

## Modeling Chemical Reactivity in Ionic Detergent Micelles: a Review of Fundamentals

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Ionic detergent micelles have the capacity to solubilize organic substrates, interact selectively with counterions, repel coions, exhibit partial “dissociation” of the counterions, grow in size with added salt, affect the position of chemical equilibria, accelerate or inhibit the rates of chemical reactions, modulate photochemical reactivity and determine the dynamics of diffusion or near-diffusion controlled processes. Many of these phenomena can be understood and analyzed quantitatively in terms of relatively simple models for binding, selectivity and electrostatics that often require no knowledge of micellar structure or dynamics (the pseudophase limit), without compromising chemical intuition. An overview is provided of our current understanding of the interplay between micellar structure and electrostatics, selectivity, solubilization, and reactivity and their role in the development of quantitative formalisms for analyzing micellar effects on reactivity and equilibria.

**Keywords:** micelles, pseudophase ion exchange, electrostatics, reactivity, equilibria

### 1. Introduction

In the mid-1970s, micellar catalysis was still viewed as a model for enzymatic catalysis and several attempts had been made to analyze and understand micellar effects on reaction rates. Notable among these were the enzyme-like substrate-binding model of Menger and Portnoy<sup>1</sup> and the model of Berezin and collaborators,<sup>2</sup> both of which were (as it later turned out) more adequate for uni- and bimolecular reactions of non-ionic species in non-ionic micelles. Micellar effects on indicator equilibria were known in the literature and attributed to interaction of the charged forms of the indicator with the oppositely charged surface. These precursor works have been reviewed,<sup>3,4</sup> including in the context of their relationship to pseudophase ion exchange (PPIE).<sup>5</sup> The present paper will outline the development of PPIE and our increased understanding of ionic interactions in micellar systems over the last 4 decades.

### 2. Micellization and the Critical Micelle Concentration (CMC)

Our starting point is the classical pseudophase treatment of the phenomenon of micellization.<sup>3</sup> The pseudophase

model for micellization treats the formation of micelles as if it were a “charged-phase”-separation at the critical micelle concentration (CMC) rather than a stepwise aggregation of monomers to form the micelles. If the micellization of an ionic detergent DY involves the association of an average number  $N_{ag}$  of monovalent detergent monomers (of concentration  $[m]_{aq}$ ) with  $\beta$  monovalent counterions of type Y (present in concentration  $[Y]_{aq}$ ) in the aqueous phase to form the micelles, M:



the corresponding equilibrium relation can be written as:

$$K_{CMC} = [M]^{1/N_{ag}} / ([m]_{aq} [Y]_{aq}^{\beta}) \sim 1 / ([m]_{aq} [Y]_{aq}^{\beta}) \quad (2)$$

The basic reason that this pseudophase description of micellization works as well as it does, despite the fact that the micelles are actually aggregates dispersed in the solution, is that micellization is typically highly cooperative, occurring over a very small concentration range, and micelle aggregation numbers,  $N_{ag}$ , are of the order of ca. 100. Thus, for typical CMC values of  $10^{-2}$ - $10^{-3}$  mol L<sup>-1</sup> and  $N_{ag}$  of ca. 70-150, the value of  $[M]^{1/N_{ag}}$  approaches unity and reduces the right-hand side of this equation to the “charged-phase”-separation equilibrium expression.

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At the CMC,  $[Y]_{\text{aq}}$  is equal to the CMC plus the concentration of added common counterion salt, i.e.,  $[Y]_{\text{aq}} = \text{CMC} + [Y]_{\text{ad}}$ . The value of the constant  $K_{\text{CMC}}$  can be calculated from  $\text{CMC}_0$ , the value of the CMC in the absence of added salt:

$$\log K_{\text{CMC}} = (1 + \beta) \log \text{CMC}_0 \quad (3)$$

This leads directly to the classic Corrin-Harkins relation for the decrease of the CMC with added common-counterion salt:

$$\log \text{CMC} = \log K_{\text{CMC}} - \beta \log [Y]_{\text{aq}} = (1 + \beta) \log \text{CMC}_0 - \beta \log (\text{CMC} + [Y]_{\text{ad}}) \quad (4)$$

Values of  $\beta$  are often in the range of  $0.7 \pm 0.1$ , similar in magnitude to values of  $1 - \alpha$ , where  $\alpha$  is the apparent degree of counterion dissociation from the micelle (as is in fact implicit in the definition of  $\beta$  above). In these and all subsequent equations, we have assumed the equivalence of concentrations and activities for convenience.

In principle, the same relationship should also allow the estimation of the free or non-micellized detergent monomer concentration  $[m]_{\text{aq}}$  in the intermicellar aqueous phase above the CMC by simply replacing CMC by  $[m]_{\text{aq}}$  and taking into account the additional counterions in the aqueous phase due to the partial dissociation of the micelles:

$$\log [m]_{\text{aq}} = (1 + \beta) \log \text{CMC}_0 - \beta \log \{ [m]_{\text{aq}} + \alpha (C_{\text{T}} - [m]_{\text{aq}}) + [Y]_{\text{ad}} \} \quad (5)$$

where  $C_{\text{T}}$  is the total concentration of added surfactant monomers, of which  $C_{\text{T}} - [m]_{\text{aq}}$  are micellized. Equation 5 predicts that the free monomer concentration of an ionic detergent will reach its maximum concentration at the CMC and then decrease as the detergent concentration is increased above the CMC. What is constant above the CMC is not  $[m]_{\text{aq}}$ , but rather the product  $[m]_{\text{aq}} [Y]_{\text{aq}}^{\beta}$ , the square root of which (for a monovalent detergent DY) is the mean ionic activity of the detergent in the intermicellar aqueous phase.

