I. INTRODUCTION

In the early 1970s, the Russian school of Berezin et al. [1,2] attempted to rationalize the unique effect that surfactants and micelles in particular had on reaction rates in solution (Fig. 1). Sufficient kinetic data involving various types of chemical reactions in micellar media had accumulated to test a hypothesis [3,4]. This hypothesis stated that in the presence of ionic surfactants some reaction rates were dramatically enhanced over a narrow concentration range in the vicinity of the critical micelle concentration (cmc) only to fall off more gradually with increasing surfactant concentration until seemingly it regained the original reaction rate observed when no surfactant was present [Fig. 1, curve (a)]. These lambda spikes often achieved heights corresponding to several thousand times the reaction rate in water. In other reactions, the observed rates rose more gently to plateaus in enzyme-like fashion [Fig. 1, curve (b)]. Undoubtedly, in more concentrated micellar solution, a drop off in rate would be observed as [Fig. 1, curve (a)] but, because micelles changed size and even shape in concentrated micellar solution, the upper limit of the range of investigation of catalysis effects was usually arranged to be about five times the cmc. A further series of reactions in the presence of surfactants displayed the opposite behavior beyond the cmc. For example, reaction rates decreased seemingly exponentially to many times less than the original values [Fig 1, curve (c)]. Usually, this rate of inhibition occurred, as with the enhancement effects, over a narrow surfactant concentration range.

The interest that arose quite strongly in the 1980s and 1990s in this particular catalysis phenomenon came from many areas. Industry was obviously tantalized by the time, energy, and materials that might be saved [5], but what seemed to appeal most to researchers were the biochemical implications. Nearly all chemical processes in the living cell occur at interfaces, such as at the active site of an enzyme on a membrane. As a result, chemical reactivity in biochemical situations is critically dependent on the local microenvironment, the local concentrations, and relative orientations of the bound reactants at cell interfaces. Thus, the realization that micelles could be realistic cell mimicks has become a major reason for this ongoing drive on the part of investigators in figuring out the specifics of micellar catalysis.

When micelles were present in solution, Berezin pictured bimolecular reactions as occurring in two sites, the micellar region and in bulk solution. The overall reaction rate was determined by the partitioning factor by which each of the reactants was assimilated.
into the micelles from the bulk solution. A rate promotion occurred when both reactants were preferentially located in the micelles. A rate decrease followed if only one of the reactants had been incorporated into the micelles. In this pseudo-phase treatment of micellar effects, the partitioning coefficients between bulk solution and micelles of the reactants and the product are critical data in the evaluation of the overall rate of reaction:

\[
\begin{align*}
A_B + B_B & \leftrightarrow P_B \\
K_A & \downarrow \quad K_B & \downarrow \quad K_P & \downarrow \\
A_M + B_M & \leftrightarrow P_M
\end{align*}
\]

where A and B are reactants, P is the product, and the subscripts B and M refer to the bulk solution and micellar regions, respectively. \(K_A\), \(K_B\), and \(K_P\) are the binding coefficients for the reactants and products partitioning between the bulk solution and micelles. The kinetic equations developed from this scheme can be used to obtain partitioning constants that agree with the experimentally determined values from techniques such as solubilization and gel filtration [1].

The immediate success of the Berezin model in accounting almost quantitatively for the observed catalysis effect of micelles has an interesting implication. Is this truly a case of catalysis? In many instances, the micelles bring about considerable shifts in equilibrium positions, which forced Berezin to admit that the term “micellar catalysis” was “somewhat incorrect” [2]. He justified its continued use on the basis that the surfactant is not consumed in the reaction and that for most surfactants the concentration required to bring about marked effects is usually very low. Some workers in the field have opted for less controversial terms such as “micellar rate enhancement” or “rate promotion.” The title of a recent review, “Micellar Catalysis, a Useful Misnomer” [3], sums up the prevalent attitude of researchers today.

