Rehfeld, *J. Colloid Interface Sci.*, 1970, **34**, 518.
[36b] K. Kalyanasundaram and J. K. Thomas, in ref. 1*b*, Vol. 2, p. 569.
[37] B. Selinger and K. Zacharaisse, unpublished work, quoted in ref. 29*b*; K. Kalyanasundaram and J. K. Thomas, unpublished results.
[38] B. Katusin-Razem, M. Wong, and J. K. Thomas, *J. Amer. Chem. Soc.*, 1978, **100**, 1679.
[39] H. Masuhara, K. Kaji, and N. Mataga, *Bull. Chem. Soc. Japan*, 1977, **50**, 2084; Y. Waka, K. Hamamoto, and N. Mataga, *Chem. Phys. Letters*, 1978, **53**, 242.
[40] Ch. Wolff and M. Grätzel, *Chem. Phys. Letters*, 1977, **52**, 542.
[41] B. K. Selinger, *Austral. J. Chem.*, 1977, **30**, 2087.

(Igepal CO-630), methanol, cationic micelle (CTAB), and anionic micelle (NaLS).

E. Fluorescence Depolarization.—Studies of the depolarization of fluorescence from solubilized probes in macromolecular systems provide information concerning the mobility of the probe and its orientation as well as the microviscosity of the probe environment. When a fluorescent molecule is excited by a plane polarized light, its emission will be maximally polarized if, during its excited state lifetime, the probe does not change its position as in a viscous medium. If the molecule is not rigidly held, Brownian motions of the probe will tend to remove the orientation imposed by the polarized excitation. The theory associated with the depolarization of fluorescence due to this random Brownian motion, has been determined[42] and the observed polarization p is given by the Perrin's equation. A fluorescence probe, loosely bound in a micelle, probes the molecular motions in its immediate environment. The 'η' thus derived is termed 'microviscosity' in order to distinguish it from the bulk viscosity of the medium in which the micelles are present.

Molecules such as perylene, 2-methylanthracene, and diphenylhexatriene (DPH) have been used in the steady state fluorescence depolarization studies[43] to measure microviscosities for the inner hydrophobic regions of aggregates of micelles and lipid vesicles. For micellar systems the measured microviscosities are of the order of 15—30 cP. Although these values are high compared with 1—2 cP observed for pure hydrocarbon liquids, they nevertheless stress the fluid nature of the micellar core. N.m.r. relaxation[44] and laser Raman scattering studies[45] of the segmental mobility of various units in micelles indicate a gradient in the motional freedom of the hydrocarbon chains with the last three—four carbon atoms at the end of the chain (in the core) behaving as though they are in neat hydrocarbon liquids. In micelles, formed by the bile acids,[22] the microviscosities are comparatively high ($\eta > 100$ cP) and in lipid vesicles, at temperatures below the lipid phase transition, η is again of the order of a few poises.

Recently an extension of the above steady state method has been introduced wherein the dynamical aspects of the depolarization are examined on the nanosecond time scales. In the dynamic polarization experiments, the probe is excited by a short (nanosecond) polarized light pulse and the fluorescence decay of ($I_{\parallel}$ and $I_{\perp}$) the components are directly monitored separately. The time-dependent fluorescence depolarization anisotropy $r(t)$ thus measured provides additional (more direct) information on the degree of anisotropy of the medium and on the type of rotational diffusion the excited probe executes inside the aggregate. There

[42] G. Weber, *Ann. Rev. Biophys. Bioengg.*, 1972, **1**, 553.
[43] M. Shinitzky, A. C. Dianoux, C. Gitler, and G. Weber, *Biochemistry*, 1971, **10**, 2106; M. Shinitzky, *Israel J. Chem.*, 1974, **12**, 879; R. C. Dorrance and T. F. Hunter, *J.C.S. Faraday I*, 1977, **73**, 89.
[44] E. Williams, B. Sears, A. Allerhand, and E. H. Cordes, *J. Amer. Chem. Soc.*, 1973, **95**, 4871; R. T. Roberts and C. Chachaty, *Chem. Phys. Letters*, 1973, **22**, 348.
[45] K. Kalyanasundaram and J. K. Thomas, *J. Phys. Chemistry*, 1976, **80**, 1462; H. O. Ashi, M. Okuyama, and T. Kitagawa, *Bull. Chem. Soc. Japan*, 1975, **48**, 2264.

have been few studies[46] of this type in lipid vesicles. Analysis of the decay profiles of $r(t)$ indicate that the orientational motion of molecules such as DPH in the lipid phase can be described by a wobbling diffusion restricted by a certain anisotropic potential and the wobbling diffusion confined to a cone with a uniform diffusion constant.

