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MICELLAR SOLUTIONS AS REACTION MEDIA

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1. INTRODUCTION

It is well established that, in many cases, rates and pathways of all kinds of chemical reactions can be altered by performing the reactions in micellar media instead of pure bulk solvents. Micelles can: concentrate the reactants within their small volumes;[1-13] stabilize substrates, intermediates or products;[14-27] and orient substrates [9,14,15,28-36] so that ionization potentials and oxidation-reduction properties,[37,38] dissociation constants,[2,3,13,32,39-46] physical properties, quantum efficiencies and reactivities [9-11,15,24,31,36,47-54] are changed. Thus, they can alter the reaction rate, mechanism, and regio- and stereochemistry.[6,22,35,55-67] For many reactions rate increases of 5 to hundreds-fold over reactions in homogeneous solutions have been reported. For some reactions rate increases may be much higher and increases in the order of 10^6-fold have been noted. Ionic colloidal assemblies, *e.g.*, micelles, microemulsions, hemimicelles (solloids), bilayers and vesicles are believed to be mimetic agents for membranes in biological systems. It has also been noted that, there are structural similarities between globular proteins and spherical micelles, and analogies between the catalytic effects of enzymes and functional micelles

and between micellar catalysis and phase-transfer catalysis.[15,16,68-74] For these reasons, numerous investigators have focused attention on micelles and reactions in micellar media.

This report contains a comprehensive review of micelles and micellar behaviour. The two main processes that play the most important roles in micellar rate enhancement or inhibition, *i.e.*, substrate solubilization and reactive counterion binding to micelles, together with the mechanism and utilization of micellar effects, and the factors affecting micellar behaviour are discussed in detail below.

1. Formation of Micelles

Micelles are dynamic colloidal aggregates formed by amphiphatic surfactant molecules. Such molecules are amphiphilic in character, *i.e.*, they possess hydrophilic and hydrophobic regions in their molecules.[75] They have a long hydrocarbon tail and a relatively small ionic or polar head group. Amphiphiles can be ionic (cationic, anionic), zwitterionic, or non-ionic depending on the nature of their head groups. Their micelles are classified in the same way.

In dilute solutions, amphiphile molecules exist as individual species in the media and these solutions have completely ideal physical and chemical properties. As the amphiphile concentration increases, these properties deviate gradually from ideality and at the concentration where aggregation of monomers into micelles occurs, an abrubt change is observed. This concentration is called the critical micellization concentration (CMC).

Experimentally CMC is found by plotting a graph of a suitable physical property of the surfactant solution as a function of concentration (c). Some CMC definitions give different percentages of micellized monomers.[76-81] The most practical and experimentally applicable definition is that of Phillips: If ø denotes an ideal colligative property, CMC is the concentration at which the slope of a graph of ø vs. c is changing most rapidly; that is $d^3/dc^3 = 0$.[76] A version of this definition given by Hall uses the chemical potential of the solvent instead of ø, and is applicable to multicomponent solutions.[79,80] CMC values are affected by different factors, *e.g.*, temperature, the length of the hydrocarbon tail, the nature of the counterions and the existence of salts and organic additives; and amphiphiles have characteristic CMC values under given conditions.[9,28,37,70,81-118] However it must be noted here that, for a given surfactant, small differences can be observed between the CMC values determined by different methods.[7] Even when the same data is plotted in different ways, different CMC values can be obtained.[117]

During the formation of micelles head group repulsions are balanced by hydrophobic attractions; and for ionic micelles, also by attractions between head groups and counterions. H- bonds can also be formed between adjacent head groups.[119]

At concentrations below the CMC ion pairs or submicellar aggregates of surfactant molecules may exist.[8,120,121] Their formation can be reduced by the addition of salts to the media.[122] Depending on the nature of the solvents and surfactants, other kinds of assemblies can also be formed.[66,123-128]

The concentration of micelles, C_M, is given by [17,70]

$$C_M = (C_D\text{-CMC}) / N \qquad (1)$$

where C_D is the total surfacant concentration and N is the aggregation number, *i.e.*, the number of monomers assembled to form a micelle. In all of the kinetic expressions, the concentration of monomeric surfactant is assumed to be given by the CMC.

The aggregation numbers of micelles (N) are affected by many factors.[80,88,95,98,101-103,105,108,115,129-142,157-170] Since micellar aggregates have highly dynamic molecular structures, micelles in solution do not have a well defined aggregation number and micellar solutions are polydisperse. Mean aggregation numbers are therefore used in calculations.

Micellization does not occur at the characteristic CMC of the surfactant in ternary systems, which consist of a solvent, surfactant, and a substance to be solubilized in micelles; since the solubilized material leads to a change in the monomer-micelle equilibrium. The micellization concentration in such systems is called solute micellization concentration (SCMC).[21,143,144] Hence, micellization concentrations to be used in kinetic expressions should be determined under the reaction conditions.[145,146]

When two self-assembling compounds coexist in the same solution, mixed micelle or comicelle formation can occur as a result of the mutual solubilization. Sometimes comicelles are formed with micellar-solubilized substrates or catalyzers.[28] Such micelles are made up of molecules of both substances.[147-159] Ionic surfactants of like charges, and nonionic and ionic ones form stable mixed micelles with each other over a range of ratios. Reversely charged surfactants, however, can form mixed micelles at only certain ratios.[160] The catalytic effectiveness of some surfactants can be increased by adding another surfactant to the medium, and using a mixed micelle system, *e.g.*, mixed micelles of cationic or anionic surfactants with nonionic ones, or monovalent ionic surfactants with divalent ones.[18,28]

2. Micellar Structure and Properties

In polar solvents such as water, monomers assemble to form a micelle in such a way that their hydrocarbon tails huddle in the core of the micelle, and the polar head groups project outwards into the polar bulk solution an locate at the micelle-water interface such that the hydrophobic tails are shielded from water (Figure 1) These micelles can also form in solvents such as 1,2-diols and formamide; as well as in 100% H_2SO_4 , D_2O and in sol-gel systems.[161-165]

Electrical charge on a micelle is neutralized by counterions in the electrical double layer around it. The first layer immediately adjacent to its surface is called the Stern Layer.[148] In this layer the counterions are adsorbed so strongly that there is no thermal agitation and they migrate together with the colloidal micelle in an electrical field. According to the most widely accepted model, head groups of surfactant molecules also situate in this layer. The remainder of the double layer is called the diffuse (Gouy-Chapman) layer since the ions are diffused into the bulk solution as a consequence of the thermal motion. The decrease in counterion concentration with the distance from the micellar surface has an exponential form.[90,102,166] The core radius is about the length of the fully extended alkyl chain of the amphiphile. The core is believed to consist of two regions, namely the inner and outer core. The outer core contains approximately the first four methylene groups. There is also another defined region within micelles called palisade layer (mantle) which includes the head groups and the first few methylene groups. On the basis of the Hartley model, the overall volume of a micelle is approximately twice that of Stern Layer.[21,167,168]

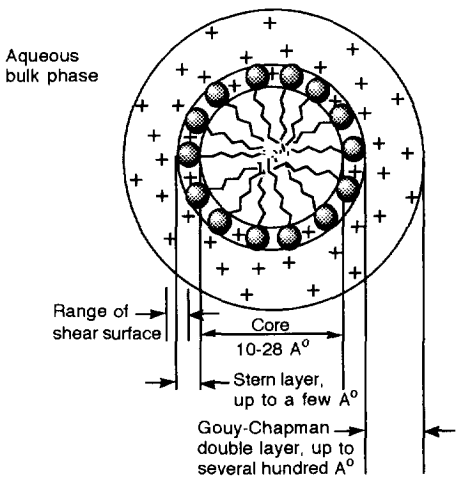


Fig.1. A two-dimensional schematic representation of the regions of a spherical ionic micelle.The counterions (+), the head groups (●), and the hydrocarbon chains (~~~) are schematically indicated to denote their relative locations but not their number, distribution, or configuration (Reproduced From ref.15b; copyright 1975 Academic Press, New York).

At concentrations close to CMC, micelles are small and spherical, rarely spheroidal.[15b,99] As the surfactant concentration increases they become larger, and after a certain concentration they elongate and convert into rodlike micelles. The presence of salt or organic additives can also lead to this conversion or affect the conversion concentration depending on the nature of the additives.[28,106,119,120,147,163,169,170]

Aggregates can also form in apolar solvents: In such cases head groups of surfactant molecules locate inside to form a polar core and hydrocarbon tails are directed towards the bulk solvent, to form the outside shell of the micelle. These are called reversed (reverse) or inverted (inverse) micelles.[171-178] If there is any water in the medium, it will be entrapped in the core.[173] This surfactant solubilized water is often referred to as a water pool and reverse micelles are sometimes called microemulsions. They are able to solubilize relatively large amount of water in their cores and this enables them to solubilize water soluble substances in nonpolar solvents. They are also reported to form in near- and supercritical fluids.[179]

In this review, the term "micelle" stands for micelles in aqueous solutions not for reversed micelles unless otherwise stated.

Micelles are also classified as non-functional and functional. Functional micelles are usually formed by surfactants which bear one (functional) or two (bifunctional) reactive groups, at the hydrophilic head, which

can act as catalyzers. Comicelles of some reactive group containing catalyzer compounds with nonfunuctional or functional surfactants are also used as functional micelles.[61,62,65,66,128,180-190]

Polarity and water content in different regions of the micelle play an important role in the rate of reaction in these regions. The surface layer of a micelle resembles a concentrated electrolyte solution with a dielectric constant lower than that of the bulk water. The micellar phase is less polar than water and the ionic micelles have a polarity near to that of pure ethanol even at the Stern layer.[15,37c,44,191-193] An increase in the aggregation number causes a decrease in the surface polarity.[194]

NMR results indicate that some of the water solvating the surfactant head group is lost on micellization.[31] Experimental results for the extent of water penetration into a micelle are contradictory.[81,98,132,147] Of the proposed models, the porous-cluster model in accordance with the "fjord" model, but with more disordered monomers, is likely to be the most realistic one. According to this model, micelle structure is dynamic and there are water molecules also deep within the micelle. Micelles are loose assemblages of oscillating amphiphile molecules, bearing water-filled cavities.[195-197] This is consistent with other evidence derived from kinetic and other techniques.[34,81,141,196,198-204] There are, however, experimental results which support the Reef and Hartley models with water free cores.[167,205]

The fluidity and liquid-drop character of micelles has been supported by ESR spectroscopy and fluorescence depolarization measurements. In ESR studies micelle-bound molecules (solutes) can rotate almost as rapidly as if they were water-soluted individually.[206] There is a dynamic equilibrium between aggregated molecules and monomers. Water molecules and counterions are also exchanged between the micelles and the bulk solvent. Micelles form and break up so rapidly that both aggregation and dissolution of monomers occurs at the same time.[164] Hence, the term "micellar boundary" is an arbitrary one sometimes considered to explain the behaviour of micelles. The law of Mass-Action can be applied to a micellar solution since micelles are dynamic aggregates and there is a dynamic equilibrium between monomers and micelles.[164b] Thus, a surfactant solution can be referred to as a two-component one-phase system. When a third component (solute) is added to this system, it affects the monomer-micelle equilibrium. Nevertheless, when estimating the distribution of solubilizate between micelles and the bulk solvent, it is useful to treat the micelles as a separate phase. That Hill's formulation for thermodynamics of small systems can be applied to micellar systems satisfactorily supports the validity of such an assumption.[207,208]

2. SUBSTRATE SOLUBILIZATION

One of the most important processes leading to micellar effects on reactions is the solubilization of substrates in micellar interiors. It is possible to solubilize water insoluble substances or to increase the solubilities of slightly soluble ones in aqueous micellar solutions. They penetrate towards the hydrocarbon-like cores of the micelles.[50,143,169,204,209-217] Since the solvent molecules penetrate beyond the polar head groups, solute in the solvent phase can interact both with the nonpolar chains of the surfactant molecules and with their polar head groups. Thus, the micellar phase may be referred to as amphiphatic, having affinity for both polar and nonpolar species. Micellar cores behave like an organic phase and the hydrophobic forces play an important role in the solubilization process.[121] The opposite holds for reverse micelles, *i.e.*, polar substances can be solubilized in different regions of reversed micelles depending on the nature of both the micelles and the solutes.[171,172,175,179,218-222]

The solubilization of substances in micellar media leads to a dynamic equilibrium of solute between micelles and the bulk phase. The solute replaces some water of hydration inside the micelles. Substrates incorporated into the micelles still form hydrogen bonds with water, *i.e.*, they are in contact with water in the micellar interior.[206-223] In general, the presence of a solute leads to both an increase in micellar size and a shape conversion from spherical to ellipsoidal or rodlike, and a bulky substrate may perturb the micellar structure.[28,31,99,144,213]

Long-chain polyelectrolytes in the media can also increase the solubility of substrates. However, macroions as individual molecules, are not as effective as their micelles.[224-228]

One can take advantage of the solubilization of polar substances in reverse micelles in order to extract polar substances, even selectively, from their aqueous solutions in contact with an organic phase containing surfactant micelles.[179,219,229,230] Conversely, non-polar substances can be extracted from organic solvents into aqueous micellar solutions.[176] These processes are called carrier-facilitated transport, where the micelle is the carrier.

