Ion Binding and Reactivity at Charged Aqueous Interfaces[†]

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Received November 26, 1990 (Revised Manuscript Received October 7, 1991)

Introduction

In 1913, McBain postulated that in dilute aqueous solution fatty acid salts spontaneously form dynamic aggregates, now called micelles, Figure 1.[1] Aggregation occurs cooperatively[2] in solutions of natural and synthetic amphiphiles, usually called surfactants or detergents, with hydrocarbon chains attached to ionic or polar head groups, Scheme I. Dilute solutions of micellized single-chain surfactants are optically trans-

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Scheme I.
Representative Micelle-Forming Surfactants

Anionic

$$CH_3(CH_2)_nOSO_3^- \, M^+$$

$$CH_3(CH_2)_nSO_3^- \, M^+$$

$$CH_3(CH_2)_nCO_2^- \, M^+$$

$$M^+ = Li^+, Na^+, K^+, NMe_4^+, etc.$$

Cationic

$$CH_3(CH_2)_nN^+(CH_3)_3 \, X^-$$

$$CH_3(CH_2)_n^+N\bigcirc X^-$$

$$X^- = Cl^-, Br^-, OH^-, etc.$$

$$n = 8 - 18$$

parent, but scatter light.[2] Micelles and other association colloids act as "microreactors", compartmentalizing and concentrating or separating and diluting reactants and thereby altering, sometimes dramatically, apparent rate and equilibrium constants of chemical reactions.[3]

[†] Collective Fantasies in Soap Solution Kinetics (or It All Comes Out in the Wash).

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(2) (a) Physics of Amphiphiles: Micelles, Vesicles and Microemulsions; Degiorgio, V., Corti, M., Eds.; Elsevier: Amsterdam, 1985. (b) Fendler, J. H. Membrane Mimetic Chemistry; Wiley-Interscience: New York, 1982. (c) Fendler, J. H. Pure Appl. Chem. 1982, 54, 1809. (d) Lindman, B.; Wennerstrom, H. Top. Curr. Chem. 1980, 65, 45. (e) Tanford, C. The Hydrophobic Effect: Formation of Micelles and Biological Membranes, 2nd ed.; Wiley: New York, 1980. (f) Muller, N. Acc. Chem. Res. 1990, 23, 23.
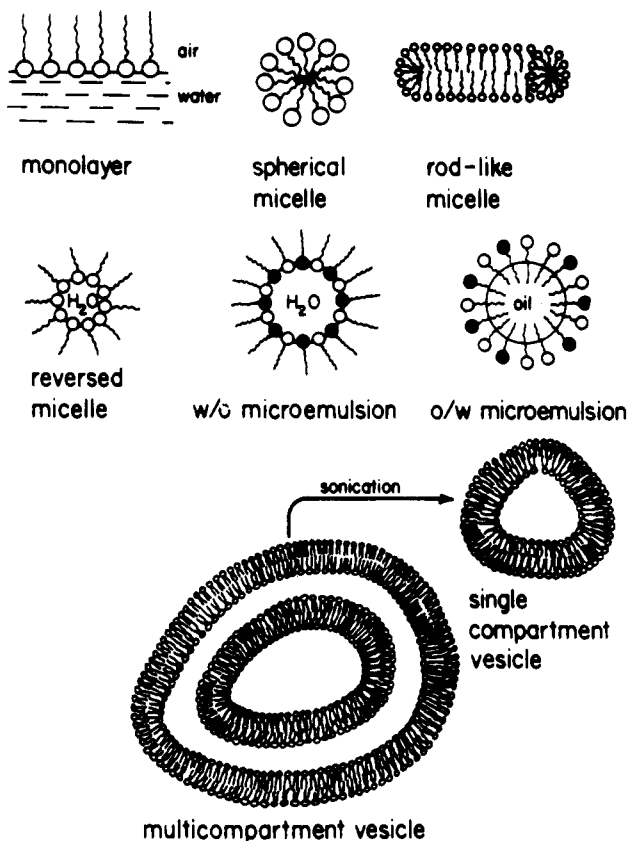
Figure 1. An oversimplified representation of some organized structures. Adapted from ref 2c with permission of the author and Pergamon Press, Ltd.

Spontaneous organization of amphiphiles in water creates dynamic aggregates that impart unique properties to the solution and whose varied forms, Figure 1, depend upon amphiphile structure and solution composition, but all have, as a common feature, interfacial regions separating the polar bulk aqueous phase from an apolar hydrocarbon-like region.[2] In micelles (Figure 2), monolayers, and vesicles, this region is formed by hydrophobic tails, and in microemulsions (and reversed micelles), it also contains added oil. Similar regions are formed by intramolecular aggregation of hydrophobic segments of amphiphilic polyelectrolytes.