F. Excitation Energy Transfer.—Transfer of excitation energy under suitable conditions between the excited electronic states of two different chromophores find application in the biophysical studies as a spectroscopic ruler in the determination of interchromophore distances. In micellar media, with proper choice of conditions, one can construct a model system in which the donor-acceptor pairs are placed in well-defined geometry and proximity and also set up conditions wherein there is a fairly high local concentration of the solutes inside the micelle.

The ability to solubilize chlorophyll *a* in non-ionic micelles at concentrations close to the *in vivo* level in chloroplasts ($\sim$ 0.1M) has enabled a study[47] of the process of energy transfer between two Chl *a* molecules by concentration depolarization of the fluorescence. By appropriate choice of solutes to micelle ratio, it is possible to study energy transfer under various multiple occupancy conditions. These studies, in addition to demonstrating the localization of the solutes, also confirm the operation of the Förster type of inductive resonance. Self energy transfer between the built-in naphthalenes has also been examined[48] in the micelles formed by cetylaminonaphthalenesulfonates.

When both the donors and the acceptors are localized inside the micelle, the local concentration of solutes is high giving very efficient energy transfer. Such enhanced efficiency in the energy transfer has been demonstrated between various types of laser dyes[49] such as Rhodamine 6G and between a thionine-methylene blue pair.[50] Recently there have been several studies which indicate that desegregation of the hydrophobic dyes in micellar media enhances considerably the CW lasing of dyes such as Rhodamine 6G and also leads to superior temporal stability for polymethine dyes compared with that in the non-aqueous solvent systems which are normally employed.

While there is no energy transfer between naphthalene and the heavy metal salt, terbium chloride, in homogeneous solvents, very efficient energy transfer has been demonstrated [51] in aqueous anionic micelles. Here again the role of micelles is to allow compartmentalization of no more than one donor per micelle and at the same time concentrate a large number of acceptors at the micellar surface. In

[46] S. Kawato, K. Kinoshita, and A. Ikegami, *Biochemistry*, 1977, **16**, 2319; K. Kinoshita, S. Kawato, and A. Ikegami, *Biophys. J.*, 1977, **20**, 289; J. H. Easter, R. P. DeToma, and L. Brand, *ibid.*, 1976, **16**, 571; L. A. Chen, R. E. Dale, S. Roth, and L. Brand, *J. Biol. Chem.*, 1977, **252**, 2163.

[47] K. Csatorday, E. Lehoczki, and L. Szalay, *Biochim. Biophys. Acta*, 1975, **376**, 268.

[48] M. Shinitzky, *Chem. Phys. Letters*, 1973, **18**, 247.

[49] G. A. Kenney-Wallace, J. H. Flint, and S. C. Wallace, *Chem. Phys. Letters*, 1975, **32**, 71.

[50] G. S. Singhal, E. Rabinowitch, J. Hevesi, and V. Srinivasan, *Photochem. Photobiol.*, 1970, **11**, 531.

[51] J. R. Escabi-Perez, F. Nome, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1977, **99**, 7749.

homogeneous media, triplet–triplet annihilation rapidly deactivates naphthalene triplets before they can transfer their excitation energy.

Efficient transfer of excitation energy from the built-in phenyl group in surfactants such as phenyl undecanoate to solubilized aromatic molecules such as naphthalene and pyrene has been advanced[36b,52] as evidence for the solubilization of these aromatics inside the micelle close to the phenyl group. A recent application using micelles as a medium to study photoreaction of water-insoluble solutes involves[53] studies of reactions of singlet oxygen produced by triplet energy transfer from sensitizers. In these studies singlet oxygen is produced by energy transfer from the triplet state of methylene blue or 2-acetonaphthone and its reactions studied indirectly by monitoring the concentration of dibenzofuran with which it reacts.