The confirmation of this predicted behavior for the free monomer concentration of sodium dodecyl sulfate (SDS) using a dodecylsulfate ion-selective electrode<sup>6</sup> led us to attempt to measure  $[m]_{\text{aq}}$  of *N*-hexadecylpyridinium chloride (HPCI) above the CMC using fluorescence quenching. Thus, we chose the water-soluble cationic fluorescence probe, 9-(3-(*N,N,N*-trimethylammonium) propyl)-anthracene (TMPA<sup>+</sup>), the fluorescence of which is efficiently quenched by pyridinium ions. Although we had

naively expected the probe to remain in the intermicellar aqueous phase, we soon realized that, because it was also an amphiphilic molecule, it could be partially incorporated into the quencher micelles. Indeed, the fluorescence quenching obeyed the Stern-Volmer equation for mixed static-dynamic quenching, the static component being due to the incorporation of the probe into the HPCI micelles:

$$\frac{\Phi_f^0/\tau_f^0}{\Phi_f/\tau_f} = (1 + K_{\text{SV}}[m]_{\text{aq}}) \{ 1 + K_{\text{S}}(C_{\text{T}} - [m]_{\text{aq}}) \} = (\tau_f^0/\tau_f) \{ 1 + K_{\text{S}}(C_{\text{T}} - [m]_{\text{aq}}) \} \quad (6)$$

In this equation,  $\Phi_f^0(\tau_f^0)$  and  $\Phi_f(\tau_f)$  are the fluorescence quantum yields (lifetimes) of the probe in the absence and presence of HP<sup>+</sup>,  $K_{\text{SV}}$  is the Stern-Volmer constant for quenching of the probe in the intermicellar aqueous phase by the non-micellized HP<sup>+</sup> monomers, and  $K_{\text{S}}$  is the equilibrium constant for incorporation of the probe into the micelles. In the micelles, the probe is non-fluorescent because it is totally quenched by the high local concentration of HP<sup>+</sup>. On the other hand, the fluorescence lifetime ratio depended on the dynamic quenching of the probe by HP<sup>+</sup> monomer free in the aqueous phase, i.e.,  $\tau_f^0/\tau_f = (1 + K_{\text{SV}}[m]_{\text{aq}})$ . Because  $K_{\text{SV}}$  could be determined from the quenching behavior below the CMC, the fluorescence lifetime ratio then permitted estimation of  $[m]_{\text{aq}}$  above the CMC as a function of detergent concentration as initially planned.<sup>7</sup>

This initial study led to two new investigations. In order to understand the incorporation of amphiphilic organic ions like TMPA<sup>+</sup> into like-charged ionic micelles, the experimental system was switched to the partitioning of the carboxylate anion of 1-pyrenebutyric acid (PBA<sup>-</sup>) into micelles of SDS.<sup>8</sup> The relatively long-lived fluorescence of PBA<sup>-</sup> in the aqueous phase could be selectively quenched by the iodide anion, which was shown to be micelle-excluded because it did not alter the lifetime of PBA<sup>-</sup> in the micellar phase. This permitted the determination of the fraction of PBA<sup>-</sup> in each phase and hence the incorporation constant  $K_{\text{S}}$  of PBA<sup>-</sup>. The value of  $K_{\text{S}}$  was found to be highly dependent on  $[\text{Na}]_{\text{aq}}$ , the concentration of sodium counterions free in the intermicellar aqueous phase. Indeed, in order to obtain coherent results,  $[\text{Na}]_{\text{aq}}$  had to be maintained constant by appropriate additions of the non-quencher salt NaCl to compensate for variations in the free Na<sup>+</sup> derived from micellar dissociation and added NaI. This study<sup>8</sup> provided two important lessons: (i) the proposal by Larry Romsted<sup>9</sup> that the apparent degree of counterion dissociation from ionic micelles,  $\alpha$ , might be relatively constant and insensitive to detergent or added salt concentration appeared to work quite nicely; and (ii) when highly charged interfaces are involved, the

important parameter is the net counterion concentration (and composition) and it is this that must be maintained constant in the aqueous phase, not the ionic strength.

In the second investigation, we opted to use the very long-lived emission of the tris(bipyridine)ruthenium(II) dication,  $\text{Ru}(\text{bpy})_3^{2+}$ , as the water-soluble probe and *N*-dodecyl-4-cyanopyridinium (DCP<sup>+</sup>) bromide as the surfactant as an alternative to our previous anthracene-derived probe/HPCl system to determine DCP<sup>+</sup> free monomer concentrations via emission quenching. We also prepared the short-chain, hydrophilic, non-micellizing *N*-methyl-4-cyanopyridinium cation (MCP<sup>+</sup>) in order to determine the dependence of the quenching rate constant  $K_{\text{SV}}$  on added salt concentration (using the extended Debye-Hückel relationship with the ionic strength replaced by the aqueous counterion concentration). From the quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  by MCP<sup>+</sup> in the absence and presence of micellar hexadecyltrimethylammonium bromide (CTAB), it was possible to show that both of these ions were indeed excluded from cationic micelles, i.e., resided exclusively in the intermicellar aqueous phase.

A literature search (prompted by a question from Henrique Toma following a presentation of our preliminary results) indicated that MCP<sup>+</sup> undergoes alkaline hydrolysis to give two products,<sup>11</sup> but at appreciable rates only for  $\text{pH} > 10$ . However, at the micelle surface, micellar catalysis of the hydrolysis of DCP<sup>+</sup> might occur at much lower pH values. Bunton *et al.*<sup>12</sup> had just reported the binding of protons to the surface of SDS micelles based on pH measurements in the aqueous phase, but the same method failed for the hydroxide ion binding to CTAB (in part because the CTA<sup>+</sup> cation binds strongly to the glass electrode, creating a junction potential that prevents accurate pH measurements). Together with Hernan Chaimovich, we realized that, because the MCP<sup>+</sup> cation was restricted to the aqueous phase of CTAB, the rate constant for alkaline hydrolysis of MCP<sup>+</sup> as a function of [CTAB] should be proportional to the amount of hydroxide ion free in the intermicellar aqueous phase. Indeed, this proved to be the case and we soon were ready to publish<sup>13</sup> the first actual measurements of the intermicellar hydroxide ion concentration as a function of [CTAB]. The problem was then how to describe the observed behavior using what we knew at the time about ionic micellar systems and counterions. The solution of the kinetic system of successive replacements of bromide ions by hydroxide ions at the CTAB micelle surface (ensconced in a footnote in reference 14) proved to be a binomial distribution of micelles with zero, one, two, three, etc. bound hydroxide ions. In hindsight, it was obvious that binding to a fixed number of sites in which occupied sites are no longer available would necessarily lead to a binomial distribution,

but at the time, it provided the impetus for understanding how to count ions in ionic micellar systems in a very straightforward manner.<sup>14</sup>