FIG. 1 Effect of surfactants on the rates of reaction in the region of the critical micelle concentration (cmc). Curves (a) and (b) represent micellar catalysis while curve (c) is a typical example of micellar inhibition.
II. DYNAMIC NATURE OF MICELLES

A major difference between micelles and many other catalysts is that micelles are dynamic and fluid reaction sites. They are continually in the process of forming and disintegrating and this must be taken into account when interpreting micellar rate enhancements. Two relaxation times are found in micellar solutions. The faster time is usually in the microsecond range and the other in the millisecond range [6–10]. The faster time is associated with the exchange of surfactant monomer between the bulk solution and the micelle while the so-called slow relaxation pertains to the overall breakdown of the micelle. The latter process occurs as a result of the size fluctuation in the micelles that results from the fast exchange. When the micelle size dips below a certain critical value, the micelle is unstable and falls apart. When this happens, a replacement micelle will spontaneously form elsewhere in the solution to maintain the overall equilibrium. The slow relaxation is related to the cmc because both are measures of the overall stability of the micelle. The micelle will be more stable the lower the cmc and the longer the relaxation time. These findings mean that reactants in relatively slow reactions occurring within micelles experience a continually changing chaotic environment. Surfactant monomers slide into and out of solution from the micelles, and the micelles themselves explode and reform elsewhere in the solution while the reaction proceeds. Kinetic techniques that involve perturbing a system at equilibrium by means of an externally applied temperature, pressure, pH, or concentration jump can promote micelle breakdown while leaving the faster exchange process unaffected [8]. Micelle break-up times can significantly affect the control of technological processes such as foaming, wetting, emulsification, and oil solubilization [10]. The short lifetimes of micelles are in sharp contrast to those of vesicles, which are the bilayer aggregates formed by phospholipids in aqueous solution. The lifespan of vesicles can range from weeks or months [11]. This means that catalysis effects observed with these stable, cell-mimetic, micellar look-alikes are much more easily interpreted than the situation with the more problematic, continually changing micelles.

Another implication of the dynamic nature of micelles is that careful delineation of the micelle into regions having specific characteristics is of limited use in reaction kinetics. In aqueous solution, the headgroups are in the micelle surface and the hydrocarbon chains occupy mainly the micelle interior where significant wetting of the methylene groups occurs [8]. Each micellar region can only be vaguely defined given the prevalent general state of flux. Thus, the micelle is divided crudely into a polar exterior and a nonpolar interior. Considerable leeway normally exists as to the location and positioning of solubilizes during the course of any interaction between the two roughly defined regions. Even practitioners of the art of micellar catalysis often fall into the trap of fruitlessly attempting to situate the reactants carefully in specific regions of the micelle, hence, ignoring its fluid and short-lived structure. Therefore, micelles presenting moving and changing targets to reactant molecules is not usually what is found when considering other forms of catalysis.

III. PRE-CMC CATALYSIS

In many instances, it is found that rate enhancements in surfactant systems appear to begin below the cmc (Fig. 1). This seemingly premature behavior is usually ascribed to premicellar aggregates of various types [12–18] although hard evidence for their existence is too difficult to obtain. The fact that this is found with some experimental methods while
other techniques appear not to be sensitive to anything unusual in the pre-cmc region is disconcerting. On top of this, the range of suspected candidates is wide ranging from surfactant dimers to substrate–surfactant complexes to oligomers of various forms. Premicelles, as the culprits, are a too facile explanation. One of the more convincing studies is that of Brinch et al. [19] who postulated premicelles as accelerating agents in an examination of the hydrolysis of dinitroalkoxyphenylphosphate with cationic surfactants. On the other hand, Drennan et al. [20] found that, for the case of a particular metal–ion complexation occurring in anionic surfactant solutions, the “premicelles” were most likely mixed, true micelles formed early through the intervention of the metal–ion reactant. A similar explanation was given for the pre-cmc catalysis found for the chromium(VI) oxidation of dimethyl sulfoxide in picolinic acid solutions containing surfactant [21]. Clearly, the pre-cmc region requires more probing to discern the mechanism by which catalysis is commonly effected.

IV. CATALYSIS WITH CATIONIC SURFACTANTS

Reactions between organic substrates and hydrophilic anions have received perhaps the most attention as suitable candidates to test and extend Berezin’s ideas on micellar catalysis because of their importance industrially. Cationic surfactants are the surfactants of choice for this class of reaction in order for both reactants to be induced to enter and to reside preferentially in the positively charged, hydrophobic micelle rather than in bulk aqueous solution. The solution behavior of the observed rate coefficient in these micellar systems generally is represented by the enzymic-like curve (b) of Fig. 1. Romsted and coworkers [3,22] pioneered the work in this field with a successful model that has come to be known as the pseudophase ion-exchange (PIE) treatment. A similar approach had received earlier airing by Menger and Portnoy [23]. The strengths and weaknesses of the PIE model have received extensive coverage [24,25] with the model being found applicable also to some situations where anionic micelles were used as the catalysts [26].