G. Excited State Acid–Base Equilibria.—In Section 2A reference was made to those compounds whose fluorescence properties are dependent on the solvent polarity (dipole moment and dielectric constant). There is another class of compounds, such as aromatic amines and phenols, whose fluorescence is pH dependent and there has long been an interest[54] in the use of these fluorescent pH indicators as probes for micellar surface. Most of these compounds have two pK_a values, one for the ground state protonation (pK_a)

$$ROH \rightleftharpoons RO^- + H^+ \; ; \; RNH_2 + H^+ \rightleftharpoons RNH_3^+ \qquad (4)$$

and another for the excited state (pK_a^*)

$$ROH^* \rightleftharpoons RO^{-*} + H^+ \; ; \; RNH_2^* + H^+ \rightleftharpoons (RNH_3^+)^* \qquad (5)$$

The fluorescence from these molecules at a given temperature is thus dependent on (i) the relative magnitudes of pK_a, pK_a^* with respect to the pH of the medium, (ii) how efficiently the equilibration occurs in the excited state within its lifetime and, (iii) how efficiently the solvent or other quenchers quench each of the two fluorescent species. Thus, 2-naphthol in water, in the pH range pK_a—pK_a^* fluoresces from both ROH* and RO^{-*} due to inefficient equilibration in the excited state while 1-naphthol fluoresces only from RO^{-*}.

Studies of ground and excited state acid–base equilibria for various molecules have shown[54,55] that micelles have a pronounced influence on both pK_a and pK_a^*. For coumarins (which are stronger acids in the excited state and hence relative fluorescence intensity is a measure of ground state dissociation) changes in pK_a can be monitored either by absorption or by fluorescence. For amines, most

[52] M. Almgren, *Photochem. Photobiol.*, 1972, **15**, 297.

[53] A. A. Gorman, G. Lowering, and M. A. J. Rodgers, *Photochem. Photobiol.*, 1976, **23**, 399; A. A. Gorman and M. A. J. Rodgers, *Chem. Phys. Letters*, 1978, **55**, 52; I. B. C. Matheson, J. Lee, and A. D. King, *ibid.*, 1978, **55**, 49; Y. Usui, M. Tsukada, and H. Nakamura, *Bull. Chem. Soc. Japan*, 1978, **51**, 379.

[54] L. K. J. Tong and M. C. Gleismann, *J. Amer. Chem. Soc.*, 1957, **79**, 4305; P. Mukerjee and K. Banerjee, *J. Phys. Chem.*, 1964, **68**, 3567; M. Montal and C. Gitler, *Bioenergetics*, 1973, **4**, 363; M. S. Fernandez and P. Fromherz, *J. Phys. Chem.*, 1977, **81**, 1755.

[55] B. K. Selinger, *Austral. J. Chem.*, 1977, **30**, 2087; B. K. Selinger and A. Weller, *ibid.*, 1977, **30**, 2377; U. Khuanaga, R. McDonald, and B. K. Selinger, *Z. Phys. Chem. (NF.)*, 1976, **101**, 209; J. R. Escabi-Perez and J. H. Fendler, *J. Amer. Chem. Soc.*, 1978, **100**, 2234.

often the free base is an efficient quencher while the protonated form is not. Thus a fluorescence-quenching titration as a function of pH in compounds of the type anthracene-$(CH_2)_3$-DMA provides a direct measure of the pK_a of the amine. In all cases, micelles (both ionic and neutral) alter the pK_a by 1—2 units. The pK_a of acid–base reactions in micelles is influenced, firstly, by the effective dielectric constant at the solubilization site and, more predominantly, by the effect of the charge dissociation of the counterions at the micellar double layer. (Estimates of local electric field strengths at the micellar surface are several kV per cm.)

Micellar effects on the excited state acid–base equilibria in 1- and 2-naphthol and pyrene-1-amine have been recently investigated. 1-Naphthol and pyrene-1-amine, which show complete equilibration for excited state reactions in homogeneous solvents, show only partial equilibration in micelles; 2-naphthol was found to go from partial equilibration to complete lack of reaction. This 'suppression of pK_a^* effect' has been attributed to the higher micellar viscosity. Increased efficiency of some dyes as laser media when solubilized in the micelles has also been attributed to this micellar effect.

3 Triplet State Studies

All the processes described in Section 2 are singlet state reactions taking place at nanosecond time scales or less. On these time scales, the micellar aggregate can be considered as a rigid (permanent) specie and micelles dispersed in water can be treated conveniently as a two-phase system. There are, however, several much slower processes connected with the micellar association equilibria, processes such as exchange of monomer with the micelle, the complete collapse of the micelle ('dissolution equilibria'), and exit and re-entry of the solubilizates in and out of the micelle. These slower (micro or millisecond) processes are conveniently probed by studies with the triplet excited states.

