

## Micellar Effects upon the Reaction of N-Alkyl-2-chloropyridinium Salts with Hydroxide Ion

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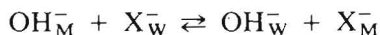
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**ABSTRACT.** Cationic micelles of myristyltrimethylammonium bromide (MTABr) and cetyltrimethylammonium bromide (CTABr) inhibit the reactions of hydroxide ion with N-alkyl-2-chloropyridinium salts (alkyl = Me, Et, propyl, *i.e.*, A<sub>1-3</sub>) because the substrates are largely in the aqueous pseudophase which is depleted in OH<sup>-</sup> by cationic micelles. Added Br<sup>-</sup> displaces OH<sup>-</sup> from the micelles and decreases micellar inhibition. The corresponding reaction of decyl (A<sub>4</sub>) and tetradecyl (A<sub>5</sub>) derivatives is catalyzed by both MTABr and CTABr which bind both reactants. These diverse rate effects can be accounted for quantitatively in terms of the pseudophase ion-exchange model, which considers reactions in both the aqueous and micellar pseudophases and the distribution of both reactants between these pseudophases.

Micellar effects upon the bimolecular reactions have been extensively studied (Fendler and Fendler 1975 and Al-Lohedan *et al.* 1982) and it is generally accepted that incorporation of reactants into micelles is of major importance. For example, cationic micelles catalyze bimolecular reactions of nucleophilic or basic anions by incorporating both reactants into the small volume of the micellar pseudophase (Cordes 1978 and Al-Lohedan *et al.* 1982).

For a number of bimolecular reactions, micellar effects can be interpreted quantitatively by estimating the concentrations of the two reactants in the aqueous and micellar pseudophase (Almgren and Rydholm 1979, Al-Lohedan *et al.* 1981, and Underwood and Anacker 1984). It is difficult to measure directly the concentration of hydrophilic ions in the micellar pseudophase, especially OH<sup>-</sup>. An indirect approach to this problem is to assume that the interaction of two (or more) counterions with ionic micelles is governed by an ion-exchange equilibrium (Romsted 1977) similar to that which governs interaction with ion-exchange resins.

This approach explains qualitatively a number of micellar effects upon reactions rate and equilibria and leads to equations which describe the competition between counterions for an ionic micelle. This approach is illustrated by an ion-exchange model (Romsted 1977).



where  $\text{X}^-$  is the micellar counterions and M and W denote the micellar and aqueous pseudophases respectively. The ion-exchange constant is given by:

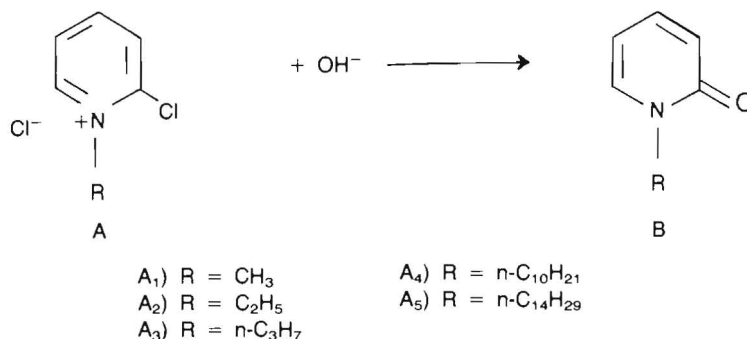
$$K_x^{\text{OH}} = [\text{OH}_W^-] [\text{X}_M^-] / [\text{OH}_M^-] [\text{X}_W^-] \dots\dots\dots (1)$$

The ion-exchange constant can be measured directly by using interior competition or estimated by simulating the variations of rate or equilibrium constants with surfactant concentration, in terms of various parameters including  $K_x^{\text{OH}}$  (Almgren and Rydholm 1979, Chaimovich *et al.* 1979, and Funasaki and Marata 1980). These treatments depends on the assumption that  $K_x^{\text{OH}}$  and rate constant in the micellar pseudophase are independent of the concentrations of surfactants, reactants and added counterions, and that  $\beta$ , the fraction of bound counterions to ionic micellar head groups, is also independent of these concentrations (Romsted and Cordes 1968, Romsted 1975, and Gunnarsson *et al.* 1980). Today this general treatment has been applied to several hydroxide ion reactions (Al-Lohedan *et al.* 1981).