The basic assumptions of the PIE model are as follows:

1. The micelles act as a separate phase; they are uniformly distributed throughout the solution and are invariant in composition throughout the micellar range.
2. The degree of counterion ionization remains constant irrespective of ion type or concentration or of surfactant concentration.
3. The micellar surface region can be thought of as ion-exchange resin where exchange processes can be handled mechanically in the same way as for a resin.

The emphasis placed on the last assumption is responsible for the name of the model. It is now well known that these assumptions, especially the first two, are reliable with impunity only over very narrow and dilute micellar concentration ranges. Nevertheless, the PIE model has provided invaluable insight over the past 25 years in elucidating micellar catalysis. Its “failures” [27–31] are usually attributable to clear-cut violations of its simple assumptions. Refinements or alternatives to these basic premises such as solving the nonlinear Poisson–Boltzmann equation for the cell model have not proved to be particularly enlightening nor more helpful [32]. The extension of the PIE model to complicated micellar systems where anomalous rate behavior is more often than not the rule rather than the exception is probably unwarranted [33]. Sudhölter et al. [34] have critically reviewed the Berezin model and its Romsted variation, the PIE model, as matters stood 20 years ago. In
a recent joint publication, a worker from each camp compares the two approaches and applies each to the particular case of amide exchange in micelles [35].

The kinetic equation at the heart of the PIE model is simply

$$k_{obs} = k_W[A_W][B_W]/[A_T] + k_M[A_M][B_M]/[A_T][V_M]$$ (1)

with the two terms respectively denoting the contributions from the reaction occurring in each pseudophase, the bulk solution, and the micelles, where A is the organic substrate and B is the anionic nucleophile. The total concentration of A is [A_T]. The binding constant of A to the micelle (K_A) provides values of [A_W] and [A_M] and the independently obtained ion-exchange constant generates values of [B_W] and [B_M]. The term $V_M$ is defined as the reaction volume in the micelle and is usually assumed to be the molar volume of the surfactant in the micelle. This term is required dimensionally because the reaction is perceived as occurring essentially in the necessarily nebulous surface region of the micelle. Its determination is problematic, but all evidence indicates that $V_M$ does not differ appreciably from the molar volume of the surfactant measured in water. Crucial to the model are accurate assessments of substrate/micelle binding constants and the ion-exchange parameters. Diverse techniques such as spectrofluorimetry [36], linear solvation free energy relationship analysis [37], and ion-selective electrode measurements [38] have been brought to bear on the determination of the requisite binding constants. The confidence level in the PIE model is now such that observed rate constants for many reactions can be successfully predicted [39]. Despite its shortcomings, it is the theoretical approach most often first invoked by workers in micellar catalysis [40–42].

In acting as catalysts, cationic micelles are usually found to invoke no change in mechanism from the reaction in water alone [43], but occasionally they provide an alternative route to the end result. Xiang et al. [44] found that the hydrolysis of p-nitrophenyl picolinate by Cu(II) and Zn(II) tripeptide complexes involved a ternary complex intermediate that was more stable in the micelle than in water. Broxton and Duddy [45] noted that cetyltrimethylammonium bromide (CTAB) micelles induced a change in mechanism in the basic hydrolysis of substituted N-methyl-p-toluidines. Mixed cationic micellar systems where either the counterion [46] or the surfactant ion [47] was varied have also been investigated. Kaneko et al. [46] discovered that the mechanism unexpectedly differed when bromide ion was substituted for chloride ion in the photolysis of a phenylhydroxylamine. Muñoz et al. [48] introduced an interesting twist when they reversed the kinetics of the dehydrochlorination of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) in tetradecyltrimethylammonium bromide micelles in aqueous alcohol solution to discover the dissociation constants of the micelles themselves.