The interfacial region or Stern layer, Figure 3, having a width about the size of the surfactant head group, contains the ionic head groups of the amphiphile, a fraction of the counterions (0.6–0.9/ionic head group), and water.[2,4,5] The Stern layer is an extremely anisotropic region with properties intermediate between those of water and hydrocarbon (alcohol-like is the common description of its polarity[2]). Thermal motion creates a diffuse electrical double layer, called the
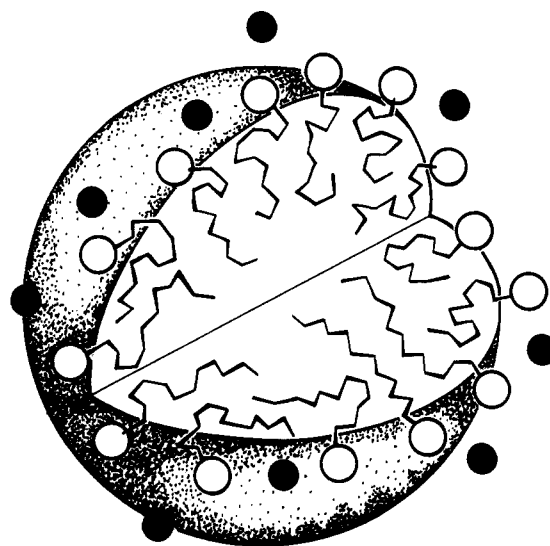
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Figure 2. Cartoon of a spherical cationic micelle adapted from a representation of an SDS micelle by Gruen.[4] Faces of the empty section show the core filled by flexible surfactant tails with a radius approximately equal to the extended length of the surfactant chain and surrounded by the Stern layer containing the head groups (O) and a fraction of the counterions (●). Micellar bound substrates and reactive ions react at this surface; see Figure 3.

Table I
Qualitative Micellar Rate Effects[a]

[a] CTAX = $C_{16}H_{33}N^+Me_3X^-$, X^- = Br^-, Cl^-, NO_3^-; SDS = $C_{12}H_{25}OSO_3^-Na^+$; Ar = p-nitrophenyl; Nuc⁻ = anionic nucleophiles, e.g., OH^-, imidazolide, benzimidazolide, RS^-, ArS^-, RO^-, ArO^-; + and – denote enhancement or inhibition, respectively.

Gouy–Chapman layer, which extends out into the aqueous phase and contains the remaining counterions.

For several decades, many workers have explored the varied and often pronounced effects of micelles, synthetic and natural vesicles, monolayers, microemulsions, and polyelectrolytes on a wide variety of ground- and excited-state reactions and equilibria.[3,6] Kinetic models were developed concurrently and provide good qualitative, and often quantitative, descriptions of many seemingly disparate observations. Here we describe the salient features of the pseudophase ion exchange, PIE,[3] and the Poisson–Boltzmann equation, PBE,[7] models, two distinct approaches for describing ionic distribu-

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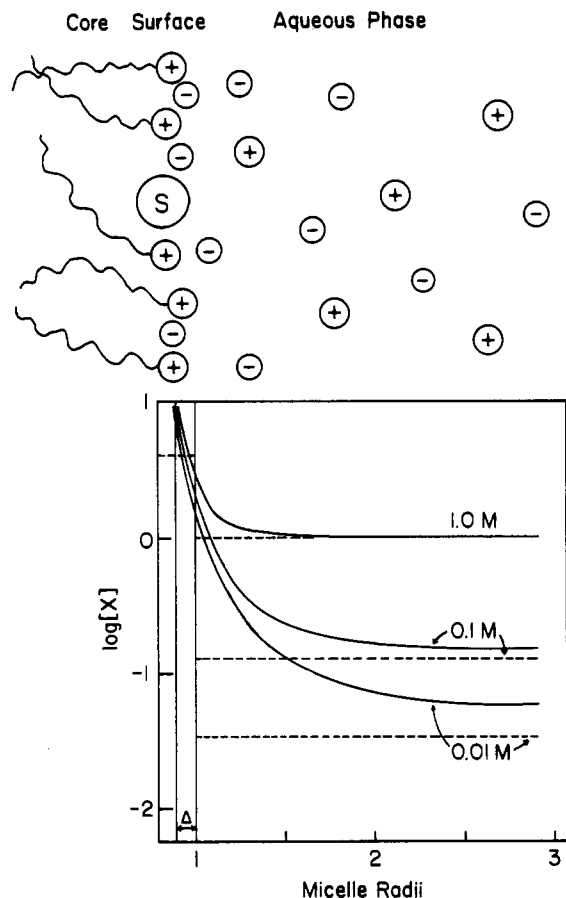
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Figure 3. Top: Cartoon illustrating locations of substrate, surfactant, co-ions, and counterions across a small cross section of a cationic micelle interface. Bottom: Illustration of the radial counterion distribution at three salt concentrations as described by solution of the PBE in spherical symmetry (solid lines) and by the PIE model assuming that $\beta = 0.75$, cmc = 0, and interfacial counterion concentration = 4 M (broken lines). $\Delta = 2.4$ Å, a typical assumed width of the reaction region in the PBE model.[7e]

tions at charged aqueous interfaces. Effects of ionic micelles on slow, thermal bimolecular reactions between organic substrates and counterions are used to illustrate some of the commonly observed rate profiles, the strengths and weaknesses of the PIE model, and how the PBE model overcomes some of these weaknesses. Applications to spontaneous and co-ion reactions, to equilibria, and to reactivity in other types of association colloids are briefly discussed.