### 3. Counting Counterions in Ionic Micellar Systems - the Basics of Pseudophase Ion Exchange

The Romsted<sup>9</sup> assumption of a constant degree of micellar dissociation ( $\alpha$ ), together with our initial studies, showed that, in a micellar solution of detergent  $\text{D}^+\text{Y}^-$  containing a common-counterion salt, e.g., NaY, the analytical concentrations of Y in the micellar ( $[\text{Y}]_{\text{m}}$ ) and aqueous ( $[\text{Y}]_{\text{aq}}$ ) compartments or pseudophases of the solution could be expressed as:<sup>14</sup>

$$[\text{Y}]_{\text{m}} = (1 - \alpha)C_{\text{D}} \quad (7)$$

$$[\text{Y}]_{\text{aq}} = \alpha C_{\text{D}} + \text{CMC} + [\text{Y}]_{\text{ad}} \quad (8)$$

where the concentration of micellized detergent,  $C_{\text{D}}$ , can be approximated as the total detergent concentration ( $C_{\text{T}}$ ) minus the CMC and  $[\text{Y}]_{\text{ad}}$  is the concentration of the added salt. Upon addition of a foreign counterion salt, e.g., NaX, the assumption that a part  $[\text{X}]_{\text{m}}$  of the total added X counterions,  $[\text{X}]_{\text{T}}$ , dislocate an equivalent amount of Y ions from the micelle surface into the aqueous phase is equivalent to the equilibrium:



This equilibrium is governed by an ion exchange selectivity coefficient  $K_{\text{X/Y}}$  reflecting the difference in affinity of X and Y for the micellar surface:

$$K_{\text{X/Y}} = [\text{X}]_{\text{m}}[\text{Y}]_{\text{aq}}/([\text{X}]_{\text{aq}}[\text{Y}]_{\text{m}}) \quad (10)$$

where the concentrations of X and Y in the two phases can be written as:

$$[\text{X}]_{\text{aq}} = [\text{X}]_{\text{T}} - [\text{X}]_{\text{m}} \quad (11)$$

$$[\text{Y}]_{\text{m}} = (1 - \alpha)C_{\text{D}} - [\text{X}]_{\text{m}} \quad (12)$$

$$[\text{Y}]_{\text{aq}} = \alpha C_{\text{D}} + \text{CMC} + [\text{Y}]_{\text{ad}} + [\text{X}]_{\text{m}} \quad (13)$$

*A priori*, this system of four equations has only two unknowns, the analytical concentration of X in either the micellar or aqueous phase and the value of  $K_{\text{X/Y}}$ . Hence, by assuming different values of  $K_{\text{OH/Br}}$  for the selectivity of hydroxide ion binding to CTAB micelles, we could predict  $[\text{OH}]_{\text{aq}}$  as a function of [CTAB] and compare the results to our experimental values<sup>13</sup> obtained from the rate of alkaline hydrolysis of MCP<sup>+</sup>.

#### 4. Pseudophase Ion Exchange (PPIE) and Reaction Kinetics

If the total concentration of X is known, the analytical concentration at the micelle surface,  $[X]_m$ , in mol L<sup>-1</sup> of micellar solution, can then be converted into the local concentration  $[X]_{mloc}$  at the micellar surface by dividing  $[X]_m$  by the volume fraction of the micelles in liters of micellar pseudophase/liter of micellar solution.<sup>14</sup> We assumed (purely for simplicity) this volume fraction to be the concentration of micellized detergent times the molar volume of the detergent,  $V_m$ :

$$[X]_{mloc} = [X]_m / (C_D V_m) \quad (14)$$

For CTAB, with  $\alpha = 0.2$  and  $V_m = 0.37$  L mol<sup>-1</sup>, the total local counterion concentration at the micelle surface, given by the expression  $[X]_{mloc} + [Y]_{mloc} = (1 - \alpha)/V_m$ , is of the order of 2.2 mol L<sup>-1</sup>. For SDS, with  $\alpha = 0.25$  and  $V_m = 0.25$  L mol<sup>-1</sup>, the local counterion concentration is ca. 3 mol L<sup>-1</sup>. These high counterion concentrations at the micelle surface can have a large influence on bimolecular reaction rates simply as the result of a local concentration effect.

The application of these ideas to local concentration effects on the rates of chemical reactions performed in micellar solutions was then straightforward.<sup>5,14,15</sup> For a bimolecular reaction between a non-ionic substrate S and a foreign counterion X, the observed rate constant,  $k_{obs}$ , under pseudo-first-order conditions (excess X) will depend on the fraction of S in each pseudophase  $f_m$  and  $f_{aq}$ , where  $f_{aq} = 1/(1 + K_S C_D)$ , governed by the micellar incorporation coefficient of the substrate,  $K_S$ , the "true" second-order rate constants ( $k_{2m}$  and  $k_{2aq}$ ) and the local reactive ion concentrations in each phase:

$$k_{obs} = f_m k_{2m} [X]_{mloc} + f_{aq} k_{2aq} [X]_{aq} \quad (15)$$

If  $K_S$ ,  $K_{X/Y}$ ,  $k_{2aq}$  and  $\alpha$  are known or can be estimated independently, the only parameter that is needed to fit kinetic profiles of  $k_{obs}$  vs. detergent concentration is  $k_{2m}$ , the second order rate constant in the micellar pseudophase.

On the other hand, many bimolecular reactions of interest in micelles are performed in buffered solutions. If the solution is correctly buffered (*vide infra*), then it is the concentration of the reactive ion in the aqueous phase,  $[X]_{aq}$ , that is constant and not the total concentration of X, which varies as the detergent concentration is varied.<sup>5,14,16</sup> However, using the known value of  $[X]_{aq}$  in the expression for  $K_{X/Y}$  (equation 10), together with equations 12 and 13 for  $[Y]_m$  and  $[Y]_{aq}$ , respectively,  $[X]_m$  can also be calculated in

the presence of buffer if  $K_{X/Y}$  is known. Hence, the same ion counting approach can be employed to analyze reaction rate constants for bimolecular reactions in which the reactive counterion is appropriately buffered.