Tee and coworkers [49, 50] have pushed the mechanistic analysis harder in seeking the preferred reaction paths that the micelles must be providing in reactions such as the thiolysis of p-nitrophenyl alkanoates where the “concentration effect,” i.e., the partitioning of both reactants into the micelle, which is at the heart of the PIE model, fails to explain sufficiently the observed catalysis or inhibition brought about by CTAB micelles. For example, in a follow-up study the efficiency of CTAB-mediated aminolysis of p-nitrophenyl acetate increased systematically from five-fold retardation to 70-fold enhancement as the amine chain was lengthened to n-octyl [51]. Advantage was taken of Kirby’s dissection of the binding of the activated complex into passive and dynamic states in order to gain insight into the binding sites of the reactants in the micelle [52]. Focusing on the interaction of the micelles with the activated complex is being increasingly viewed as the next step in elucidating the mechanism of micellar catalysis beyond what can reasonably be expected of the PIE model [53]. Another direction in which improvement is required is
V. CATALYSIS WITH ANIONIC SURFACTANTS

Another active area in micellar catalysis has been metal-ion complexations where anionic surfactants are used to attract positive ions and hydrophobic solutes into the micellar aggregate. The rate coefficients in these cases often show curve (a) (Fig. 1) behavior in micellar solution where the initial increase defies careful characterization with its sudden precipitous climb occasioned principally by the strong coulombic forces between the micelles and multivalent cations. As opposed to the PIE approach, the focus instead in the modeling has been on the gradually descending portion of the $k_{\text{obs}}$ curve that occurs with increasing micelle concentration. Following Berezin’s view, the basic equilibria operating in this region are assumed to be those of Fig. 1 and the observed attenuation of the catalysis effect is ascribed to the dilution of the micelle-bound reactants as the micelle concentration is increased. The micelle concentration dictates the relative amounts of reactant in each pseudophase through the partitioning constants. Thus, as with the PIE model, these binding parameters play an important role in analyzing the observed kinetic behavior even on the downslope of the curve.

One development that has proved fruitful and insightful in this area is due to Robinson and coworkers [55–58]. Inhibition as would occur when indicator anions are present in anionic micellar solutions is also well accommodated by this view [18,59–61]. The kinetic relationship that emerges from the Robinson treatment is

$$k_{\text{obs}} = k_W[A_T]/[C V_M(1 + (C K_A)^{-1})(1 + (C K_B)^{-1})]$$  \hspace{1cm} (2)

where $C$ is the concentration of the micellized surfactant, i.e., the total surfactant concentration less the cmc, $A$ is the metal-ion reactant, and $B$ is the ligand [56,57,62]. It is assumed that $k_W = k_M$ and that the backward step in the metal-ion complexation is of little kinetic consequence especially when micelles are present. The binding parameters $K_A$ and $K_B$ are obtained independently as with the PIE approach through such studies as ligand solubilization. The molar reaction volume $V_M$ is usually initially approximated by the surfactant molar volume in water and then computer fitted to Eq. (2) to yield a more useful measure of the micelle structuring as envisioned by the reactants. It is often found that best-fit $K_A$ values are more precise and just as accurate as independently measured values. Insight into the structure of mixed or unusual micelles is often gained through the $V_M$ and, to a lesser extent, $K_A$ estimates that emerge from this modeling [62,63]. Useful information has been gained about the micelles formed by two-tailed [64], two-headed [64], short-tailed [57], and fluorocarbon anionic surfactants [65], and in the presence of additives such as urea [63], benzene [66], and inorganic salts [67] through this method. Confidence in the essential legitimacy of this modeling approach is now such that the use of kinetics to reveal subtleties in micelle structure is becoming more widespread, even with cationic surfactants [68]. Given the common source and the similar methodology, it follows that the Robinson model has the same limitations as that for the PIE model.

A probe reaction that has seen much use in this context is the formation of the complex between Ni$^{2+}$ ion and the bidentate organic ligand, *trans*-pyridine-2-azo-p-dimethylaniline (PADA). The kinetics of this reaction is conveniently studied by the stopped-flow technique under pseudo-first-order conditions with nickel ions in excess.
Anionic micelles can provide a successful reaction site for positively charged reactants which otherwise do not react to any extent in aqueous solution. Dash and Mohammed [69] used sodium dodecyl sulfate (SDS) micelles to enable oxalatopentaaminecobalt(III) to undergo complexation with Ni(II) and Fe(III) metal ions. That the situation is not always that simplistic is demonstrated by the metal-ion complexation of Pyrogallol Red in micellar dodecyltrimethylammonium bromide solution where a rate enhancement was observed despite the similar charges of the ions and the micelle [70]. On the other hand, metal–ligand complex formation between Cu(II) and benzoylacetone in anionic and cationic micellar solutions occurred as expected, i.e., with rate increases and decreases, respectively [71]. Stability constants for Cu(II) and Cd(II) ion complexes with several common ligands in micellar SDS are available [72].