A. Phosphorescence and the Triplet State.—The rare observance of phosphorescence emission from aromatic molecules in fluid solutions is often attributed to the impurity quenching of the excited states. Studies on singlets, discussed earlier, indicate that the micellar environment tends to shield or screen the excited state of a probe located within the lipid phase from reactions with molecules located in the bulk aqueous phase; it is thus reasonable to expect sufficient protection of the triplet state in micelles that phosphorescence may be observed at room temperature. Recently, phosphorescence emission from a variety of aromatic molecules has been observed[56] in anionic sodium lauryl sulphate micelles. Molecules such as 1-bromonaphthalene and 1-bromopyrene emit phosphorescence quite strongly in fluid aqueous micellar solutions at room temperature. With non-halogenated aromatics such as pyrene or naphthalene, intense phosphorescence was observed in the presence of thallous (Tl^+) ions which bind strongly to the negatively charged micellar surface. The success of these experiments is partly due to the intra/intermolecular heavy atom effects and partly due to the micellar protection

[56] K. Kalyanasundaram, F. Greiser, and J. K. Thomas, *Chem. Phys. Letters*, 1977, **51**, 507.

of the triplet state from the aqueous quenchers and from the triplet–triplet annihilation process. Each of these effects by themselves leads only to extremely weak emission. The successful observation of phosphorescence enables one to monitor some of the slower processes mentioned earlier. Quenching studies on 2-bromonaphthalene emission with water-soluble quenchers such as I^- indicate that the solute leaves a NaLS micelle in 2 msec and re-enters with a rate constant of about 1×10^9 M^{-1} sec^{-1}.

There have been few studies of reactions of the triplet state by direct monitoring of the triplets by laser flash photolysis.[16] Quenching of anthracene triplets by Cu^{2+} ions in cationic CTAB micelle give the rate constant for anthracene exit to be of the order of 2×10^2 sec^{-1}. In all cases, the triplet lifetimes (either by phosphorescence or by T–T absorption) in micelles are much larger compared with that in homogeneous solvent systems. For water-insoluble solutes with very low exit rates, one can produce and use fairly high concentrations of the triplets without appreciable deactivation by triplet–ground state and triplet–triplet quenching mechanisms. This is very important, if one wants to utilize all the triplets efficiently in triplet-photosensitized reactions, as will be discussed later.

B. Photoionization.—Photoionization of molecules and subsequent electron transfer reactions are being investigated in a wide variety of systems because of their importance in our understanding of primary photophysics, solar energy storage, and their relevance to biological electron-transfer processes. In the photolysis of aromatic and heterocyclic molecules in polar solvents, depending on the light intensity, one observes, in addition to the triplets, their ionization products, solute cations, and solvated electrons. The photoionization occurs by one or two photon absorption processes. The relative efficiency of the two channels—photoionization *versus* triplet—is dependent on the nature of the medium. Micelles have been found[57,58] to have a pronounced influence on these reactions.

The efficiency of photoionization is greatly influenced when molecules are photolysed in anionic micelles. For tetramethylbenzidine, for example, the ratio of the yields of solute cation to the triplet is 6.0 in anionic NaLS micelles compared with 0.17 in methanol. This is due to the increased probability of electron escape to the bulk water, effective stabilization of the cation, and prevention of the re-entry of the solvated electron by the negatively charged micellar surface. A photoejected electron with an excess energy > 1.1 eV is capable of escaping the micellar charge and is solvated in the bulk water. The range, energy, and the reactivity of the photo-ejected electron prior to thermalization and solvation and also of the hydrated electron, have been examined in detail. In cationic micelles, as with the exciplex dissociation case mentioned earlier, the probability of

[57] S. C. Wallace, M. Grätzel, and J. K. Thomas, *Chem. Phys. Letters*, 1973, **23**, 359; M. Grätzel and J. K. Thomas, *J. Phys. Chem.*, 1974, **78**, 2248; D. J. W. Barber, D. A. N. Morris, and J. K. Thomas, *Chem. Phys. Letters*, 1976, **37**, 481; P. Picuolo, Doctoral Dissertation, University of Notre Dame, 1977.

