The Pseudophase Model of Micellar Catalysis. Addition of Cyanide Ion to *N*-Alkylpyridinium Ions

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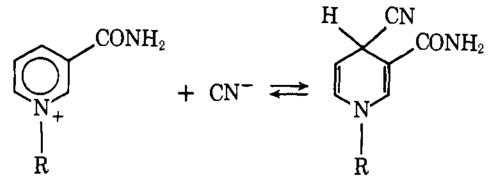
Abstract: Cationic micelles speed addition of cyanide ion to the 4 position of *N*-alkyl-3-carbamoylpyridinium bromide (alkyl = n-$C_{12}H_{25}$, n-$C_{14}H_{29}$, n-$C_{16}H_{33}$). At high concentration of cetyltrimethylammonium cyanide [CTACN] the reaction rates become almost independent of [CTACN] as substrate binding approaches completion. The rates of these reactions in 0.005 M CN^- go through maxima with increasing concentration of cetyltrimethylammonium bromide [CTABr]. The rate-surfactant profiles in both surfactants fit a pseudophase model of micellar catalysis. Using measured binding of the substrates to micelles of CTABr, the second-order rate constants in the micellar pseudophase are almost the same as that in water. Thus, the entire rate enhancement is due to concentration of reactants in the micellar pseudophase.

Cyanide ion adds reversibly to the 4 position of *N*-alkyl-3-carbamoylpyridinium ions (**1**)[1,2] and the rate and equilibrium constants of addition have been measured by Cordes and his co-workers.[2] Cationic micelles of *n*-alkyltrimethylammonium bromides increase both the rate and equilibrium constants of addition, and the effects increase markedly with increasing length of the *n*-alkyl group of **1**.[3]



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Two factors could be involved in these micellar effects:[4] (1) The micelle could concentrate the two reactants in the Stern layer at the micelle–water interface. (2) The micelle could increase the reactivity of the bound reactants, i.e., exert a medium effect. This second hypothesis is particularly attractive because transition-state formation results in charge neutralization and therefore a decrease in the Coulombic repulsions between the substrate and the cationic head groups of the micelle.[3,7]

Increasing substrate hydrophobicity will increase the extent of substrate incorporation, but it may also change the location of the substrate in the micelle and both effects could increase the reaction rate.[3] However, the rates of cyanide ion addition to **1**, R = $C_{12}H_{25}$, go through a maximum with increasing concentration of the surfactant, tetradecyltrimethylammonium bromide. Such rate maxima are typical of bimolecular micellar catalyzed reactions, and must be accounted for in any model of micellar catalysis.

Our aim was to establish the relative importance of these medium and concentration effects, and to do this we had to estimate the concentration of each reactant in the micellar pseudophase. The distribution of an organic substrate between the aqueous and micellar pseudophases can usually be measured directly. However, it is more difficult to do this for small, hydrophilic ions, e.g., CN^-, and competition for the micelle between the reactive cyanide ion and an unreactive halide ion is an added complication.

This problem is simplified by using a reactive counterion surfactant, e.g., hexadecyltrimethylammonium cyanide (CTACN), because the concentration of cyanide ion in the Stern layer should depend directly upon β, the extent of micellar charge neutralization, which for most ionic micelles is in the range 0.7–0.9.[9] The pseudophase kinetic model predicts that above the critical micelle concentration (cmc) the rate of addition of CN^- to **1** should increase to a plateau value as **1** becomes fully micellar bound. This kinetic form has been observed for acetal hydrolysis in solutions of micellized sulfonic acids.[10]

The rate constant in the plateau region allows direct estimation of the second-order rate constant in the micellar pseudophase, and comparison of this rate constant with that in water measures the importance of the medium effect of the micelle. In addition, the rate constant in the micellar pseudophase can be used to evaluate the role of competition between CN^- and Br^- in reactions of **1** in solutions of CTABr.

A similar approach has been applied to acid-catalyzed reactions such as acetal hydrolysis, the benzidine rearrangement, and the hydration of dihydronicotinamides in micelles of sodium dodecyl sulfate.[10,11] For each of these reactions the reactivity of the hydrogen ion in the micellar phase is less than that in water. However, there are a number of micellar-catalyzed reactions of hydrophobic anions for which the reaction of the anion in the micelle is very similar to that in water.[5,8] Our results with cyanide ion fit this pattern, and show that micellar rate enhancements of the addition of CN^- to **1** are due almost completely to increased concentration of the reactants in the micellar pseudophase.