Micellar Effects on Bimolecular Reactions

Many of the reactions studied in micellar solutions have "well-understood" mechanisms in homogeneous solution.[3] A few examples are shown in Table I. Reactions are generally monitored spectrophotometrically under first-order conditions. Typically a reaction solution contains surfactant; substrate, S (ca. 10^{-5} M); excess second reactant, N ([N] $\geq$ 10[S]); and sometimes salt. The observed rate is given by

$$\text{rate} = k_{\text{obsd}}[S_T] = k_2[S_T][N_T] \tag{1}$$

where subscript T denotes the total or stoichiometric concentration, [ ] concentration in moles/liter of solution, k_{obsd} the observed first-order rate constant, and k_2 the apparent second-order rate constant. Alternatively, when N is OH⁻ or H_3O^+, buffers can be used to "control" [N] (see below).

Addition of sufficient ionic surfactant, at constant [N_T], creates micelles and often produces dramatic changes in k_{obsd} (and k_2). Profiles of k_{obsd} versus surfactant concentration are generally multiphasic well below 0.1 M surfactant with maxima or minima in k_{obsd} which differ from k_{obsd} in water by factors up to several orders of magnitude. Added salts have marked effects on rates of bimolecular reactions in micellar solutions, well beyond typical salt effects in water. Nevertheless, rate profiles for a wide variety of bimolecular reactions show characteristic patterns which depend upon substrate charge and hydrophobicity, surfactant head group charge and chain length, and counterion concentration and type. It is these patterns which we attempt to simulate.

Menger and Portnoy[8] proposed the first kinetic model which treated micelles as enzyme-like particles and successfully fitted inhibited bimolecular reactions. This model also fitted spontaneous reactions,[3a,e–g] but could not simulate the rate maxima characteristic of micellar-enhanced bimolecular reactions. Berezin and co-workers developed the first general treatment based on the pseudophase model and successfully simulated spontaneous and bimolecular reactions between neutral organic reactants.[3a,9] We modified the pseudophase model to simulate bimolecular, ion–molecule, reactions.[3b–f]

The major problem is modeling interfacial concentrations and distributions of ionic reactants, although in favorable cases they can be measured directly.[3b,d–f] The micellar surface is a dynamic ensemble (Figures 2 and 3) which interacts with ions coulombically and specifically, as shown by specific counterion effects on micellar properties.[2,3] Coulombic interactions depend upon micellar surface charge density and ionic valency, whereas specific interactions are largest for low charge density, polarizable ions. As with other ion-selective surfaces, specificity is a balance of hydration and ion-head group interactions.[10,11] NMR results suggest that simple univalent counterions are hydrated at the micelle surface, although their solvent shells may be disrupted.[12] The concentration of counterions in the reaction region depends on ionic strength, although calculations show that counterion concentration near the surface is not very sensitive to salt concentration[2d,7e] (Figure 3). Estimating interfacial compositions is more complex under typical kinetic conditions because the solutions contain mixtures of counterions.

We model ion distributions in two ways. In the PIE model, micellar surfaces are treated as selective ion exchangers saturated with counterions.[3] In the PBE model, ion distributions are computed within a reaction region at the micelle surface by using the Poisson–Boltzmann equation modified for specific ion interactions.[7] Simulations of kinetic data typically require complex, second-order and sometimes higher order

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(11) Micelles probably form only when specific interactions are weak and head groups and counterions are hydrated. Strong specific interactions, which increase the crystal lattice energy, make surfactants water insoluble, e.g., the infamous soap scum formed by fatty acid salts in hard water.

(12) Lindman, B.; Soderman, O.; Wennerstrom, H. In *Surfactant Solutions: New Methods of Investigation*; Zana, R., Ed.; Marcel Dekker: New York, 1987; p 295.

Scheme II

$$S_w \rightleftharpoons S_m$$

$$+ \qquad +$$

Aqueous $N_w \rightleftharpoons N_m$ Micellar

Pseudophase   Pseudophase

          $\downarrow k_2^w$ $\downarrow k_2^m$

      Products   Products
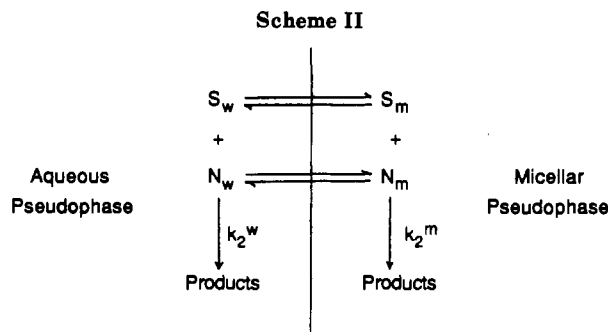
equations. However, simple "back of the envelope" calculations often give good estimates of k_{obsd}[3f] because much of the complexity is in the algebra and the unfortunate variety of formalisms created by different research groups (including our own). Our focus here is on basic concepts.