[58] S. A. Alkaitis, M. Grätzel, and A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1975, **79**, 541; S. A. Alkaitis, G. Beck, and M. Grätzel, *J. Amer. Chem. Soc.*, 1975, **97**, 5723; S. A. Alkaitis and M. Grätzel, *ibid.*, 1976, **98**, 3549.

geminate ion-recombination is enhanced and hence the photoionization efficiency is low. The very low yields of ions and high yields of excited states in the photolysis in homogeneous non-polar solvents are also attributed to the very efficient recombination of the geminate ion-pair. Studies on the mechanisms of photoionization indicate that the thresholds for photoionization are also significantly reduced in aqueous micellar solutions in comparison with that in non-polar alkane liquids or in the gas phase. In micellar solutions, the ionization potentials for solutes are estimated to be at least 2—3 eV less than those in the gas phase.

4 Photoredox Reactions

Photoredox reactions, in which an electron is transferred from a low energy donor to a high energy acceptor using visible light, are currently receiving wide attention as a possible means of solar energy conversion and storage, and also as simple models to simulate photosynthetic electron-transport. A heterogeneous system, such as micelles containing a strongly absorbing photo catalyst, offers several advantages over homogeneous solvent systems. Firstly, most of the water-insoluble sensitizers can be used. By keeping the solute to micelles ratio fairly low, it is possible to use high concentrations of the sensitizer without appreciable loss in the overall efficiency. Secondly, the low ionization thresholds in micelles enables usage of visible light. In the third place, the rate of geminate ion-recombination can be kept low in anionic micelles. In energy-storing redox reactions, a major cause for the overall inefficiency in homogeneous solvent systems is the very fast, thermodynamically favourable back reactions of the redox products in the dark. Studies of electron transfer reactions[59] in micelles, using triplet excited states of molecules as donors or as acceptors and also those involving hydrated electrons and solutes outlined below, indicate that, with proper choice of conditions, these undesirable back reactions can be reduced to some extent.

A. Reactions of Hydrated Electrons.—Micellar effects on the reactivity of the hydrated electron, $e_{\overline{aq}}$ (produced in the bulk water by pulse radiolysis) with solutes solubilized perferentially in the micellar phase have been investigated for a wide variety of solutes[60] in different micelles. Electron transfer reactions of the type

$$e_{\overline{aq}} + S \rightarrow S^- \qquad (6)$$

which occur at diffusion-controlled rates in the homogeneous solvent systems, are

[59] For a detailed review of these studies, see A. Henglein and M. Grätzel in 'Solar Polar and Fuels', ed. J. R. Bolton, Academic Press, New York, 1977, p. 53; M. Grätzel in ref. 1*b*, p. 531; A. J. Frank in ref. 1*b*, p. 549.

[60a] K. M. Bansal, L. K. Patterson, E. J. Fendler, and J. H. Fendler, *Internat. J. Rad. Phys. Chem.*, 1971, **3**, 321; J. H. Fendler, H. A. Gillis, and N. V. Klassen, *J.C.S. Faraday I*, 1974, **70**, 145; M. Grätzel, J. K. Thomas, and L. K. Patterson, *Chem. Phys. Letters*, 1974, **29**, 393; L. K. Patterson and M. Grätzel, *J. Phys. Chem.*, 1975, **79**, 956; A. J. Frank, M. Grätzel, A. Henglein, and E. Janata, *Ber. Bunsengesellschaft Phys. Chem.*, 1976, **80**, 547; A. J. Frank, M. Grätzel, and A. Henglein, *ibid.*, 1976, **80**, 593.

[60b] M. Grätzel, J. J. Kozak, and J. K. Thomas, *J. Chem. Phys.*, 1975, **62**, 1632.

subjected to large retardation or enhancements if the solute is solubilized in an ionic micelle. The large positive charge on the cationic micelles attracts the e_{aq}^- to the micelle, giving rise to abnormally high rate constants ($> 5 \times 10^{11}$ M^{-1} sec^{-1}). Anionic micelles similarly repel the e_{aq}^- and reduce the rate. Cases are also known where the micelles promote electron-transfer reactions such as

$$CO_2^- + Py \rightarrow CO_2 + Py^{-\cdot} \quad (7)$$

$$3DQ^* + CO_3^{2-} \rightarrow DQ^{-\cdot} + CO_3^{-\cdot} \quad (8)$$

(Py = Pyrene and DQ = Duroquinone) which do not occur in homogeneous solutions. For micelles with reactive headgroups, as in cetylpyridinium chloride, the net positive charge on the micelle catalyses the rate of the reaction of e_{aq}^- with the headgroup leading to rate constants as high as 1.5×10^{12} M^{-1} sec^{-1}. It is to be noted that these electron transfer reactions are complimentary to the photoionization studies where an electron is ejected into the bulk water.

