Photoprocesses in Microaggregates

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ABSTRACT
Despite the potential complexity of microaggregate-containing systems, photophysical probe techniques have made important fundamental contributions to our understanding of the structure and properties of the aggregates and of the dynamics and reactivity of small molecules added to the system. By appropriate choice of the probe and quencher, one can often reduce the behavior of such microheterogeneous systems to that of a simple pseudophase system, amenable to study by steady-state fluorescence techniques. Rather general photophysical probe-based methods are now available for measuring equilibrium constants for solute incorporation and exchange selectivity coefficients for counterion binding to various types of microaggregates, including micelles, vesicles, and reverse micelles.

Introduction

Small aggregates, such as micelles, liposomes, and reverse micelles, formed by self-assembly of amphiphilic subunits, have been extensively employed as "microreactors" for the modification and manipulation of thermal and photochemical processes. The relevant components of such an organized system include the microaggregates themselves and the continuous bulk phase in which they are dispersed. Furthermore, the internal structure of the microaggregates can consist of more or less well-defined regions, such as the internal water pool of a vesicle or reverse micelle. In addition, if the amphiphile is ionic, the aggregates will bear a net charge and can have a significant electrostatic surface potential. This potential will affect the extent of association and exchange of counterions at the aggregate surface and the radial distribution of counterions and co-ions in and around the aggregates.[1,2]

The time scale on which most thermal or ground-state reactions occur is typically much longer than that required for redistribution of the reagents or reactive species between the aggregates and the bulk phase(s) and often exceeds the average lifetime of the microaggregates themselves (e.g., milliseconds in the case of typical aqueous micelles,[2] much longer in vesicles). Under these conditions, the observed effects of the aggregates on reactivity depend primarily on the total amount of aggregated amphiphile (the interfacial pseudophase) present in the solution. Thus, in this limit, known as the pseudophase limit, reaction kinetics can be interpreted without explicit consideration of the structure and state of dispersion of the aggregates or of the statistics and dynamics of incorporation of the reactive species into the aggregates. Thus, for example, the observed effects of aqueous micellar solutions on most bimolecular ground-state reactions can be successfully reproduced by the pseudophase ion exchange model,[1,2] which assumes the existence of two independent reaction channels, that is, one in the micellar pseudophase and the other n the intermicellar aqueous phase. The relative importance of these two channels is governed by the relative amounts of the two pseudophases, by the intrinsic reactivities in each pseudophase, and by the difference in the average local concentrations of the reagents in the micellar and aqueous phases.[1,2]

In contrast, photochemical reactions and photophysical processes such as fluorescence and triplet-state decays occur on a time scale that is very short relative to the lifetime of the aggregates and often comparable to or faster than solute or counterion exchange between the aggregates and the surrounding medium. In addition, because they require the photon as one of the reagents, photoinduced processes can be initiated rapidly (in nanoseconds or picoseconds) and selectively under controlled conditions, providing fast kinetic information unavailable from studies of ground-state reactions. Consequently, photochemical and photophysical probe techniques have proven to be invaluable tools for the elucidation of many of the structural and dynamic properties of these microaggregates.

Minimum Reaction Scheme

The simplest framework for interpreting the kinetics of photochemical or photophysical processes in a microheterogeneous medium is outlined in Scheme 1 (adapted from Kleinman and Bohne[3]). Even this highly oversimplified scheme emphasizes the potential complexity of these systems. In particular, it should be noted that the population of initially formed excited states of the probe, A*, cannot be assumed to be homogeneous. Thus, if the probe partitions between the aggregates and the external medium, excitation will produce two distinct classes of excited states, that is, those initially associated with the aggregates and those initially free in the external medium. Within the former class, further inhomogeneities may arise due to differences in the site of incorporation of the probe within the aggregate phase. Thus, for example, in a reverse micelle, an aggregate-associated excited state can potentially be formed on either the organic-rich or the aqueous-rich side of the interface or localized in the water pool; in a vesicle, the