Pseudophase Treatment of Bimolecular Reactions

Two basic assumptions are common to all pseudophase kinetic models: (a) micelles act as a separate phase from water; and (b) changes in k_{obsd} (and k_2) due to added surfactant and salt depend largely upon the distribution of S and N between micelles and bulk water.

Micelle formation is a highly cooperative phenomenon. When the surfactant concentration exceeds the critical micelle concentration (cmc), all additional surfactant forms micelles. In dilute solution, ionic micelles are approximately spherical (Figure 2), with aggregation numbers ranging from ca. 50 to 150,[2] but at higher surfactant concentration or with added salt, they may grow into flexible ellipsoids or rods. Both the cmc and growth depend upon surfactant chain length, head-group structure and charge, counterion type and concentration, and organic additives. Nevertheless, many surfactant properties such as conductivity, solubilization, and effects on chemical reactivity are insensitive to changes in micelle size and shape and depend primarily on the concentration of micellized surfactant, $[D_n]$:[2,3]

$$[D_n] = [D_T] - cmc \qquad (2)$$

where $[D_T]$ is the stoichiometric surfactant (detergent) concentration and the cmc is that obtained under experimental reaction conditions. Often $[D_T] \gg$ cmc and the cmc can be neglected.

Surfactant monomer, organic molecules, and ions associate with micelles at nearly diffusion controlled rates, and they exit at a rate, governed by the strength of binding,[13] that is generally much faster than those of most thermal reactions. Thus micellized surfactant is at thermal equilibrium with solutes throughout the reaction, and observed rates can be treated as the sum of rates of concurrent reactions in each pseudophase, Scheme II, where subscripts m and w indicate micellar and aqueous pseudophases, respectively, and k_2^w and k_2^m are second-order rate constants.

Micellar binding of an organic substrate, S, is governed by both coulombic and hydrophobic interac-

tions[2,3,14] and is generally described by a binding constant, K_s:[8,14]

$$K_s = \frac{[S_m]}{[S_w][D_n]} \qquad (3)$$

Values for K_s can usually be estimated, in the absence of N, by spectroscopy, solubility, liquid chromatography, or ultrafiltration,[14,15] and they increase with increasing substrate hydrophobicity (e.g., in Table I, with the length of the alkyl chain, R, of the substrate). Spectroscopic methods show that bound polar substrates are located at the micellar surface and not in the hydrophobic core.

Combining the rate expression for k_{obsd} based on Scheme II with eq 3 gives

$$k_{obsd} = \frac{k_2^w[N_w] + k_2^m K_s N_m[D_n]}{1 + K_s[D_n]} \qquad (4)$$

The term N_m in eq 4 is the local, molar concentration of the ionic reactant within the micellar pseudophase:

$$N_m = \frac{[N_m]}{[D_n]V_m} \qquad (5)$$

where V_m is the molar volume in liters/mole of reactive region and $[D_n]V_m$ denotes the micellar fractional volume in which the reaction occurs. Concentrations of ions and molecules in the aqueous phase are generally expressed in units of moles/liter of total solution volume because the micellar pseudophase volume seldom exceeds 3% (for about 0.1 M surfactant) of the total solution volume.

Equation 4 shows that the relative proportions of the overall reaction occurring in the aqueous and micellar pseudophases depend on both $[D_n]$ and K_s. Equation 5 illustrates a fundamental property of all pseudophase models, that reaction rate within the micellar pseudophase depends upon the *local* concentration of N within the micellar pseudophase and *not* its stoichiometric concentration. The local interfacial counterion concentration is estimated to be about 3–5 M by PBE calculations[7e] and from simple micellar models[3b] (Figure 3), which is orders of magnitude greater than the corresponding stoichiometric concentration. Conversely, interfacial co-ion concentrations are orders of magnitude lower than their stoichiometric concentrations.[7e,25]

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(15) Equation 3 is strictly valid only for dilute, nonionic substrates. K_s is not a thermodynamic constant, and added salts sometimes increase it modestly, probably by "salting out" the substrate into micelles.[16]

(16) Romsted, L. S. *J. Phys. Chem.* 1985, 89, 5113.

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(25) Quina, F. H.; Politi, J.; Cuccovia, I. M.; Martins-Franchetti, S. M.; Chaimovich, H. In *Solution Behavior of Surfactants: Theoretical and Applied Aspects*; Mittal, K. L., Fendler, E. J., Eds.; Plenum Press: New York, 1982; Vol. 2, p 1125.

Much of the effect of micelles and other association colloids on k_{obsd} of bimolecular reactions is caused by compartmentalization of reactants within each pseudophase. When N is a counterion to ionic micelles, binding S brings it into a microenvironment, i.e., the "microreactor", having a high local concentration of N, which increases k_{obsd}. When N is a co-ion, binding S brings it into a microenvironment with a much lower concentration of N, which reduces k_{obsd}.