The behaviour of the neative ions such as e_{aq}^- in the presence of highly charged ionic micelles are governed largely by the sign and the relative magnitude of the electric field ('zeta potential') at the micellar surface. The high surface potential (in the range 50—200 mV) present over the few angstroms thickness of the Stern-layer decreases rapidly with an increase in distance in the Gouy–Chapman layer. The surface potential–distance profiles have been computed[60b] from the numerical solutions of the Poisson–Boltzmann equation and the rate constants for the various e_{aq}^- reactions have been correlated in terms of the drop in the micellar surface potentials.

Mechanistically, the reactions of e_{aq}^- with acceptors solubilized in ionic micelles have been treated[61] as tunnelling processes. Under these mechanisms, whether or not a given electron-transfer will occur under a given set of conditions depends on the extent of the overlap in the estimated distributions of the occupied and unoccupied redox levels of the redox systems e_{aq}^-/e and A^-/A.

B. Electron-Transfer Reactions of the Triplets.—Micellar effects on the triplet excited state redox reactions have been investigated under conditions wherein the donor–acceptor pair is spatially separated with a charged electrical interface introduced between the two. Under such conditions, significant differences in the electron-transfer rates have been observed[58,62,63] for a diverse class of molecules such as pyrene, nitroanthracene, tetranitromethane, phenothiazine, tetramethylbenzidine, and duroquinone.

Instructive among these studies are the intramicellar electron-transfer between the triplet state of solubilized aromatic molecules and ionic acceptors adsorbed strongly on the micellar surface. Consider, for example, the electron transfer from

[61] A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 1078; *ibid.*, 1975, **79**, 129; M. Grätzel, A. Henglein, and E. Janata, *ibid.*, 1975, **79**, 475.

[62] A. J Frank, M. Grätzel, A. Henglein, and E. Janata, *Ber. Bunsengesellschaft Phys. Chem.*, 1976, **80**, 294.

[63] R. Scheerer and M Grätzel, *J. Amer. Chem. Soc.*, 1977, **99**, 865; *Ber. Bunsengesellschaft Phys. Chem.*, 1976, **80**, 979; M. Grätzel, A. Henglein, R. Scheerer, and P. Toeffl, *Angew. Chem.*, 1976, **98**, 690.

tetramethylbenzidine (TMB) triplets to Eu^{3+} ions absorbed on the surface of anionic (NaLS) micelles.

$$^3TMB^* + Eu^{3+} \rightarrow Eu^{2+} + TMB^{+\cdot} \quad (9)$$

In a homogeneous solvent system, as in methanol, the rate constants for the forward and back transfer are 6.4×10^9 sec^{-1} and 1.4×10^7 M^{-1} sec^{-1}, respectively. In anionic micelles, in the absence of acceptor cations, the triplets decay very slowly (first $t_{\frac{1}{2}}$ for $^3TMB^*$ is about 800 μsec). In the presence of small amounts of Eu^{3+} (3×10^{-3} M) the triplets decay extremely rapidly ($t_{\frac{1}{2}} \sim 30$ nsec) giving rise to the redox products $TMB^{+\cdot}$ and $Eu^{2+\cdot}$.

In homogeneous solvents, following the electron transfer the products back react by second order, equal concentration kinetics. In micelles, however, there are isolated ion pairs and the back transfer can be considered as a summation of intramicellar events occurring between the donor ($D^{+\cdot}$) and acceptor ($A^{-\cdot}$) pair on the micellar surface. Considering the micelle as a macromolecule, such back reactions should follow first-order kinetics, as has been observed experimentally. Such types of very fast intramicellar electron transfer followed by a pseudo first-order back reaction has been demonstrated for a variety of redox pairs. If the acceptor is a neutral hydrophobic molecule, *e.g.* duroquinone in anionic micelles, following the intramicellar electron-transfer, part of the redox pair recombines efficiently while some of the solute anions ($DQ^{-\cdot}$) escape from the anionic micelles by solute ejection mechanisms referred to earlier (see p. 39). A phenomenological model[64] which takes into account the influence of the compartmentalization, as well as the statistical distribution of reactants, has been developed to describe the redox kinetics of fast intramicellar redox reactions. The rate laws derived differ significantly from those in homogeneous kinetics. In cases where the back reaction between $D^{+\cdot}$ and $A^{-\cdot}$ is reduced as in the micelles, it allows build-up of the redox products on steady state irradiation.