1. Substrate Binding Constant

According to the pseudophase ion-exchange kinetic model, there is an equilibrium between free (S_W), in the aqueous phase, and micellar-bound (S_M) substrate as follows:

$$S_W + D_n \xrightarrow{K_S} S_M D_n \qquad (2)$$

D_n refers to micellized surfactant and K_S is the binding constant of the substrate to the micelle. When the surfactant (D) is present in a large excess compared to the solute, K_S is given by [41,169]

$$K_S = [S_M] / [S_W] ([D] - CMC) \qquad (3)$$

For cases where the surfactant is not present in a large excess compared to S_M, eq. 3 is modified as

$$K_S = [S_M] / [S_W] ([D] - [S_M] - CMC) \qquad (4)$$

by taking into account the amount of surfactant attached to the solute.[23]

It has been shown that the amount of substrate solubilized within micelles can be calculated from the relative solubilities of the substrate in surfactant solution and water by assuming that the increase in its solubility in the presence of surfactant is caused wholly by its incorporation into the micelles. Thus, the value of K_S can be calculated from the following equation:[85]

$$(K_S / N) = S_M / (1-S_M) (C_D - CMC) \qquad (5)$$

2. Solubilization Loci in Micelles

The pathways and the rates of reactions in micellar systems depend to a great extent on how deep the solubilized species are located within the micelle.[197,231] The results have shown that solubilized molecules interact with the polar head groups of a micelle and penetrate towards the core. They reside in the inner core,[171,218] outer core,[213,232] palisade layer [31,233,234] or between the polar head groups.[39,225] Sometimes micellar effects can also be observed as a result of the stabilization of substrates as counterions, i.e., without solubilization, with the substrates not hydrophobic enough to be solubilized in the micellar interior.[56]

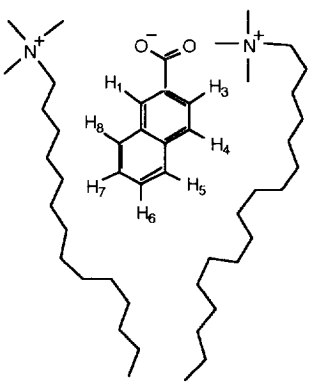


Fig. 2. Proposed orientation and location of 2-naphthoate anion embedded in the palisade layer of an aqueous cationic micelle to form a comicelle (Reproduced from ref. 144 ; copyright 1991 American Chemical Society).

Both electrostatic and hydrophobic factors play a role in determining the binding site of a solute to the micelle. Therefore both the structures of the amphiphile and the solute are of great importance in determining the extent of solubilization and the penetration of solute into the micelle.[8,86,120,143,147c,232] If the hydrophobicity of one partner increases, the association constant of the solute increases and the solute penetrates deeper into the micelle.[235] For example, naphthalene-2-sulfonate ion locates one or two carbons closer to the micellar surface than its methyl ester.[31] Similarly, while sulfonated N-alkyl phenothiazines reside near the micellar interface, unsulfonated ones penetrate more deeply into the micelle and the degree of penetration depends on the length of their alkyl chains.[36] An increase in the size of the surfactant head group also increases the depth of penetration by solute.[31]

Micellar-bound polar solutes reside largely in the Stern layer at the micellar surface, and reactions of polar solutes probably occur in this region. If the compound has both a polar and a hydrophobic end, the polar region orientates itself toward the head groups of the surfactant molecules, while the other end becomes involved with the hydrocarbon tails of the micelle interior. It has been shown that aromatic anions situate near the micelle-water interface.[9,31,233,234] The aromatic section of the molecule is embedded in the palisade layer whilst the charged parts locate near to the micellar interface so that they can still be solvated by water.[9,28,31,233,234,236] Bachofer *et al.* have concluded that the location and orientation of 2-naphthoate anion in TTAB micelles, determined from ^{1}H NMR chemical shift, NOESY and surface tension data can be represented schematically as in Figure 2.[144]

The location of both the substrate and reactive ion, in the transition state of the reaction between methyl naphthalene-2-sulfonate (MeONs) and Br^- in CTA halide micelles, is estimated from NMR results and can be represented schematically as in Figure 3.[9]

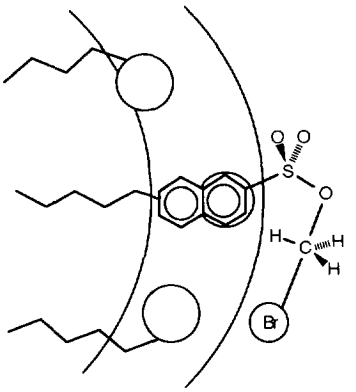


Fig. 3. Proposed location and orientational assignment of reacting species, MeONs and Br^-, in cationic micellar and aqueous phases, respectively (Reproduced from ref. 9; copyright 1989 American Chemical Society).

The solubilization of weakly polar substances in non-ionic micelles is believed to occur in the polyoxyethylene layer, however, it may occur in the micellar core including the outer core.[39,86,209,225,237-240] Short chain alkyl amine cations bind to the anionic surface of SDS micelles as their counterions, not only by electrostatic interactions, but also by such forces as hydrogen bonding.[56]

Similar photoionization yields of alkylsulfonate derivatives with different alkyl chain lengths, which were thought to locate at different positions, in reversed micelles of CTABr and AOT indicated that the branched chains of AOT molecules favor the bending of the alkyl chain of the chromophore such that the chromophore can locate in the organic phase nearer to the interface (Figure 4).[48a]

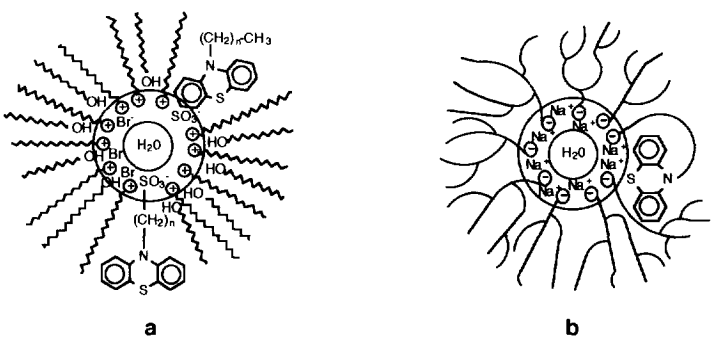


Fig. 4. Schematic representation of location and orientation of photoionizable guest Na 10-alkyl phenothiazine sulfonate and Na phenothiazinylalkane-1-sulfonate molecules in (a) CTABr and (b) AOT reverse micelles. HO~~~ represent an 1-alcohol as cosurfactant in *n*-octane (Reproduced from ref. 48a; copyright 1990 American Chemical Society).

The evidence for a polar environment with solubilized probes in micelles may be an indication of partially adsorped probes at micellar surfaces. Mukerjee and Cardinal have proposed a two-state model for the solubilization of several benzene derivatives and naphthalene, which invokes an equilibrium between a "dissolved state", associated with micellar core, and an "adsorbed state", associated with the micelle-water interface. They have also noted that the purely "dissolved" state may be difficult to obtain in practise for any solute and that the amount solubilized in the core increases with increasing aliphatic carbon number, *i.e.*, with increasing interfacial tension.[235] The adsorbed / dissolved ratio also depends upon the solute concentration. As the mole ratio of solubilizate to surfactant is increased to values approaching 0.7, the solubilization in the hydrocarbon core becomes predominant. All these results are consistent with the results from other studies.[232,235,241-244] Ramachandran *et al.* reported values for the fraction of solubilizate in the adsorbed state, for some aromatics, even close to 100%.[193a]

3. Factors Affecting Solubilization

The most important factor is the hydrophobicity of the surfactant and the substrate. The binding constant of the substrate to the micelle (K_S) is affected by the nature of the surfactant in such a way that it decreases rapidly with decreasing length of the alkyl group. The more hydrophobic the substrate the higher value of K_S and the deeper the penetration into the micelle is observed. The molecular weight of solubilizate, chain length and head group structure of amphiphile, temperature, and the existence of added salts in the medium are the other factors. The concentration of the compound to be solubilized and the pH of the bulk phase also affect the quantity solubilized.[32,99,143,160,216,219]

As a rule, aromatic acids and sorbic acid which have double bonds or aromatic systems conjugated with the carboxyl group are much less soluble than the corresponding aliphatic acids. Crystalline substances are more difficult to solubilize than a liquid of approximately the same molecular weight. It has also been observed that the amount of material solubilized in micelles depends upon the pH of the medium for sparingly water soluble ionizable substrates.

Additional salts may induce the "salting in" or "salting out" of the substrate, *i.e.*, a reduction or increase in K_S values, depending on the nature of the salt, and this should be taken into account when fitting the rate data.[90,100,245-247] The presence of salts in reverse micellar systems effects the solubilizate uptake from the bulk phase by decreasing the amount of surfactant solubilized water entrapped in the water pool. At high salt concentrations the amount solubilized is drastically decreased.[177b,178c,179,219]

3. COUNTERION BINDING

Another fundamental process in micellar catalysis or inhibition is the counterion binding to micelles. Micelles can either attract the reactive ions or repell them depending upon the electrical charge of their head groups. Thus, micelles may bring the solubilized substrates and reactive ions together or keep them apart such that the reactions are speeded up or inhibited. Another way by which micelles can catalyze a reaction is the stabilization of intermediates as bound counterions.[17,160] Sometimes, even substrates are bound to micelles as their counterions.[56]

Head groups of ionic micelles are generally about 30% ionized, *i.e.*, 70% neutralized by the counterions in the Stern layer, though there are experimentally estimated values of 10-70% for extent of ionization of micelles, at the CMC. The degree of counterion binding depends on several factors.[9,17,51,77,82,100,107b,248-252]

Counterions interact with the head groups not only electrostatically, but also hydrophobically. Some ions bind largely Coulombically, *e.g.*, $SO_4^=$ ion; while both specific and Coulombic interactions control binding of some others, *e.g.*, halide ions. Some lyotropic series have been established for the relative affinities of both anions and cations to the micelles.[2,6-9,17,31,41,70,82,90,100-102,124,125,145,147,170,192,248,249,251-268]

The neutralization degree of the micelles are given in terms of the fraction of micellar head groups neutralized by counterions, β, and β has values between 0.3-0.9. The relationship between the fractional ionization of a micelle, α, and β is given by $\beta = 1 - \alpha$ and α can be formulated as $m = N(1 - \alpha)$ where m is the average number of ions associated with each micelle. When only surfactant counterions Y exist in the medium; as in case of micelles composed of reactive counterion surfactant molecules which have the reactive ions as their own counterions:

$$\beta = [Y_M] \; / \; C_M \qquad (6)$$

In some cases there is also another type of counterion, X, in the medium; X competes with Y for micellar surfaces, and here β is given by

$$\beta = [Y_M] + [X_M] \; / \; C_M \qquad (7)$$

When salts are added to micellar solutions, the counterions of salts compete for the ionic head groups of micelles with the surfactant counterions which already exist in the solutions. Thus, displacements can occur depending on the nature of counterions and the head groups, *i.e.*, on the relative affinities of counterions for the head groups.[248,249] When the added counterions are "reactive" ions, after displacement, micellar rate enhancements are observed. Conversely, when they are inert ions and the reactive species are the surfactant counterions, they can cause inhibition by excluding the reactive ions from the micellar surfaces.[269] Salt effects on reactions in micellar media will be discussed later in Chapter 5 in more detail.

4. MECHANISM OF MICELLAR EFFECTS

1. Concentration Effect

Kinetic treatments and substrate solubilization data have made it apparent that detergents affect reaction rates by incorporating the substrate into the micellar aggregate, rather than by changing the solvent properties of the water, *i.e.*, the concentration of reactants into a small volume through hydrophobic and electrostatic interactions is the main factor involved in the rate enhancement of bimolecular reactions (Figure 5).[1-13,22,70,208,252]

The incorporation of substrate into the micellar phase may bring it into proximity with the reagent which may either be attracted to the micelles electrostatically; or may be incorporated into the functional micelles by chemical forces. All of these factors affecting the extent of substrate solubilization and reactive counterion binding also affect reaction rates in micellar solutions.[2,6,9,23,170,248a,269]

For bimolecular reactions, the degree of micellar rate enhancement depends largely on the extent of reactive counterion binding to micelles. Reactions occur between the micellar solubilized substrate and the bound counterions in the Stern layer. The frequency of molecular collisions increases as a consequence of the close association of the two reacting species at the micellar interface. In cases where micelles solubilize the substrate but repell the counterions or do not attract them effectively, the reactants are separated and as a result the reactions are inhibited. The extent of inhibition depends upon how deeply the substrate is buried into the micelle.[13c,86,270-272]

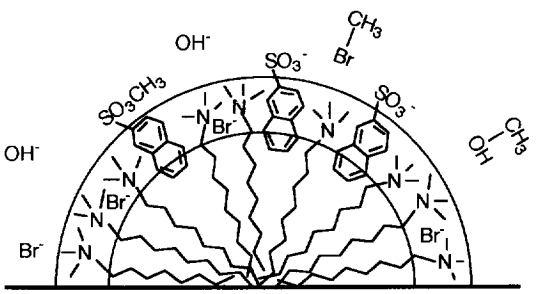


Fig. 5. Oversimplified two-dimensional schematic representation of the concentration effect of micelles.

Substrate micellization increases the reaction rate because on micellization counterions can be attracted or repelled more effectively. As a result, additives may also become effective even if they are not effective at concentrations below the CMC of the self micellizing substrate.[119,273-275]

2. Medium Effect

Together with the concentration effect, micelles also exert a medium effect that changes the reactivities of both the substrate and the reactive ion.[53,275,276] This effect arises from a combination of cage, preorientation, microviscosity, polarity and charge effects.