Two assumptions are made in the PIE model in estimating $[N_m]$ in eq 5.[3b-f] (a) The micellar surface acts as a selective ion exchanger, and competition between inert counterions, X, and reactive counterions, N, is given by

$$K_N^X = \frac{[N_w][X_m]}{[N_m][X_w]} \tag{6}$$

(b) The fraction of the surface occupied by the two counterions is assumed to be constant and given by the degree of counterion binding, β:

$$\beta = \frac{[N_m] + [X_m]}{[D_n]} \tag{7}$$

Experimental estimates of β, usually from the fractional micellar charge α ($\alpha = 1 - \beta$), are in the range $\beta = 0.6–0.9$ for a variety of counterions and head groups and are usually insensitive to surfactant and salt concentration, indicating significant specific interactions at the micelle surface.[2d,3] However, β for very hydrophilic counterions, e.g., for binding of OH⁻ and F⁻ to cationic micelles,[3e,f,7,18] appears to increase significantly, with their total concentrations indicating that they interact primarily coulombically and that a substantial fraction of these ions are in the diffuse double layer. Equation 7 fits the data, however, when nonreactive counterions that bind strongly, e.g., Br⁻, are in excess over reactive counterions, e.g., OH⁻, and thus control the value of β.

The key parameter in the PIE model is the ion-exchange constant.[3b-f,19] Ionic competition at the micellar surface is governed by differences in the specific interactions of two counterions, and coulombic effects are assumed to cancel.[20,21] Values of K_N^X for a variety of counterions are similar to those of loosely cross-linked ion-exchange resins[3b-f] and generally follow a Hofmeister series, i.e., large, weakly hydrated, polarizable anions displace hydrophilic anions. Values of K_N^X have been estimated from rate and equilibrium data, spectrally, by ultrafiltration, and electrochemically.[3d,19] The PIE model works with univalent ions because activity coefficient ratios essentially cancel for similarly charged ions (eq 6), except at high electrolyte concentrations. Exchange between uni- and bivalent anions can be successfully treated if effects on the cmc and activity coefficients are included.[19]

Successful Applications of the PIE Model

We and others have combined eqs 4–7 with mass balance equations in various forms to simulate micellar effects on a variety of reactions at moderate surfactant (<0.1 M) and salt (<0.4 M) concentrations.[3b-f,19,21] Independent estimates or reasonable values are used for the parameters k_2^w, β, K_s, K_N^X, and the cmc. We assume that the term k_2^m/V_m (obtained by combining eqs 4 and 5) is constant and select its value from the best
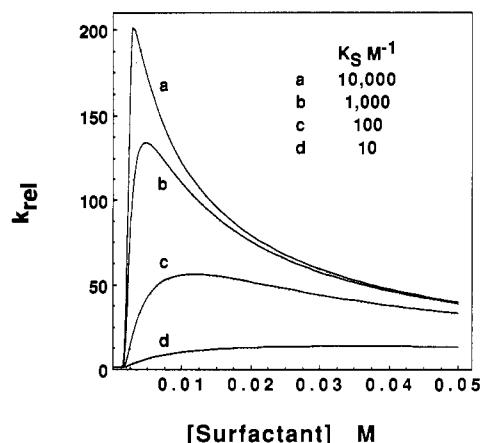

Figure 4. Effect of increasing substrate hydrophobicity on k_{rel} as a function of surfactant concentration. Parameter values are cmc = 0.002 M, $[N_T]$ = 0.01 M, K_N^X = 4, k_2^m/k_2^w = 1.0, β = 0.7, and V_m = 0.15 M⁻¹. K_s values are listed in the figure.
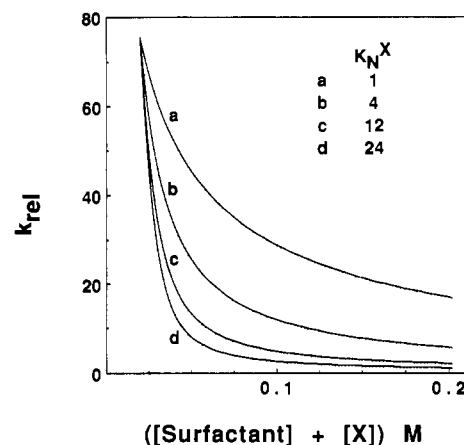

Figure 5. Specific salt effects on k_{rel} as a function of added NaX, [X], for typical K_N^X values (see figure), at surfactant concentration = 0.02 M and K_s = 1000 M⁻¹. Other parameters are as in Figure 3. Surfactant and salt have the same counterion in curve b.

fit of the data over a range of experimental conditions. We estimate k_2^m by assuming that V_m is equal to the volume of the micelle[3c] (e.g., V_m = 0.37 M⁻¹) or of the Stern layer[3d-f] (e.g., V_m = 0.14 M⁻¹). On this basis, values of k_2^m differ by no more than factors of 2–3. Estimated values of k_2^m for different types of reactions are generally close to or somewhat smaller than k_2^w, consistent with reaction at a water-rich micellar surface.[3c-f] However, this generalization may reflect the types of bimolecular reactions chosen for study, e.g., Table I, which are not very sensitive to solvent polarity. Some unimolecular reactions, whose reaction rates depend strongly on solvent polarity, have very different rate constants in micelles and water.[3e,f]

Figures 4 and 5 are theoretical plots based on eqs 3–7 and mass balance equations which illustrate the basic features of rate–surfactant concentration profiles. To focus attention on the concentration effect, we plot the observed rate constant relative to that in water, k_{rel} = $k_{obsd}/k_2^w[N_T]$, with k_2^m = k_2^w, and use typical values of the other parameters (see figure captions).