Experimental Section

Materials. The substrates were prepared by alkylating nicotinamide with the alkyl bromide.[2,3] Cetyltrimethylammonium bromide was purified by recrystallization from Et_2O-EtOH. Cetyltrimethylammonium chloride (CTACl) was prepared by heating hexadecyl chloride in 25% Me_3N under reflux in *i*-PrOH for 3 days with periodic addition of Me_3N (25%). The volatiles were removed and traces of H_2O were removed by addition of EtOH followed by distillation. The product was recrystallized (Et_2O-EtOH). The critical micelle concentration (cmc) was 1.8×10^{-3} M, by surface tension, with no minimum in a plot of surface tension vs. log [CTACl]. Cetyltrimethylammonium cyanide (CTACN) was prepared from CTACl and a tenfold excess of NaCN in the minimum EtOH. The mixture was stored overnight and NaCl was removed by filtration. After four treatments there was no residual Cl^- and EtOH was removed and CTACN and NaCN were separated using hot MeCN. CTACN was recrystallized from MeCN. The cmc of CTACN determined by surface tension was 8.6×10^{-4} M, and there was no minimum in a plot of surface tension against log [CTACN]. The experiment was done in the presence of OH^- to suppress protonation of CN^-, and [CTACN]/[NaOH] = 5. The cmc of CTACN is almost the same as that of CTABr.[12]

Kinetics. Reactions were followed spectrophotometrically at 340 nm and 25.0 °C, with 10^{-5} M substrate,[9] and the observed first-order rate constant, k_ψ, is in s^{-1}. Protonation of CN^- was suppressed by addition of OH^- and in all experiments $[CN^-]/[OH^-] = 5$.

Addition of CN^- to **1** is reversible,[2,3] but reaction goes to completion in the presence of CTACN. For reaction in the presence of CTABr allowance was made for the contribution of the reverse re-

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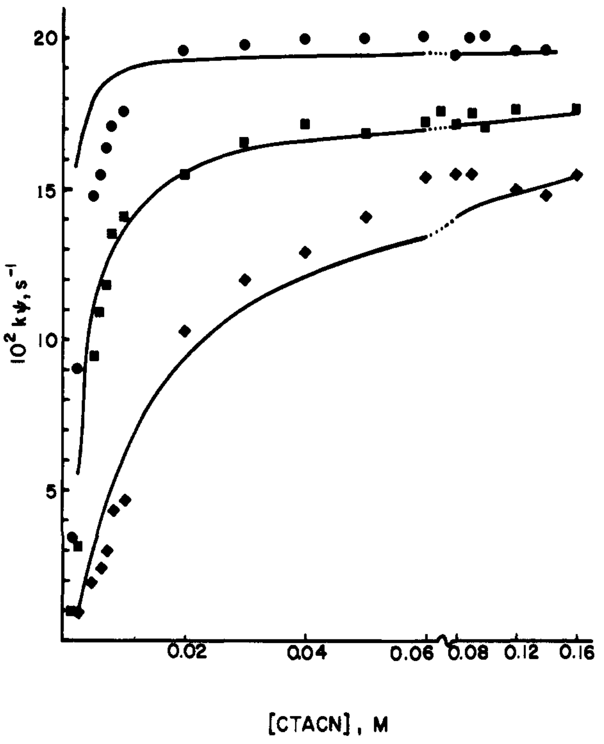

Figure 1. Variation of first-order rate constants with [CTACN]: ◆, ■, ●, R = $C_{12}H_{25}$, $C_{14}H_{29}$, and $C_{16}H_{33}$, respectively.

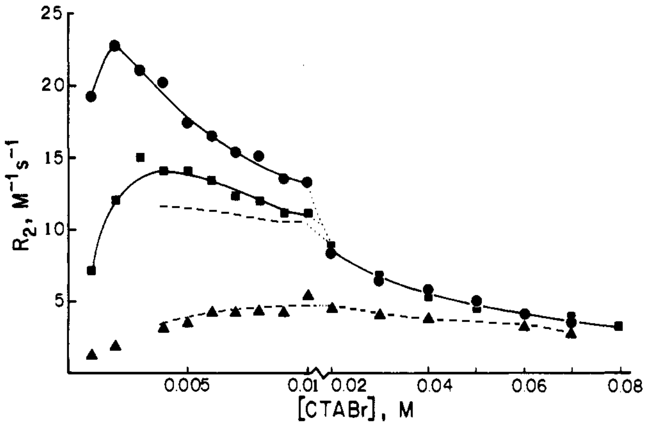

Figure 2. Variation of second-order rates with [CTABr] in 0.005 M NaCN: ◆, ■, ●, R = $C_{12}H_{25}$, $C_{14}H_{29}$, and $C_{16}H_{33}$, respectively. The broken lines are calculated.