How then can one buffer a micellar solution so that  $[X]_{aq}$  is indeed reasonably constant? There are in principle two ways to buffer an ion concentration: (i) use an excess of a slightly soluble salt of the reactive species X {e.g., Mg(OH)<sub>2</sub> to maintain  $[OH]_{aq}$  in micellar CTAB} or (ii) use a buffer for which the ions involved in the buffering equilibrium are both coions (or a coion and a very hydrophilic neutral species) and the counterions of the buffer are the same as those of the detergent. Thus, for SDS, appropriate buffers for maintaining the intermicellar pH might be sodium H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>. For CTAB, bis-tris hydrobromide or low concentrations of tris hydrobromide are adequate. In both cases, the contribution of the buffer components to  $[Y]_{ad}$  is known and the buffer ions are restricted primarily to the aqueous phase. An inappropriate choice, that probably will not adequately buffer the intermicellar pH, for example, would be H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> in micellar CTAB because the mono- and divalent phosphate counterions bind differently to the micelle, altering their relative concentrations in the aqueous phase, and they compete with Br<sup>-</sup> and OH<sup>-</sup> for the micelle surface. Knowing how to buffer micellar solutions properly permitted the analysis of ionic micellar effects on the dissociation of weak acids, HA, like phenols and thiols, in CTAB, where the conjugate base, A<sup>-</sup>, is a counterion.<sup>5,14</sup> In this case, the apparent dissociation constant,  $pK_{ap}$ , is defined as:

$$pK_{ap} = [H^+]_{aq} \{ [A^-]_{aq} + [A^-]_m \} / \{ [HA]_{aq} + [HA]_m \} \quad (16)$$

Once  $[A^-]_m$  is known, one can then analyze bimolecular reactions such as the thiolysis or oximolysis of esters where the reactive nucleophile is the weak-acid-derived anion.<sup>5,17</sup>

#### 5. Implications of Simple PPIE

This simple PPIE approach, which included most of the previous models as limiting cases, nicely reproduced most of the known reactivity patterns in ionic micellar solutions.<sup>5,14,15</sup> Moreover, when the apparent rate constants of bimolecular reactions were corrected by PPIE for the effects of the local concentration of the reagents at the micelle surface, the true second-order rate constants in the aqueous and micellar pseudophases ( $k_{2aq}$  and  $k_{2m}$ ) usually were found to be remarkably similar in magnitude.<sup>15</sup> The inescapable conclusion was that, in most cases, intrinsic micellar effects on reactivity were not particularly large and perhaps even non-existent (for unimolecular reactions,

there are modest effects<sup>15</sup> that have been interpreted in terms of an equivalent homogeneous medium, see reference 18). As a consequence, PPIE could do more than just analyze reactivity patterns. By assuming that  $k_{2m} = k_{2aq}$ , one could now actually make predictions of the expected reactivity patterns when reasonable estimates of the requisite parameters such as substrate incorporation coefficients, ion exchange selectivities and degrees of micellar dissociation were available.

On the other hand, the ability to make predictions of the "expected" reactivity patterns also permitted the detection of situations in which the simple PPIE approach apparently failed. Early on, inadequacies were found in the treatment of reactivity patterns in hexadecyltrimethylammonium hydroxide or fluoride, CTAOH<sup>19</sup> or CTAF,<sup>20</sup> i.e., cationic micelles with highly hydrophilic hydroxide or fluoride counterions. The micelles of both of these detergents have aggregation numbers that are substantially smaller than those of CTAB and their size and apparent degree of micellar dissociation,  $\alpha$ , change with detergent concentration. Hence, the apparent breakdown of PPIE in these surfactants was not a problem of the model *per se*, but rather of the inadequacy of the assumption of constant  $\alpha$ , as shown by the agreement between PPIE and experiment when the variation of  $\alpha$  was taken into account.<sup>15,20</sup>

One particularly useful way of estimating incorporation coefficients,  $K_s$ , for neutral substrates is via the use of multiparametric linear solvation free energy relationships (LSERs) to correlate  $\log K_s$  with the structure of the solute for a given detergent.<sup>21-23</sup> LSERs based on Abraham solute parameters have been particularly useful for this purpose. In the Abraham approach, the transfer of a solute from water to the micelle is assumed to be the sum of five free energy contributions: (i) the difference in cavitation energy between water and the micelle, which is proportional to the (appropriately scaled) molar volume of the solute,  $V$ ; (ii) the solute polarizability in excess of that of an alkane,  $E$ , which can be calculated from the refractive index of the solute; (iii) the solute dipolarity,  $S$ , which accounts for dipolar interactions; (iv) the solute hydrogen bond basicity,  $B$ , or propensity to accept hydrogen bonds; and (v) the solute hydrogen bond acidity,  $A$ , or hydrogen bond donating ability. Values of these solute parameters are currently available for several thousand molecules.<sup>24</sup> Transforming this into a LSER for  $K_s$  gives an equation of the form:

$$\log K_s = \text{constant} + eE + sS + aA + bB + vV \quad (17)$$

For SDS, multiple regression of a large number of  $K_s$  values provided the following quantitative relationship, in which the coefficients reflect the relative contribution of

each term to the overall free energy change for incorporation of the solute into the micelle:

$$\log K_s = 0.08 + 0.58 E - 1.09 S + 0.03 A - 3.40 B + 3.81 V \quad (18)$$

Similarly, for CTAB, the corresponding relationship was found to be:

$$\log K_s = -0.57 + 0.57 E - 0.15 S + 0.85 A - 3.61 B + 3.36 V \quad (19)$$

In both cases, the coefficients with the greatest magnitude are those associated with the size of the solute and its hydrogen bond basicity. Greater solute size, which encompasses the hydrophobic effect, favors incorporation of the solute into the micelle, reflecting the much higher cavitation energy of water relative to the micelle. In contrast, a greater solute hydrogen bond basicity disfavors incorporation in the micelles, indicating that the aqueous phase is a much better hydrogen bond donor than the solubilization environment sensed by the solute in the micelle. An important point that should not be overlooked is that this type of LSER should work well only if the nature of the average solubilization environment is reasonably similar for all of the solutes, despite their structural diversity. Thus, although it has been speculated for decades that solutes of different hydrophobicities might solubilize in different regions of micelles (hydrocarbon core, micelle-water interface, etc.), solute incorporation into micelles, as measured by  $K_s$ , provides no evidence for the necessity to assume the existence of distinct micellar solubilization environments for different classes of solutes, at least for SDS and CTAB micelles. Although difficult to apply to multifunctional solutes, this LSER approach does provide a qualitative framework for estimating reasonable magnitudes of solute incorporation coefficients from solute structure.