C. Photosensitized Redox Reactions.—An extension of the direct photoredox reaction between a donor–acceptor pair is the photo-sensitized electron transfer in which a third component (sensitizer) receives the visible light and sensitizes the electron transfer. An advantage of the three-component system over the two is that it allows the build-up of considerable amounts of the redox products, much more than the concentration of the compound that receives the light. In functionalized micellar systems, such three-component electron transfer can be carried out[65] with a proper organization of the reactants at the molecular level. One study where a comparison has been made on the overall efficiency in micelles, as against the homogeneous solvent system, is the chlorophyll *a* sensitized reduction of methylviologen in non-ionic micelles. (Sensitized reduction of methylviologen is of interest as a simple model of photosystem I and hydrogen gas can be

[64] M. Maestri, P. P. Infelta, and M. Grätzel, *J. Chem. Phys.*, 1978, in the press.

[65] K. Kalyanasundaram and G. Porter, *Proc. Roy. Soc.* (*Lond.*), 1978, in the press; K. Kalyanasundaram, *J.C.S. Chem. Comm.*, 1978, 628; Y. Moroi, A. Braun, and M. Grätzel, *J. Amer. Chem. Soc.*, 1978, in the press. K. Kalyanasundaram, J. Kiwi, and M. Grätzel, *Helv.Chim. Acta*, in the press.

released from reduced viologen through the use of enzymes or metal catalysts.) Here, the water-insoluble sensitizer is solubilized in the neutral micelle and the D/A pair (both water-soluble) randomly dispersed in the bulk aqueous phase. Such spatial separation of the sensitizer leads to significant differences in the redox kinetics. With respect to the overall efficiency, the reduction was found to be very efficient in methanol for low D, A concentrations and under conditions where high concentrations of the sensitizer are used (to maximize the yields at short exposure times) reactions in micelles provide better efficiency. The micellar surface charge and also the binding of either the donor or the acceptor to the micelle have been found to play a major role in controlling the overall efficiency in similar reductions in anionic micelles with tris-bipyridylruthenium(II) as the sensitizer. *N*-methylphenothiazine and di-indole derivatives have been used in similar studies.

5 Photophysics in Reversed Micelles

A. General Features of the Reversed Micelles.—Certain types of surfactants such as dialkylsulphosuccinates (Aerosols) form aggregates in non-polar organic solvents and these are termed[66] 'reversed' or 'inverted' micelles. In reversed micelles, the polar headgroup of the amphiphiles constitute the core and the hydrophobic tails extend into and are surrounded by the bulk apolar solvent. Reversed micelles formed by surfactants such as Aerosol-OT solubilize relatively large amounts of water. The water is present in the polar centres where it forms spherical pools, the sizes of which are controlled by the surfactant-to-water ratio. Studies of reversed micelles have been of interest from their industrial importance as in dry cleaning and also as simple model systems to simulate the water pockets often found in various bioaggregates.

The state of the solubilized water, interactions, and reactions of various solutes are being investigated by a variety of physical methods. The physical properties of the solubilized water have been found to be quite different from that of the bulk water. ^{1}H, ^{23}Na n.m.r. studies, for example, on the sodium di-iso-octylsulphosuccinate–heptane–water system indicate[67] that until there is sufficient water molecules for the solvation of all the sodium counterions ($H_2O : Na^+$ *ca.* 6) water protons behave as co-ordinated water and only at higher water concentrations behave like normal hydrogen-bonded water.