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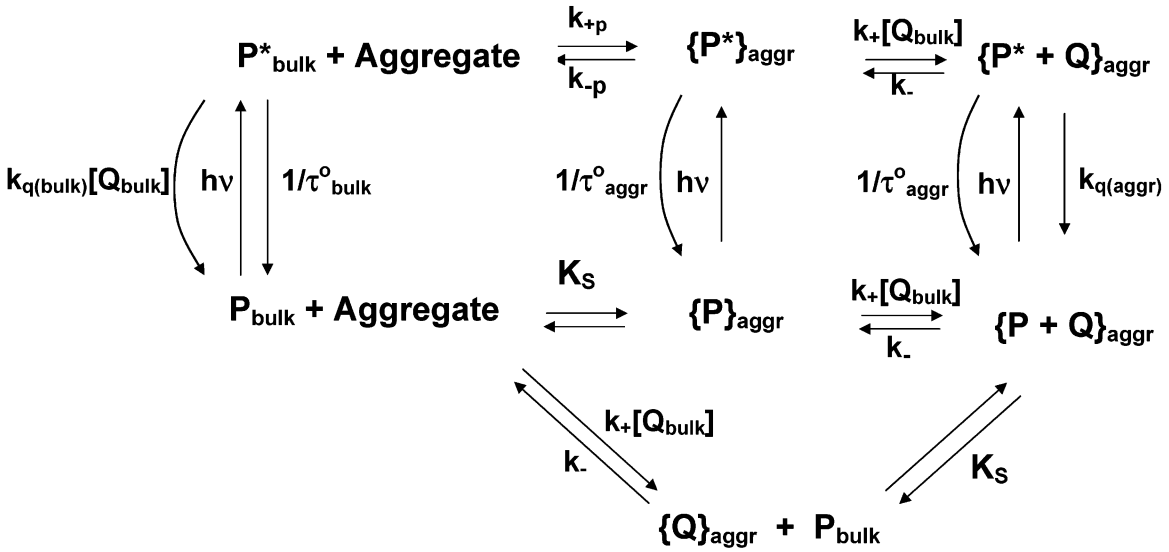
Scheme 1. Simplified Kinetic Scheme for Interpreting the Kinetics of Photophysical Processes in a Microheterogeneous Medium[a]



[a] In this scheme, P and P* refer to the ground-state and excited probe, respectively, τ to the probe lifetime, Q to the quencher, and the subscripts to the localization in either the continuous phase (bulk) or the aggregate (aggr). The equilibrium constant for incorporation of the ground-state probe is K_S, and the rate constants refer to quencher entry (k_+) and exit (k_-), excited probe entry (k_{+p}) and exit (k_{-p}), bimolecular quenching in the bulk phase ($k_{q(bulk)}$), and pseudo-unimolecular quenching in the aggregate ($k_{q(aggr)}$).

initial excited state may be formed in the internal water pool, within the lipid bilayer, or on the internal or external vesicle surfaces. In each region, the micropolarity and microviscosity sensed by the probe will be distinct, which can in turn influence or determine its mobility, accessibility to potential quenchers, and intrinsic lifetime.

In systems containing quencher species, the aggregates may differ in the number of quenchers that they contain. Thus, even if the individual microaggregates were internally homogeneous microphases, one would expect to observe differences in the probe/quencher collision probability relative to homogeneous solution. Furthermore, in systems such as water-in-oil microemulsions or vesicles, the interpretation of the data may require analysis in terms of a three-pseudophase system to take into account the existence of clearly different regions within the microaggregates.[4,5]

Despite the potential kinetic complexity associated with photochemical and photophysical processes carried out in microheterogeneous media, judicious choice of the probe or the probe/quencher system can provide important insights into fundamental aspects of such systems. In this brief overview, we shall concentrate primarily on applications of photophysical probe techniques developed or applied routinely in our laboratories or both. Since these have focused primarily on problems related to the interaction of small molecules and ions with microaggregates and the implications of such interactions for bimolecular reaction processes, we have intentionally omitted any consideration of a number of other important areas in which photophysical probes have made important contributions to the understanding of microaggregate-containing systems.