Micelles are capable of holding two reactive species together for a longer period of time than homogeneous solutions. As a result of this cage effect, the probability of reactions and hence the reactivities are increased. For example, due to the compartmentalization of the radical pair, the geminate character of triplet-derived geminate radical pairs or radical ion pairs sequestered in a micellar environment can often be retained for sufficiently long times that the radical pair can access the singlet surface in photoreactions. This leads to closed shell products.[270,271]

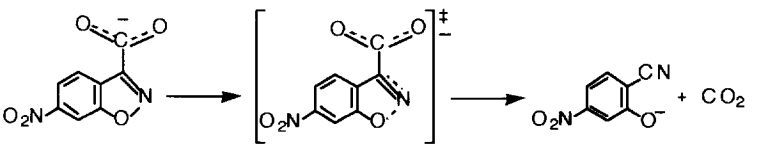
The preorientational effect, *i.e.*, the capability of micelles to solubilize substrates in specific orientations is one of the most important factors that facilitates the reactions and provides control over regio- and stereoselectivity. A favorable location and orientation of the substrate in micelles can lead to an increase in its

reactivity.[14,15,32] Charged substrates reside amongst the reversely charged head groups, with their charged groups directed towards the micellar interface, as shown in Figures 2-4. This location brings the substrates into close proximity with micellar bound reactive ions and can also provide a favorable orientation to react with them. When the substrates are aromatic anions, an interaction between the positively charged atoms in the head groups and the π-system of the aromatic rings also contributes to the increase in the reactivity of substrates.[9,14,15,28,30-34] In reverse micelles, the hydrophobic portion of the substrates is directed towards the bulk solvent; while the polar groups are located in the micellar interior. Preorganisation at the AOT reverse micellar surface in isooctane-water solvent system results in chemoselectivities of up to 60%, for the direct α-peptidation of dicarboxylic amino acids, when the condensing agent is used as a cosurfactant; thus reversing their normal preference for side chain carboxyl group amidation.[34b]

Since the microviscosity of micelles is much higher than the viscosity of the surrounding homogeneous solvent, substrate molecules incorporated in micelles have less translational and rotational freedom and this is reflected in their reactivity; and in regio-, stereo- and product selectivity.[11,173d]

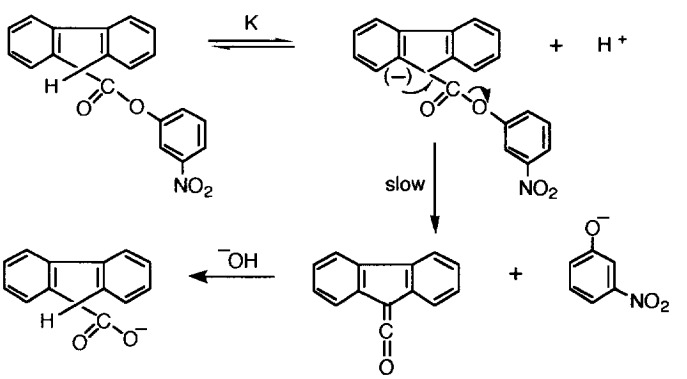
For some reactions electrostatic and hydrophobic interactions between the substrate and micelle may contribute to activation energies. Micelles that catalyze a reaction decrease the activation energy and entropy, while the inhibitory ones increase them.[72,85,86,259,270,271,277,278] For both bimolecular and unimolecular reactions, the micellar environment leads to a reduction in the free energy difference between the ground state and transition state and can stabilize intermediates electrostatically, relative to the ground state, such that the reactions are catalyzed. The low polarity environment in a cationic micelle can decrease the free energy of a bulky anionic transition state, with more delocalized charge, relative to that of the ground state. An anionic micelle can have the opposite effect.[14-21,25-28,86] Pearson's concept of hard and soft reagents operates in this respect.[261,262]

Outstanding examples of unimolecular reactions catalyzed by the stabilization of intermediates are decarboxylations and dephosphorylations (Scheme 1).[20,27,269] The rate of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion is enhanced by approximately 120-fold in the presence of mixed micelles of CTABr and Igepal DM-730.[18,28]



Scheme 1

Stabilization of the ground state, however, results in inhibition.[23,272] The inhibition by CTABr micelles of the spontaneous decomposition of m-nitrophenyl 9-fluorenecarboxylate is attributed to the stabilization of the ground state, which has highly delocalized charge, rather than the charge-localized transition state (Scheme 2).



Scheme 2

The observed inhibition by CTABr of alkene bromination has been ascribed partially to the low polarity of the micellar surface, since the reaction involves charge separation, and also to the stabilization of initial state, *i.e.*, Br_3^- ions. Br_3^- ion is formed quantitatively between Br_2 and Br^- in the presence of CTABr and is strongly stabilized by the micelles.[279]

In the absence of micelles the azide ion, N_3^-, is unreactive in aromatic nucleophilic substitutions but the unfavorable transition state interactions appear to disappear in CTABr micelles. Cationic micelles, as electrophiles, lead to the polarization of N_3^- ion, *i.e.*, to the stabilization of the resonating structure $N{\equiv}\overset{+}{N}{-}N^{2-}$, and as a result it becomes a surprisingly active nucleophile.[24,280,281]

In cases more than one class of reaction product is formed, depending on the relative stabilization of the products, product selectivity of the reactions may be varied. Micellar effects on product selectivity will be discussed in Chapter 8 in further detail.

The thymine group, as a molecular receptor, interacts with the adenine group by base-stacking rather than hydrogen bonding, in homogeneous solution, while supramolecular receptors consisting of (thyminylalkyl)-ammonium salts incorporated in SDS micelles as co-compounds bind to the adenine residue by hydrogen bonding. This is thought to be because the hydrogen-bonding groups are shielded from water in the micellar microenvironment (Figure 6). Thus, molecular recognition by means of hydrogen bonding has been realized in an aqueous solution.[282a,b] Hydrogen bonding can also occur between uncharged 1-alkylthymine and adenine derivatives in the presence of SDS.[282c]

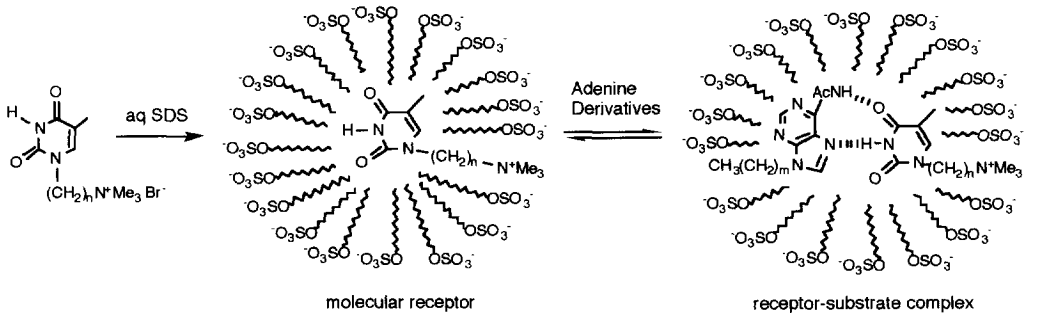


Fig. 6. Molecular recognition by hydrogen bonding in aqueous micelles (Reproduced from ref. 282a; copyright 1993 American Chemical Society).

3. Micellar Effects in Photochemical Reactions

Micellar media are reported to be a novel environment for photochemical reactions. Micelles can promote photoinduced electron or proton transfer by compartmentalization, prohibit back-charge transfer and permit the control of charge separation across the interface.[231bc,283-288]

In the photoreductions of negatively charged ethylenediaminetetraacetato cobaltate(III), $[(Co(edta)]^-$, and neutral tris (acetylacetonato) cobalt (III), $[Co(acac)_3]$, by 1-benzyl- (BNAH) and 1-dodecyl-1,4-dihydronicotinamide (DNAH), cationic micelles supress the separation of $[Co(edta)]^=$ from the micellar phase and the high internal microviscosity of the micelles depresses the diffusion of $BNAH{\cdot}^+$ from the encounter complex. The low polarity of the micellar phase also retards the formation of ionic species such as $BNAH{\cdot}^+$; but because of their concentration effect on both photo-excited substrates and $[Co(edta)]^-$, DTACl and HTABr accelerate the electron transfer while anionic SDS hinders the approach of $[Co(edta)]^-$ to micellar incorporated BNAH*. Conversely, the photoreduction of neutral $[Co(acac)_3]$ is accelerated by SDS micelles, whilst cationic micelles retard the electron transfer. This different behaviour in positively and negatively charged micelles has been explained by the different micellar effects exerted on the heterolytic dissociation of the encounter complex.[11,54]

Baglioni *et al.* have measured the effect of charge separation on the photoionization of TMB to TMB^+ by ESR. They have performed the reaction in cationic-anionic mixed micelles and altered the composition of micelles such that their charge changes from a net (+) to a net (-), in order to assess the contributions to the photoionization yield due to the "charge effect", and due to the TMB^+-water interactions.[53] They have reported that the photoyield is enhanced and that the charge effect is only produced by positively charged micelles. In such micelles the removal of the electron from the micelle is facilitated and the TMB^+-water interaction is of secondary importance.

4. Micellar Effects on Regioselectivity

Product distribution and regioselectivity in photochemical reactions depends largely on the preorientation of substrates within the micelles. Upon the irradiation of 2-substituted naphthalenes, the *cis*- dimer is formed while the major product is the *trans*- dimer in organic solvents; this is because the molecules are orientated in ionic micelles in such a way that the hydrophilic groups (R_2) are directed towards the micellar interface (Figure 7).[289]

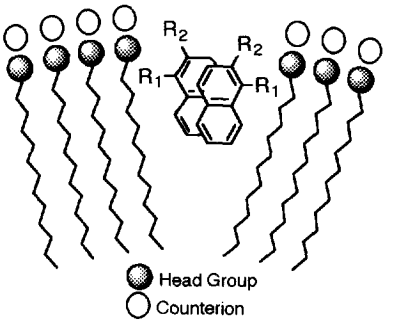
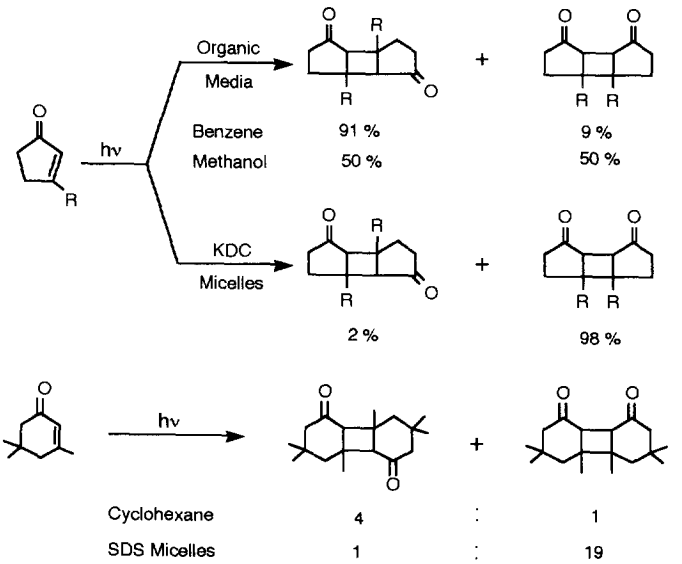


Fig. 7. The role of hydrophilic groups (R_2) in preorientation of substrate molecules at the micellar interface (Reproduced from ref. 289; copyright 1984 American Chemical Society).

Favorable head-head dimerization is encountered for 9-substituted anthracenes in ionic micellar solutions when the 9-substituent is a polar group.[290] Similarly, suitable polar derivatives of 2-phenylindene yield mainly *anti*-hh dimers upon irradiation in micellar environments.[291] Efficient dimerizations in potassium dodecanoate micelles are observed for 3-*n*-butyl- and 3-*n*-decylcyclopentenones with a reversal in regiochemistry compared to organic media due to the orientation of monomers with their carbonyl oxygen at the interface (Scheme 3).[292]



Scheme 3

The irradiation of *trans*-cinnamic acid in CTABr gives dimeric product in 35% yield with a truxinic : truxillic acid in a ratio of 19 : 1 and significantly no photodimer formation is observed in nonmicellar solutions (Figure 8).[293]

When both the diene and dienophile are surfactants, above the CMC of their mixed micelles, regioselectivity can be attained through the orientation effect of micelles, as demonstrated by the reaction between the 1,3-diene (3) and the dienophile (4) (Scheme 4). Both reactants have ionic head groups, and this favours the orientation of their head groups at the micellar interface, which leads to the formation of an excess of cycloadduct (5) over (6), up to a ratio of 3:1. Very little reaction occurs in the aqueous phase. Such an orientational effect has not been observed with nonionic reactants of comparable structures.[294]

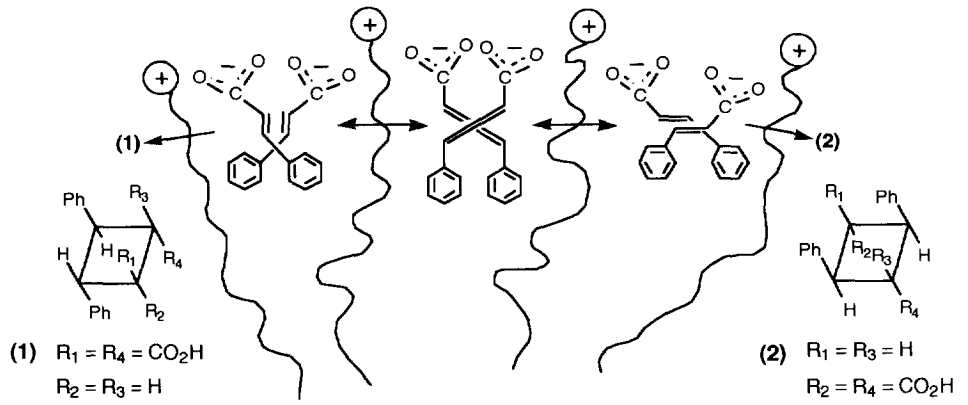
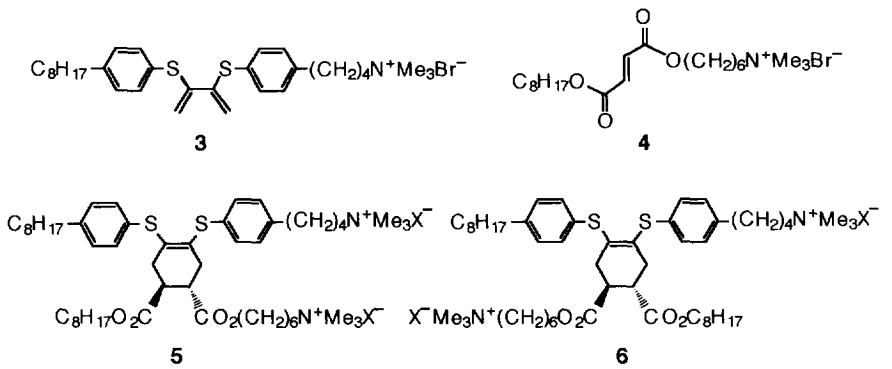


Fig. 8. Possible orientations of micelles and substrates for the formation of truxinic (1) or truxillic (2) acids (Reproduced from ref. 293; copyright 1988 American Chemical Society).