## 6. Lessons from the Simple Electrostatics of Ionic Micelles

Ionic micelles have relatively high electrostatic potentials at their surface and it is this potential that attracts the counterions to - and repels coions from - the vicinity of the surface. How then, does the PPIE approach avoid an explicit consideration of the micellar surface potential? The traditional model for counterion binding to the micelles assumes that a certain fraction of the counterions penetrate in between the ionic headgroups of the ionic surfactant, forming the Stern layer, while the remainder are distributed

around the micelle in the diffuse electrical double layer. For a planar interface, the parameter that reflects the thickness of the double layer or the (approximately exponential) decay of the potential with distance out from the interface is the Debye length  $1/\kappa$ , given by the relationship:  $1/\kappa$  (in nm) =  $0.3/I^{1/2}$ , where  $I$  is the ionic strength of the bulk aqueous phase. Thus, for a cationic micelle with a radius of 2.2 nm in a solution with an aqueous counterion concentration of  $0.005 \text{ mol L}^{-1}$  (ca.  $0.021 \text{ mol L}^{-1}$  detergent),  $1/\kappa = 4.2 \text{ nm}$  and the double layer should extend out at least 10-15 nm from the micelle center. On the other hand, for an aggregation number,  $N_{\text{ag}}$ , of about 90, corresponding to a micelle concentration of  $C_D/N_{\text{ag}} = 0.0002 \text{ mol L}^{-1}$ , the average midpoint between the centers of any two micelles is only  $0.735/(C_D/N_{\text{ag}})^{1/3} = 12.2 \text{ nm}$ . Consequently, except at low detergent concentrations in the presence of high concentrations of added salt, the electrical double layers of adjacent ionic micelles will overlap, i.e., the micelles will interact electrostatically with each other and the electrostatic potential will pass through a minimum at the midpoint between micelles rather than decay to zero far from the micelles. This results in a continuous variation of the electrostatic potential, and hence of the local concentrations of counterions and coions, throughout the solution, as shown schematically in Figure 1 and more quantitatively for the potential in Figure 2. The micellar counterions that are at the midpoint between micelles, where the potential goes through the minimum, no longer pertain to the peripheral regions of the double layer but rather to the intermicellar aqueous phase, i.e., these are the counterions that give rise to the apparent dissociation of the micelles.

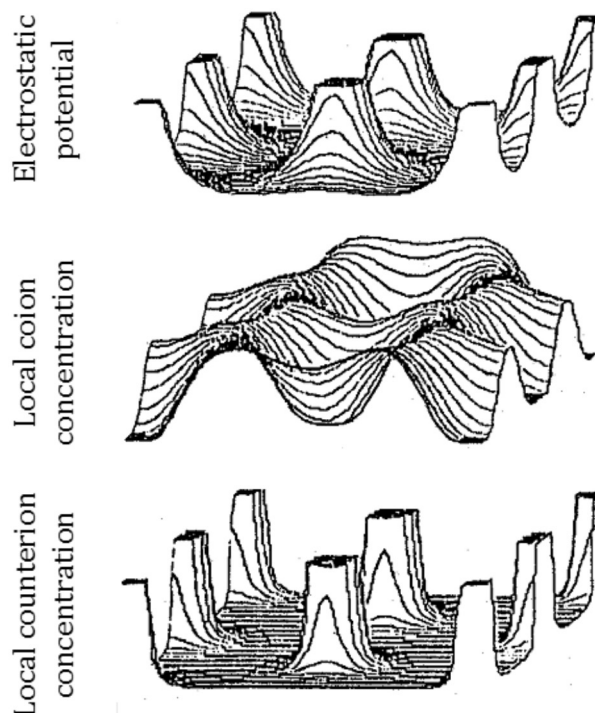
An important parameter in colloidal electrostatics is the dimensionless charge density parameter  $\xi_o$  dependent on the geometry of the charged particle.<sup>25</sup> Thus, for an infinitely long rod-like particle:

$$\xi_{\text{or}} = 2\pi\lambda_B(\sigma/e)a_{\text{rod}} = \lambda_B/L \quad (20)$$

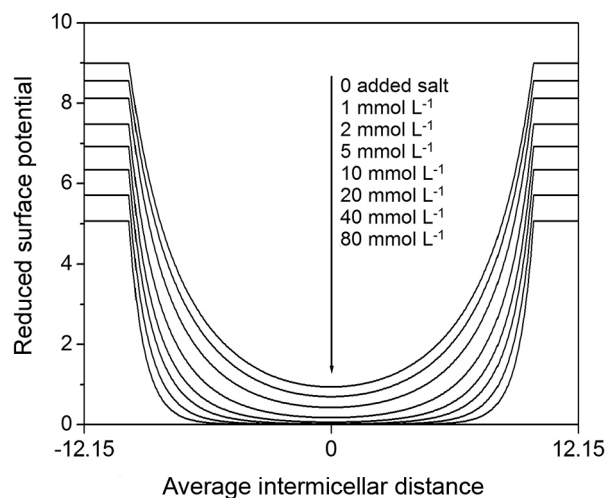
where  $L$  is the distance between primary charges along the polyelectrolyte chain. For a charged spherical micelle:

$$\xi_{\text{om}} = \pi\lambda_B(\sigma/e)a_m = \lambda_B N_{\text{ag}}/(4a_m) \quad (21)$$

where  $a_{\text{rod}}$  and  $a_m$  are the radii of the rod or spherical micelle and  $\sigma/e$  is the charge *per* unit area on the surface of the colloidal particle [=  $N_{\text{ag}}/(4\pi a_m^2)$  for a spherical micelle]. The Bjerrum length,  $\lambda_B$ , corresponds to the distance at which the interaction between two elementary charges is equal to the available thermal energy. For a medium of relative dielectric constant  $\epsilon_r$ , the value of  $\lambda_B$  is given by:<sup>25</sup>



**Figure 1.** Three-dimensional cartoon representation of the electrostatic potential in the solution around a hexagonally-packed ensemble of charged spheres ( $a_m = 2.3 \text{ nm}$ ;  $N_{\text{ag}} = 75$ ;  $\text{CMC} = 1 \text{ mmol L}^{-1}$ ,  $C_D = 30 \text{ mmol L}^{-1}$ ) and the corresponding local concentrations of coions and counterions.