Figure 4 also illustrates the effect of increasing substrate hydrophobicity.[3a,b,21] For K_s = 100, the rate maximum is at ca. 0.01 M surfactant, where S is ca. 47% bound. The rate maximum does not indicate complete substrate binding, but is the crossover point
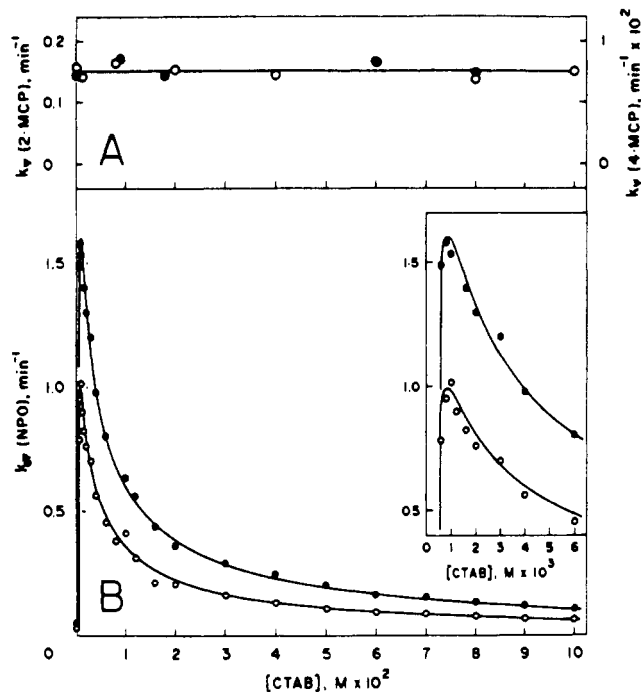
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Figure 6. Effect of CTABr on the observed first-order rate constants, k_ψ, for alkaline hydrolysis reactions of MCP and NPO in the presence of 0.02 M borate buffer: (A) 2-MCP at pH 9.50 (O) and 4-MCP at pH 9.80 (●); (B) NPO at pH 9.5 (O) and pH 9.8 (●). Inset shows data at low [CTABr]. Solid lines are calculated using the PIE model, β = constant. Reprinted with permission from ref 21b. Copyright 1980 American Chemical Society.

between a concomitant rate increase caused by transfer of S from water into the micelles (eq 4) and a rate decrease caused by dilution of N with added surfactant (eq 5). When $k_2^m < k_2^w$, the model predicts that this dilution effect makes the overall reaction at high surfactant concentration slower than in water, giving net inhibition.[22]

Figure 5 illustrates the typical marked inhibition caused by added salts at constant surfactant concentration.[3b-f,21] Added X displaces N with the selectivity given by K_N^X (eq 6).

The PIE model,[3b-f] initially restricted to unbuffered solutions, was later extended to buffered systems.[21] Rate profiles for alkaline reactions of N-methyl-2- and -4-cyanopyridinium ions, 2- and 4-MCP, respectively (Table I, **3**, R = CH₃), and p-nitrophenyl octanoate, NPO (Table I, **1**, R = C₇H₁₅), in CTABr and borate buffer, Figure 6, illustrate both buffer effects and a typical simulation using the PIE model.[21b] The very hydrophilic MCP ions remain in the aqueous pseudophase, where pH is buffer controlled and reaction rate is unaffected by added surfactant. In contrast, NPO partitions strongly into micelles, $K_s \sim 15\,000$ M^{-1} (eq 3), and is more than 99% bound at ca. 0.01 M CTABr. The similarity of the biphasic rate profiles for NPO in Figure 6 to those in unbuffered solutions shows that buffers do not hold the micellar surface pH constant as surfactant concentration is varied.

Other Applications of the PIE Model

The PIE model fits micellar effects on indicator equilibria;[16,23] reactions of ionizable nucleophiles in functional, mixed micelles and vesicles;[3e] reactions in microemulsions;[24] and reactions with co-ions[25,26] and in

polyelectrolytes.[27] Systems with marked differences in reactivity are briefly discussed.