In some systems, reaction occurs in both the aqueous and micellar pseudophases so that the substrate distribution has to be taken into account (Funasaki and Marata 1980, and Bunton *et al.* 1980). In other systems the hydrophobicity of substrate was such that it was located in only one pseudophase (Al-Lohedan *et al.* 1981, 1982). Such is the case for methyl, N,N-trimethylglycinate, which does not bind to micelles (Al-Lohedan *et al.* 1981). However, in this reaction it was necessary to take into account the kinetic salt effect of the surfactant upon the rate of reaction in the aqueous pseudophase. This problem also exists for the reaction of 4-methyl-4-cyanopyridinium ion (Quina and Chaimovich 1979).

Our aim was to examine micellar effects upon reaction of hydroxide ion with a series of chemically similar substrates of different hydrophobicities chosen so that reaction would occur either wholly in the aqueous pseudophase or wholly in the micellar pseudophase. If the pseudophase ion-exchange model is correct, consistent values of parameter such as  $\beta$  and  $K_x^{\text{OH}}$  should be applicable to reactions of structurally similar substrates occurring in either the micellar or aqueous pseudophase.

We studied a series of N-alkyl-2-chloropyridinium ions (Scheme 1) whose hydrophobicities could be changed without changing the reaction mechanism.



Scheme 1

The surfactants used were cetyltrimethylammonium bromide (C<sub>16</sub>H<sub>33</sub>NMe<sub>3</sub>Br, CTABr) and myristyltrimethylammonium bromide (C<sub>14</sub>H<sub>29</sub>NMe<sub>3</sub>Br, MTABr). The reaction of halopyridinium ions with aqueous hydroxide ion have been studied in detail and the mechanism is well established (Barlin and Benbow 1974).

## Experimental

### Materials

The N-alkyl-2-chloropyridinium chlorides were prepared by heating equimolar 2-chloropyridine and the alkyl chlorides under reflux in MeCN for 5 days (Barlin and Benbow 1974). The solvent was removed by evaporation and the products were recrystallized from EtOH/Et<sub>2</sub>O.

Preparation or purification of the surfactants has been described (Bunton *et al.* 1980). Redistilled deionized CO<sub>2</sub> free water was used as solvent.

### Kinetics

Formation of the pyridone (B) was followed spectrophotometrically at 296 nm. Repetitive scanning of the spectrum of the reaction mixture showed that no intermediate buildup during reaction (Fig. 1). We used  $(2-3) \times 10^{-5}$  M substrate and 0.01 M NaOH, so that the individual runs were first-order for most of the reaction. Reactions were carried out in water at 25.0°C and first-order rate constant  $k_{\psi}$ , are expressed in reciprocal seconds.

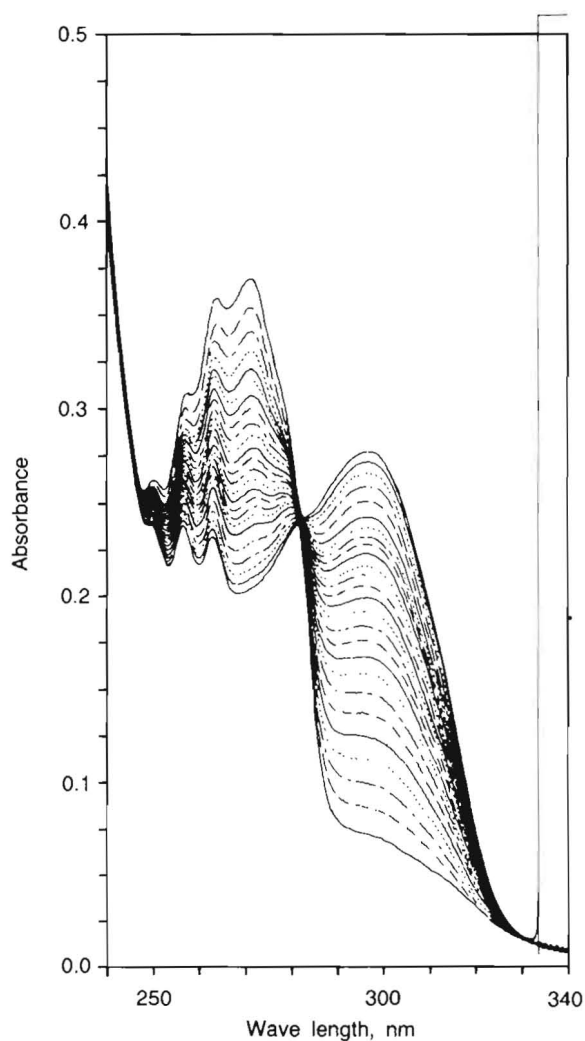
### Substrate Binding to Micelles

The binding constants  $K_s$  were determined by ultrafiltration using an Aminco 202 Cell with a PM 10 membrane (Bunton *et al.* 1978).  $K_s$  Values are given in terms

of the concentration of micellized surfactant, eq. 2, where  $S_M$  and  $S_W$  are substrate in micellar and aqueous pseudophases,  $D$  is the surfactant and  $cmc$  is the critical micelle concentration.

$$K_s = [S_M] / (S_W ([D] - cmc)) \dots\dots\dots (2)$$

The solute concentrations in the filtrate were determined spectrophotometrically.