Pseudophase-Limit Situations Exhibiting Simple Exponential Decays or Amenable to Study by Steady-State Fluorescence Techniques

Photochemical or simple photophysical measurements on microheterogeneous systems containing a photophysical probe and a quencher can potentially provide information regarding the distribution of the ground-state probe, the excited state probe, or the quencher. On a nanosecond to microsecond time scale, the interpretation of quenching phenomena in microaggregate systems can be drastically simplified by utilizing either a probe or a quencher that is excluded from the microaggregate. Thus, if the probe remains exclusively in the bulk aqueous (normal micelle or vesicle) or organic (reverse micelle) phase of the system during its entire lifetime, the excited probe population decays monoexponentially and simple Stern−Volmer quenching behavior is observed:

$$\tau^\circ/\tau = I^\circ/I = 1 + K_{SV}[Q_{bulk}] \qquad (1)$$

where τ° and I° are, respectively, the excited probe lifetime and emission intensity in the absence of added quencher and τ and I are the corresponding values in the presence of quencher. Since the Stern−Volmer constant (K_{SV}) can be measured in the pure bulk phase under comparable conditions in the absence of the microaggregates, eq 1 can be used to determine the concentration of the quencher in the bulk phase ($[Q_{bulk}]$). This strategy has been applied to various types of quenchers, in particular co-ions[6] and counterions.[7−9] An analogous approach has been employed to estimate effective quencher concentrations in the aqueous pool of reverse micelles.[10] From $[Q_{bulk}]$ and the total concentration of added quencher, one can calculate ion exchange selectivity coefficients.

A complementary strategy is to use a strongly micelle-excluded quencher species that only quenches the fraction of the probe (f_{bulk}) present in the bulk phase. For a nonmigrating probe, that is, a probe of which the rate of exit from the aggregate is much slower than its decay, the total emission intensity in the absence of quencher, $I°$, is

$$I° = f_{aggr}I°_{aggr} + f_{bulk}I°_{bulk} \quad (2)$$

where $I°_{bulk}$ and $I°_{aggr}$ are the intrinsic emission intensities of the probe in the bulk phase and in the aggregate. At sufficiently high quencher concentrations, the fluorescence intensity approaches

$$I_{highQ} = f_{aggr}I°_{aggr} \quad (3)$$

Combination of these two equations with eq 1 (where $[Q_{aq}]$ is now the total added quencher concentration) gives the expression[11]

$$I°/(I° - I) = (f_{aggr}I°_{agg}/(f_{bulk}I°_{bulk}) + 1)\{1 + 1/(K_{SV}[Q_{bulk}])\} \quad (4)$$

which allows estimation of the equilibrium constant for partitioning of the probe between the bulk phase and the aggregates from the ratio f_{aggr}/f_{bulk}. One of the first examples of the application of this approach was the study of the incorporation of the 4-(1-pyrene)butyrate anion into SDS micelles using the iodide ion as the micelle-excluded quencher.[11] For cationic micelles, Cu(II) has been employed as a totally excluded quencher.[12]

When the emission of the probe is influenced by the aggregate, the partitioning of the probe can be evaluated in the absence of quencher from the change in the emission intensity as a function of surfactant concentration.[13] When we start from eq 2, it can be readily shown that

$$(I - I°_{bulk})^{-1} = (I°_{agg} - I°_{bulk})^{-1} + (I°_{agg} - I°_{bulk})^{-1}(K_S[Det])^{-1} \quad (5)$$

Thus, the intercept/slope ratio of a plot of the left-hand side of eq 5 against the reciprocal of the analytical concentration of micellized surfactant, [Det], permits estimation of the equilibrium constant for partitioning of the probe, K_S. The only assumption is that the behavior of the probe inside the aggregate is independent of the surfactant concentration. An analogous situation arises when the surfactant molecules that form the aggregate are themselves efficient quenchers of the probe emission; under these circumstances, only the probe in the aqueous phase emits. This approach was employed to study the effect of added electrolyte on the incorporation of cationic derivatives of anthracene into cationic *N*-hexadecylpyridinium micelles.[14] Other photophysical properties, such as the band position or the shape of the spectra can also be employed to monitor the probe partitioning.[15]

More detailed information can be derived from time-resolved fluorescence measurements on systems in which the probe partitions between the aggregate and bulk phases in the ground state and the quencher is excluded from the aggregate. The lifetime of the bulk-phase probe decreases with added quencher. On the other hand, if the rate constant for exit of the excited probe from the aggregate, k_{-p}, is much smaller than the rate of decay of the probe, the lifetime of the aggregate-bound probe is unaffected by the presence of the quencher. This predicts that the decay of the probe fluorescence should be the sum of two monoexponential decays, only one of which varies with the concentration of added quencher. This approach has been employed to study the partitioning of naphthalene in micellar solutions of SDS employing bromide ions as quenchers.[16]