Cationic micelles induce large rate enhancements (10^3–10^6-fold) in reactions of organic substrates with nucleophiles that are anions of weak acids such as phenols, thiols, or oximes.[3c,e,f] Weakly acidic functional groups such as imidazoles,[9] iodosoarenoic acids,[28] copper complexes,[29,30] thiols, oximes, and hydroxamic acids have also been attached directly to surfactant head groups[3e] or comicellized with inert surfactant.[31] The large rate enhancements are produced by high local anionic nucleophile concentrations generated by strong binding of the organic acids and their enhanced deprotonation by high local OH⁻ concentrations at cationic micellar surfaces.[3c,f,21,31] A striking example is the ca. 10^6-fold enhancement of the rate of thiolysis of NPO in assemblies of a twin-tail cationic surfactant, which is in the range of rate enhancements produced by enzymes; nonetheless, simulations with the PIE model show that k_2^m is only about 5 times greater than k_2^w.[32]

Structures of microemulsions, Figure 1, depend upon solution composition.[33] Oil-in-water, o/w, microemulsions behave like alcohol-modified micelles, but their structures often pass through bicontinuous phases to water-in-oil, w/o, microemulsions with additional oil. General treatments of rates in microemulsions assume that reaction can occur in the aqueous, interfacial, or oil regions.[24,34] The concept of constant β cannot be applied because cosurfactant, e.g., an alcohol, affects counterion binding. However, rates of bimolecular reactions have been treated quantitatively in alcohol-modified micelles[35] and in microemulsions[24] by estimating the amount of ionic reagent at the surface independently, e.g., by conductivity.

Reactions of organic substrates with hydrophilic co-ions are generally inhibited by micelles because the substrate is bound and the co-ion is repelled, but for fully bound substrates, added surfactant and salt increase the rate.[7e,25,26] A Donnan equilibrium, instead of ion exchange, is used to describe specific counterion effects on reactions of hydrophilic co-ions such as OH⁻ in anionic micelles[25] and H₃O⁺-catalyzed reactions in cationic micelles.[26]

Weaknesses of the Original PIE Model

Pseudophase treatments sometimes fail near the cmc because solutes may interact with surfactant monomers

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or premicelles, or induce micellization.[3d] This refractory problem is recognized by a discrepancy between the cmc estimated kinetically and by direct measurement under similar conditions.

A major weakness of the original PIE model is the assumption of constant β. This implies that the concentration of ionic reactant at the surface of micelles of a "reactive counterion" surfactant should be constant because eq 7 simplifies to $\beta = [N_m]/[D_n]$. Substitution of this relation into eqs 4 and 5 predicts that k_{obsd} will reach a plateau when substrate is fully micellar bound and will be unaffected by added reactive ion. This prediction is satisfactory for reactions of dilute Br^-, Cl^-, or CN^- in cationic micelles and for H_3O^+ in alkane- and alkoxyarenesulfonates,[3e] but not in alkyl sulfate micelles.[36] For reactions of very hydrophilic anions, e.g., OH^-, F^-, $CH_3CO_2^-$, and HCO_2^-, rate constants increase strongly with increasing $[D_n]$ and on addition of reactive anions. Even rate constants of reactions of Cl^- and Br^- increase, albeit slowly, on addition of reactive ion,[37] suggesting that their concentrations at micellar surfaces are increasing.[3f]

Two approaches have been used to simulate these data. Values of β estimated conductimetrically[18] show that β increases with increasing [CTAOH] and [CTAF]. Another approach describes the increasing fraction of bound counterions in terms of a Langmuir isotherm and uses a binding constant similar in form to that of eq 3 to simulate counterion distribution. A numerically small binding constant fits kinetic data with increasing [CTAOH] and at high added OH^-.[3e] The treatment has been applied to various counterions and to mixtures of counterions,[38] as well as to changes in Cl^- and Br^- NMR line widths.[37,39] Hydrophilic counterions have small binding constants, so that β is never constant, whereas less hydrophilic counterions, e.g., Br^-, have large binding constants, so the micellar surface becomes saturated with counterions at low surfactant concentration, and β is approximately constant. Counterion binding constants for anions follow a Hofmeister series, and their ratios are similar to ion-exchange constants (eq 6).

An Alternative Analysis of Ion–Micelle Interactions

Coulombic interactions with cylindrical or spherical micelles can be estimated by solving the PBE in the appropriate symmetry by numerical integration with allowance for coulombic and specific interactions. This approach has been applied to micellar rate effects on reactions of both counterions and co-ions.[7] Reactions are assumed to occur in a surface region of defined thickness Δ (Figure 3), and solution of the PBE gives the concentration of ions (N_m in eq 5) in this region. Interfacial ionic concentrations depend on total concentrations of ions and surfactant, micellar radius and aggregation number, and a specific binding parameter, which is large for low charge density, polarizable ions, but is small or 0 for hydrophilic ions such as OH^- and

F^-. Calculated second-order rate constants, k_2^m, are insensitive to surfactant and salt concentration, and ratios of specific ion binding parameters are numerically similar to ion-exchange constants (eq 6). Values of k_2^m for counterion reactions increase only slightly as Δ is increased, e.g., from 2.4 to 3 Å, probably because the PBE predicts that counterion concentrations at micellar surfaces are high and fall sharply with distance, as shown for coulombic interactions in Figure 3.