**Fig. 1.** Repetitive scans for the reaction of  $0.001 \text{ MOH}^-$  with  $3 \times 10^{-5}$  (N-methyl-2-chloropyridinium ion (time interval is 38 sec.)

## Results

### *Reaction in the Absence of Surfactant*

The rate of the reaction for methyl, ethyl, propyl and n-decyl derivatives ( $A_{1-4}$ ) are independent of substrate concentration in the range of  $(2-20) \times 10^{-5} \text{M}$  in  $0.01 \text{ M NaOH}$ . The second order rate constants  $k_w$  are 0.55, 0.43, 0.4 and  $0.45 \text{ M}^{-1}\text{s}^{-1}$  at  $25^\circ\text{C}$ . The slightly decreased reactivities of  $A_2$ ,  $A_3$  and  $A_4$  are probably due to steric effect. However, the second order rate constant for reaction of N-tetradecyl-2-chloropyridinium ion ( $A_5$ ) increases as its concentration increases almost certainly because of substrate micellization which attracts  $\text{OH}^-$  to the cationic aggregate. However, we used  $2 \times 10^{-5} \text{M}$  of  $A_5$  which is well below its cmc which is  $2 \times 10^{-3}$ . The effect of substrate concentration on reactivity is under study.

Added electrolyte decreases the rate of reaction, the negative salt effect in water upon the reaction of the methyl derivative ( $A_1$ ) is unaffected by the nature of the salt (Tables 1,2) but, in some cases, it increases slightly with increasing charge density of the anion of the added electrolyte but change in the cation of the electrolyte ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) has little effect.

### *Reaction in the Presence of Surfactant*

*N-methyl-2-chloropyridinium chloride ( $A_1$ )*. Reaction is inhibited by micelles of MTABr and CTABr and added NaBr decreases the inhibition (Fig. 2). The inhibition depends upon the halides anion but not on the surfactant cations.

*N-Ethyl ( $A_2$ ) and N-propyl-2-chloropyridinium chloride ( $A_3$ )*. CTABr inhibits the reaction of both derivatives  $A_2$  and  $A_3$ , but the inhibition go through minima with increasing CTABr concentration (Fig. 3).

*N-Decyl ( $A_4$ ) and N-tetradecyl-2-chloropyridinium chloride ( $A_5$ )*. For reactions of these substrates with  $\text{OH}^-$ , the first-order rate constants go through maxima with increasing [surfactant] (Fig. 4) and the rate enhancement increases with substrate hydrophobicity, which decreases the [surfactant] needed for maximum rate enhancement.

*Substrate binding to micelles*. The binding constants  $K_s$  of methyl, ethyl and propyl derivatives increase with increasing [CTABr] (Table 3). These increase can be ascribed to micellar binding of an ion pair (Bunton *et al.* 1978), or one can assume that the micelle has a constant charge which is maintained by entry of both cationic substrate and chloride ion. However, the binding constants for the decyl and tetradecyl derivatives to micelles of CTABr are 60,  $240 \text{M}^{-1}$  respectively with  $2.5 \times 10^{-5} \text{M}$  solute and up to  $0.2 \text{ M}$  CTABr.