**Figure 2.** Solutions of the Poisson-Boltzmann equation for the electrostatic potential between two positively-charged CTACL-like charged spheres ( $a_m = 2.2 \text{ nm}$ ;  $N_{\text{ag}} = 90$ ;  $\text{CMC} = 0$ ;  $C_+ = C_- = 0.020 \text{ mol L}^{-1}$ ) in water at  $30 \text{ }^\circ\text{C}$ .

$$\lambda_B = e^2/(4\pi\epsilon_0\epsilon_r k_B T) \quad (22)$$

where  $e$  is the elementary charge,  $k_B$  the Boltzmann constant and  $\epsilon_0$  the permittivity of vacuum. In water at  $25 \text{ }^\circ\text{C}$ , the value of  $\lambda_B$  is  $0.72 \text{ nm}$ .

For an infinitely long rod-like polyelectrolyte, it was well-known that the value of  $\xi_{\text{or}}$  determines whether

or not part of the counterions will “condense” on the polyelectrolyte; when they do, the apparent degree of counterion dissociation can be estimated from the Manning<sup>26</sup> relationship  $\alpha_{\text{rod}}$  ca.  $1/\xi_{\text{or}}$ . Thus, a decrease in the spacing,  $L$ , between the charges on the polyelectrolyte backbone increases  $\xi_{\text{or}}$  and decreases  $\alpha_{\text{rod}}$ . From Poisson-Boltzmann calculations for finite concentrations of charged spheres in the absence of added salt, we obtained the following analogous expression for the apparent degree of micellar dissociation:

$$\alpha_{\text{mic}} \sim 1.7/(1 + \xi_{\text{om}}) \quad (23)$$

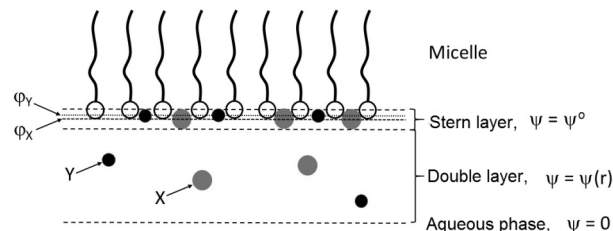
This equation nicely rationalizes the general features of the behavior of  $\alpha$  for micelles. Thus, for a CTAB-like micelle with a radius of  $a_m = 2.3$  nm and an aggregation number of ca. 100 ( $0.66 \text{ nm}^2$  per detergent headgroup charge),  $\xi_{\text{om}} = 7.8$  and  $\alpha_{\text{mic}} = 0.19$ , in good agreement with the experimental  $\alpha$  value of ca. 0.2. A CTAOH micelle with about half the aggregation number of a CTAB micelles should have an  $\alpha$  about twice that of CTAB. On the other hand, the value of  $\alpha$  should decrease gradually as the chain length of the detergent increases and approach zero for particles with very large radii, such as the external surface of charged vesicles.

A particularly useful relationship between counterion selectivity and the electrostatic potential was first derived by Plaisance and Ter-Minassian-Saraga<sup>27</sup> in 1976 in a study of specific ion effects on cationic polyelectrolyte monolayers. In a micellar solution of the monovalent cationic detergent  $D^+Y^-$ , three locations are assumed for the  $Y$  counterions derived from the micelle (Figure 3): (i) a fraction  $\alpha$  of the micellar counterions in the intermicellar aqueous phase; (ii) counterions that have penetrated into the Stern layer, interact with the detergent headgroups with the average binding energy  $\phi_Y$  and compensate a fraction  $\theta_Y^\circ$  of the headgroup charge; and (iii) a fraction  $1 - \alpha - \theta_Y^\circ$  of counterions in the electrical double layer around the micelle. The local concentration of  $Y$  ions in the double layer is a function of the electrostatic potential difference,  $\psi(r)$  relative to that at the midpoint between micelles:

$$[Y(r)]_{\text{DL}} = [Y]_{\text{aq}} \exp(F\psi/RT) \quad (24)$$

where  $F$  is the Faraday. Assuming that the affinity of the  $Y$  ions for the surface depends on the concentration of  $Y$  ions just outside the Stern layer, equal to  $[Y]_{\text{aq}} \exp(F\psi^\circ/RT)$ , where  $\psi^\circ$  is the micellar surface potential,  $\theta_Y^\circ$  can be expressed in terms of the simple binding isotherm:

$$\theta_Y^\circ = K_Y [Y]_{\text{aq}} \exp(F\psi^\circ/RT) / \{1 + K_Y [Y]_{\text{aq}} \exp(F\psi^\circ/RT)\} \quad (25)$$



**Figure 3.** Cartoon representation of the distribution of ions according to the model of Plaisance and Ter-Minassian-Saraga,<sup>27</sup> with indications of the corresponding electrostatic ( $\psi$ ) and Stern-layer ( $\phi$ ) potentials.

where the affinity constant is:

$$K_Y = K_Y^\circ \exp(\phi_Y/RT) \quad (26)$$

For a CTAB-like micelle with  $\alpha = 0.2$ , a typical estimate of  $\theta_Y^\circ$  would be about 0.60-0.65, meaning that only about 15-20% of the counterions pertain to the double layer. Rearrangement of this last equation provides the following relationship for the reduced surface potential  $F\psi^\circ/RT$ :

$$F\psi^\circ/RT = \ln [\theta_Y^\circ/(1 - \theta_Y^\circ)] - \ln K_Y - \ln [Y]_{\text{aq}} \quad (27)$$

For the case of two monovalent counterions  $X$  and  $Y$ , the corresponding expression for the net fraction of counterions in the Stern layer,  $\theta_{XY}$ , can be written as:

$$\theta_{XY} = (K_Y [Y]_{\text{aq}} + K_X [X]_{\text{aq}}) \exp(F\psi^\circ/RT) / \{1 + (K_Y [Y]_{\text{aq}} + K_X [X]_{\text{aq}}) \exp(F\psi^\circ/RT)\} \quad (28)$$