If, on the other hand, the probe excited-state lives long enough to migrate out of the aggregate into the surrounding bulk medium during its lifetime, the lifetime of the probe approaches the value of $1/(1/\tau_o + k_-)$ at high concentrations of a quencher that is micelle-excluded (if the aggregate is ionic, the quencher can be a hydrophilic co-ion; finding an adequate quencher would be more difficult for nonionic aggregates). In our laboratories, we used this approach, with bromide ion as the micelle-excluded quencher, to demonstrate that the triplet states of short-chain *n*-alkyl 3-nitrophenyl ethers migrate quite efficiently in micellar SDS solutions.[17] Other important cases of excited probe migration in micelles include the triplet state of the 1-pyrenesulfonate ion, which was shown by monitoring triplet−triplet annihilation to migrate between SDS micelles,[18] and the triplet state of xanthone, the exit of which from micelles can be detected by monitoring the medium-dependent shift of its transient absorption spectrum.[3] In reversed micellar systems, micelle−micelle collisions resulting in probe or quencher migration or both can be diffusion- or near-diffusion-controlled.[19]

Known cases of significant excited probe migration are limited to long-lived states. To be solubilized predominantly in the microaggregate phase, the species exit rate must be similar to or greater than the product of the rate constant for entry into the microaggregate times the concentration of microaggregates, that is, $k_{-p} \gg k_{+p}$[microaggregate]. For a typical aqueous micellar solution with a maximum detergent concentration of 0.1 M and an aggregation number of 100, the micelle concentration is on the order of 10^{-3} M or less, while the rate constant for solute entry is usually found to be diffusion-controlled or on the order of $10^{10}-10^{11}$ M^{-1} s^{-1}. Thus, the residence time of an initially micelle-bound photochemical probe can be expected to be at least 1 μs ($k_{-p} < 10^6$ s^{-1}; comparable to the microsecond time scale for entry and exit of detergent monomers from aqueous micelles[2]) in a micelle and correspondingly longer in vesicular systems.

In the case of alkyl *m*-nitrophenyl ethers,[17] the excited triplet state exits from SDS micelles significantly faster than the ground state, indicating that the ground state partitions more strongly to the micelle than the triplet state. Recent analyses of solute incorporation into micelles[20] in terms of a five-parameter (solute molar volume, polarizability, dipolarity, and hydrogen bond acidity and basicity) linear solvation free energy relationship (LSER)

provide insight into the origin of changes in the affinity of solutes for micelles upon electronic excitation. For most micellar systems studied to date, LSER analyses have shown that the incorporation of neutral organic molecules is governed primarily by two factors: solute molar volume and solute hydrogen bond basicity. An increase in the former favors micellar incorporation, while an increase in the latter disfavors micellar incorporation of the solute. Since electronic excitation does not appreciably affect solute molar volume, large changes in affinity for the micelle should require large changes in the hydrogen bond acceptor properties of the solute upon excitation. For an aromatic hydrocarbon such as naphthalene, the hydrogen bond basicity should be relatively unaffected by excitation to the first excited singlet state.[16] In the case of the 3-nitrophenyl ethers, we have suggested that electronic redistribution in the excited triplet state increases the π-electron density on the nitro group.[17] This enhances its hydrogen bond basicity, provoking the observed decrease in the affinity of the triplet state for the SDS micelle. A similar change in hydrogen bond basicity of the π,π^* triplet state of xanthone may also contribute to its rate of migration.[4]