action to k, using the equation

$$k_2 = k_\psi/(K_d + [CN^-]) \quad (1)$$

where k_2 is the second-order rate constant for the forward reaction and K_d is the dissociation constant of the reverse reaction, determined by the method of Cordes and Lindquist.[2] After attainment of equilibrium, small amounts of solid NaCN were added until the absorbance became constant, and K_d was estimated from the change in absorbance.[13] The correction for the reverse reaction is smaller with 0.005 M CN^- than in the reactions studied earlier.[2,3]

Micellar Binding of the Substrates. Binding of **1** to micelles of CTABr was measured by ultrafiltration,[14] using an Aminco 202 cell with a PM-10 membrane. Equilibrium across the membrane was established by recycling 3-mL aliquots of the filtrate until the absorbance of the filtrate was constant. The membrane discriminates between water and the substrates and for **1**, R = $C_{12}H_{25}$ and $C_{14}H_{29}$, the transport number was 1.1. We used this value for **1**, R = $C_{16}H_{33}$, which could not be studied in the absence of micelles because of its very low solubility in water.

We calculated $[S_M]/[S_W]$, the relative concentration of **1** in solutions of CTABr and in water, with a correction for the transport number. Plots of $[S_M[/[S_W]$ were linear with [CTABr] and their slopes gave the binding constant, K_S, where[15,16]

$$K_S = [S_M]/\{[S_W]([CTABr] - cmc)\} \quad (2)$$

Absorbances of the filtrate and filtrand were measured at 265.5 nm and 3-mL samples were diluted to 10 mL with EtOH or MeCN to break up the micelles. The maximum [CTABr] were 0.05, 0.03, and 0.005 M for **1**, R = $C_{12}H_{25}$, $C_{14}H_{29}$, and $C_{16}H_{33}$, respectively.

The values of the binding constants, K_S (M^{-1}), to CTABr micelles are respectively dodecyl, 70; tetradecyl, 390; hexadecyl, 3500. The incremental free energy of binding is 580 cal mol^{-1} per methylene group, which is similar to the values for surfactant incorporation into a micelle[17] and micellar incorporation of hydrophobic esters.[18] This agreement suggests that the *N*-alkyl groups of the substrate penetrate deeply into the apolar region of the micellar core. The incremental free energies of binding are much smaller for *p*-alkylphenols and phenoxide ions with micellized CTABr,[19] suggesting that here alkyl groups of these solutes did not penetrate so deeply.

Reaction in CTACN. As predicted, the first-order rate constants, k_ψ, approach plateau values with increasing [CTACN],[10] and for **1**, R = $C_{16}H_{33}$, k_ψ is constant over a wide range of [CTACN]. These plateau values are only slightly affected by substrate hydrophobicity (Figure 1), which does, however, strongly affect the steepness of the plots of k_ψ against [CTACN], by changing the extent of micellar binding of the substrate.

Reaction in CTABr. The rate-surfactant profiles for addition of 0.005 M CN^- to **1** follow the usual pattern in that the second-order rate constants, k_2, go through maxima and the maximum rate constants increase with increasing substrate hydrophobicity (Figure 2).

Discussion

Analysis of Rate Constants in CTACN. The plateau values of k_ψ are only slightly dependent upon substrate hydrophobicity (Figure 1). This observation suggests that in reactions of CN^- in micelles of quaternary ammonium halides the major effect of substrate hydrophobicity (ref 2 and 7, Figure 2) is to increase micellar incorporation of the substrate rather than to change substrate reactivity in the micellar pseudophase. These observations confirm the predictions of the pseudophase ion-exchange model for the micellar binding of ionic reactants,[6] and they accord with the effects of micellized sulfonic acids on acetal hydrolysis.[10]

The pseudophase kinetic model for reaction of a nucleophile, N, leads to the following relation between the first-order rate constant, k_ψ, and the surfactant concentration, [D]:[10,11,20]

$$k_\psi = \frac{k_W[N_W] + k_M K_S m_N{}^s([D] - cmc)}{1 + K_S([D] - cmc)} \quad (3)$$

In eq 3, the concentration of monomeric surfactant is assumed to be constant and given by the critical micelle concentration (cmc), k_W is the second-order rate constant in water, and k_M that in the micelles. The concentration of the nucleophile in water, $[N_W]$, is expressed as molarity, whereas that in the micelles, $m_N{}^s$, is expressed as a mole ratio,[10,11] i.e.

$$m_N{}^s = [N_M]/([D] - cmc) \quad (4)$$

where the quantities in square brackets denote moles of solute per liter of total solution.[22]

Several assumptions are made in deriving eq 3. For example, it is assumed that the nature of the micelle as a reaction medium is unaffected by added solutes, i.e., that k_M, k_W and K_S are constants for a given substrate. Equation 3, and others like it,[5,8,11,23-25] are only approximate kinetic models, and seldom fit the experimental data exactly. However, in many systems the model fits the data within the limits of experimental error, except at very low surfactant concentrations where the solutes can markedly perturb the micellar structure and the cmc.[15]

For CTACN

$$m_{CN}{}^s = \beta = [CN_M{}^-]/([CTACN] - cmc) \quad (5)$$

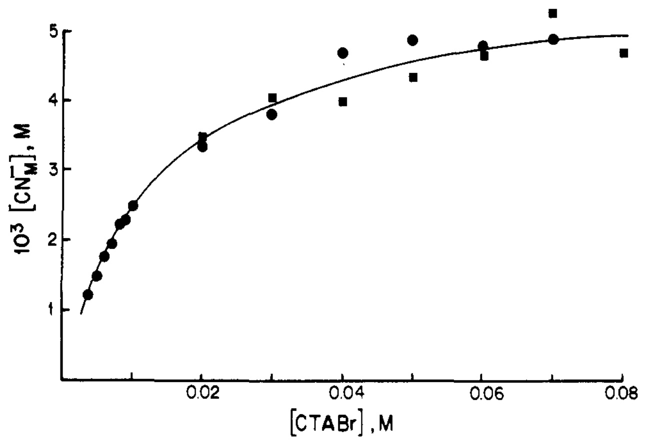

Figure 3. Dependence of micellar bound cyanide ion on CTABr, calculated using eq 9. Squares and circles are from k_2 values for **1**, R = $C_{14}H_{29}$ and $C_{16}H_{33}$, respectively.

Table I. Second-Order Rate Constants in Micellized CTACN[a]

substrate	βk_M, s^{-1}	k_2^m, M^{-1} s^{-1}	K_S, M^{-1} [b]
1, R = $C_{12}H_{25}$	0.17	0.032	70
1, R = $C_{14}H_{29}$	0.18	0.034	390
1, R = $C_{16}H_{33}$	0.19	0.036	3500

[a] At 25.0 °C with $\beta = 0.75$. [b] In CTABr.

where β is the fraction of micellar head groups neutralized by CN^- in the Stern layer.[6,9] The reaction in water is so slow that it can be neglected,[2] so that for reaction of CN^- eq 3 simplifies to[10]

$$k_\psi = \frac{\beta k_M K_S([\mathrm{CTACN}] - \mathrm{cmc})}{1 + K_S([\mathrm{CTACN}] - \mathrm{cmc})} \qquad (6)$$

When all the substrate is micellar bound, as with **1**, R = $C_{16}H_{33}$, when [CTACN] > 0.04 M (Figure 1)

$$k_\psi = \beta k_M \qquad (7)$$

The values of βk_M for **1**, R = $C_{12}H_{25}$, $C_{14}H_{29}$, were obtained by fitting the rate-surfactant profile to eq 6 (Table I). The binding constants, K_S, of the substrates were assumed to be the same in CTACN as in CTABr (Results).

The solid lines were calculated using eq 6 and the parameters in Table I, and a cmc of 8×10^{-4} M. The agreement between observed and calculated values is satisfactory, except that k_ψ for **1**, R = $C_{16}H_{33}$, increases more sharply than predicted. The assumption that the concentration of monomeric surfactant is constant, and is given by the cmc in water, is a major problem in this type of calculation, especially when the substrates are so hydrophobic that they may induce micellization or interact with submicellar aggregates.[15,26]

The agreement between observed and calculated values of k_ψ for the less hydrophobic substrates suggests that the simple kinetic model with the assumed constancy of β is satisfactory. Similar conclusions have been drawn for hydronium ion reactions in the presence of micellized sulfonic acids, but this simple model fails for reactions in micellized quaternary ammonium hydroxide[10] and fluoride,[27] suggesting that the failure of the simple model may be related to the hydrophilicities of the reactive counteranions.