Scheme 4

However, regioselectivity has only been attained in cases where the inherent forces controlling regioselectiviy are weaker than the hydrophobic association energies that induce the preorientational effect.[33,295]

5. Mechanism for Functional Micelles

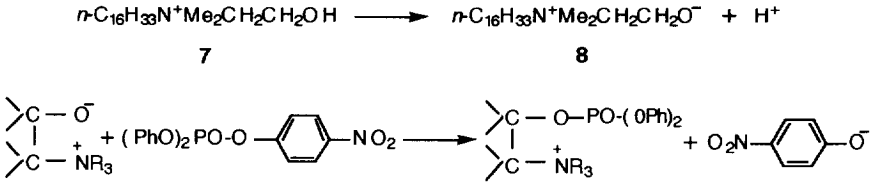
Functional micelles can function as effective bases or nucleophiles, by virtue of the reactive groups on either their surfactant molecules or on co-components in comicelles, and hence catalyze reactions. Due to this additional catalyzing action, rate enhancements by functional micelles are considerably larger than those by non-functional micelles of comparable structure; and bifunctional micelles are better catalyzers than monofunctional micelles.[128,180-190,296-308]

The most widely reported functional groups are hydroxyl,[306-308] imidazole,[58,69,183,186] thiol,[181,182,303] and some -OH bearing groups such as hydroxyalkyl,[185,187a,190a,273,297-301,304,306,308] hydroximino alkyl,[184,302,308] hydroxylamine,[305] and hydroxamic acid.[184]

There is evidence that nucleophilic catalyzers generally act in their anionic form, and the reactivities of nucleophiles are increased at relatively high pHs due to pK_{app} decreasing, in cationic micellar media. The increased activities in micelles is due to the formation of hydrophobic ion pairs between the functional group and cationic head groups such that the rate is increased by the amount of anionic species present. The concentration effect of micelles and the type and position of the deprotonated micelle functional group are the other important factors.[41,180,308]

Functional surfactants have been utilized in dephosphorylations,[58,184,185,189,297,302,305] deacylations,[152,180-183,186,189,273,296,301] nucleophilic additions and substitutions,[185,298-300,303,306-308] and elimination reactions.[298,304,308] The most widely used functionalized surfactants contain imidazole and hydroxyalkyl moieties. The catalytic

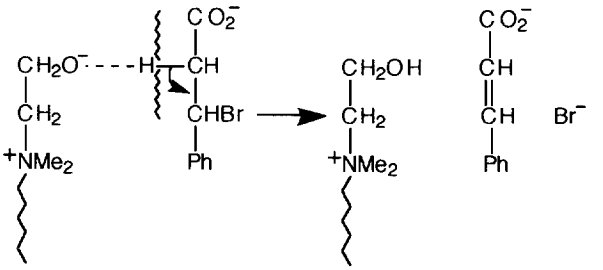
efficiency of hydroxyalkyl surfactants is mostly due to the nucleophilic attack by their alkoxide zwitterion (8) generated at high pH (Scheme 5).



Scheme 5

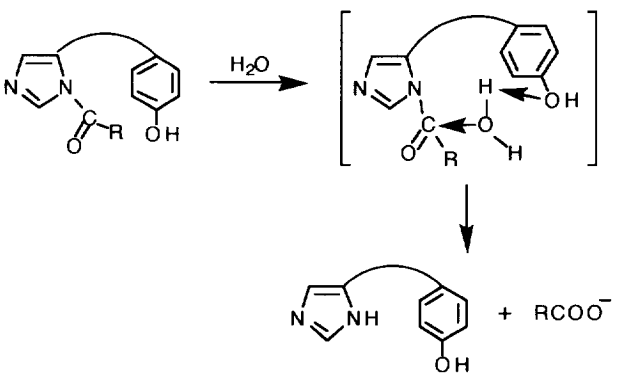
Bulky alkoxide ions are much better reagents than OH^- for deacylations. 1-Hydroxyethyl-2-dimethylhexyl ammonium bromide (7) provides approximately 600-fold rate enhancement over OH^- for the decomposition of malachite green.[300]

1-Hydroxyethyl-2-dimethylalkyl ammonium bromide micelles enhance the E2 elimination of 3-bromo-3-phenyl propionate, rather than S_N1 decomposition, by means of its alkoxide centre acting as a base (Scheme 6).[298]



Scheme 6

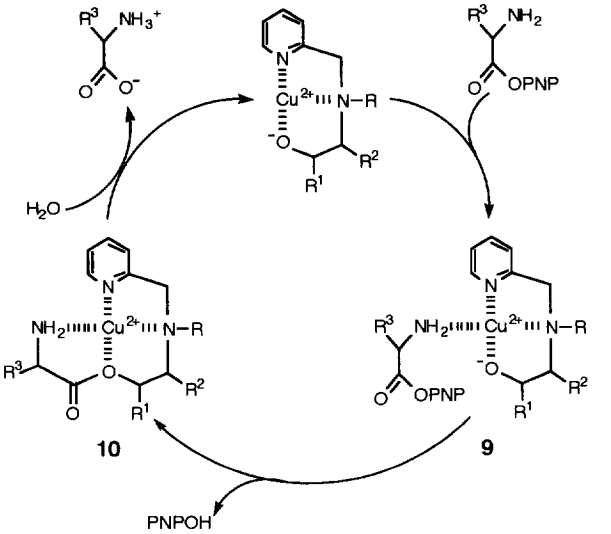
Reactions in imidazole-functionalized micelles occur *via* acylation followed by deacylation of the imidazole group. Reactions in comicelles of bifunctional catalysts containing both imidazolyl and hydroxyl groups with a cationic nonfunctional surfactant gave 5000 fold or more catalytic efficiency than when the catalyst contained either of these groups.[180,188] A possible mechanism for a catalytic effect with this type of surfactant micelles on deacylation processes is illustrated in Scheme 7. The results suggest that, for a deacylation mechanism, acyl transfer from the imidazolyl to the hydroxyl group is less probable than general base catalysis by the neighbouring phenolic hydroxyl group.[188]



Scheme 7

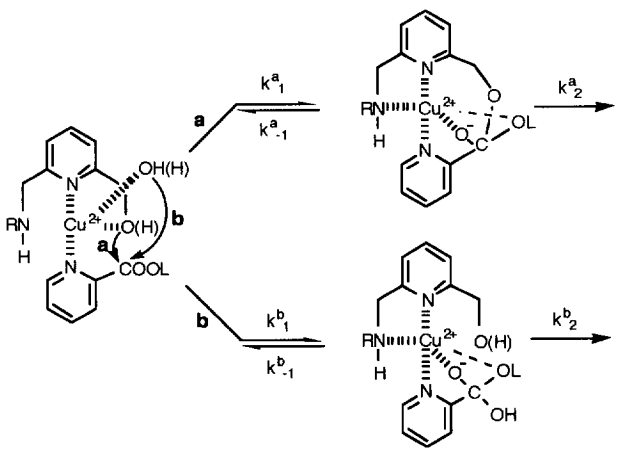
Micelles of a thiol functionalized surfactant, *N*-*n*-cetyl-*N*,*N*-dimethyl-*N*-(β-thioethyl) ammonium chloride (n-$C_{16}H_{33}N^+(CH_3)_2CH_2CH_2SHCl^-$), has been reported to be the best micellar esterolysis reagent for

p-nitrophenylacetate (PNPA) and -hexanoate (PNPH) when compared to other functional micelles other than comicellar blends of N-OH reagents and CTA halides.[182,303] It cleaves PNPA and PNPH with k_{cat} (second order catalytic rate constant) 485 and 1037 L/mol·s, respectively.



Scheme 8

Outstanding examples of functionalized micelles are called "metallomicelles", and they bind substrates with enzyme-like efficiency. They are made up of either transition metal complexes of surfactants containing imidazole or pyridine moieties or comicelles of ligand complexes with surfactants, and are utilized in the hydrolysis of carboxylic and phosphoric acid esters and amides.[189,309,310] The existence of a hydroxyl group on the surfactant molecule induces rate enhancements. Hydroxyl groups are activated by metal ions and act as effective nucleophiles in neutral aqueous media. Rate accelerations of up to 10^6-fold have been reported when compared to the uncatalyzed hydrolysis of substrates. The observed rate enhancements are also considerably larger than those in the presence of the nonmicellar analogs of the complexes or of the free metal ions. The hydroxyl group is involved as a nucleophile in the hydrolytic cleavage leading to a transacylation intermediate that undergoes a rapid, metal ion assisted hydrolysis and results in turn over of the catalyst (Scheme 8).[310b] In cases where the surfactant does not bear a hydroxyl group, a hydroxide ion, formed from a water molecule that has lost a proton after binding to the metal, functions as a nucleophile.



Scheme 9

The observed metallomicellar rate enhancement is due to both concentration and medium effects: (i) Micelles bring the substrate into a small volume together with the ligand and metal ions (ii) The local pH at the micellar surface favours the dissociation of hydroxyl groups in the complex. The pK_a of metal-bound water molecules is reduced both by the effect of the metal and the highly cationic Stern region where the water resides. Moreover, the release of a proton from Cu-OH_2 will be promoted by a low dielectric constant at micellar surfaces (iii) Micellar media promote the electrophilicity of the metal ions toward micellar bound substrates due to the positive charge of Stern layer.

However, it has been reported that leaving group effect may be of importance. For instance, in the cleavage of some picolinic acid esters by 6-((*n*-dodecylamino)methyl)-2-(hydroxymethyl)pyridine, rate enhancements have been observed only with activated substrates. With regards to competition between the hydroxide ion from metal-bound water and the ligand hydroxyl group for nucleophilic attack to the carbonyl carbon of the esters (Scheme 9); the hydroxyl of the ligand is favored in the case of good leaving groups, whilst in the case of picolinates having poor leaving groups the hydroxide ion becomes the effective nucleophile.[310d]

6. Micellar Effects on Stereoselectivity

The stereoselectivity of a reaction can also be altered in micellar systems. In this respect, the main factor is again the preorganizational function of micelles. The formation of a supramolecular chiral organization on the surface of a chiral surfactant micelle, which can provide chiral recognition, has been illustrated in Figure 9.

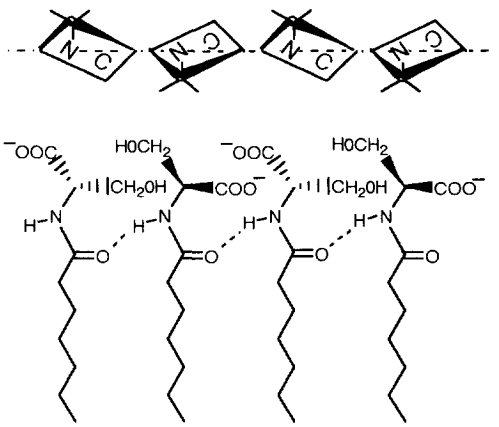


Fig. 9. Side and upper views, of an assembly of four adjacent *N*-stearoyl-L-serine molecules in a micellar aggregate (Reproduced from ref. 119c; copyright 1993 American Chemical Society).