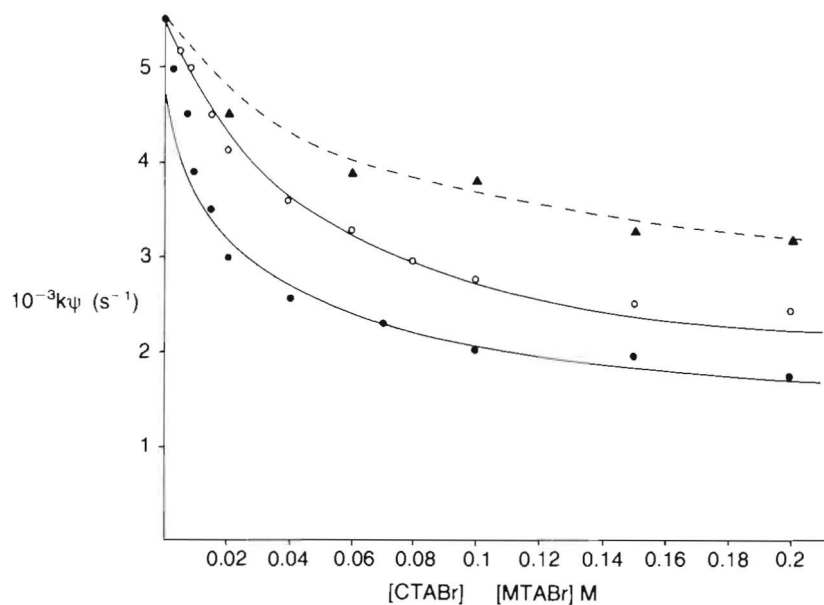


Fig. 2. Reaction of N-methyl-2-chloropyridinium chloride with 0.01 M  $\text{OH}^-$  in CTABr and MTABr.

(●) in CTABr; (○) in MTABr; (▲) in CTABr+0.1 M NaBr.  
Solid Lines are predicted.

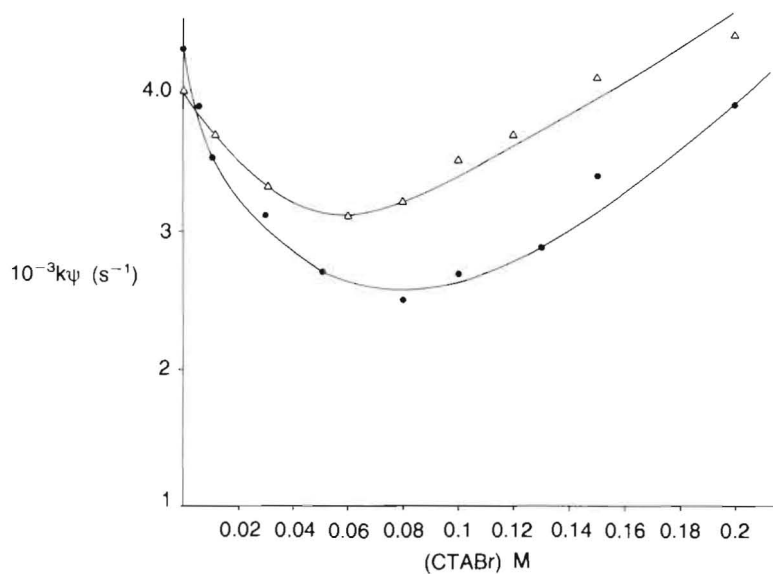


Fig. 3. Reaction of N-ethyl- and N-propyl-2-chloropyridinium ion with 0.01 M  $\text{OH}^-$  in CATBr.

(●) R = ethyl; (△) R = propyl.

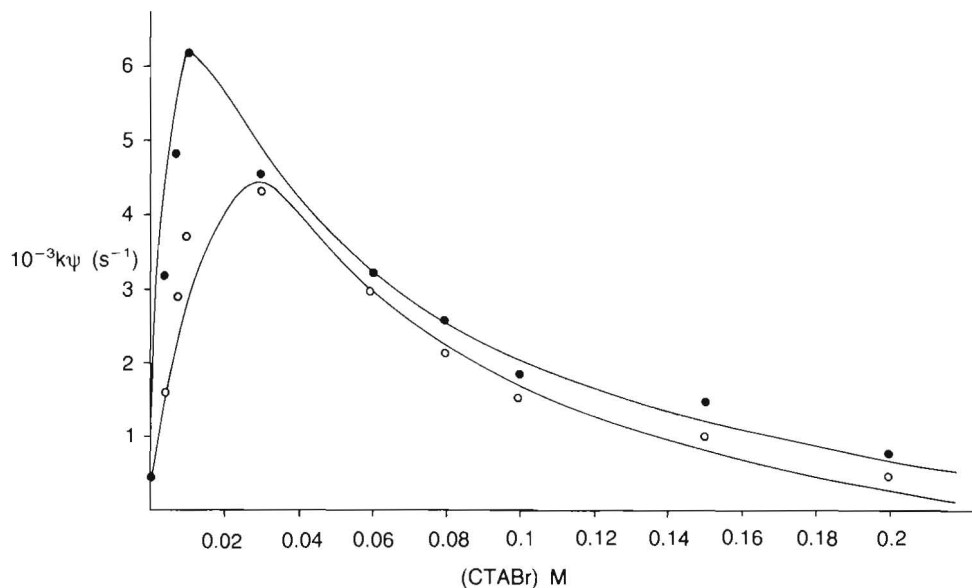


Fig. 4. Reactions of N-decyl- and N-tetradecyl-2-chloropyridinium ion with 0.01 M OH $^{-}$  in CTABr.