When the probe is nonmobile, that is, is localized in the microaggregate during its entire lifetime (τ_o), a simple and general methodology for obtaining equilibrium constants for the partitioning of quenchers between the microaggregate and the external solvent is via the analysis of steady-state fluorescence measurements performed at several different microaggregate concentrations. The procedure has the advantage that it is independent of the quenching mechanism and the type of quantitative relationship between the probe fluorescence intensity and the quencher concentration.[13,21] Also, it can be applied to the evaluation of the partitioning of probes between the bulk solvent and aggregates that are not quenchers as long as these modify some property of the probe emission. We have employed this approach to evaluate the incorporation of neutral molecules in micelles,[13,22] reverse micelles,[23] liposomes,[13,22] and biological membranes.[24] The method is insensitive to the quencher distribution and kinetics and only requires that the properties of the microaggregates be independent of the surfactant concentration over the concentration range utilized.[13] Furthermore, it can be used to determine the dependence of the apparent distribution constant on the probe occupancy, that is, to evaluate nonideality effects. This method has been extended[25] to the evaluation of ion exchange selectivity at the surface of ionic aggregates. The basis of the methodology is exemplified in Figure 1 for the case of an additive that influences the probe emission.

Quenching of excited states by molecular oxygen is an important special case in which rate constants for quenching of aggregate-bound probes can be readily determined. In most of the microaggregate systems studied to date, the decay of excited probes is essentially monoexponential in the presence of oxygen.[26] Since the rate constant (k_-) for exit of oxygen from surfactant aggregates is typically much larger than the pseudo-unimolecular rate constant for quenching (k_q) within the microaggregate, the local quencher concentration becomes averaged over the micelles prior to quenching (corresponding to the pseudophase limit for excited-state processes), and the quenching exhibits simple Stern−Volmer kinetic behavior:

$$1/\tau_{+Ox} - 1/\tau_{NoOx} = k_{Ox} = k_{qOx}[O_2] \qquad (6)$$

where τ_{+Ox} is the probe lifetime in oxygen-saturated solutions and τ_{NoOx} the corresponding lifetime under an inert gas such as argon or nitrogen. Values of k_{Ox} have been measured for a variety of microaggregate systems, including micelles, reverse micelles, liposomes, and biological membranes.[27−29] Representative data obtained in our laboratories, collected in Table 1, show, for example, that there is very little difference between the efficiencies of quenching of probes by oxygen in water and in micelles. In cationic dioctadecyldimethylammonium chloride (DODAC) vesicles, there is a significant increase in the k_{Ox} values above the gel-to-liquid crystalline phase transition temperature (ca. 35 °C). In red blood cell ghosts, the quenching depends somewhat on the localization of the probe chromophore within the membrane. In Aerosol OT reverse micelles, there is a dependence on both the viscosity of the bulk organic phase and the localization of the probe chromophore relative to the interface. The values measured in reverse micelles are, in all the systems, smaller than those obtained in the corresponding bulk solvent. This can be due to both an increased viscosity and a lower solubility of oxygen in the micelles, both of which decrease the rate of encounter of oxygen molecules with micelle-incorporated probes. This methodology requires only that the gaseous species of interest be a

Table 1. Pseudo-Unimolecular Rate Constants for Quenching by Oxygen (1 atm) in Microheterogeneous Systems (Data from Refs 28 and 29)

system[a]	probe[b]	T (°C)	k_{ox} (10^7 s^{-1})
water	PS	25	0.22
	PMTMA	25	0.24
	PBTMA	25	0.24
SDS (micelles)	PMTMA	25	0.22
	PBTMA	25	0.25
CTAC (micelles)	PS	25	0.20
DODAC (SUVs)	MP	22	1.1
		50	3.5
DODAC (LUVs)		22	0.3
		50	3.5
red cell ghosts	PMTMA	37	0.9
	PBTMA	37	1.4
	PUTMA	37	2.0
	PHA	37	2.0
isooctane (neat)	MP	25	10.0
dodecane (neat)			3.7
AOT/isooctane, $W = 20$[c]	PMTMA		3.0 (1.7)[d]
	PBTMA		3.6 (1.9)[d]
	PUTMA		5.1 (2.4)[d]

[a] SDS, sodium dodecyl sulfate; CTAC, hexadecyltrimethylammonium chloride; DODAC, dioctadecyldimethylammonium chloride; SUVs/LUVs, small and large unilamellar vesicles, respectively; AOT, Aerosol-OT. [b] PS, 1-pyrenesulfonic acid; MP, 1-methylpyrene; PMTM, 1-pyrenemethyl trimethylammonium ion; PBTMA, 4-(1-pyrene)butyltrimethylammonium ion; PUTMA, 11-(1-pyrene)undecyltrimethylammonium ion; PHA, 16-(1-pyrene)hexadecanoic acid. [c] Reverse micelles, W = water/AOT = 20. [d] Values in parentheses in neat dodecane.