Enantioselective reactions with chiral substrates can either be performed in micelles of chiral surfactants or in comicelles of chiral catalyzers with achiral surfactants. Surfactants may be functional or nonfunctional but higher stereoselectivities can be achieved by using micelles of functional surfactants.[58-67,127,145,310-314] Substrate chirality is most important and a chiral surfactant is not always required for diastereomeric selectivity as observed for the cleavage of LL- and DL-*N*-carbobenzyloxyalanylproline *p*-nitrophenyl esters; achiral surfactants provided much greater selectivities.[64]

The most widely studied stereochemical reactions are the hydrolyses of *p*-nitrophenyl esters of *N*-protected D- or L- amino acids, in the presence of dipeptide or tripeptide catalyzers containing generally L-His residue at the N- or C- terminal positions. Ono *et al.* reported a (k_D / k_L) value of 5.68 for such a system by using an optically active hydroxamic acid derivative of *N*-protected L-lysine, in the presence of CTABr micelles at 0°C.[63a] Similarly, values of 131 for the k_L / k_D ratio in various hexadecyltrialkylammonium bromide micelles have been reported.[63b] In the LauHisLeu+ CTABr and MyrHisLeu + CTABr catalytic systems, higher enantioselectivities can be attained (k_L / k_D = 12 and 9.13, respectively) for the deacylation of *p*-nitrophenyl *N*-dodecanoyl-D(L)phenylalaninate.[66,127] The addition of a bilayer surfactant to the latter system raises the rate ratio to 16.[127] The tripeptide $C_4H_9O_2C$-L-Phe-L-His-L-Leu-OH cleaves *p*-nitrophenyl esters of *N*-protected L- and D-phenylalanine in micellar media with an enantioselectivity of k_L / $k_D \approx 40$.[311]

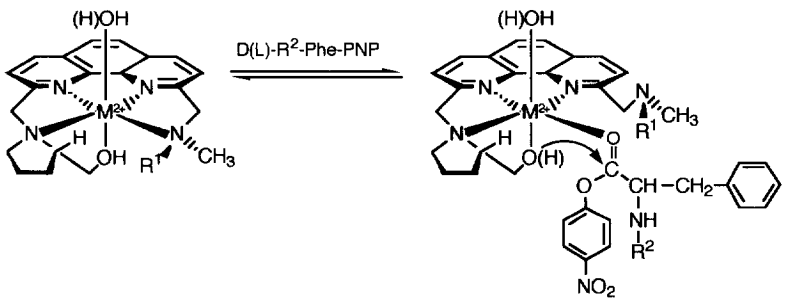
Together with hydrophobic and electrostatic interactions, orientation of the substrate by hydrogen bonding between the surfactant and substrate molecules can provide chiral recognation giving rise to unfavorable and favorable interactions between their bulky groups.[311,312] When mixed micelles of chiral surfactants with achiral

ionic surfactants are formed, the bulk water is excluded more efficiently from the hydrogen bonding section of the chiral surfactant compared to the pure chiral surfactant micelles. This provides a chiral microenvironment for enantiomeric recognition, due to hydrogen bonding between the chiral micelle and the solubilized enantiomeric compound.[282b]

Cationic micelles show little or no effect on the rate and stereochemistry of solvolytic displacement reactions of some co-micellizable sulfonates while anionic SLS micelles strongly inhibit these reactions and drastically decrease the percentage of inversion of the product alcohol (from 100%, to 56% net inversion).[61]

Zhang *et al.* have attained enantiomer in excesses of up to 40 % in the addition of carbenes to aromatic aldehydes and up to 15% in the oxidation of some phenyl alkyl sulfides with $NaIO_4$ in micelles of various chiral surfactants. The configuration of the product is opposite to that of the surfactant which contains only one chiral center.[67]

Stereoselective hydrolysis of *p*-nitrophenyl esters of *N*-protected amino acids can be realized in mixed metallomicellar systems containing metal-ion complexes of hydroxy functionalized 1,10-phenantrolines. The enantioselectivity that can be achieved depends on both the nature of the bivalent metal ion and the surfactant. Depending on the nature of the co-surfactant, an inversion in enantioselectivity can be observed.[310a] The nature of the substrate is also relevant. Greater stereoselectivity can be attained by increasing the hydrophobicity of the substrate since this introduces an extra orientation requirement between the complex and the substrate due to the hydrophobic interaction. This can be provided, for example, by the substitution of R^2 group of the substrate and/or R^1 group of the surfactant, which has been illustrated in Scheme 10, with more hydrophobic groups.[310a] Scrimin *et al.* suggest that the chiral ligand reacts faster with the substrate of opposite absolute configuration.[310b]



Scheme 10

Stereospecificity can also be attained on substrate micellization. In the nitrous acid deamination of chiral primary amines, when the alkyl group of the substrate is sufficiently hydrophobic to form micelles, the stereochemistry of alcohol formation is switched from inversion to retention, at concentrations above the CMC of the amines. This is thought to be due to the mainly frontal attack of water molecules upon the intermediate. The overall stereochemistry is a weighted sum of the stereochemistries for the micellar and nonmicellar reactions. The nonmicellar reactions commence after the concentration of substrate falls below the CMC.[274]

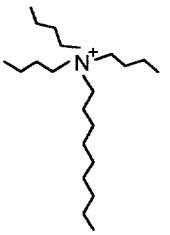
5. FACTORS AFFECTING THE MICELLAR BEHAVIOR

1. Surfactant Structure

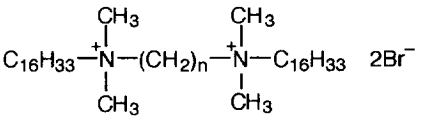
The nature of the surfactant plays a very important role in micellar catalysis. A small change in surfactant structure can induce changes in the surface properties and the rigidity of the micelle which markedly affect the reactivity of the substrates.[19,27,315-316] The size, nature and position of the head group and the length of its hydrophobic chain are all important factors.[317]

As a rule, the reactivity in micelles increases with increasing head group bulk. Two factors are involved in this increase: The first is related to the polarization and the disruption of the hydration of reactive counterion, and the second is the electrostatic interaction between the substrate and ionic head groups which increase with the head group bulk.[9,24,28,31,316] The binding parameters of counterions to micelles decrease with increasing head group bulk but second order rate constants at the micellar surface and overall first order rate constants increase. This is attributed to the increased disruption in the hydration of reactive ions by bulkier head groups, that leads to increased nucleophilicity of these ions together with the increased electrostatic interactions between the substrates and head groups.[8,9,31,51,52,318] With respect to the rate enhancement, the folding back of the alkyl groups at the head groups towards the micellar surface is also of importance. This reduces water-alkyl group contact so that

the reaction takes place in a region of relatively low polarity (Figure 10, a).[31,81,316]



a



b

Fig. 10. a) Orientation of the alkyl groups at the head group along the micellar surface, b) kuaternized *N,N'*-tetramethyldiamines which function as dicationic surfactants.

Counterion binding coefficients also depend on the hydrophobicity of the head groups and the existance of folded back residues at the head groups.[31,52] Folding back at the micellar surface reduces the space between head groups available for counterions.

The insertion of hydroxyethyl groups, instead of methyl groups, in CTACl causes a decrease in the reactivity of Cl^- ions because their -OH groups solvate Cl^- by hydrogen bonding and displace water molecules.[52] In the hydrolyses of a series of 2-(substituted phenoxy) tetrahydropyrans, the introduction of a methyl group at the 1- position of sodium hexadecyloxyethyl sulfate markedly reduces its catalytic effectiveness.[19]

In the hydrolysis of methyl orthobenzoate in the presence of various Na hexadecyl sulfates, catalytic efficiency is markedly dependent on the position of the head group. As it moves further from the terminus of the chain, the catalytic efficiency decreases.[315]

These factors also affect the substrate binding constant, *i.e.*, the amount of micellar bound substrate.[52] The binding parameters for both counterions and substrates increase with increasing length, *i.e.*, increasing hydrophobicity of the alkyl chain of the surfactants.[8,9,32,36,48,72] Even when the substrate is essentially completely associated with micelles, it is more reactive when the micelles are formed from more hydrophobic surfactants.[14-16] The longer the alkyl chain of the surfactant, the stronger inhibitor it also becomes.[298]

The observation that the more hydrophobic the surfactant the better the catalyst it is may reflect a more favorable geometrical disposition of the substrate with respect to the Stern layer. Also, electrostatic effects resulting from the formation of better organized micellar surfaces with increased N and surface charge, perturbation of the hydrogen bonding of adjacent water molecules, and the direct contribution of hydrophobic forces to the activation energy and free energy changes may also be important.[51,275,319]

The increase in enantioselectivity with the hydrophobicity of the surfactant molecule depends upon the presence and the position of a functional group on it.[67] Alternatively, it has been reported that the photoionization yield decreases with increased micelle surfactant chain length. This is attributed to the fact that micelles formed from shorter chain surfactants have more water penetration and polarity at the interface.[36]

Those micelles composed of surfactants bearing two negative charges are particularly effective catalysts.[315] Bunton *et al.* have studied the decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate ion and the reactions of OH^- and F^- ions with some substrates: they concluded that micelles of dicationic surfactants are better catalysts than monocationic surfactants of the same chain length (Figure 10, b), probably because aggregation is assisted by the linkage between the cationic head groups such that micellar incorporation of initial and transition states is more effective.[28,320] A similar effect has been observed with methylene-bridged dicationic surfactants, and it is thought that the bridging $-CH_2$ groups force water molecules away from the micellar surface and can induce larger rate enhancements.[316]

Comicelles of ionic-nonionic surfactants may be more effective catalysts for some reactions relative to pure ionic surfactant micelles because of the lowered charge density at the micellar surface.[18]

The behavior of micelles also depends largely on their charge and some generalizations can be made in this respect:

Nonionic micelles often have little or no effect on the rates of bimolecular reactions with ionic reactive counterions, especially when the substrates are located near the water-rich micellar surface.[85,86] Since they cannot attract the reactive counterions effectively, they sometimes even inhibit these kind of reactions especially when the substrates are hydrophobic enough to enter the micellar interior where they are protected from ionic reagents.[68,122,259,272,321] Thus, they behave like cationic or anionic micelles in their mode of inhibition.[32,34,55,68,321] Cationic, anionic and nonionic micelles may also have similar effects on the reactions of nonionic reagents.[68,321]

For reactions involving carbonium ions, of the following types behaviors of anionic and cationic micelles can be predicted:

$$(R-X)_M + H^+_W \longrightarrow R^+_M + HX_M \quad (A)$$

$$R^+_M + X^-_W \longrightarrow (R-X)_M \quad (B)$$

For reactions of type A, anionic micelles are expected to stabilize the bulky carbonium ion in the transition state relative to the ground state, which involves a neutral reactant and a small reactive ion (See Chapter 4), and therefore to catalyze these kind of reactions. Cationic micelles are predicted to have an inhibitory effect, since they will repell the reactive ions.[16,19,68,315,317]

The reaction of a carbocation that is sufficiently hydrophobic to be incoporated into micelles, with an anion from the bulk phase is expected to be catalyzed by cationic micelles, since they can both attract the reactive ions effectively and destabilize the cationic substrate electrostatically relative to the zwitterionic transition state. Anionic micelles inhibit these reactions since they keep the reactants apart.[14,21,280] Nevertheless, if the anionic nucleophilic reagent in reaction B were to replaced by a neutral one, both the substrate and transition state would have a (+) charge and so catalysis by cationic surfactants could not be predicted.[317]

Ionic micelles generally inhibit spontaneous hydrolyses, probably because of the relatively nonpolar character of the micellar interior compared to that of water.[12,197,322] However, they sometimes may not have any effect on the rate and it has been reported that the attack of water upon substrates such as 2,2',4,4',4"-pentamethoxytrityl cation and methyl naphthalene-2-sulfonate is even catalyzed by cationic micelles.[51,280] Cationic micelles, as large macroions, can effectively bind carbocations because of hydrophobic and dispersive attractions.[187,261,262] The spontaneous decomposition of *m*-nitrophenyl-9-fluorene carboxylate is slightly enhanced by nonionic, catalyzed by anionic, and inhibited by cationic and zwitterionic micelles (See Scheme 2).[272]

As a general rule, anionic micelles increase the rate of bimolecular reactions with positively charged reactive counterions, *e.g.*, protonation of indicator bases, metal-ligand substitution reactions and acid catalyzed reactions.[55,57,68,264,269,323-326] Conversely, they inhibit bimolecular reactions of neutral substrates with anionic nucleophiles because they repell the reactive anions and keep them away from the micellar solubilized substrate.[68,70,85,86,259,327] However, addition of high concentrations of electrolyte reduces the potential at the micellar surface such that anions may approach the surface to achieve some reaction with the substrate. Anionic micelles increase the rate of bimolecular reactions of nonionic nucleophiles.[23]

Cationic micelles increase the rate of bimolecular reactions between a neutral substrate and an anion, *e.g.*, basic hydrolysis reactions[5,12,22,30,51,70,73,85,86,91,259,272,307,308,327-329] and nucleophilic substitution reactions;[4,8-10,23,40,51,52,72,91,93,245,257,259] as well as dephosphorylations,[23,189,330] deacylations,[189,257] decarboxylations,[18,27,28,316] intramolecular nucleophilic anionic cyclizations,[27,325] and *cis*- to *trans*- isomerizations.[142a] Bimolecular reactions of nonionic nucleophiles are also speeded up by cationic micelles, but the reactions of nonionic and ionic electrophiles are retarded.[269a,321,331-333]

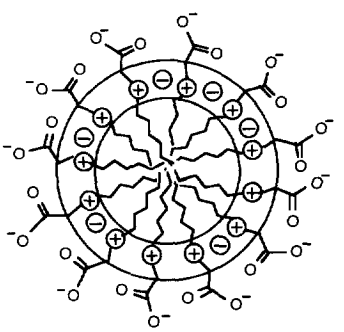


Fig. 11. Simplified schematic representation of the structure of a zwitterionic micelle (Reproduced from ref. 334; copyright 1991 Pergamon Press plc).

Zwitterionic micelles do not generally have as big an effect on reaction rates as do cationic and anionic micelles.[19,72,298,305,322,334] However, there are some exceptions: Dodecyltri- and dimethylammoniopropanesulfonates are reported to be excellent catalysts for the addition of cyanide ion to pyridinium ion derivatives.[72,278] Similar rate - [surfactant] profiles can be obtained with nonreactive zwitterionic micelles to those obtained with

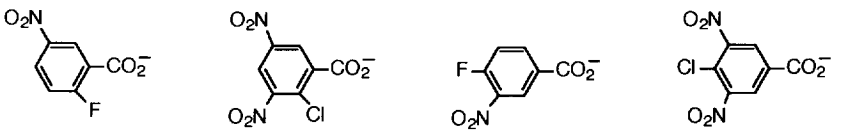
reactive ion cationic micelles.[334] Zwitterionic micelles can be considered as spheres with anionic residues extending outwards, with cationic centers residing further inside. Therefore, the charge density at cationic centers is greater than that at the anionic centers. Hence these kind of micelles can bind anions, and their catalytic effect on reactions with reactive anions can be understood this way (Figure 11).[16,27,305,334]

2. Substrate Structure

The nature of the substrate is another factor affecting reaction kinetics in micelles. Two aspects of substrate structure play an important role in micellar rate effects: Substrate hydrophobicity and the nature of its polar substitutents.