(○) R = C<sub>10</sub>H<sub>21</sub> $^{-}$ ; (●) R = C<sub>14</sub>H<sub>29</sub> $^{-}$

Lines are predicted:

## Discussion

### Reactions of Methyl, Ethyl and Propyl Derivatives (A<sub>1,3</sub>)

Micellar effects upon reactions of methyl derivatives (A<sub>1</sub>) are similar to those observed with 4-methyl-4-cyanopyridium ion (Quina and Chaimovich 1979) and methyl N,N,N-trimethylglycinate (Al-Lohedan *et al.* 1981) because these substrates bind only weakly to micelles. Therefore, reaction occurs largely or completely, in the aqueous pseudophase, and this reaction is inhibited because OH $^{-}$  is taken up by the micelle by exchange with the halide counterion (eq. 1).

However, there is a complication because the surfactant ions might exert a kinetic salt effect upon the rate of reaction in the aqueous phase similar to the salt effect in (Table 1 and 2). It is, sometimes, possible to correct for this salt effect (Quina and Chaimovich 1979 and Al-Lohedan *et al.* 1981), but it introduces uncertainty in the quantitative treatment, and with the methyl derivative (A<sub>1</sub>) added salt and surfactants decreases the inhibition.

The situation is more complicated for reactions of the ethyl and propyl derivatives (A<sub>2</sub> and A<sub>3</sub>) where  $k_{\psi}$  goes through minima with increasing

[surfactant]. Qualitatively, these observations suggest that in dilute surfactant the substrate is in the aqueous pseudophase, which is depleted in  $\text{OH}^-$  by the cationic micelles, but that with increasing [surfactant], the substrate becomes micellar bound, and there is a contribution from reaction in the micellar pseudophase. This possibility is supported by the observation that at high [surfactant] the propyl derivative has more catalysis than the ethyl derivative probably because it is more hydrophobic (Fig. 3). Also the binding studies (Table 3) are consistent with this possibility.

We did not attempt to interpret these micellar rate effects quantitatively because the complexity of opposing effects, introduces a large number of adjustable parameters into the treatment.

**Table 1.** Salt effects upon reactions of methyl derivative ( $\text{A}_1$ ) with No added surfactant\*

| [Salt]M | LiBr   | NaCl   | NaBr   | KBr    |
|---------|--------|--------|--------|--------|
| 0.004   | 0.0052 | 0.0054 | 0.0051 | 0.0049 |
| 0.008   | 0.0047 | 0.0049 | 0.0046 | 0.0045 |
| 0.01    | 0.0042 | 0.0045 | 0.0042 | 0.0041 |
| 0.02    | 0.0039 | 0.0042 | 0.0038 | 0.0037 |
| 0.04    | 0.0036 | 0.0039 | 0.0036 | 0.0036 |
| 0.08    | 0.0035 | 0.0035 | 0.0034 | 0.0033 |
| 0.1     | 0.0033 | 0.0033 | 0.0032 | 0.0032 |
| 0.15    | 0.0031 | 0.0032 | 0.0030 | 0.0031 |
| 0.2     | 0.0030 | 0.0032 | 0.0029 | 0.0030 |

\* Values of  $k_{\text{p}}$  ( $\text{s}^{-1}$ ) at  $25.0^\circ\text{C}$  with  $3 \times 10^{-5}$  M substrate and 0.01 M NaOH.

**Table 2.** Effects of hydroxide ion concentration\* upon the reaction of N-alkyl-2-chloropyridinium ions with no added surfactant

| [NaOH] M | Alkyl  |        |        |
|----------|--------|--------|--------|
|          | Me     | Et     | Propyl |
| 0.004    | 0.0023 | 0.0018 | 0.0016 |
| 0.008    | 0.0045 | 0.0036 | 0.0031 |
| 0.01     | 0.0055 | 0.0043 | 0.0040 |
| 0.028    | 0.0152 | 0.012  | 0.009  |
| 0.05     | 0.02   | 0.021  | 0.016  |
| 0.12     | 0.064  | 0.045  | 0.041  |
| 0.16     | 0.085  | 0.072  | 0.058  |
| 0.22     | 0.110  | 0.091  | 0.079  |

\* Values of  $k_{\text{p}}$  ( $\text{s}^{-1}$ ) at  $25^\circ\text{C}$  with  $3 \times 10^{-5}$  substrate.