Solving for the surface potential gives:

$$F\psi^\circ/RT = \ln [\theta_{XY}/(1 - \theta_{XY})] - \ln K_Y - \ln ([Y]_{\text{aq}} + K_{X/Y} [X]_{\text{aq}}) \quad (29)$$

where we have expressed the ion exchange selectivity coefficient  $K_{X/Y}$  as:

$$K_{X/Y} = (K_X^\circ/K_Y^\circ) \exp[(\phi_X - \phi_Y)/RT] \quad (30)$$

The salient feature of equation 29 is that it tells us that the effect of a mixture of common ( $Y$ ) and non-common ( $X$ ) counterions on the properties of the ionic micelle  $DY$  will be determined by the equivalent counterion concentration  $[Y]_{\text{aq}} + K_{X/Y} [X]_{\text{aq}}$ . Thus, the contribution of  $X$  is modulated by its selectivity relative to the common counterion  $Y$ . Equations 27-30 can be readily generalized to the case of mixtures of mono- and divalent counterions by replacing  $F\psi^\circ/RT$  by the more general term  $-z_X F\psi^\circ/RT$  or to micelles formed by divalent detergent ions. Although this is beyond the scope of the current review, the general result is that the effect of counterion valence on the micellar properties

scales as the selectivity times the ion concentration raised to the inverse power of the valence of the ion, i.e., monovalent ions scale as their concentration, divalent ions as the square root of their concentration and trivalent ions as the cube root of their concentration in the aqueous phase. The simple scaling of the relative electrostatic effects of counterions nicely rationalized the effects of cations of different valences on zwitterionic sulfobetaine micelles saturated with perchlorate ion.<sup>28</sup>

We can now interpret the consequences of the addition of a non-common counterion salt on a variety of micellar properties, some of which puzzled researchers for years.<sup>29</sup> Thus, the CMC of an ionic detergent should obey the modified Corrin-Harkins relationship (compare to equation 4):

$$\log \text{CMC}_{XY} = (1 + \beta_Y) \log \text{CMC}_{oY} - \beta_Y \log ([Y]_{\text{aq}} + K_{X/Y}[X]_{\text{aq}}) \quad (31)$$

where  $\beta_Y$  is the slope of the common-salt Corrin-Harkins plot and  $\text{CMC}_{oY}$  is the CMC of  $DY$  in the absence of added salt. As shown in Figure 4, this is indeed the case. As the micellar surface potential decreases, the free detergent monomer concentration,  $m_{\text{aq}}$ , will also decrease. This can be investigated indirectly by looking at the effect of added salt on the incorporation of a monomer-like molecule (or pseudomonomer)<sup>30,31</sup> such as the *N*-hexadecylpyridinium cation into a like-charge CTACl micelle, for which the incorporation can be formulated as a monomer (m)-pseudomonomer (PM) exchange equilibrium:



The apparent incorporation coefficient of the pseudomonomer reflects the added-salt induced changes in the free monomer concentration, which in turn depends on the equivalent counterion concentration  $[Y]_{\text{aq}} + K_{X/Y}[X]_{\text{aq}}$ :

$$\log K_{\text{PM}/\text{m}} = \log \left\{ \frac{[\text{PM}]_{\text{m}}}{([\text{PM}]_{\text{aq}} C_{\text{D}})} \right\} + \log [m]_{\text{aq}} \quad (33)$$

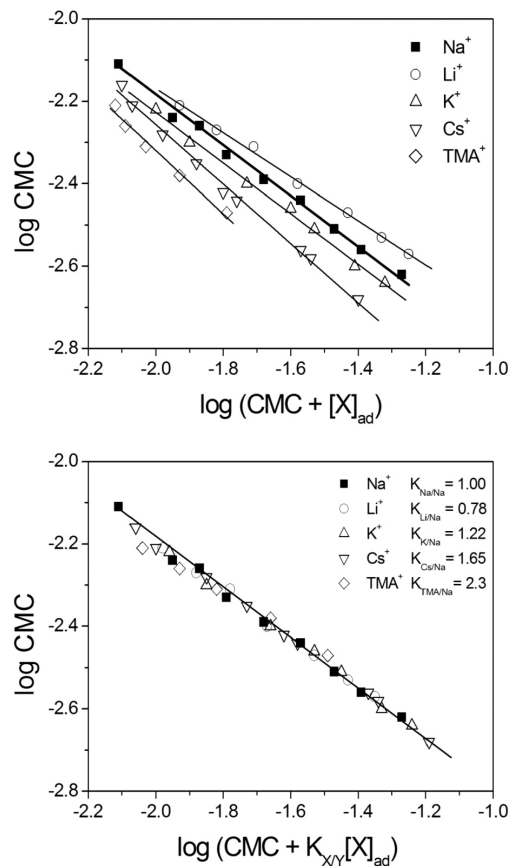
Since the rates of entry and exit of ionic species from ionic micelles depend on the electrostatic field around the micelle, the question arises as to what extent the field affects the individual entry and exit rates.<sup>31,32</sup> The ratio of entry ( $k_+$ ) and exit ( $k_-$ ) rates for a counterion:

$$k_+/k_- = (k_+^0/k_-^0) \exp(F\psi^0/RT) \quad (34)$$

can be separated into the individual rates:

$$k_+ = k_+^0 \exp[(1 - \delta)F\psi^0/RT] \quad (35)$$

$$k_- = k_-^0 \exp(\delta F\psi^0/RT) \quad (36)$$



**Figure 4.** Correlation of foreign counterion effects on the CMC of SDS via: (upper panel) a Corrin-Harkins type relationship (equation 4); or (lower panel) the relationship modified to include ion exchange selectivity (equation 31). Experimental data from reference 29.

by introducing a parameter  $\delta$ , which provides a measure of the fraction of the overall electrostatic work that must be overcome for the ion to escape from the micelle;  $1 - \delta$  is then the corresponding fraction at which capture of the ion by the surface becomes irreversible. Studies of the dynamics of the incorporation of thiosulfate ion into CTACl micelles and of the *N*-ethylpyridinium ion and  $\text{Cu}^{\text{II}}$  in SDS showed that both  $k_+$  and  $k_-$  are sensitive to salt concentration.<sup>32</sup> For pseudomonomers like *N*-alkylpyridinium ions in CTACl, however, the rate constants for micellar entrance were very sensitive to salt concentration ( $\delta$  close to zero), but insensitive to the alkyl chain length. In contrast, the exit rate constants were relatively insensitive to salt concentration but very sensitive to the alkyl chain length, i.e., the exit rate constants are controlled almost entirely by the hydrophobicity of the pseudomonomer, becoming larger as the alkyl chain length decreases.<sup>30</sup>