Substrate reactivity depends largely on the extent of its penetration into the micelle, that changes with its hydrophobicity. As a rule, the increasing hydrophobic character of the substrate increases the influence of the micellar phase on the velocity of the reaction, *i.e.*, increases either catalysis or inhibition.[15,32,36,41,70,72,197,319,330c, 335] For example, the hydrolysis of methyl *ortho*-benzoate and -valerate are subject to catalysis by SDS but the hydrolysis of methylorthoacetate is not.[68] Alkaline hydrolyses of *N*-dodecyl- and *N*-hexadecyl-4-cyanopyridinium ions are catalyzed by CTABr but not the reactions of the *N*-methyl- derivatives which reside extensively in the aqueous phase.[22] The product distribution is also not effected for the latter derivatives. The binding constants of adenine residues by thymine derivatives, due to hydrogen bonding in the micellar interior, are increased with increasing hydrophobicities of both the receptors and the ligands. Base pairing is not observed when the receptor is not sufficiently hydrophobic to be incorporated into micelles (See Figure 6).[282c] The reactions of *N*-alkyl-2-bromopyridinium ions with OH^- are inhibited by CTA chlorides or bromides when the substrates are methyl and ethyl derivatives which do not bind to micelles, while the reactions of more hydrophobic derivatives which can be solubilized in the micellar interior are catalyzed.[252] However, there may be an optimum substrate chain length to achieve maximum catalysis or inhibition.[279]

Broxton and Marcou have selected some nitroactivated halobenzoates with halogen substitutents in *ortho* and *para* positions, to locate the substrate at the micellar interface (11,12) and more deeply into the micellar core (13,14), respectively (Scheme 11). The reactions of aniline, which resides at the micellar interface, with



11 **12** **13** **14**

Scheme 11

ortho compounds have been catalyzed by CTABr, while its reactions with *para* compounds are inhibited. Conversely, reactions of tertiary amines, which reside in the micellar interior, with more deeply buried substrates were catalyzed more effectively than their reactions with the substrates residing at the micellar interface.[29,34a]

The location of the chromophore with respect to the aqueous micellar interface, which depends on the length of its alkyl chain length, is an important factor that affects the efficiency of charge separation in photoreactions.[36,47,48,53,231b] In the photosubstitution reactions of nitroaryl esters with the OH^- ion, the observed decrease in the quantum yields with increased *n*-alkyl chain length can be attributed to the deeper penetration of the substrate into the micellar interior.[231c] Their longer chains do not facilitate the preorientation of some coumarins in micelles prior to photodimerization, but when the alkyl chain of the substrate is very much longer than that of the surfactant chain surprisingly the anti head-tail dimer is formed presumably because of a change in the mode of solubilization of the substrate.[295b]

The shape of the curve of reaction rate versus [surfactant] may also change depending on the hydrophobicity of the substrate.[22,46,100]

A reaction in the micellar phase is more sensitive to the nature and the position of polar substitutents of substrates than the same reaction in water.[35,317] It has been reported that the k^+/k^- ratio, where k^+ and k^- stand for values of pseudo first order rate constants in cationic and anionic micelles respectively, for reactions of fully micellar bound substrates may change depending on the nature of the substitutents on the substrate molecules.[19,197,280,315,336,337] The sensitivity of the substrate to catalysis by cationic micelles increases with electron withdrawal in its polar substitutents, while the extent of catalysis by anionic micelles increases with increasing electron donation of the polar substitutents (since the existence of electron donating groups predominates the bond breaking in the transition state, with some exceptions). For example, in the hydrolyses of acid chlorides

k^+ / k^- becomes >1 or <1 when the substitutents are electron attracting or donating, respectively, indicating that the mechanism of the reaction changes depending upon the nature of polar substitutents.[322]

Regioselectivity can be attained in cases where there is a hydrophilic group on the substrate molecule. This leads to preorientation of the substrate as observed in photocycloaddition reactions (See Figure 7 and Scheme 3).[289-292,338]

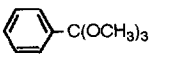
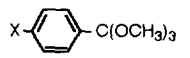
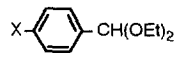
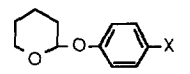
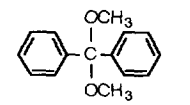
SUBSTRATE	SURFACTANTS	EFFECT
 Methyl Orthobenzoate	Sodium Alkylsulfates Isomeric Hexadecylsulfates Substituted Oxyethylenesulfates Sodium 2-Dodecylbenzenesulfonate Disodium Sulfoalkylsulfates Alkyldisulfonates Sulfoalkylcarboxylates α-Sulfoalkyl Esters	Catalysis
	Dodecyldimethylphosphine Oxide Dodecyldimethylammoniumpropane-sulfonate Dodecyldimethylammoniumacetate Cetyltrimethylammoniumbromide	Inhibition
 p-Substituted Methyl Orthobenzoates X = -OMe, -Me, -H, -F, -Cl, $-NO_2$	Sodium Dodecylsulfate	Catalysis
 p-Substituted Benzaldehyde Diethyl Acetals X = -OMe, -Me, -H, -F, -Cl	Sodium Dodecylsulfate Sodium Decylsulfonate	Catalysis
 2-(p-Substitutedphenoxy)-tetrahydropyrans X = -OMe, -Me, -H, -Cl, $-NO_2$	Sodium Dodecylsulfate Sodium 2-Hexadecyloxyethylsulfate Sodium 2-Hexadecyloxy-1-methyl-sulfate	Catalysis
	Dodecyldimethylammoniumpropane-sulfonate Dodecyldimethylphosphine Oxide	Inhibition
 Benzophenone Dimethyl Ketal	Sodium Dodecylsulfate Octadecyldimethylammonium Bromide	Catalysis Inhibition

Table I. Effects of several surfactants on the rate of hydrolysis of some acetals, ketals and ortho esters.

In spontaneous hydrolyses, inhibition by cationic micelles increases with increasing ability of the substrates to generate a carbocation, which is dependent on the structure of their alkyl groups. Conversely, anionic micelles catalyze the reactions of such substrates through electrostatic stabilization of the developing carbonium ion in the transition state (Table I). Non-ionic and zwitterionic surfactants inhibit hydrolysis of the substrates in Table I probably because of the lower polarity at the micellar surface compared to the bulk phase.[317]

In some cases the number of substituents on the aryl group of the substrate is more important than its chain length.[339] For photoreactions the relative charge of the electron donor and the micelle is also relevant.[283a]

3. Nature of the Counterions

The nature of the counterions affects a number of properties of micelles such as N,[340,341] CMC,[342,343] surface potential,[39] substrate and water penetration,[344,345] the amount of the hydrocarbon chains exposed at the micellar surface, and water organization at the micellar interface.[251,346] Reactive and inert counterion micelles and micelles with different counterions behave in different ways.[4,6,30,51,255,324] The main factors are the hydrophobicity and polarizability of the counterions, which affect the amount of reactive counterions bound to the micelle and the extent of the disruption of their hydration.[8,31,260]

There are clear differences in the behaviour of cationic micelles with very strongly, moderately and weakly hydrophilic anions, *e.g.*, OH^-, Cl^- and Br^-, respectively. The more hydrophilic ions such as OH^- or $SO_3^=$, locate in the more aqueous region of the micellar surface, compared to Br^-; therefore they are further away from

the micellar bound substrate and are less reactive. The ratio of the second order rate constant at the micellar surface to the rate constant in water decreases with increasing hydrophilicity, or decreasing polarizability of the nucleophile, *i.e.*, it follows the sequence $Br^- > Cl^- > SO_3^= > OH^-$.[257]

In aromatic nucleophilic substitution reactions of 2,4-dinitrohalobenzenes with OH^-, PhO^- and PhS^- ions catalysis increases in the order $OH^- > PhO^- > PhS^-$;[86,247,347] and the catalysis of reactions of carbocations with BH_4^- and CN^- ions, in cationic micelles, are much greater than that with the OH^- ion, indicating the importance of the hydrophobicity of the reactive ion.[21,269b,280]

The reactivities of counterions depend on their solvation shell, which may be perturbed by interactions with the micelle. The deeper a counterion penetrates between the head groups, the more its hydration is disrupted, *i.e.*, the more nucleophilic an ion it becomes.[9,31,51,52] Hydrophilic OH^- ions interact so strongly with water that their hydration is only slightly perturbed by cationic micelles, regardless of the head group of the surfactant. However, the hydrations of Br^- and Cl^- are decreased considerably and moderately, respectively, when they interact with the micellar surface.

The nucleophilicity of the Br^- ion is better than that of the Cl^- ion also because hydrogen bonding reduces the nucleophilicity of anions and this effect is most significant with small hydrophilic anions of high charge density.[245,246] The rate enhancements with OH^- reactions are larger in CTACl than those in CTABr because Br^- is more effective than Cl^- at excluding OH^- from a cationic micelle.[91]

In photoreactions, heavy atoms are known to modify singlet-triplet intersystem crossing efficiencies, resulting in changes in reactivities. Therefore the *cis/trans* ratio of the formed acenaphtylene dimers is reduced considerably in micellar HTABr when compared to that in HTACl micelles. This has been attributed to the quenching of the excited singlet state and to the promotion of the triplet state reactivity by the Br^- ions.[348,349] For the same reason, on irradiation, alkoxycoumarins show a high degree of reactivity in CTACl compared to CTABr micelle since heavy atom induced intersystem crossing will be negligible in the presence of Cl^- ions.[295b] The enhanced reactivity in CTACl micelles compared to CTABr micelles is also observed in the photodimerization of 2-substituted naphthalenes.[289]

It has been suggested that with very hydrophilic ions that interact largely Coulombically, the second order rate constant in the micellar pseudophase will not be very sensitive to the head group bulk. However, bulky head groups will speed up reactions of anions that bind specifically to micellar surfaces.[51] On the other hand, however, the second order rate constant for the additional reaction pathway across the micellar interface proposed by some investigators, is found not to depend on the nature of the counterion, as an indication of its similarity to phase-transfer catalysis.[73,276]

4. Salts and Other Additives

All of the factors affecting the size, shape, CMC and other properties of the micelles may affect their effectiveness in altering reaction rates and pathways. One of these factors is the existence of salts or organic additives in the micellar media.[4,41,51,85,93,100,101,218,269,257,273,298,325b,321,350-353] By inducing changes in the properties of micelles, salts and organic additives control the extent of substrate solubilization and counterion binding to micelles.[90] On the addition of organic salts to the medium, the incorporation of the organic ion into the micelle may prevent the incorporation of the substrate.[28,277] The larger the K_S value for the organic ion, the greater is the inhibitory effect. The addition of alcohols also reduces binding of both substrates and reactive ions.[90]

Inert salts, especially the inorganic ones, and organic additives have generally been found to decrease the rates of reactions. On the other hand, their rate increasing effects have also been reported for some reactions.[20,28,42,246,354] Thus micellar catalyzed reactions can be inhibited, or micellar inhibition can be suppressed, by the addition of electrolytes to the medium.[170]

Various series related to the effectiveness of added ions as inhibitors, or catalyzers, have been developed.[7,14,16,28,39,72,86,101,147,251,259,265]

The salt effects are specific and depend upon the nature of the ion which has a charge opposite to that of the micelle, suggesting that both electrostatic and hydrophobic factors play a role. The effects are greatest for large, low charge density and hydrophobic ions which interact most strongly with the reactive counter ionic micelle. In general, the more hydrophobic a character possessed by the ion, the better inhibitor it becomes. The inhibitory effect of an ion increases with its ability to lower the CMC and surface potential, to increase N, and to decrease the ionization degree of micelles.[39,355]

Added salts inhibit micellar catalysis by excluding ionic reagents from the micellar surfaces, as a result of ionic competition for micellar head groups, and by reducing the electrical potential of the micellar surface, so that affinity for reactive ions is weakened. An increase in N, induced by added salts, leads to deeper penetration of the substrate into the micelle, and a reduced number of micelles at any given [surfactant], and hence to inhibition.[15,16,28,82,259,275] It has been reported that upon the addition of salts or organic solvents, micellar surfaces

become more hydrated and the water content of the micellar interface plays an important role in inhibition.[47]

Following a decrease in the micellar surface charge density, due to additives, the transition state is either stabilized or destabilized in an organic reaction compared to the ground state and rate enhancement or retardation is observed.[15,20,39,47,273,356] It has also been suggested for catalyzing effect of added salts that shrinkage of the Stern layer by an increased concentration of counterions might lead to a concentration of reactants.[100] Salts of high solubility in the aqueous phase can also increase the binding constant of substrate to the micelles by "salting out" the substrate from the aqueous pseudophase and this results in rate enhancement.[7,41,245,246,252] The rate enhancement is also observed when a common salt is added to the medium in which a reaction in reactive counterion micelles occurs.[8,10,42,52,102]

Additives also affect the pK_{app} values as well as reaction rates in micellar solutions.[2,21,39,41,357] There is an interesting report about the dissociation of thymol blue, indicating that the addition of CTABr increases the pK_{app} values at high salt concentrations, while the opposite is observed at low salt concentrations.[2]

From hydrolysis reactions in buffered micellar systems Quina and Chaimovich suggested that the most appropriate buffer systems for micellar solutions will be those whose buffer species are highly hydrophilic, are of the same charge as the surfactant monomer, and whose counterions are identical with those of the surfactant used.[231] Under these conditions, the influence of added buffer can be analysed as an added common salt effect.[358] Salt effects on the reaction rates can be explained satisfactorily by theoretical treatments.[10,245,246,273,359]

Salt effects may be smaller on reactions in functional micelles, than those in comparable nonfunctional ones.[273]

5. *Factors for Reverse Micelles*

All of the factors mentioned above are also applicable to reactions in reversed micellar systems. In such systems micellar solubilized water plays an important role: depending upon the nature of the reaction, rate retardation or enhancement is observed with increasing amounts of water, *i.e.*, dielectric constant. The nature of the bulk solvent also has great importance in this respect.[173,204,218,360,361]

The [H_2O]/[surfactant] ratio (w) has been reported to affect the rate and other features of the reactions in a number of studies.[361b,362,363] For example, the efficient and selective formation of the *syn* head-to-head photodimer of *trans*-4-stilbazolium cations, in reversed micellar system of hexane-AOT-water, can be correlated with a ground state association that is controlled by the stilbazolium / surfactant ratio and w.[362] In cases where water pools are small, the orientation of stilbazolium ions with respect to the charged interface of a reversed micelle is constrained, and the charged interface presents an organized surface that can lead to a topological control.[362] The amount of solubilized water can be reduced, and hence the reactivity can be altered, by salt addition.[177b,178c]

The extent of micellar catalysis also depends on the temperature. An increase in the temperature leads to an increase in micellar catalysis but to a decrease in the stereoselectivity.[16,28,66,86,277] Hydrophobicity of the catalyzer compounds is also relevant.[330b]

6. MODES OF STUDY IN MICELLAR SYSTEMS

In order to utilize micellar effects, reactions are generally performed in micellar or comicellar solutions of surfactants. Co-compounds are either other kinds of surfactants or catalyzers.