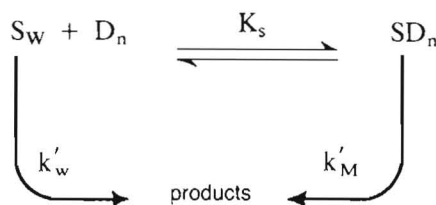
**Table 3.** Micellar binding of methyl, ethyl and n-propyl derivatives\*

| (CTABr),M | Me   | Et   | Propyl |
|-----------|------|------|--------|
| 0.1       | 0.16 | 0.24 | 0.36   |
| 0.13      | 0.26 | 0.42 | 0.88   |
| 0.17      | 0.29 | 0.56 | 1.85   |
| 0.2       | 0.33 | 0.83 | 2.56   |

\* Values of  $K_s$  ( $M^{-1}$ ) at 25°C with  $3 \times 10^{-5}M$  pyridinium ion.

*Reaction of long chain substrates.* The micellar rate enhancement of the decyl- and tetradecyl- derivatives ( $A_4$ ,  $A_5$ ) can be treated quantitatively by considering the distribution of both reactants between aqueous and micellar pseudophases and the rate constants in each pseudophase. The treatment is based upon Scheme II, where

Scheme II



$[D_n] = [D] - \text{cmc}$  and  $k'_w$  and  $k'_M$  are first-order rate constants.

The observed rate constant is given by eq. (3) (Menger and Portony 1967)

$$k_\psi = \frac{k'_w + k'_M K_s ([D] - \text{cmc})}{1 + K_s ([D] - \text{cmc})} \quad (3)$$

The first-order rate constants are given by:

$$k'_w = k_w [\text{OH}'_w] \quad (4)$$

$$k'_M = k_M m_{\text{OH}}^s \quad (5)$$

where  $[\text{OH}'_w]$  is a molarity in terms of total solution volume and the second-order rate constant,  $k_M$  is written in terms of the mole ratio of micellar bound  $\text{OH}^-$  to micellar head groups (Bunton *et al.* 1978).

$$m_{\text{OH}}^s = [\text{OH}_M^-] / ([D] - \text{cmc}) \quad \dots\dots\dots (6)$$

Equations (3-6) give:

$$k_{\psi} = \frac{k_w[\text{OH}_W^-] + k_M K_s m_{\text{OH}}^s ([D] - \text{cmc})}{1 + K_s ([D] - \text{cmc})} \quad \dots\dots\dots (7)$$

Simulation of the rate-surfactant profiles, therefore, requires analysis of the distribution of  $\text{OH}^-$  between aqueous and micellar pseudophases.

### **Distribution of $\text{OH}^-$**

The variation of  $m_{\text{OH}}^s$  with [surfactant] can be predicted for assumed values of the ion-exchange constants,  $K_x^{\text{OH}}$ ,  $\beta$  and cmc, provided that these parameters are constant over a range of [surfactant]. With these assumptions eq. 7 and mass balance give the quadratic eq. 8 (Al-Lohedan *et al.* 1981, 1982), where subscript T denotes total concentration.

$$(m_{\text{OH}}^s)^2 + m_{\text{OH}}^s \left( \frac{[\text{OH}^-]_T + K_x^{\text{OH}} [\text{X}^-]_T}{(K_x^{\text{OH}} - 1) [D]} - \beta \right) - \frac{[\text{OH}^-]_T}{(K_x^{\text{OH}} - 1) [D]} = 0 \quad \dots\dots\dots (8)$$

Equation 8 has the same general form as that used elsewhere (Quina and Chaimovich 1979 and Funasaki and Marata 1980) except that we express the concentration of micellar bound  $\text{OH}^-$  as a mole ratio  $m_{\text{OH}}^s$ .

### **Simulation of Dependence of $k_{\psi}$ on Surfactant**

Equations 7 and 8 were combined and the variation of  $k_{\psi}$  with [D] was simulated by using assumed values of the parameters in these equations. The rate constants of reaction in water,  $k_w$  were directly measured (Results). We did not correct for salt effects on  $k_w$ , because most of the reactions occurs in the micellar pseudophase. Reported values of  $\beta$  are generally in the range 0.6-0.9 (Romsted 1977 and Gunnarsson *et al.* 1980) and of  $K_{\text{Br}}^{\text{OH}}$  Ca 10-20 (Quina and Chaimovich 1979, Bunton *et al.* 1980, Al-Lohedan *et al.* 1981 and Vera and Rodenas 1986). We took the cmc as  $8 \times 10^{-4} \text{M}$  for CTABr (Mukerjee and Mysels 1971), but our surfactant concentrations were such that the simulated fits were insensitive to the cmc. The values of the substrate binding constants  $K_s$  were measured in CTABr (results). However,  $K_s$  has only a small effect on the fitting of the data.