VI. CATALYSIS WITH NONIONIC AND ZWITTERIONIC MICELLES

When neither reactant is charged, micelles formed from nonionic surfactants will not be expected to have a pronounced catalytic effect on the reaction rate because the charged species will have little incentive to be solubilized within the micelle. Thus, Harada et al. [73] found that the polyoxyethylene alkyl ether of hydrocarbon chain length 12 was only 25% as effective as a catalyst as an anionic surfactant of the same chain length such as dodecyltrimethylammonium chloride in the hydroxide ion reaction with tetrinitromethane. The kinetics of complexation of some azophenol derivatives with Ni$^{2+}$ and Cu$^{2+}$ ions was depressed in the presence of Triton X-100 micelles in keeping with the incorporation of the azophenols within and the exclusion of the metal ions from the nonionic micelles [74]. Carbone et al. [75] took advantage of this lack of attraction of ionic species to nonionic micelles to gain insight into the dominant hydrophobic attractive forces between reactants and nonionic Triton X micelles. However, this exclusion of polar reactants is not always complete and may in fact be significant enough to account for the sometimes observed micellar inhibitions [76].

Like their nonionic counterparts, zwitterionic micelles have not received much attention as catalysts although they present an interesting opportunity to explore the effect of charge separation in the surfactant monomer on the catalysis effect. Conceivably, the negative and positive charges on the surfactant monomer might be sufficiently removed from each other in the micelle so that charged reactants could be preferentially solubilized within the micelle with resulting marked rate enhancements. The above situation is noted in the Ni$^{2+}$ complexation of PADA where Ni$^{2+}$ ions apparently readily enter carboxybetaine micelles, but are excluded from sulfobetaine micelles [77]. The more delocalized sulfonate group does not afford the same degree of attraction for the Ni$^{2+}$ ion as does the carboxylate charge center. In the carboxybetaine micellar situation, the tetra-alkylammonium positively charged center is ineffective in preventing the small and hard Ni$^{2+}$ ion from residing in the micelle. Ghosh et al. [78] have noted that the acid hydrolysis of hydroxamic acids in two zwitterionic sulfobetaine surfactants was inhibited, but that alkaline hydrolysis was accelerated.

Another diagnostic kinetic application with zwitterionic micelles was that of Rodriguez et al. [79], who investigated the reaction of DDT with hydroxide ions in micellar sulfobetaine solutions to determine the role cations play in the process. Micellar charge plays an important role in micellar catalysis [80]. The use of nonionic micelles affords a sensitive and refining means to measure the operative hydrophobic
forces by providing a situation where the overall coulombic forces are essentially eliminated [81].

VII. ELECTRON TRANSFER REACTIONS

The use of micelles as rate promoters or inhibitors in electron transfer reactions has been recently reviewed by Prado-Gotor et al. [82]. Possible applications lie in the fields of solar energy conversion and storage, DNA modification, gated electron transfer reactions, and the testing of the PIE and analogous models. Another purpose in using micelles in electron transfer reactions is to ascertain how electrons might behave in biological systems for which micelles are fitting mimicks [83–85]. Micelles can also possess intense surface electric fields which would be expected to exert a powerful influence on electron transfer reactions. In fact, the surface potential of micelles is often revealed through electron transfer reactions as surface probes [86]. Micelles can also have a major influence on electron transfer fluorescence reactions [87].

It must be noted that the dynamic nature of micelles must especially be borne in mind in dealing with electron transfers which invariably are fast processes. The seminal work of Bruhn and Holzwarth [88], an examination of the kinetics of diffusion-controlled electron transfer reactions in micellar sodium dodecyl sulfate solutions, disclosed that sufficient heed must be paid to the continuous disintegration and reconstitution of the micelles in this time range.

An interesting twist in using micelles in electron transfer reactions is to slow rates so that they might be measured more conveniently. Bunton and Cerichelli [89] found that ferrocene is too rapidly oxidized in water by ferricyanide but, in the presence of anionic micelles into which ferrocene is preferentially partitioned, the reaction rate is easily obtained. The rate attenuation results because the concentration of the negatively charged ferricyanide is lower in the vicinity of the anionic micelles than in bulk solution.