What then does a consideration of micellar electrostatics tell us about the PPIE model for treating reactivity patterns in ionic micellar solution? The first conclusion is that, although the ratio of local concentrations is equal to



that of the analytical concentrations for the exchange of counterions of the same valence, the same is not true for the exchange of counterions of different valences. Hence, the ion exchange selectivity coefficients should really be expressed in terms of the local concentrations of the micellar ions and the valences of the ions involved in the exchange:<sup>33</sup>

$$K_{X/Y} = \{[X]_{\text{mloc}}/[X]_{\text{aq}}\}^{1/|Z_X|} \{[Y]_{\text{aq}}/[Y]_{\text{mloc}}\}^{1/|Z_Y|} \quad (37)$$

The second conclusion is that, instead of just having micellar and aqueous counterions, we actually have micellar Stern-layer counterions, micellar double layer counterions and aqueous counterions. By assuming that the micelles contribute  $\alpha C_D$  counterions to the aqueous phase, ascribing  $(1 - \alpha)C_D$  counterions to the micellar pseudophase lumps the counterions in the double layer together with those in the Stern layer. In principle, monovalent-divalent counterion selectivities determined in the aqueous phase (by ultrafiltration) and at the micelle surface (by fluorescence quenching) should be different if this were a significant problem for the model; however, these measurements failed to show differences in the selectivities.<sup>33</sup>

Micellar electrostatics also identified an additional limitation of the way the local concentrations at the micelle surface were expressed in the original formalism. By assuming that there are  $(1 - \alpha)C_D$  counterions at the micelle surface, the original PPIE ion counting scheme fails to count the additional contribution of the aqueous ions to the local counterion concentration at the micelle surface (it counts only the surface excess of counterions). Consequently, the local counterion concentration extrapolates to the wrong limit as  $\alpha$  goes to unity, i.e., in this limit it predicts that there are zero counterions at the micellar surface and hence zero reaction. Indeed, the true local counterion concentrations should be written as:

$$[Y]_{\text{mloc}} = [Y]_{\text{m}}/(C_D V_{\text{m}}) + [Y]_{\text{aq}} \quad (38)$$

which goes to the proper limit of  $[Y]_{\text{mloc}} = [Y]_{\text{aq}}$  when  $[Y]_{\text{m}} = 0$ . In most cases the concentration in the aqueous phase are small relative to the local concentrations at the micelle surface. However, inclusion of this last term will become essential, e.g., for the situation of a reaction involving an ionic nucleophiles in mixed ionic-nonionic detergent micelles, where  $\alpha$  will tend to unity as the proportion of ionic detergent decreases. In addition, as shown by Romsted,<sup>34</sup> this term is necessary in order to reproduce the measured local concentrations of counterions at the micelle surface of CTACl in the presence of very high added ( $> 0.2 \text{ mol L}^{-1}$ ) concentrations of NaCl.

## 7. Conclusions

In this work, we have touched on just a few of the potential effects of charged interfaces like ionic detergent micelles on reactivity and equilibria. These effects typically derive from the capacity of these ionic surfactant aggregates to solubilize organic substrates, interact selectively with counterions, repel coions, exhibit partial “dissociation” of the counterions, grow in size with added salt, and determine the dynamics of diffusion or near-diffusion controlled processes. Most micellar effects on equilibria and ground-state chemical reactions can be understood in terms of the relatively simple PPIE formalism, which is still the chemically most satisfying approach for analyzing and predicting the effects of the charged interfaces of ionic association colloids such as micelles,<sup>15</sup> vesicles,<sup>17</sup> microemulsions,<sup>35</sup> etc. on reaction rates and equilibria. The model does not require explicit consideration of factors such as size, shape, curvature or dynamics of the aggregates or interaggregate interactions. The coulombic and specific interactions of the ions with the surface are incorporated into the model via ion exchange selectivity coefficients and the non-uniform distribution of the ions throughout the aqueous phase of the solution need not be taken into account.

Treating the aggregates as if they were a separate pseudophase, ignoring the structure or dynamics of the charged interface, can be shown to be valid as long as the equilibration of at least one of the reactive species between the aqueous and micellar phases and among the ensemble of micelles is faster than the rate of reaction (the pseudophase limit).<sup>36</sup> This is true for all equilibria, essentially all ground-state reactions and even for many excited state processes. On the down side, pseudophase limit phenomena reflect time-averaged properties of the system, rather than instantaneous properties of the charged interface. Hence, these phenomena cannot and do not provide meaningful insight into things like the dynamics or structure of the aggregates, the sites of reaction within the aggregate, the orientation of molecules in the aggregates, etc.

Over the years, several limitations of the original formulation have been identified and can be readily incorporated into the model when necessary. The assumption of a constant degree of counterion binding to the surface breaks down for highly hydrophilic counterions, but this can be taken into account by employing the requisite variable values of  $\alpha$  in the model. The consequences of the failure to add the contribution of the aqueous counterion concentration to the local counterion concentration at the surface are manifested only in certain situations that can

now be readily anticipated. Thus, PPIE provides us with a working understanding of how counterions compete at the surface and the relationship between the properties of the interface and the ionic composition of the medium. The counterion types and concentrations in the aqueous phase modulate the surface potential and hence the size and shape of the aggregates. The proper counting of the ions and the ability to attribute them unambiguously to either the aqueous or micellar pseudophases requires a thorough knowledge of the ionic composition of the medium. The use of ions that will certainly cause undesirable interferences (such as buffer ions that interact with the interface) must be avoided.

Finally, since the medium effects of micelles on the reactions of polar organic molecules and ions generally appear to be similar to those in water, PPIE is more than a model for deriving rate or apparent equilibrium constants from kinetic or equilibrium data. Fairly reliable methods are available for estimating counterion exchange selectivities, the binding constants of neutral substrates and the values of  $\alpha$ . Hence, the assumption of similar reactivity in water and the micelle allows PPIE to be employed as a tool for experimental design, i.e., to predict *a priori* the expected effects of a charged interface on the reaction or equilibrium of interest.

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