The rate constants that we estimated are given in Table 4, and we took  $\beta = 0.7$  and  $K_{\text{Br}}^{\text{OH}} = 8.5$  (cf. ref. Mukerjee *et al.* 1967), Anacker 1979, Quina and Chaimovich 1979, Bartet *et al.* 1980 and Bunton *et al.* 1980). As has been found for other systems the fit between experimental and calculated values of  $k_{\psi}$  is satisfactory (Almgren and Rydholm 1979, Quina and Chaimovich 1979, Funasaki and Marata 1980 and Al-Lohedan *et al.* 1982), but this agreement does not prove that our values of  $K_x^{\text{OH}}$  or  $k_M$  are correct (Bunton *et al.* 1980 and Al-Lohedan *et al.* 1981).

### Rate Constants in Aqueous and Micellar Pseudophase

The second-order rate constants  $k_M$  in the micellar pseudophase are given in terms of mole ratio rather than molarity as the unit of concentration and cannot be compared directly with the second-order rate constant,  $K_w$ , in water whose dimensions are  $M^{-1} s^{-1}$ . The comparison can be made provided that the volume element of reaction in the micellar pseudophase is specified. We estimated the molar volume of the Stern layer of micelles of CTABr as Ca. 0.14 L, so that the second-order rate constant,  $k_2^m$  in terms of moles reagent in 1 L of Stern layer is (Bunton *et al.* 1978)

$$k_2^m = 0.14 k_M$$

Alternatively, we could take the volume of micelle as the volume elements, which would approximately double the values of  $k_2^m$  (Funasaki and Marata 1980). The values of  $k_2^m$  for reaction of decyl and tetradecyl derivatives are in Table 4.

Table 4. Rate constants in the micellar pseudophase\*

| R                                 | $k_M(s^{-1})$ | $k_2^m(M^{-1} s^{-1})$ |
|-----------------------------------|---------------|------------------------|
| n-C <sub>10</sub> H <sub>21</sub> | 0.56          | 0.09                   |
| n-C <sub>14</sub> H <sub>29</sub> | 0.58          | 0.09                   |

\* In cetyltrimethylammonium bromide (CTABr).

It appears that for reactions of the various N-alkyl-2-chloropyridinium ions in the micellar pseudophase  $k_2^m$  is  $0.09 M^{-1}s^{-1}$  Table 4, and is smaller than  $k_w$  in water, which is 0.43,  $0.40 M^{-1}s^{-1}$  (Table 2) for reactions of A<sub>4</sub> and A<sub>5</sub> respectively. The differences are not unexpected because there is a negative salt effect on reactions of OH<sup>-</sup> with N-alkyl-2-chloropyridinium ions in water and the high ionic concentration in the Stern layer should inhibit reaction.

We do not include in our treatment a term for an assumed electrostatic effect on reaction in the micellar pseudophase. Some worker explicitly includes such a term which obviously affects the estimated ion-exchange parameters (Almgren and Rydholm 1979). However, all the treatments suggest that concentration of reactants into a small volume of the micellar-water interface is the main factor in rate enhancements of bimolecular reactions.