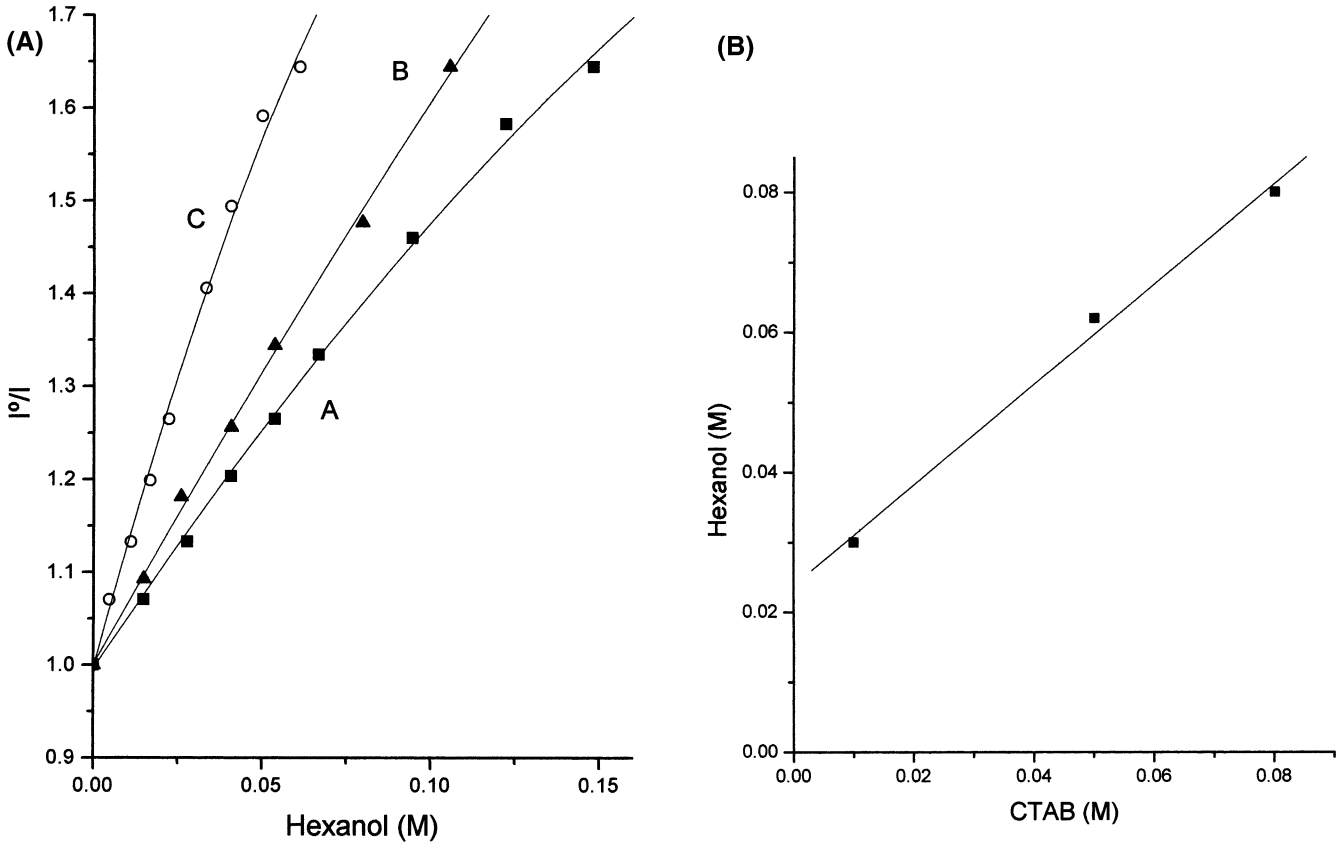


FIGURE 1. Method of Encinas and Lissi[21] for determining equilibrium constants for solute incorporation in microaggregate systems. Panel A shows Stern−Volmer plots (data from ref 13) for the change in the intensity of anilinonaphthalenesulfonate (ANS) fluorescence upon addition of *n*-hexanol to aqueous micellar solutions of hexadecyltrimethylammonium bromide (CTAB); [CTAB] = 0.010 (○), 0.050 (▲), and 0.080 M (■). The analytical additive concentrations necessary to produce the same amount of quenching at each CTAB concentration were determined from the points of intersection of the straight line parallel to the *X*-axis, drawn at $I^\circ/I = 1.4$, with the quenching curves. In panel B, the analytical quencher concentrations derived from Figure 1A that produce the same net quenching ($I^\circ/I = 1.4$) are plotted against the surfactant concentration. The intercept provides the additive concentration in the bulk pseudophase and the slope the number of additive molecules that are associated with the micelle per molecule of micellized CTAB. From the slope/intercept ratio, one can estimate the equilibrium constant for incorporation of the additive. Repeating this treatment at different I°/I values allows one to determine the dependence of this equilibrium constant on the intra-aggregate concentration of the additive.

quencher and is thus not limited to oxygen. For example, we have employed an entirely analogous approach to study the distribution of nitrous oxide in liposomes and lipoproteins.[30]

In micelles and reversed micelles, where most of the probes are located in microaggregates devoid of oxygen at the moment of excitation,[28,29] the quenching is dominated by the dynamics of oxygen entry. On the other hand, in much larger aggregates such as giant unilamellar vesicles, which can contain several oxygen molecules per aggregate, the dynamics of oxygen entry and exit are almost irrelevant. The quenching rate is then determined by the intramolecular quenching rate constant and the ratio k_+/k_-, that is, by the partition constant of the quencher (oxygen) between the bulk solvent and the microaggregates. It is important to note that the validity of this simple treatment requires that the quenching rate constant be independent of the probe localization and lifetime, a condition that frequently does not hold, reflecting the intrinsic inhomogeneity of microaggregates.[28,29]

As a consequence of its relatively long lifetime (typically $> 1\ \mu$s) and low reactivity, singlet oxygen generally equilibrates between the various compartments of the microaggregate system prior to reaction. Examples of singlet oxygen reactions that are amenable to treatment by the pseudophase model include studies in micelles, reverse micelles, and small vesicles.[5,29] In sufficiently large vesicles, however, it can be shown that singlet oxygen does not live long enough to equilibrate completely in the internal aqueous pool of the vesicle when it is generated exclusively in the external aqueous phase.[29] Interestingly, it has been found that the reactivity of methylindole with singlet oxygen in SDS micelles is consistent with that predicted from an LSER correlation of singlet oxygen reactivity in homogeneous solvents.[31]

Situations That Require Nanosecond Time-Resolved Measurements

Situations in which the details of the distribution of the quencher in the ensemble of microaggregates are important or in which one wishes to study the dynamics of quencher entry and exit require the use of nanosecond time-resolved quenching (TRFQ) measurements. These

are routinely analyzed in terms of the Infelta−Tachiya equation[32−36] for the temporal decay of the fluorescence intensity. In addition to the assumption that the probe is nonmobile,[37] this classical treatment also assumes that (1) for a given set of conditions, a single set of rate constants is adequate to describe the pseudo-unimolecular quenching process within the aggregate (k_q) and quencher exit from the aggregate into the surrounding medium (k_-), and (2) the incorporation of the quencher obeys a Poisson distribution. Since the Poisson distribution is verified at low occupation numbers, the latter condition can be attained by maintaining the average number of quenchers per micelle, $\langle n \rangle$, relatively small.[26]

Numerous studies of time-resolved fluorescence quenching in microaggregate-containing systems have employed the Infelta−Tachiya equation to extract values of k_q, k_-, $\langle n \rangle$, and, in favorable cases, k_+, the rate constant for quencher entry into the aggregate, since

$$\langle n \rangle = (k_+/k_-)[Q_{bulk}] \qquad (7)$$

When a quencher is employed that is also solubilized completely in the microaggregate, the aggregation number (N_{ag}) and polydispersity of small microaggregates (e.g., micelles containing at most ca. 150−200 detergent monomers) can be estimated from the values of $\langle n \rangle$.[34,35,42,43] For mobile quenchers that partition between the microaggregate and bulk phases, values of $\langle n \rangle$ together with values of N_{ag} can be used to calculate the analytical concentration of quencher in the micelle and, hence, its equilibrium constant for partitioning (if it is a neutral organic molecule) or its ion exchange selectivity coefficient (if it is a counterion[8,44,45] or co-ion[46]). As shown in Figure 2, for counterions[26] and amphiphilic co-ions,[46] the rate constants for quencher entry (k_+) into and exit (k_-) from ionic aggregates depend on aggregate concentration and added electrolyte concentration. These dependencies, which are related to the variation in the electrostatic surface potential of the aggregate, can be used to examine details of the incorporation of co-ionic[46] and counterionic[26] species into ionic aggregates.

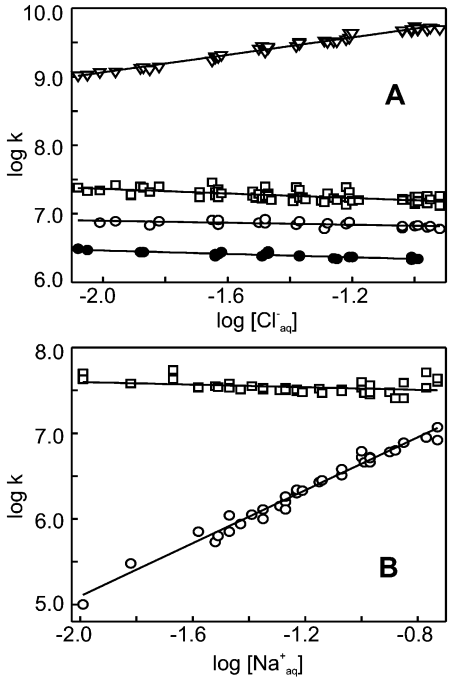


FIGURE 2. Added salt dependence of the dynamics of co-ion (A) and counterion (B) binding to ionic micelles. Panel A shows the dynamics of the incorporation of *N*-alkylpyridinium ions (alkyl = *n*-nonyl, *n*-decyl, and *n*-dodecyl) in cationic hexadecyltrimethylammonium chloride (CTACl) micelles determined from time-resolved fluorescence quenching data with pyrene as probe.[45] The rate constants for quencher entry (log k_+ (▽), alkyl chain length independent) into the micelle, for intramicellar quenching (log k_q (□), alkyl chain length independent) and for quencher entry (log k_-, *n*-nonyl (○); *n*-decyl (●)) are plotted as a function of the log of the concentration of chloride ion in the aqueous phase. The entry rate of these co-ionic quenchers is governed by the micellar surface potential and the exit rate by the alkyl chain length. Panel B shows the dynamics of the incorporation of Cu^{2+} in anionic sodium dodecyl sulfate (SDS) micelles determined from time-resolved fluorescence quenching data with pyrene as probe.[26] The rate constants for intramicellar quenching (log k_q, □) and for quencher entry (log k_-, ○) are plotted as a function of the log of the concentration of sodium ion in the aqueous phase. The micellar surface potential affects primarily the exit rate of this counterionic quencher.

Concluding Remarks

Microaggregate-containing systems are intrinsically nonhomogeneous. Small molecules and ions present in the bulk phase can migrate rapidly in and out of the aggregates, while those incorporated in the microaggregate can migrate within the aggregate. By appropriate choice of the probe and quencher, one can often reduce the behavior to that of a simple pseudophase system amenable to study by steady-state fluorescence techniques. Rather general photophysical probe-based methods are now available for measuring equilibrium constants for the incorporation of solutes and exchange selectivity coefficients for counterion binding to various types of microaggregates, including micelles, vesicles, and reverse micelles. These data have played a central role in the development of models for ground-state reactivity in micelles and vesicles and for linear free energy relationship analyses of the solubilization of neutral molecules by micelles. Time-resolved emission measurements can be utilized to obtain information with respect to the migration of quenchers and excited states, including both ground and singlet molecular oxygen, to infer sizes of the microaggregates, and to develop models for the dynamics of entry and exit of ions from ionic aggregates. Thus, despite the potential complexity of such microheterogeneous, aggregate-containing systems, simple photophysical probe techniques have made important fundamental contributions to our understanding of the structure and properties of the aggregates and of the dynamics and reactivity of small molecules present in the system.

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