B. Fluorescence Probe Studies in Reversed Micelles.—The nature of the inner aqueous core and various substrate–surfactant interactions have been examined[68]

[66] J. H. Fendler, *Accounts Chem. Res.*, 1976, **9**, 153.
[67] M. Wong, J. K. Thomas, and T. Nowak, *J. Amer. Chem. Soc.*, 1977, **99**, 4730.
[68a] M. Wong, M. Grätzel, and J. K. Thomas, *Chem. Phys. Letters*, 1975, **30**, 329; M. Wong, J. K. Thomas, and M. Grätzel, *J. Amer Chem. Soc.*, 1976, **98**, 2391; D. J. Miller, U. K. A. Klein, and M. Hauser, *J.C.S. Faraday I*, 1977, **73**, 1654; U. K. A. Klein, D. J. Miller and M. Hauser, *Spectrochim. Acta*, 1976, **324**, 379.
[68b] G. D. Correll, R. N. Cheser, F. Nome, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1978, **100**, 1254.
[68c] M. Wong and J. K. Thomas in ref. 1*b*, p. 647.

recently by fluorescence probe analysis. The emission properties of 1,8-anilinonaphthalene sulphonate in the reversed micelles were found to be extremely sensitive to the size of the solubilized water clusters. The quantum yields and lifetime for the fluorescence decrease with increasing radius of the core while the position of the emission maximum shifts to a longer wavelength. At low water content the fluorescence from probes such as Rhodamine B are strongly polarized, indicating a very rigid core ($\eta > 40$ cP). Under these conditions, the quenching of fluorescence of water-soluble probes, such as pyrene-1-sulphonate (solubilized at the interface) by ionic quenchers, is also very inefficient.

Steady state fluorescence depolarization results on 8-hydroxy-1,3,6-pyrenetrisulphonate (pyranine) at various water contents in the dodecylammoniumpropionate (DAP)–cyclohexane–water system have been interpreted[68b] in terms of the number of water molecules involved in the solvation of the surfactant headgroups. Intramicellar prototropic changes in the fluorescence of pyranine

$$ROH^* + H_2O \rightleftharpoons RO^{-*} + H_3O^+ \qquad (10)$$

has also been examined[69] in reversed micelles. In the DAP–cyclohexane–water system, efficient triplet energy transfer between solubilized pyrene-1-butyrate and terbium chloride (which does not occur in the absence of micelles) has been demonstrated.

C. Electron-Transfer Reactions in Reversed Micelles.—Effects due to the charge on the donor, the availability of the acceptor, the microenvironment around the acceptor or the electron, and energy transfer from a biphenyl anion and triplets (produced by nanosecond pulse photolysis and radiolysis) to acceptors located at different sites, have been investigated[68c] in the reversed micelles Aerosol-OT–heptane–water system. Cu^{2+}, H_3O^+ and pyrene-1-sulphonic acid were used as electron-acceptors and several pyrene derivatives were used as energy acceptors. Increasing the micellar size and the water content tend to increase the rate of these reactions if the two reactants are hydrophilic and are in the micelle, *e.g.*, the electron transfer from biphenyl anion to Cu^{2+}. Here, increase in water content also increases the mobility of the two solutes. If one reactant is hydrophobic (and hence located in the alkane phase) and the other hydrophilic, then increase in the water content decreases the rate of the reaction. For non-charged reactants, if one is located in the micelle, the rates decrease slightly due to the clustering of this reactant in one phase.

6 Concluding Remarks

Studies of the photophysics of molecules, reviewed here, continues to be a very fruitful area of research. As indicated in several places, these studies have provided more direct information on several dynamical aspects of the micellar association: permeability, counterions binding, surface charge and its variations, solute entry and exist rates, *etc.* Studies in micelles also have clearly indicated the variations/complications that can arise when one attempts to use some of the

[69] U. Klein and M. Hauser, *Z. Phys. Chem.* (*NF.*), 1974, **90**, 215.

well-defined photophysical processes as probes for biological macroaggregates. With studies in the simpler micellar-model system, one is better equipped for the study of larger aggregates using these methods. In various places it has been pointed out how the solubilization of a solute molecule in the micelle alters the photoreactions undergone by the solute. Organization of the reactants at the molecular level with ease is something peculiar to the micelles. Advantages in our ability to desegregate the solutes from each other and at the same time use high concentrations of photo-sensitizer solute are only now beginning to be appreciated and one can definitely expect several useful applications based on this to be developed. Applications in the area of solar energy conversion and in the usage of laser dyes have been indicated. The number of studies of slower processes with the triplet state have been few compared with those using fluorescence.

One can anticipate extensive applications of phosphorescence in the near future, especially on the dynamics of micellar association equilibria. As mentioned in the introduction, only in photophysical methods has one a very wide range of time scales to work with, from a few picoseconds to several seconds.

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