Photochemical reactions are most frequently carried out in frozen micellar solutions. An external magnetic field has also been applied to study the magnetic field effects in micellar media.[48,53,235b,283a,285,287,288,364]

In reactions with water insoluble organic liquid compounds, and water soluble reagents, surfactants disperse the organic liquids in the aqueous phases, on stirring. Thus a heterogeneous reaction may be catalyzed by the formation of both emulsion and micelles. This can be utilized in large scale reactions and in reactions that require the minimum contact of water immiscible reactants with the aqueous phase.[365]

Some reactions are performed utilizing intermicelle solubilizate exchange between the micelles. After mixing two reversed micellar solutions, each of which contains only one of the two reactants as solute, micelles begin to collide due to Brownian motion and sometimes coalesce to form short-lived dimers that redisperse again to form new micelles. Meanwhile solubilizates are exchanged and so the reaction occurs (Figure 12).[221] A similar study has been performed with two reversed micellar solutions; one of them containing the catalyzer (imidazole) and the other containing the ester to be hydrolyzed, in their water pools.[172]

A new area of application in micellar systems is to prepare homogeneous colloidal dispersions of ultrafine metal, metal oxide, selenide or sulfide particles so that they have improved catalytic activities. Micelles serve as microreactors as well as protective colloids, and thus control the particle size. For this purpose; Me salts are

reduced by hydrogen, N_2H_4, $NaBH_4$ or preferably by photoreduction, in micellar solutions. The micelles surrounding the colloidal particles also solubilize and control the orientation of substrates, resulting in novel regioselective hydrogenations and photoinduced electron transfers. The size of the microreactors and thus the size of the colloidal clusters can be controlled by changing the amount of solubilized water in reversed micelles.[284,366-370]

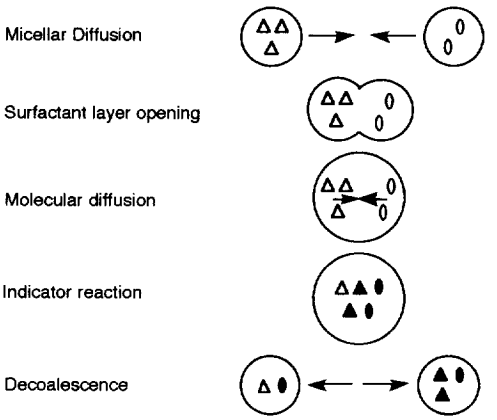


Fig. 12. Elementary steps associated with reversed micellar coalescence, solubilizate exchange and reaction (Reproduced from ref. 221a; copyright 1990 American Chemical Society).

Quantitative analysis methods have been developed in micellar systems. The precision of the present methods may also be increased in micellar media.[371]

The extraction and purification of lipophilic or lipophobic substances by the Micellar Enhanced Ultrafiltration Technique (MEUF) is sometimes performed using micelle-solubilized complexing agents as extractants. This new technique is called Ligand-Modified MEUF. This technique can also be utilized in the separation of cations in the same solution (Figure 13).[372-374]

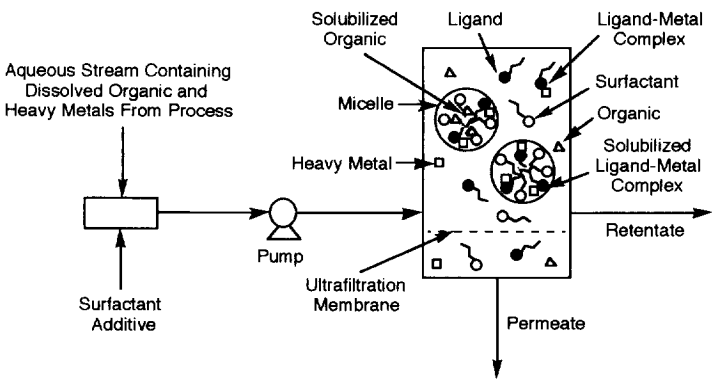


Fig. 13. Schematic of the ligand-modified micellar-enhanced ultrafiltration process (Reproduced from ref. 374a; copyright 1991 Marcel Dekker, Inc).

As mentioned before, micelles have a very short life time due to the rapid exchange of detergent molecules between aggregates and bulk water. With the consideration that such a dynamic equilibrium may not be favorable to the catalytic process in micelles, it has become a field of interest to build polymerized micelles from polymerizable surfactant molecules to prevent this exchange. Upon polymerization, the degree of counterion binding is also increased. Surfactant molecules may bear polymerizable groups in their alkyl chains or head groups, and the resulting products are called T and H polymers, respectively.[17,375-385]

In a catalytic study of the hydrolyses of *p*-substituted benzaldehyde diethylacetals in the presence of polimerized micelles (16) of sodium 10-undecenyl sulfate (15), the maximum catalytic activity was observed to be roughly two times higher for reactions in solutions of (16) than for reactions in solutions of (15), and the rate

effect appeared at low concentrations, even below the CMC of the surfactant monomer. The T-type polymeric micelles provided more favorable microenvironments for reactions compared to those of H-type polymeric micelles.[386]

$$CH_2=CH-(CH_2)_9-OSO_3^-Na^+ \quad (15)$$

$$-(CH_2-\underset{|}{CH})_n-(CH_2)_9-OSO_3^-Na^+ \quad (16)$$

7. ESTIMATION OF IONIC CONCENTRATIONS AT MICELLAR SURFACES

Micellar rate effects are generally treated in terms of concentrations of micellar-solubilized substrate and reactive counterions at the micellar surface, *i.e.*, in terms of the reactant distribution between aqueous and micellar pseudophases. Kinetic expressions for unimolecular reactions in micelles include substrate binding constant to micelles, K_S. Kinetic expressions for bimolecular reactions with reactive ions include both K_S and the reactive ion concentration at the micellar surface. The reactions performed in micellar solutions are generally bimolecular and micellar rate effects for such reactions are directly related to the reactive ion concentration at micellar surfaces.

In order to estimate the ionic concentration at the micellar surface, the ionization (α) or neutralization (β) degree of micelles can be measured directly by methods such as electrophoresis, ultrafiltration, gel filtration, diffusion, NMR; and by the measurements of conductivity, pH, solubility, osmotic pressure, ion activity, light absorbance, light scattering and the effect of added electrolyte on CMC.[4,6,7,9,10,41,51,100,114,147a,168,192,269a,252,273,328,351,358,387-390] There may be some differences between the α and β values determined by different methods.[7,31,90,101]

Direct measurement methods are not generally applicable to hydrophilic inorganic ions. For these, sometimes electrochemical methods can be used, except for OH^-.[248,251] The determination of $[OH^-_W]$ *via* pH or conductivity measurements has proven to be less than satisfactory.[248a] An alternative and more reliable approach is the indirect determination of either $[OH^-_W]$ or $[OH^-_M]$ from kinetic data for a reaction involving OH^-, in which the substrate is completely localized in either the micellar or the intermicellar aqueous phases. When a reactive substrate resides exclusively in the micellar aqueous phase the following rate expression can be written for the pseudo first order rate constant, k_ψ:

$$k_\psi = k_2' \ [OH^-_W] \quad (8)$$

Thus, by using the values of the second order rate constant, k_2' measured in the absence of detergent, one can analyse a reaction with OH^- ion as a function of [surfactant] in terms of $[OH_W]$.[253]

The α or β values for ionic reactants, which are generated by the dissociation of weak acids, cannot generally be estimated by direct measurements since the micelles affect the acid dissociation equilibrium.[2,41] Indirect methods proposed for these kind of ions, *e.g.*, imidazole anion, may also not be reliable.[391] However, Bunton *et al.* were able to measure the binding of phenoxide ions to CTABr spectrophotometrically under conditions in which phenol was partially ionized.[23]

In some cases when the ionization is complete under the reaction conditions, *e.g.*, ionization of thiol in deacylations by thiolate ions, the micellar concentration of anionic nucleophiles can be measured directly. It is also straightforward to estimate the concentration of a nonionic reactant in the micellar pseudophase by direct measurements.[2,21,145,276,392]

Some theoretical treatments have been developed to estimate reactive ion concentrations at micellar surfaces, for cases reliable results are difficult to obtain by direct measurements. The most widely used treatment to predict ionic micellar effects on reaction rates is the pseudophase ion exchange model (PPIEM).[1-13,17,21,26,30,31,39-42,50-52,70,72,73,82,86,90-93,99-102,113,114,145,168,191,245-248,251-253,255-257,263,265,273,274,276,308,321,324,328,329,332,352,355,387-405]

The concentration of reactive ions at the micellar surface can also be estimated by solving the Poisson-Boltzman Equation (PBE) in spherical symmetry for finite [surfactant] and [electrolyte].[2,6,39,90,102,140,192,230b,245,257,265,352,396,406,407] Other models have also been developed to assess the ionic distribution in micellar systems, however, they have not yet been so widely applied.[39,168,254,257,352,396,400,408,409]

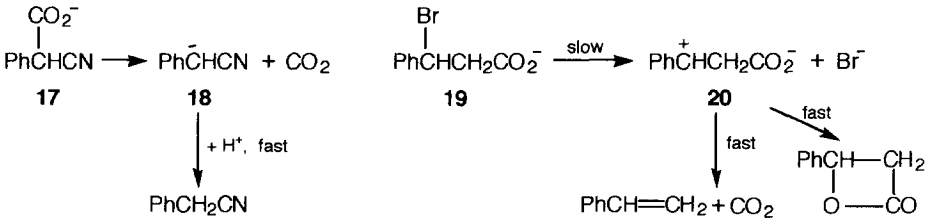
A number of kinetic equations have been developed that account for the micellar rate enhancement and inhibition in various micellar systems.[7,11,13,23,32,46,70,71,86,93,100,145,168,231,252,255,259,276,277,324,390,410-412]

8. MICELLAR EFFECTS ON REACTION MECHANISMS

1. Micelles as Probes and Directors for Preferential Routes

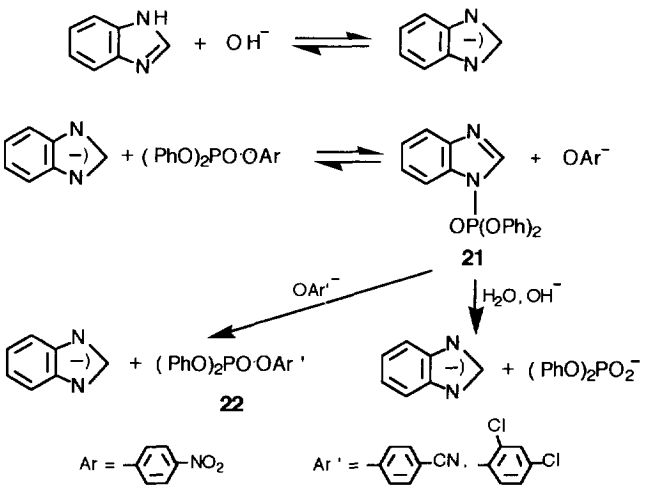
In recent years results from an increasing number of studies provided evidence that micelles can alter reaction mechanisms, molecularities and orders by virtue of their medium effect; and that they can be utilized as mechanistic probes for reaction mechanisms.[330]

k^+/k^- Values (See Chap. 5.2) can provide evidence about the reaction mechanism because micelles catalyze the reactions which involve reversely charged transition states with respect to their own charges.[197,337] Cationic micelles catalyze decarboxylations *via* a carbanion intermediate while they inhibit those *via* an intermediate carbonium ion (Scheme 12).[20] Conversely, anionic micelles catalyze the spontaneous hydrolyses where the transition state has carbocationic character, while they inhibit the ones with transition states of anionic character. Related to the k^+/k^- ratio for the spontaneous reactions, the following generalization has been made : If bond making is dominant in the transition state (S_N2 mechanism), $k^+/k^- > 1$; but if bond breaking predominants (S_N1 mechanism), $k^+/k^- < 1$. Thus, the k^+/k^- ratio appears to be indicative of reaction mechanism.[197,280,317,336]