VIII. EXCITED STATE CHEMISTRY IN MICELLAR SOLUTION

The diffusion-controlled deactivation of excited states in micelles is essentially more complicated than for ordinary, slower reactions occurring in micellar media. As noted above, concentrative effects are chiefly responsible for the change in rate. First, quencher molecules must be present in each micelle and thus it is important to know the statistical distribution of the reactants among the micelles. Second, due to the very close proximity of the quencher with the excited species in the micelle, additional slow deactivation processes may occur as the contents of the micelles undergo mixing after the initial rapid deactivation step [90]. Factors such as polydispersity, quencher or excimer migration and exchange, excimer reformation (a particular problem with pyrene which is the most common excited probe used), and even the extent of counterion binding (for ionic quenchers) must be taken into account [90]. These additional concerns have meant that the elucidation of the kinetic mechanism whereby excited states are defused in micelles has not experienced the same refinement as for ordinary reactions reacting in micelles. However, probing these problems is ongoing [11]. The potential rewards, however, of persevering in the hunt for a satisfactory model for deactivation in micelles are so manifest that a lively recent literature in this field exists.
IX. MICELLAR CATALYSIS IN INDUSTRY

The earliest interest in micellar catalysis was in searching for quicker and more efficient routes to synthesizing industrially important organic compounds. Fendler and Fendler [4] is a comprehensive compendium of the work performed in this area previous to 1975. Since then the chief emphasis in micellar catalysis has been on the theoretical or mechanistic side even with potentially commercially significant products, e.g., Diels–Alder reactions [91]. In spite of the level of sophistication achieved in modeling and the wide range of reactions investigated theoretically, industry has been slow in finding applications for micellar catalysis although a quick look at the patent literature shows that technologists consider many surfactant-mediated processes to have commercial promise. Emulsion polymerization has been touted as a notable exception where the scaling up of the process has been singularly successful [92,93]. Hydrophobic monomers concentrated within micelles may undergo polymerization much more quickly than in solution and in the process higher degrees of polymerization are often achieved [94]. Another advantage of using micelles is that the degree of solubilization of the monomers in aqueous solution is usually much enhanced without the system becoming too viscous and less easily temperature controlled. Ionic monomers are concentrated in the surface region of the micelles by counterion binding and a similar catalysis effect is noted [95].

Other specific areas of micellar catalysis in which industry has expressed interest are in micellar phase-transfer catalysis and in the synthesis of mesoporous molecular sieves [92]. In the first example of the latter application, investigators at Mobil were able to control pore size and properties by synthesizing the desired mesoporous material in the presence of appropriately sized, structured, and charged micelles [96]. The burst of research activity in this area that occurred in the next few years after this discovery has been reviewed by Huo et al. [97].

X. MICELLAR CATALYSIS AND THE ENVIRONMENT

Concern for the well-being of the environment is expected to have a major impact on micellar catalysis in two directions: the remediation of pollutants and the switch to less toxic detergents. The little that has been done to date on either score in this field has been reviewed recently by Mackay [98]. In the first area, the dehydrochlorination of DDT in sulfobetaine micelles [99] and the micellar destruction in soils of neurotoxic phosphorus esters such as fenitrothion, a commonly used pesticide for the control of spruce budworm [100], have been investigated. The latter involves cationic surfactants which can effect nucleophilic displacements on the esters with rates as high as 5400-fold. In the second area, surfactant workers are turning their attention to natural surfactants [101] and to the benign, nonionic sugar surfactants, the alkyl glucopyranosides, and the maltosides in both their monomeric and polymeric forms [102], to determine their basic properties. As far as is known, no micellar catalysis studies have been reported with these “green” detergents.