Our model is based on Stigter's Stern layer model for micellar structure.[28] In formulating the kinetic model for reactivity in micelles of CTACN, and in calculating k_M, we assume that β is constant and unaffected by ions in the aqueous pseudophase. There are no experimental values of β for CTACN, but we estimated $\beta = 0.75$ for CTABr, based on deprotonation of benzimidazole,[29] and we use that value of CTACN. There is support for this assumption of the constancy of β from experiments with polyelectrolytes,[30] including nucleic acids.[31,32] In any event, errors so introduced with k_M are small because $\beta \approx 1$.

The second-order rate constants, k_M, can be converted into k_2^m, which is the second-order rate constant expressed in terms of moles of reactant per liter of Stern layer using the molar volume of the Stern layer. This quantity has been estimated to be 140 mL for CTABr,[10,15] and if we use this value for CTACN we obtain

$$k_2^m \approx 0.14 k_M \qquad (8)$$

The various rate constants are in Table I. The values of k_2^m are very similar to the second-order rate constant of 0.014 M^{-1} s^{-1} for the reaction of the iodide of **1**, R = n-C_3H_7, in 0.5 M NaCN in water,[2] suggesting that the observed rate enhancements stem almost wholly from concentrating the reactants in the Stern layer at the micelle–water interface. Coulombic destabilization of the initial state relative to the zwitterionic transition state plays at most a minor role in speeding the reaction. This observation appears to be general because second-order rate constants of a number of reactions in the micelle are similar to, or smaller than, those in water.[5,8,10,11,23-25,33] These conclusions depend on estimation of reactant distribution between water and the micelles and on the volume element of reaction; for example, some investigators use the total volume of the micelle rather than that of the Stern layer,[5,23-25] but these assumptions do not affect the overall conclusions because the volume of the Stern layer is approximately 40–50% of that of the micelle.

Analysis of Rate Constants in CTABr. The rate–surfactant profiles for reaction with 0.005 M CN^- in the presence of CTABr should follow eq 3 and 4, which can be written for convenience in terms of the second-order rate constant, k_2. The reaction in the aqueous phase is so slow that k_W can be neglected, giving the second-order rate constant with respect to CN^- as

$$k_2 = k_M K_S[CN_M^-]/0.005\{1 + K_S([\mathrm{CTABr}] - \mathrm{cmc})\} \qquad (9)$$

In analyzing the rate data we assume that k_M is unaffected by the nature of the counterion. From reactions in CTACN we estimate k_M to be 0.25 s^{-1} for **1**, R = $C_{14}H_{29}$ and $C_{16}H_{33}$, and 0.23 s^{-1} for **1**, R = $C_{12}H_{25}$. There is a problem in assuming that the concentration of monomeric CTABr is constant and given by the cmc in water because added solutes often promote micellization and reaction may be mediated by submicellar aggregates.[15,26] In order to minimize these problems we apply our analysis to solutions of [CTABr] > 0.004 M, which is well above the cmc of 8×10^{-4} M.[12]

The values of K_S were determined in CTABr in the absence of salt. However, preliminary results indicate that added salts may increase the binding of cations to cationic micelles, and may increase K_S. Some added salts appear to increase the binding of Malachite Green to CTABr,[15a] and we are finding similar effects in the binding of a betaine ester and bromopyridinium ion to cationic micelles, although these results were obtained with salt concentrations much higher than those used in the present work. However, K_S for **1**, R = $C_{16}H_{33}$, is so large (Results) that it should be also fully bound above 0.003 M CTABr, and this should also be true for **1**, R = $C_{14}H_{29}$, above 0.02 M CTABr, and we use k_2 values under the conditions (Figure 2) combined with the k_M values to calculate [CN_M^-]. There are two important conclusions to be drawn from the calculated values of [CN_M^-] (Figure 3) and the rate–surfactant profiles. First, the values calculated for the two substrates agree reasonably well and the corresponding values of k for the two substrates are also very similar at high [CTABr] (Figure 2). Second, in high [CTABr] the values of [CN_M^-] approach 0.005 M; i.e., under these conditions almost all the

Table II. Estimation of Ion Exchange Constant[a]

10^2[CTABr], M	$10^2[CN_W^-]$, M	K_{Br}^{CN}
0.4	0.37	1.0
0.5	0.35	1.2
0.6	0.32	1.0
0.7	0.31	1.0
0.8	0.28	0.8
0.9	0.27	0.9
1.0	0.25	0.8
2.0	0.16	0.6

[a] In CTABr with 5×10^{-3} M CN^- and 10^{-3} M OH^-.

cyanide ion is micellar bound. However, the *concentation* of CN^- in the micellar pseudophase, m_{CN}^s (eq 5), decreases at high CTABr simply because the micellar concentration of CTABr increases; i.e., there is a dilution of CN^- in the micellar pseudophase.

The values of $[CN_M^-]$ (Figure 3), K_S (Results), and k_M can be used to calculate k_2, eq 9. The dashed lines in Figure 2 are calculated for reactions of **1**, R = $C_{12}H_{25}$ and $C_{14}H_{29}$, using the calculated values of $[CN_M^-]$. The agreement is satisfactory in view of the approximations of the treatment, and the agreement for reactions of **1**, R = $C_{14}H_{29}$, would be improved if K_S were increased by addition of CN^- to CTABr. In any event, we conclude that the second-order rate constants in micellized CTACN (Table I) and the rate-surfactant profile (Figure 2) can be explained in terms of the distribution of the substrates and CN^- between the aqueous and micellar pseudophases. The medium effects of the micelle in the rates are relatively unimportant despite the decrease of net charge in forming a zwitterionic transition state from oppositely charged reactants.

Ion Exchange. Estimation of $[CN_M^-]$ (Figure 3) allows us to evaluate the relative affinities of CN^- and Br^- for a cationic micelle in terms of the equation[6]

$$K_{Br}^{CN} = [CN_W^-][Br_M^-]/[CN_M^-][Br_W^-] \qquad (10)$$

where the subscripts W and M denote the aqueous and micellar pseudophases, respectively. We consider only solutions of CTABr where CN^- was between 20 and 80% bound (Figure 3), so that

$$[CN_W^-] = 0.005 - [CN_M^-]$$

$$[Br_M^-] = \beta([\mathrm{CTABr}] - \mathrm{cmc}) - [CN_M^-]$$

$$[Br_W^-] = [\mathrm{CTABr}] - [Br_M^-]$$

([CTABr] denotes the stoichiometric concentration of surfactant, and $\beta = 0.75$).

The treatment cannot be used at high [CTABr] where $[CN_W^-]$ is given by a small difference between large numbers, but K_{Br}^{CN} (Table II) is reasonably close to 1 between 0.004 and 0.02 M CTABr using values of $[CN_W^-]$ estimated from the kinetics of the reaction of **1**, R = $C_{16}H_{33}$, in CTABr (Figure 2). The calculation depends on unconfirmed assumptions, viz., that β is constant and unaffected by the nature of the counterion and that K_{Br}^{CN} is itself a constant, and that OH^-, used to suppress protonation of CN^-, has no effect on micellar binding of the other ions.

Our conclusion that the ion exchange constant K_{Br}^{CN} is close to 1 is supported by an empirical relation between the micellar bound and total CN^-.

The binding of hydrogen ions to micelles of sodium lauryl sulfate follows the empirical relation[35]

$$m_{H^+}^s = 0.8[H^+]/([H^+] + [Na^+]) \qquad (11)$$

suggesting that H^+ and Na^+ have very similar affinities for an anionic micelle, and we find a very similar relation for the binding of CN^- to micellized CTABr in that a plot of m_{CN}^s, i.e., $[CN_M^-]/([\mathrm{CTABr}] - \mathrm{cmc})$, against $[CN^-]/([CN^-] + [Br^-])$ is approximately linear with a slope of ca. 0.7. (The concentrations $[CN^-]$ and $[Br^-]$ are stoichiometric.) Empirical relations akin to eq 11 seem to be followed when ion exchange constants (eq 10) are close to unity and they then provide a convenient method of estimating concentrations of micellar-bound counterions.

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(33) The situation is completely different for spontaneous unimolecular reactions whose rate constants in the micelle are often very different from those in water.[34]
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