Co-ion concentration is also sensitive to distance from the micellar surface and has a small, finite value within the reaction region, Δ. Application of the PBE to reactions of OH^- as a co-ion with p-nitrophenyl alkanoates (Table I, 1) and p-nitrophenyl diphenylphosphinate in SDS shows that this approach fits the dependence of rate constants upon concentrations of SDS, OH^-, and added salts, and it has been adapted to include specific ion–micelle interactions.[7e] The model also fits effects of cationic surfactants and specific anion effects on the co-ion (H_3O^+) catalyzed hydrolysis of dioxolanes (Table I, 4).[40]

Despite differences in basic assumptions, the PIE and PBE models lead to similar conclusions for micellar effects on bimolecular reactions, and calculated values of k_2^m are similar.[7] Both models also satisfactorily treat reactions of uni- and bivalent counterions. Unlike the PIE model, the PBE predicts a rate dependence upon micellar radius, aggregation number, and shape, e.g., on the sphere-to-rod transition.

Perspectives and Guidelines for Future Work

Pseudophase treatments of reactivity in association colloids provide a chemically satisfying approach with predictive power. Estimation of the distribution of reactants factors out the contribution of transfer free energies to overall reaction free energies and shows that medium effects of micellar microreactors on reactions of polar organic molecules and ions are generally similar to those of water.[41]

The PIE model treats effects of charged interfaces on rate and equilibrium constants in micelles and other association colloids without explicit consideration of such factors as size, shape, surface dynamics or curvature, aggregate interactions, and the relative significance of coulombic and specific interactions. The PIE formalism, like the PBE, postulates an equilibrium distribution of reactants and no interaction with surfactant monomer. It works best at moderate concentrations of amphiphile and salt and when the dominant counterion at the micelle surface is not very hydrophilic.

The PBE model succeeds under some of the conditions where the simple PIE model, with constant β, has problems, and its predictions of growth effects on reactivity are being explored. It is computationally more demanding, although not excessively so because of the availability of inexpensive microcomputers.

Further progress depends not only upon the development of better kinetic models but also on increasing our understanding of colloidal structure and of ionic interactions with association colloids composed of ionic,

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nonionic, zwitterionic, and amphoteric surfactants and their mixtures, which are more typical of biological membranes and commercial applications.

Ion–Neutral Complexes

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An ion–neutral complex (INC) consists of an incipient ion coordinated to a putative neutral. The two components of the INC are not connected by a normal covalent bond, but they remain bound together by ionic forces such as ion–dipole attraction. INCs are significant because their charged and neutral components are sufficiently separated that they show reactivities similar to those expected for the isolated species. In particular, the components are able to rotate with respect to one another, thus permitting the occurrence of reactions which would be geometrically impossible if the partners were joined by a covalent bond. Consequently, the chemistry of the species within the INC becomes manifest at energies below those needed to cause complete separation to products. One component of the INC may react individually (e.g., an incipient cation may isomerize); alternatively, the ionic and neutral species may react with each other (e.g., by hydrogen transfer).

INCs are potentially relevant in all forms of science in which ions react in dynamic environments. For instance, the behavior of charged species, especially the rearrangement of carbocations, is a central theme of organic chemistry. The ion in an INC occupies a position intermediate between that of the "bare" (unsolvated) ion and that of the corresponding species in solution. Therefore, analysis of the reactions of INCs should reveal the effects induced by a single solvent molecule (the coordinated neutral) on the intrinsic chemistry of the ion. Thus, the archetypal cation isomerization, $CH_3CH_2CH_2^+ \rightarrow (CH_3)_2CH^+$, can be investigated. Furthermore, the influence of the solvent molecule on the rearrangement may be studied by generating INCs containing a variety of different neutral components attached to the $C_3H_7^+$ cation.

The idea that INCs might be important in the unimolecular reactions of ions was developed independently in several laboratories.[1–4] We first postulated INCs to understand the unusual reactivity of certain metastable ions. Metastable ions dissociate after being partly transmitted through the mass spectrometer. Consequently, they are long-lived species, having lifetimes of typically 10–100 μs, and their reactions usually take place with excess energies in the transition states that are small and comparable to those found in solution experiments.[5] Analysis of the fragmentation of metastable ions offers an almost ideal method of investigating the chemistry of ions.[6] Thus, the $C_4H_9O^+$ oxonium ions 1 and 2 (Scheme I) undergo the same reactions (~85% H_2O loss and ~15% CH_2O expulsion) with the same kinetic energy releases. It is not possible to explain this phenomenon by mechanisms involving only "conventional" intermediates (i.e., those in which the connectivity of atoms is adequately described solely in terms of covalent bonds and the normal rules of valency apply). However, the identical behavior of 1 and 2 was logically explained by supposing that these ions interconvert via the INCs 1a and 2a, prior to fragmentation.[1,2,7] Equilibration of 1a and 2a corresponds to a 1,2-hydride shift in the incipient propyl cation. Since such shifts are known to be extremely facile, both in solution and in the absence of solvent, we considered that interconversion of 1a and 2a via this route was a reasonable hypothesis. Subsequent elaboration of the mechanism rationalized the chemistry of 1 and 2 in detail.[2a] Moreover, parallel mechanisms could be used to explain the reactivity of many other ions of diverse structure and functionality.[2b,8]

A further refinement of this general mechanism is the suggestion that 1a represents the transition state for

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