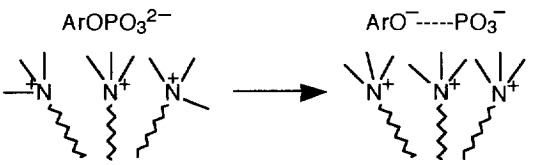
Scheme 12

Bunton *et al.* have utilized of micellar media to elucidate the mechanism of the reaction of *p*-nitrophenyldiphenylphosphate with benzimidazolide and naphth-2,3-imidazolide ions which can act either as general bases or nucleophiles. For this purpose, the reactions were performed in the presence of different phenoxide ions (ArO^-), which were expected to have similar inhibitory effects as if the areneimidazolide ions were acting as general bases by competing for the OH^- ions at micellar surfaces. If the areneimidazolide ions acted as nucleophiles, added phenoxide ions would attack the phosphorylated intermediate (21) and react with it to regenerate the substrate or a new triaryl phosphate (22). In this case they would have different and much stronger inhibitory effects, and this was observed (Scheme 13). Such a mechanistic study cannot be carried out in nonmicellar systems since the reactions of areneimidazolide ions contribute to the overall rate to such a small extent in water, and trapping of the intermediate by phenoxide ions is much more effective in a micellar medium since these ions bind much more strongly than OH^- ions to cationic micelles.[330]



Scheme 13

The hydrolyses of *p*-nitrophenyl phosphate monoanion and of the dianion of glucose-6-phosphate, which involve proton transfer, are not catalyzed by cationic micelles, while hydrolyses of dianions of dinitrophenyl phosphates are catalyzed, and this suggests that each dianion is decomposed into two monoanions which have a higher electrostatic energy to interact with the head groups (Scheme 14).[277]



Scheme 14

In the presence of SDS the hydrolyses of oxazepam and 2'-methyldiazepam is catalyzed over a range of HCl concentrations indicating that there is initial amide hydrolysis, because azomethine hydrolysis is inhibited by SDS. The observed inhibition of the basic hydrolysis of oxazepam, in the presence of CTABr, has been attributed to the increased ionization of oxazepam in CTABr micelles. It has been reported that the mechanism of basic hydrolysis of diazepam can be changed, from initial azomethine attack to initial amide hydrolysis, either by performing the reaction in CTABr micellar solution or by the introduction of a methyl group in the 2' position on the phenyl ring at C5.[57]

In Broxton and Marcou's study on the reactions of nitroactivated halobenzoates, reactions with primary amine nucleophiles, in the presence of CTABr micelles, proceeded *via* aminodehalogenation. With the more sterically bulky tertiary amines hydroxydehalogenation was observed. This behavior of tertiary amines, which reside deeply within the micelle, as specific base catalysts, confirmes the existance of water in the micellar interior (See Scheme 11).[34a]

The photodehydrochlorination of pentachlorobenzene in CTABr micelles proceeds mainly *via* the conversion of triplet state to excimer followed by fragmentation, not *via* the fission of the triplet state. Excimer formation is enhanced by 100-fold or more, compared to the reaction in acetonitrile solution.[54]

In the photooxidation of *N*, *N*-diethylhydroxyamine (DEHA) by Rose Bengal (RB), upon the incorporation of RB into micelles, the contribution of the singlet oxygen pathway increases at the expense of electron transfer from DEHA to the RB triplet, since the electron transfer is inhibited by the less polar micellar environment.[284c]

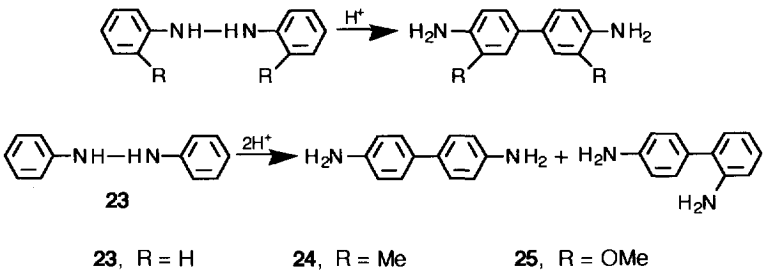
The dediazoniation reactions of *sec*-alkanediazonium ions are known to proceed by reaction mechanisms that range from inverting nucleophilic displacement to the intervention of solvated carbocations. Micellization can influence the relative contributions of the competing pathways.[413]

The catalytic efficiency of micelle- and ion-catalyzed reactions determines the preferential route through which the reaction products are formed in the reaction between cerium(IV) and arsenic(III), catalyzed by metal ions, in DTABr micelles.[44]

The rate determining step in the base dissociation of short-chain alkylamines is the intramolecular proton transfer process in the presence of SDS micelles, while it is the diffusion process in the absence of them. Catalytic and mechanistic effects of SDS micelles have been attributed to the strong interaction between the sulfate head groups and the amine cation at the transition state, *i.e.*, to the stabilization of the transition state.[56] Micelles also induce changes in the rate-limiting step of substituted benzoate ester thiolysis, leading exclusively to rate-limiting thiolate attack.[414]

2. *Order and Molecularity of Reactions*

The micellar effects on the benzidine rearrangement of 1,2-diphenylhydrazine (23), which acquires two protons, and of 1,2-di-*o*-tolylhydrazine (24) and 1,2-di-*o*-anisylhydrazine (25), which are one-proton reactions, provide evidence for the rate limiting proton transfer (Scheme 15). Micellar catalysis is dependent on the acidity of the medium. In dilute acid, rearrangement of (23) is inhibited by CTABr and nonionic Brij micelles as predicted. Anionic NaLS strongly catalyzes the reaction. NaLS also very strongly catalyzes the two-proton rearrangements of (24) and (25). For compound (24) which undergoes mainly one-proton rearrangement in the absence of micelles, only the two-proton rearrangement is observed. The rearrangement of (25) is close to first order with respect to $[H^+]$ in dilute acid, but has an apparent order of 1.73 for the reaction catalyzed by NaLS micelles.[55]



Scheme 15

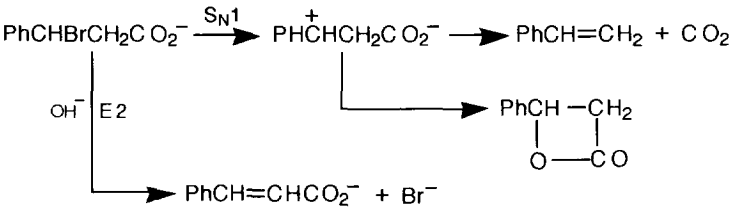
The oxidative degradation of tryptophan by acid permanganate is 1st order in $[MnO_4^-]$ and fractional order in [tryptophan], but in the presence of SDS the reaction is 1st order in each reagent.[415]

For spontaneous hydrolyses, the first order rate constant in the micellar pseudophase is usually smaller than the rate constant in the aqueous pseudophase in cationic and zwitterionic micelles and generally the difference is much smaller for bimolecular than for unimolecular hydrolyses, while the opposite holds for anionic micelles. This gives an indication to the relationship between the charge effect of micelles and the molecularity of the reactions.[6]

3. Micellar Effects on Product Selectivity

Micellar control of reaction products can be achieved when one of the two reactions that a given substrate can undergo, is catalyzed while the other is inhibited in a micellar medium (See also Chapter 4).[145]

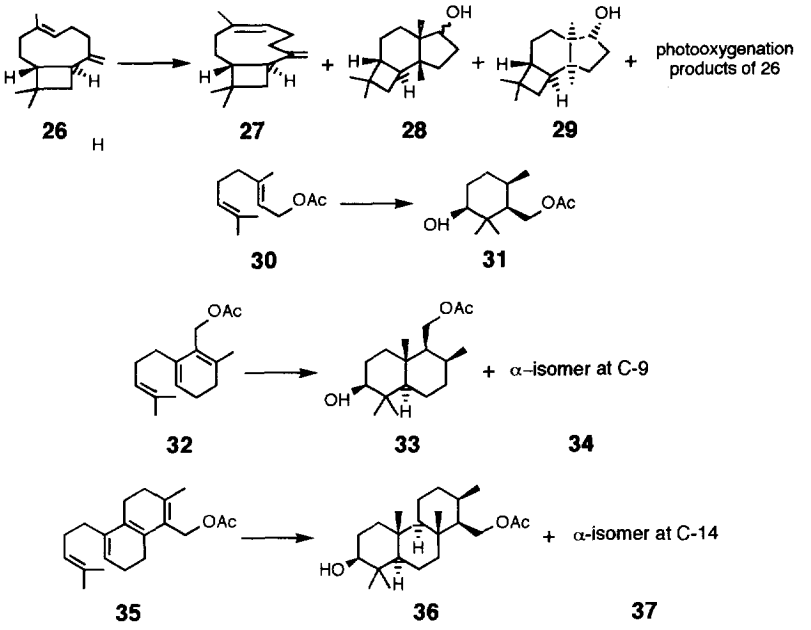
In dilute aqueous alkali, styrene is formed as the major product in the S_N1 decomposition of 3-bromo-3-phenyl propionate. In the presence of micelles of 1-hydroxyethyl-2-dimethylalkyl ammonium bromide this S_N1 reaction is inhibited. Instead, *trans*-cinnamate ion becomes the major product as a result of E2 reaction intervention. In the absence of micelles this E2 elimination is only found in much more concentrated alkali (Scheme 16).[298]



Scheme 16

CTABr significantly catalyze the hydroxydefluorination of 1,5-difluoro-2,4-dinitrobenzene. Monohydroxy functionalized micelles of cetyl (2-hydroxyethyl) dimethylammonium bromide and (2-hydroxycetyl)-trimethyl-ammonium bromide catalyze the reaction by a nucleophilic mechanism in which an aryl ether is formed prior to conversion by a second S_NAr reaction to 2,4-dinitrophenol, the normal product of the hydroxyde-fluorination reaction. On the other hand, the transient formation of a micellar-bound spiro-Meisenheimer complex from the intermediate aryl ether is observed in the presence of bifunctional micelles of cetyl-(2,3-dihydroxypropyl)-dimethylammonium bromide.[307]

CTABr has been observed to increase the amount of aryl alkyl ether product relative to the amount of phenol product in the reactions of 1-fluoro-2,4-dinitrobenzene and 2-fluoro-5-nitrobenzoate with OH^-, in aqueous binary mixtures with alcohols. The results have been attributed to the increased ionization of alcohols by CTABr micelles and to the differences in the orientation of the substrates. Micelles have little effect on the product distribution of 4-fluoro-3-nitrobenzoate which is more deeply buried in the micellar interior. In addition, in the presence of CTABr micelles, the ethers derived from 1-fluoro-2,4-dinitrobenzene and 2-fluoro-5-nitrobenzoate undergo a subsequent S_NAr reaction with OH^- ions during which the alkoxide ions are displaced and the corresponding phenol is produced. Such a reaction is not observed for 4-fluoro-3-nitrobenzoate , for which the reaction centre is buried deeper, since the ethers are shielded from subsequent attack by OH^- ions (See Scheme 11).[35]



Scheme 17

Light-induced polyene cyclizations can be realized in micellar media (Scheme 17).[416] The irradiation of *trans*-caryophyllene (26) in homogeneous solution in the presence of an electron acceptor causes merely (*E*) / (*Z*) isomerisation (26 ⇌ 27), while competing transannular cyclization, affording (28) and (29), is observed in anionic micellar media. Similarly, the cyclic products (31),(33) and (36) are the major components upon the irradiation of *trans*-geranyl acetate (30), *all-trans*-farnesyl acetate (32) and *all-trans*-geranylgeranyl acetate (35), respectively.

In the nitrous acid deamination reaction of [1-^{2}H]-1-octanamide in homogeneous solution, [1-^{2}H]-1-octanol is obtained with ca. 95% inversion of configuration. Upon substrate micellization, the enantiomeric purity of [1-^{2}H]-1-octanol decreases while [1-^{2}H]-1-nitrooctane is surprisingly formed with ca. 90% retention of configuration. 1-Octyl· ·NO_2 radical pairs, rather than ion pairs are likely to intervene on the retentive route in the micellar phase. Micellar media also induce the formation of dioctyl ethers due to the concentration effect of micelles.[417]

In alkali hydrolyses of *N*-dodecyl- and *N*-hexadecyl-4-cyanopyridinium ions a marked preference for pyridone formation is observed in the presence of CTABr, leading to a reversal of the product ratios at low external pH values. Even at high pH values higher ratios of pyridone / amide are observed.[22]

Benzoin autoxidizes to a 1:1 mixture of benzil and benzoate. CTACl micelles catalyze this reaction and favour only the formation of benzoate. On the other hand, the reaction is inhibited in the presence of NaLS micelles and the only product to be obtained is benzil .[418]

9. PROSPECTS FOR THE FUTURE

One can alter the rate, mechanism, product distribution, regio- and stereoselectivity of reactions by performing them in micellar solutions instead of homogeneous solvents. It is also possible to perform reactions with insoluble or labile substrates in such systems. Because of this, many more investigators in every field of chemistry are expected to focus attention on reactions in micellar media. Micellar structure and properties will continue to be studied and it will become an important challenge to synthesize new amphiphiles with different head groups, alkyl chains and functional groups in order to achieve improved micellar effects.

10. ABBREVIATIONS

N, aggregation number; CMC, critical micellization concentration; [ ], molar concentration, in general meaning, concentration; K_S, substrate binding constant to micelles; subscripts M and W, micellar and aqueous pseudophases, respectively; PPIEM, pseudophase ion-exchange model; PBE, Poisson-Boltzman equation; ASA, acetyl salicylic acid; SDS, sodium dodecyl sulfate; TTAB, tetradecyltrimethylammonium bromide; CTA, DTA and HTA: cetyl-, dodecyl- and hexadecyltrimethylammonium cations; AOT, sodium bis(2-ethyl-1-hexyl)sulfosuccinate; TMB, *N,N,N',N'*-tetramethylbenzidine; Triton-X-100, octylphenol decaethylene glycol ether; NaLS, sodium lauryl sulfate; Brij, polyoxyethylene alkyl ether.

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