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## References

- Al-Lohedan, H. and Bunton, C.A. (1982) Ion binding and micellar effects upon reactions of carboxylic anhydrides, *J. Org. Chem.* **7**: 1160-1166.
- Al-Lohedan, H., Bunton, C.A. and Romsted, L.S. (1981) Micellar effects upon the reaction of betaine esters with hydroxide ion, *J. Phys. Chem.* **35**: 2123-2129.
- Al-Lohedan, H., Bunton, C.A. and Romsted, L.S. (1982) Micellar effects upon the reaction of hydroxide ion with N-alkyl-2-bromopyridinium ion, *J. Org. Chem.* **47**: 3528-3532.
- Almgren, M. and Mydholm, R. (1979) Influence of counterion binding on micellar reaction rates. Reaction between p-nitrophenyl acetate and hydroxide ion in aqueous cetyltrimethylammonium bromide, *J. Phys. Chem.* **83**: 360-364.
- Anacker, E.W. (1979) *In Solution Chemistry of Surfactants*, Vol. I, Mittal, K.L. (Ed.), Plenum Press, New York, pp. 247-265.
- Barlin, G.B. and Benbow, J.A. (1974) Kinetics of reactions in heterocycles. Part X. Reaction of substituted N-methyl pyridinium salts with hydroxide ions, *J. Chem. Soc. Perkin, Trans. II*: 790-797.
- Bunton, C.A., Carrasco, N., Huang, S.K., Paik, C.H. and Romsted, L.S. (1978) Reagent distribution and micellar catalysis of carbocation reactions, *J. Am. Chem. Soc.* **100**: 5420-5425.
- Bunton, C.A., Romste, L.S., and Sepulveda, H. (1980) A quantitative treatment of micellar effects upon deprotonation equilibria, *J. Phys. Chem.* **84**: 2611-2618.
- Chaimovich, H., Bonilha, J.B.S., Politi, M.J. and Quina, F.H. (1979) Ion exchange in micellar solutions. 2. Binding of hydroxide ion to positive micelles, *J. Phys. Chem.* **83**: 1851-1854.
- Cordes, E.H. (1978) Micellar effects upon bimolecular reaction, *Pure Appl. Chem.* **50**: 617-621.
- Fendlar, J.H. and Fendlar, E.J. (1975) *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York.
- Funasaki, N. and Marata, A. (1980) Catalysis and inhibition of the alkaline hydrolysis of benzocaine and analogs by cationic surfactant, *Chem. Pharm. Bull.* **28**: 805-814.
- Gunnarsson, G., Jonsson, B. and Wennerstrom, H. (1980) Surfactant association intomicelles. An electrostatic approach, *J. Phys. Chem.* **84**: 3114-3121.
- Menger, F.M. and Portony, C.E. (1967) On the chemistry of reactions proceedings inside molecular aggregates, *J. Am. Chem. Soc.* **89**: 4698-4703.
- Mukerjee, P. and Mysels, K.J. (1971) *Critical micellar concentration in aqueous surfactant systems*. National Bureau of Standards, Washington, D.C., U.S.A.
- Mukerjee, P., Mysels, K.J. and Kapauan, P. (1967) Counterion specificity in the formation of ionic micelles-size, hydration and hydrophobic bonding effects, *J. Phys. Chem.* **71**: 4166-4175.
- Quina, F.H. and Chaimovich, H. (1979) Ion exchange in micellar solutions. 1. Conceptual frame work for ion exchange in micellar solutions, *J. Phys. Chem.* **83**: 1844-1850.
- Romsted, L.S. (1975) *Rate enhancement in micellar systems*, Ph.D. Thesis, Univ. of Indiana, Bloomington.
- Romsted, L.S. (1977) *Micellization Solubilization and Microemulsion*, Vol. II, Plenum Press, New York, pp. 509-530.
- Romsted, L.S. and Cordes, E.H. (1968) Secondary valence force catalysis. VII Catalysis of hydrolysis of p-nitrophenyl hexanoate by micelle-forming cationic detergents, *J. Am. Chem. Soc.* **90**: 4404-4409.
- Underwood, A.L. and Anacker, E.W. (1984) Organic counterions and micellar parameters. Substituent effects in a series of benzoates, *J. Phys. Chem.* **88**: 2390-2393.
- Vera, S. and Rodenas, E. (1986) Inhibition effect of cationic micelles on the basic hydrolysis of aromatic ester, *Tetrahedron* **42**: 143-149.

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## تأثير الجزئي الغروي على تفاعل أملاح ن - الكيل - ٢ - كلوروبريدينيوم مع أيون الهيدروكسيد

حمد بن عبدالله اللحيدان

قسم الكيمياء - جامعة الملك سعود - الرياض - المملكة العربية السعودية

تقوم الجزئيات الغروية ذات الأيونات الموجبة الشحنة - لكل من ميرستاييل ثلاثي ميثايل بروميد الامونيوم (MTABR) وسيتايل ثلاثي ميثايل بروميد الامونيوم (CTABR) - بتثبيت تفاعل هيدروكسيد الصوديوم مع مشتق المثيل (أ) والاثيل (ب) والبوريل (ج). وسبب ذلك أن هذه المواد المتفاعلة توجد في الطور المائي الافتراضي، والذي يفتقر لأيونات الهيدروكسيد بسبب جذب هذه الجزئيات لها. وتقلل إضافة أيونات البروميد من هذا التثبيط بسبب احلال أيونات البروميد محل أيونات الهيدروكسيد في طور الجزئيات الغروية الافتراضي، ويدفعها إلى الطور المائي الافتراضي.

أما التفاعلات المطابقة لمشتق ديسايل (أ) وتتراديسايل (هـ) فإنها تحفز بكل من MTABR و CTABR، وذلك أن كل منهما يستطيع أن يقوم باحتضان (ارتباط) هذين المركبين. ويمكن حساب هذا التأثير المتعاكس بطريقة كمية، وذلك باستخدام نظرية الطور الافتراضي المتبادل - الأيوني - والذي يأخذ بعين الاعتبار التفاعل الذي يحدث في كلا الطورين الافتراضيين للماء وللجزئيات الغروية، وكذلك توزيع المادتين المتفاعلتين بين هذين الطورين الافتراضيين.