XI. MICELLAR CATALYSIS IN REVERSE MICELLES

Increasing the nonpolar character of the medium causes micelles to do a flip-flop into a reverse micelle with the hydrophobic alkyl tails of the surfactant pointing outwards and the hydrophilic head groups inwards occupying “shore” positions on the enclosed water
pool. These reverse micelles or vesicles constitute along with the solvent a microemulsion of the self-explanatory *water-in-oil* (w/o) type. *Oil-in-water* (o/w) microemulsions have similarities to normal micelles in water. Clearly, the same conditions for catalysis based on Berezin’s ideas of preferential partitioning of the reactants into regions of the vesicle from the solvent pertain as they would for a normal micelle. Thus, kineticists were not slow in exploring microemulsions for possible dramatic catalytic effects on test reactions. An added incentive was that reverse micelles were one step closer than normal micelles to the liposomes or bilayer structures that are the form found in the natural membrane for the two-tailed surfactants, the phospholipids. Another advantage often exploited was the greater kinetic stability of the vesicle over the micelle. Friberg and Ahmad [103,104] are usually given credit for the first catalysis study in reverse micelles when they investigated the hydrolysis of *p*-nitrophenyl dodecanoate in aqueous hexanol solution with CTAB present. An early kinetic foray into microemulsions revealed that a $7.0 \times 10^4$-fold enhancement occurred in the thiolysis of *p*-nitrophenyl acetate by *N*-methylmercaptan in dialkyl(dimethylammonium) chloride vesicles [105]. Other studies were equally as promising [106–110].

Fletcher and Robinson [58] pointed out that the kinetic scheme was basically no different for w/o microemulsions than for regular micellar solution. They investigated kinetically the Ni$^{2+}$/PADA complexation reaction in the sodium bis-(2-ethylhexyl)sulfosuccinate (AOT)/*n*-heptane system where a 10-fold rate enhancement was observed with no change in the rate coefficients. The AOT system is frequently the microemulsion of choice for w/o systems because its properties have been well characterized for different ratios of water to oil.

Despite this sanguine start, catalysis in microemulsions has not developed to the same extent as catalysis in normal micellar solution with only about one paper in five in micellar catalysis each year involving reverse micelles. Half the reason is the complexity of the system, which does not lend itself easily to modeling and characterization even in the AOT system where much is known [111]. An in-depth survey of catalysis with reverse micelles will not be attempted here because with the many opportunities the various microemulsion systems offer for research possibilities the advancing front in knowledge is thinly spread both horizontally and vertically compared with the state of the art with simpler, normal micelles. A listing of representative papers in reverse micellar catalysis published recently reveals the types of investigations that are currently of interest in this field: Azevedo et al. [112] carried out kinetic and stability studies with penicillin acylase in reversed micelles; Lee and Cho [113] used a microemulsion to synthesize nanocrystalline PbS particles; enzymes were trapped and reacted within reverse micelles [114]; and nucleophilic aromatic substitutions were performed in reverse micelles [115]. Not surprisingly, biologically interesting reactions, especially involving enzymes, feature prominently in the list. Despite this present lack of focus and of sophistication in modeling, it is safe to predict that reverse micelles will continue to be actively explored as catalysts.

**XII. MICELLAR CATALYSIS TOMORROW**

Micelles in general as catalysts have a future not only in the practical side of chemistry, e.g., in effecting the rapid disintegration of environmental pollutants, but also in the theoretical sphere of the science by revealing intimate details of reaction mechanisms, micelle structures, and the dynamics at work within micelles. Next-generation models are required to replace the PIE model and its analogs. The use of more sophisticated
techniques and the resorting to a more thorough analysis of the data in micellar catalysis should see this development soon. Two interesting new developments are chemical trapping to elucidate the interfacial regions of micelles [116] and micellar autocatalysis [117].

A look at what can be done now and a hint at what soon will be routine is seen in the work of Woodward and Sakaguchi [118]. Hydrogen removal in benzophenones in micelles was examined by pulsed microwave irradiation. By a combination of single pulse and pulse shift measurements, all the kinetic parameters were obtained for the reaction in each micellar system, resulting in a global kinetic analysis. What emerged from this comprehensive scrutiny was a clarification of the micelle interior and a better understanding of the role the ketyl radical was playing in the recombination kinetics. Pulsed microwave is just one of the many new insightful approaches to micellar kinetics now possible. Another molecular information-rich technique that has seen little use to date in following micellar kinetics is NMR with all of its acronymic variants that in the hands of the experienced can reveal such intimate details of structure. As micelle kineticists become better versed in the investigative opportunities afforded by these and other new methods, it can be confidently predicted that great strides will be made in the understanding of the micelle itself as well as of the manner by which it affects reaction rates and mechanisms.

ACKNOWLEDGMENT

Financial support was provided by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES