# The Problem of pH in Micellar Catalyzed Reactions[1]

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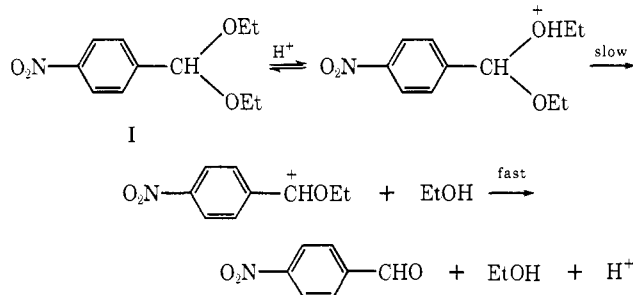
**Abstract:** The second-order rate constants, $k_\psi/C_{H^+}$ and $k_\psi/a_{H^+}$, have been measured for the hydrolysis of p-nitrobenzaldehyde diethyl acetal catalyzed by HCl in aqueous micellized sodium lauryl sulfate (NaLS). The values of the constants depend on whether the calculation is based on hydrogen ion concentration or activity, and are different from $k_\psi/a_{H^+}$ measured in dilute buffers, and those values which themselves depend on the buffer. The rate constants increase to maxima with increasing surfactant concentration, and then decrease. These anomalies disappear if allowance is made for the relative amounts of "free" and micellar bound hydrogen ions, because the reaction rate of the micellized substrate is proportional to the latter. Reduction of micellar catalysis by NaCl or Me$_4$NCl depends in part on a decrease in the concentration of micellar bound hydrogen ions. Smaller differences between $k_\psi/C_{H^+}$ and $k_\psi/a_{H^+}$ are found for the reaction inhibited by cetyltrimethylammonium bromide (CTABr).

Many of the reactions which are catalyzed by micelles are pH dependent.[2] For some reactions the rate changes with pH until all the substrate is converted into the reactive species and is then independent of pH, as in unimolecular hydrolyses of phosphate esters[7] or decarboxylations,[8] but often the hydrogen or hydroxide ions are catalysts or reagents or the reaction is general catalyzed. Many of these reactions are most conveniently followed in the pH range 3–11, where buffers are used, and the concentration of hydrogen or hydroxide ion is calculated from the pH.

In the absence of micelles, it is relatively simple to decide whether a reaction is catalyzed generally or specifically,[9] but this problem is less straightforward in the presence of micelles which can change acid dissociation constants. The situation is more uncertain with base catalysis because then we must assume that the autoprotolysis constant of water is unaffected by micelles and that pH measurement or buffer equilibria are unaffected by micelles.[3-6] When the stoichiometric concentration of hydrogen or hydroxide ions has been used in calculations, the second-order rate constants ($k_\psi/C_{H^+}$ or $k_\psi/C_{OH^-}$) have generally decreased with increasing reagent concentration.[10,11] Occasionally second-order rate constants calculated using both approaches have been compared.[12]

To determine the seriousness of this problem, we chose a specific hydrogen ion catalyzed reaction rather than one dependent on hydroxide ion, because the

glass electrode is specific for hydrogen ions. The most convenient reaction appeared to be acetal hydrolysis, catalyzed by anionic micelles of sodium lauryl sulfate, NaLS, in dilute strong acid or buffer. These reactions have been studied extensively in the presence and absence of micelles.[13-16] We used the relatively unreactive p-nitrobenzaldehyde diethyl acetal (I) as sub-



strate. Its hydrolysis is catalyzed specifically by hydrogen ions, with a convenient rate at pH 2–3 in the presence of anionic micelles of NaLS.[16] This pH can be obtained using either buffers or dilute hydrochloric acid. Some experiments were done with added salts and with cationic micelles of cetyltrimethylammonium bromide (CTABr).

The observed second-order rate constants, calculated as $k_\psi/C_{H^+}$ or $k_\psi/a_{H^+}$, in the presence of micelles varied over a factor of 4 depending upon the source and concentration of hydrogen ions. Measurements of the extent of micellar catalysis therefore have significance only under certain arbitrary conditions, and there are problems in comparing rates of micellar catalyzed reactions carried out in solutions of different acidities.

## Experimental Section

**Materials.** p-Nitrobenzaldehyde diethyl acetal (I) was prepared by standard methods and was vacuum distilled.[14,16] Its nmr spectrum (60 mHz) was consistent with the structure, and <1% of free aldehyde could have been detected.

Sodium lauryl sulfate (NaLS) was recrystallized three times from aqueous EtOH, and cetyltrimethylammonium bromide (CTABr)

(1) Support of this work by the National Science Foundation and the Arthritis and Metabolic Diseases Institute of the U. S. Public Health Service is gratefully acknowledged.

(2) For reviews of kinetic effects of micelles, see ref 3–6.

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(14) T. H. Fife and L. K. Jao, *J. Org. Chem.*, 30, 1492 (1965); T. H. Fife, *Accounts Chem. Res.*, 5, 264 (1972).

(15) R. H. DeWolfe, K. M. Ivanetich, and N. F. Perry, *J. Org. Chem.*, 34, 848 (1969).

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was recrystallized three times from EtOH-acetone and once from MeOH-ether. All the experiments were done using the same samples of surfactants.

**Measurement of pH.** A Corning Model 12 expanded scale meter was used with a Corning combination electrode; generally the ternal reference electrode were used, but a separate calomel reference electrode and a salt bridge of NaCl-agar were used occasionally. The electrode was stored in pH 7 buffer (Mallinkrodt) and was washed in deionized water before use; it was then rinsed with pH 7 buffer and the meter was standardized using first pH 7 and then pH 2 buffer. Whenever the solution was changed, the electrode was rinsed with deionized water and the surplus water removed and the meter was restandardized using the pH 7 and 2 buffers. The response of the electrode became slow after prolonged exposure to surfactant, but it was restored by soaking the electrode in 0.1 $M$ HCl.

All pH measurements were made at least in triplicate and they agreed within ±0.02. When measurements were made on solutions containing NaLS with the combination electrode, there was a very slow but steady drift of the pH reading. Potassium lauryl sulfate is only sparingly soluble in water and its precipitation at the KCl salt bridge in the combination electrode probably caused this drift. We therefore carried out some measurements using an external electrode with a NaCl-agar salt bridge and found no slow long term drift, and the initial pH readings determined using either internal or external reference electrodes agreed within 0.02. Care should be taken in using pH-Stat methods for rate measurement or pH control in the presence of some surfactants, and even though NaCl is considered to be less satisfactory than KCl in reducing liquid junction potentials at salt bridges,[17] it may be useful in the presence of anionic surfactants. Two glass electrodes were used in these experiments and they gave the same pH readings.

Some experiments were made in order to decide whether the variations of pH which we observed were artifacts due to the effects of the surfactants on the glass electrode or the liquid junction potential at the salt bridge.

(i) In an earlier study it had been shown that up to $10^{-2}$ $M$ NaLS changed the pH of water by less than 0.1,[18] and we confirmed this observation. (Professor Luis Sepulveda informs us that he has found that CTABr has no large effects upon the pH of redistilled water.)

(ii) The increase of pH on addition of NaLS to a solution of buffer or dilute HCl decreases with increasing concentration of buffer or HCl (Table I).

**Table I.** Effect of NaLS upon pH[a]

| $C_{NaLS}$, | Buffer | | | | | | | |
| $M$ | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| | 3.00 | 2.55 | 2.04 | 1.53 | 2.46 | 2.63 | 2.37 | 2.43 |
| 0.008 | 3.18 | 2.61 | 2.11 | 1.69 | 2.54 | 2.67 | 2.42 | 2.43 |
| 0.012 | 3.24 | 2.73 | 2.17 | | | | | |
| 0.018 | 3.39 | 2.81 | 2.24 | 1.75 | 2.63 | 2.82 | 2.51 | 2.46 |
| 0.024 | | 2.88 | 2.34 | | | | | |
| 0.036 | 3.62 | 2.94 | 2.40 | 1.84 | 2.71 | 2.93 | 2.60 | 2.49 |
| 0.060 | 3.79 | 3.12 | 2.51 | 1.93 | 2.79 | 3.00 | 2.63 | 2.50 |
| 0.084 | | 3.18 | | | | | | |

[a] Values of pH measured in the reaction solution: A, $10^{-3}$ $M$ HCl; B, $3.16 \times 10^{-3}$ $M$ HCl; C, $10^{-2}$ $M$ HCl; D, $2.95 \times 10^{-2}$ $M$ HCl; E, chloroacetate; HA:A = 14.5:2 m$M$; F-H, cyanoacetate; respectively HA:A = 6:4 m$M$, 13.5:5 m$M$, and 60:40 m$M$.

(iii) The pH of $10^{-2}$ $M$ HCl or cyanoacetate buffer is little affected by CTABr (Table II).

(iv) The pH of hydrogen oxalate-oxalate ion buffer is little affected by NaLS. The pH of a solution of 0.10 $M$ $(CO_2)_2H^-$ and $(CO_2)_2^{2-}$ changes from 3.65 to 3.67 in 0.069 $M$ NaLS. This observation suggests that pH changes on addition of anionic surfactants will be least if both components of the buffer are anionic. We assume that a similar principle could be used in selecting buffers

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**Table II.** Effect of CTABr upon pH[a]

| | Buffer | |
| $C_{CTABr}$, $M$ | 0.01 $M$ HCl | Cyanoacetate[b] |
|---|---|---|
| | 2.04 | 2.37 |
| 0.0076 | 2.07 | |
| 0.0076[c] | 2.05 | |
| 0.008 | | 2.37 |
| 0.008[c] | | 2.34 |
| 0.0171 | 2.11 | |
| 0.018 | | 2.36 |
| 0.0342 | 2.11 | |
| 0.036 | | 2.35 |
| 0.0571 | 2.13 | |
| 0.060 | | 2.34 |

[a] Values of pH. [b] 0.0135 $M$ cyanoacetic acid and 0.0005 $M$ sodium cyanoacetate. [c] With 0.01 $M$ NaCl.

to be used with cationic surfactants, although we have not tested this point.

**Kinetics.** The reaction was followed in the usual way at 267 nm using a Gilford spectrophotometer, with a water-jacketed cell compartment at 25.0°. A solution (0.5 $\mu$l) of the acetal in ethanol was added to 2.5 ml of the reaction solution. The aqueous solutions were prepared using water redistilled over $KMnO_4$, and $CO_2$ free water was used to make up the solutions for runs using $10^{-3}$ $M$ HCl or buffer. The first-order rate constants were generally calculated using the integrated first-order rate equation and a Hewlett Packard 9820A desk computer with a least-squares program. Guggenheim's method[19] was used for some of the slower runs, and for the slowest runs in the presence of CTABr, we could not obtain a stable infinity value for the absorbance. For these runs we used a successive approximation procedure to obtain the infinity absorbance value. This drift in the infinity absorbance could have been caused by oxidation of $p$-nitrobenzaldehyde. Micellization speeds the acid hydrolysis of alkyl sulfate ions,[20] but this reaction is very slow under our conditions, and caused no problems.

**Critical Micelle Concentrations.** The critical micelle concentrations (cmc) of NaLS were calculated using literature values for NaCl;[21] those in dilute HCl were determined using a Fisher surface tension balance.[22] Our results (Table III) are in the expected range.

**Table III.** Values of Cmc of NaLS

| $10^3C_{HCl}$, $M$ | Salt | $10^3$Cmc, $M$ |
|---|---|---|
| 1.00 | | 4.07 |
| 3.16 | | 3.55 |
| 10.0 | | 2.25 |
| 30.0 | | 1.12 |
| 10.0 | 0.053 $M$ $Me_4NCl$ | 1.05 |
| 10.0 | 0.105 $M$ $Me_4NCl$ | 0.5 |
| 10.0 | 0.05 $M$ NaCl | 1.5[a] |
| 10.0 | 0.10 $M$ NaCl | 1.0[a] |

[a] Estimated using the data of M. L. Corrin and W. D. Harkins *J. Amer. Chem. Soc.*, **69**, 683 (1947).

## Results

**Kinetics in the Absence of Surfactant.** The various values of the second-order rate constants (Table IV) were calculated using either $C_{H^+}$ for dilute HCl or $a_{H^+} = -$antilog pH for buffer solutions.

The mean value of $k_2 = 0.287$ l. mol$^{-1}$ sec$^{-1}$ agrees

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(20) J. L. Kurz, *J. Phys. Chem.*, **66**, 2239 (1962); V. A. Motsavage and H. B. Kostenbander, *J. Colloid Sci.*, **18**, 603 (1963).
(21) M. L. Corrin and W. D. Harkins, *J. Amer. Chem. Soc.*, **69**, 683 (1947).
(22) K. Shinoda, T. Nakagawa, B.-I. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., 1963, Chapter 1.
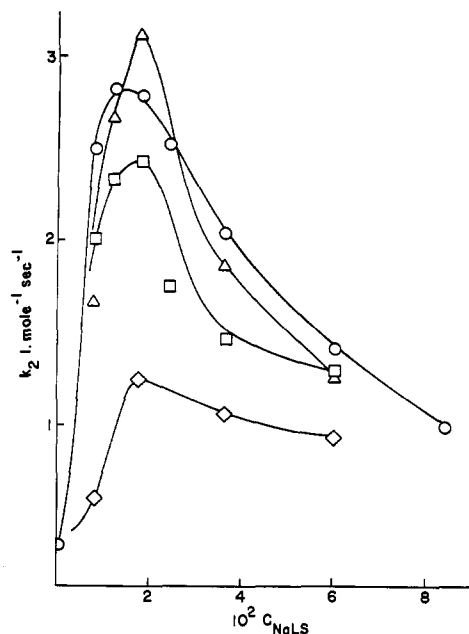
Figure 1. Variation of $k_2 = k_\psi/C_{H^+}$ with $C_{NaLS}$ in dilute HCl at 25.0°: ($\triangle$) $10^{-3}$ $M$ HCl; ($\bigcirc$) $3.16 \times 10^{-3}$ $M$ HCl; ($\square$) $10^{-2}$ $M$ HCl; ($\Diamond$) $3 \times 10^{-2}$ $M$ HCl.

Table IV. Second-Order Rate Constants for Hydrolysis in Absence of Surfactants[a]

| Acid | $10k_2$, l. mol$^{-1}$ sec$^{-1}$ |
|---|---|
| $3.16 \times 10^{-3}$ $M$ HCl | 3.00 |
| $1.00 \times 10^{-2}$ $M$ HCl | 2.67 |
| $3.00 \times 10^{-2}$ $M$ HCl | 2.98 |
| $1.00 \times 10^{-2}$ $M$ cyanoacetate | 2.67 |
| $1.85 \times 10^{-2}$ $M$ cyanoacetate | 2.88 |
| $1.00 \times 10^{-1}$ $M$ cyanoacetate | 3.20 |
| $1.65 \times 10^{-2}$ $M$ chloroacetate | 2.70 |

[a] At 25.0°; the values of $k_2$ in HCl are $k_\psi/C_{H^+}$, those in buffer are $k_\psi/a_{H^+}$.

reasonably well with the value of 0.34 l. mol$^{-1}$ sec$^{-1}$ reported by Dunlap, Ghanim, and Cordes[16] for reaction in cyanoacetate buffer in the absence of surfactant, and these variations in $k_2$ could be caused by errors in the pH measurements and by differences in the ionic strengths of the reaction solutions. These reactions are often followed at constant ionic strength, but the specificity of kinetic salt effects makes this approach suspect,[23,24] and it is useless in the presence of micelles.[25]

**Kinetics in the Presence of Surfactant.** For reactions catalyzed by dilute HCl, we calculated the second-order rate constants, $k_2^c$ and $k_2^a$, using either the stoichiometric concentration of hydrogen ions or $-$antilog pH, where pH is determined in the presence of the surfactant, so that $k_2^c = k_\psi/C_{H^+}$; $k_2^a = k_\psi/a_{H^+}$. These second-order rate constants are plotted in Figures 1 and 2 against the concentration of NaLS. As expected, $k_2$ rises steeply to maxima which are followed by a gradual decline.[3-6] The values of both $k_2^c$ and $k_2^a$ depend upon the concentration of HCl, and $k_2^a > k_2^c$ for all con-

(23) C. A. Bunton and J. D. Reinheimer, *J. Phys. Chem.*, 74, 4457 (1970).

(24) P. Salomaa, A. Kankanpera, and M. Lahti, *J. Amer. Chem. Soc.*, 93, 2084 (1971).

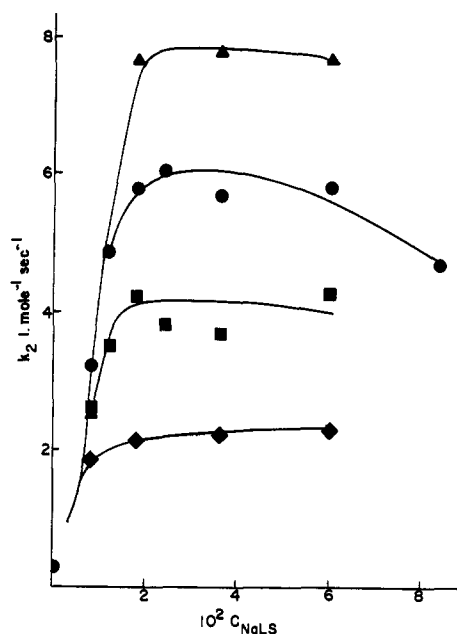(25) C. A. Bunton in "Reaction Kinetics in Micelles," E. H. Cordes, Ed., Plenum Publishing Co., New York, N. Y., 1972.

Figure 2. Variation of $k_2 = k_\psi/a_{H^+}$ with $C_{NaLS}$ in dilute HCl: ($\blacktriangle$) $10^{-3}$ $M$ HCl; ($\bullet$) $3.16 \times 10^{-3}$ $M$ HCl; ($\blacksquare$) $10^{-2}$ $M$ HCl; ($\blacklozenge$) $3 \times 10^{-2}$ $M$ HCl.

centrations of acid, with large differences between the rate constants at different acid concentrations.

The situation is even more confusing for reaction in the presence of buffers. The second-order rate constants were calculated in two ways: (i) by assuming that the pH is unaffected by added surfactant, and $k_2^b = k_\psi/a^b_{H^+}$, where $a^b_{H^+}$ is calculated from the pH of the buffer in the absence of surfactant, or (ii) by assuming that the pH of the solution in the presence of surfactant gives the activity of the hydrogen ion, $a^m_{H^+}$, and $k_2^m = k_\psi/a^m_{H^+}$. There is no reason to trust the validity of any of these assumptions, as can be seen from the various sets of values of $k_2$ which, plotted against surfactant concentration (Figure 3), show that the apparent micellar catalysis depends upon the source of the hydrogen ions, and the method of calculation. Although these second-order rate constants go through maxima with increasing surfactant concentration, the fall off is greatest for the more dilute acids, and is always greater for $k_\psi/C_{H^+}$.

Relations between micellar catalysis and substrate structure may be in error if the nature or concentration of the acid is changed from one experiment to another, as is often the case where substrate reactivities are very different. There is also a large element of arbitrariness in estimating the extent of micellar catalysis (Table V).

Table V. Maximum Rate Enhancements by Micelles of NaLS[a]

| Acidic medium | $k_{rel}$ | Acidic medium | $k_{rel}$ |
|---|---|---|---|
| $1 \times 10^{-3}$ $M$ HCl | 27.3 (10.8) | Chloroacetate[b] | 18.2 (12.1) |
| $3.16 \times 10^{-3}$ $M$ HCl | 20.9 (8.9) | Cyanoacetate[c] | 21.6 (13.2) |
| $1 \times 10^{-2}$ $M$ HCl | 13.5 (8.5) | Cyanoacetate[d] | 14.8 (10.6) |
| $3 \times 10^{-2}$ $M$ HCl | 8.0 (4.4) | Cyanoacetate[e] | 7.7 (7.0) |

[a] Values calculated from $k_2^a$ or $k_2^m$, the values in parentheses were calculated from $k_2^c$, or $k_2^b$, for optimum $C_D$. [b] $1.45 \times 10^{-2}$ $M$ ClCH$_2$CO$_2$H $+ 2 \times 10^{-3}$ $M$ ClCH$_2$CO$_2$Na. [c] $6 \times 10^{-3}$ $M$ NCCH$_2$CO$_2$H $+ 4 \times 10^{-3}$ $M$ NCCH$_2$CO$_2$Na. [d] $1.35 \times 10^{-2}$ $M$ NCCH$_2$CO$_2$H $+ 5 \times 10^{-3}$ $M$ NCCH$_2$CO$_2$Na. [e] $6 \times 10^{-2}$ $M$ NCCH$_2$CO$_2$H $+ 4 \times 10^{-2}$ $M$ NCCH$_2$CO$_2$Na.
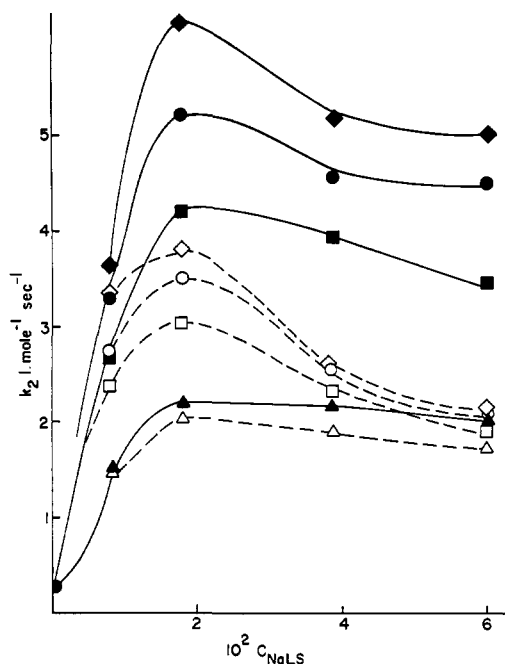
Figure 3. Variation of $k_2$ with $C_{NaLS}$ in the presence of buffers (see Table I for code). Open points are calculated using the pH in the absence of surfactant, solid points in the presence of surfactant. Buffers: (●,○) E; (◆,◇) F; (■,□) G; (▲,△) H.

However, the maximum rate of hydrolysis is always found at *ca.* 0.02 $M$ NaLS (Figures 1–3).

The measurement of pH in the normal way is subject to considerable uncertainties, both experimental and theoretical.[17,26] An error of ±0.02 unit in the pH corresponds to an error of approximately ±5% in the value of $k_2$, but although some of the scatter in plots of $k_2$ *vs.* $C_{NaLS}$ could be caused by such errors, the overall discrepancies are much too large to be explained in these terms, and a more detailed consideration of the problem is required.

**Micellar Inhibition.** As expected, cationic micelles of CTABr inhibit the reaction (Figure 4), but the various second-order rate constants are in fair agreement over a range of concentrations of CTABr. These results are understandable because micellar inhibition implies that the reaction is taking place in the bulk of the solution and not on the micelles,[3–6,27] and cationic micelles do not interact strongly with hydrogen ions and influence the pH (Table II). However, even here the agreement between the various $k_2$ values is no better than fair, and uncertainties could arise because of interactions between CTA$^+$ and the buffer anions and because the cationic micelles might influence the liquid junction potential at the salt bridge. (The pH measurements in CTABr were made using the internal reference electrode.)

**Salt Effects on Micellar Catalysis.** So far as we are aware, added salts always reduce the micellar catalysis of bimolecular reactions, unless they introduce a new reaction path, and the retardation increases with decreasing charge density of the counterion to the micelle.[3–6,25] The rate retardation can be explained in part in terms of exclusion of ionic reagents from the

(26) R. G. Bates in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 2.
(27) F. M. Menger and C. E. Portnoy, *J. Amer. Chem. Soc.*, **89**, 4698 (1967).
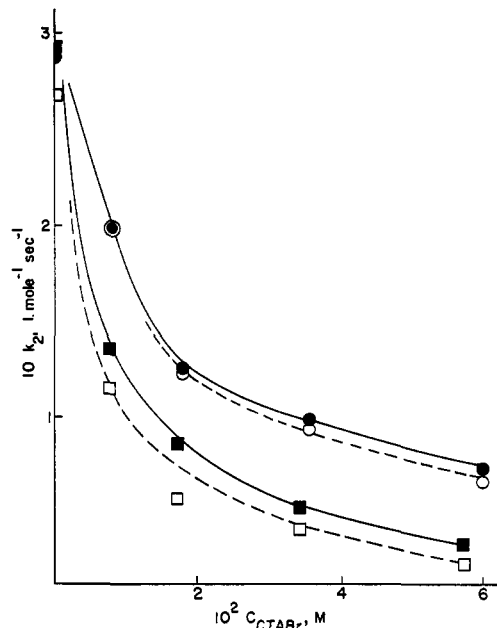


Figure 4. Inhibition in dilute HCl (squares) or cyanoacetate buffer; 0.0135 $M$ NCCH$_2$CO$_2$H, 0.005 $M$ NCCH$_2$CO$_2$Na (circles): (□) $k_\psi/C_{H^+}$; (■) $k_\psi/a_{H^+}$; (○) $k_\psi/a^b_{H^+}$; (●) $k_\psi/a^m_{H^+}$.

micellar pseudophase although changes in micellar structure may also be important.[8,25,28] We used salts only for reaction catalyzed by HCl, because they change the dissociation of weak acids, but nonetheless salt effects depend upon the scale of acidity which is used, and as shown in Table VI the values of $k_2^c$ and $k_2^a$ differ slightly.

Table VI. Salt Effects upon Micellar Catalysis[a]

| Salt | pH | $10^3 k_\psi$, sec$^{-1}$ | $k_\psi/C_{H^+}$ | $k_\psi/a_{H^+}$ |
|---|---|---|---|---|
| | 2.24 | 24.2 | 2.42 | 4.21 |
| 0.05 $M$ NaCl | 2.20 | 10.0 | 1.00 | 1.58 |
| 0.10 $M$ NaCl | 2.14 | 9.76 | 0.98 | 1.35 |
| 0.053 $M$ Me$_4$NCl | 2.12 | 5.43 | 0.54 | 0.72 |
| 0.105 $M$ Me$_4$NCl | 2.10 | 3.54 | 0.35 | 0.45 |

[a] At 25.0° with 0.018 $M$ NaLS and 0.01 $M$ HCl.

**pH Measurements in the Presence of Micelles.** Addition of NaLS to solutions of either dilute HCl or carboxylate buffers increases the pH (Table I), with the effect being largest for the most dilute acids, as would be expected if hydrogen ions are attracted into the Stern layer of the micelles. The glass electrode is specific for the hydrogen ion, but assumptions have to be made in setting up a pH scale, notably that the liquid junction potential of the salt bridge is relatively independent of the electrolyte solution.[17,26] Surfactants could affect pH measurements in several ways, for example by changing the liquid junction potential or the characteristics of the glass electrode, and affecting the dissociation of a buffer acid. Our measurements of the effect of CTABr on the pH of dilute HCl, and of acetate and benzoate at *ca.* pH 4 by Dr. Minch show that at concentrations below the cmc, this surfactant slightly increases the pH, but above the cmc the effect is small for

(28) C. A. Bunton, M. J. Minch, and L. Sepulveda, *J. Phys. Chem.*, **75**, 2707 (1971).

dilute HCl and acetate buffer, but is greater for benzoate buffer, probably because of interactions between the cationic micelles and benzoate ion.[29] These observations, and those cited in the Experimental Section, suggest that the major effect of cationic surfactants on the pH of buffers comes from changes in the ionic equilibria, and these can be minimized by using hydrophilic buffers.

Added salts compete with hydrogen ions for an anionic micelle and slightly decrease the pH of dilute HCl (Table VI).

We hoped to find evidence for the interactions of OH⁻ with CTABr by pH measurements, but the effects were only a little larger than those caused by addition of CTABr to water. In this system, changes in both the autoprotolysis constant of water in the micelle and the liquid junction potential by CTABr could complicate the measurements. Similar experiments using an Orion fluoride electrode 96-09 in sodium fluoride and CTABr were also unsatisfactory because the change in potential (12 mV) on addition of CTABr was the same in deionized redistilled water as in $10^{-3}$ $M$ NaF. However, successful use of other specific anion electrodes has been made by others.[30]

## Discussion

**Significance of Rate Measurements in Solutions of Micelles.** The disagreement between the various values of the second-order rate constants (Figures 1–4 and Table V) shows the limitations of the accepted treatment of hydrogen ion catalyzed reactions in the presence of anionic micelles and possibly of all bimolecular micellar catalyzed reactions. Possible causes of these discrepancies are as follows.

(i) The ionic media are different for these reactions, and salt effects upon the micellar catalysis could be important, except that all the solutions were dilute, and the major differences were the presence of chloride rather than carboxylate ions. Hydrophobic ions, such as arenesulfonates and tetraalkylammonium ions, have large effects upon reaction in micelles,[4,6,25] but such ions were not present in our acidic solutions.

(ii) The pH measurements may have no significance in the presence of micelles if they interfere with the functioning of the glass electrode, but this drastic hypothesis is not supported by evidence from pH studies in biological systems[17] and that cited in the Experimental Section. In addition there is extensive work on the satisfactory use of other specific ion electrodes in the presence of micelles.[30-32]

(iii) The hydrolysis of simple acetals is a multistep reaction in which the first protonation step is generally considered to be rapid and reversible, but micelles might change the nature of the rate-limiting step although there is no evidence that intermediates build up in this reaction.[13-15,33] In addition, there is no reason to believe that general acids could be catalysts in the presence of micelles. The variation of rate with buffer concentration does not fit this explanation.

Unimolecular micellar catalyzed reactions give plateaux values of rate constants when all the substrate is taken up by the micelles, as predicted by the quantitative treatment of micellar catalysis, but this treatment is unsatisfactory for bimolecular micellar catalyzed reactions which generally show rate maxima rather than the predicted plateaux.[6,7,10] However, micellar inhibited bimolecular reactions can generally be treated satisfactorily in terms of the quantitative treatment of a partitioning of substrate between the aqueous phase and the micelles.[6,10,27]

Several explanations have been given for the failure of the quantitative treatment of bimolecular micellar catalyzed reactions and the rate maxima which are observed, bearing in mind the successful treatment of micellar inhibition. It has been suggested that inhibition by the counterions of the surfactant is important,[8,34] and another explanation is that when there is sufficient surfactant to take up all the substrate, addition of further surfactant generates more micelles, so that the probability of a micelle containing both substrate and ionic reagent is reduced.[7,10] We use this second explanation to explain the differences in the second-order rate constants for the reaction catalyzed by NaLS in the presence of dilute HCl, and we believe that it may be generally applicable. In using this approach, we calculate the amount of free and micellar bound hydrogen ions from the pH following standard methods for the estimation of micellar bound ions,[30-32] i.e., we calculate the "concentration" of hydrogen ions in the micellar pseudophase for solutions of dilute HCl.

**Catalysis by Strong Acid.** We assume that all the acetal is taken up by the micelles at concentrations of NaLS greater than 0.018 $M$[35] (Figures 1–4) and use the pH in the presence of surfactant to calculate the free and micellar bound hydrogen ions by assuming that

$$-\text{antilog pH} = a_{\text{H}^+} \approx C^{\text{w}}_{\text{H}^+}$$

so that

$$C_{\text{H}^+} = C^{\text{w}}_{\text{H}^+} + C^{\text{m}}_{\text{H}^+}$$

(where $C^{\text{w}}_{\text{H}^+}$ and $C^{\text{m}}_{\text{H}^+}$ are the concentrations of free and micellar bound hydrogen ions); cf. ref 30–32.

At $C_{\text{NaLS}} \gg 0.018$ $M$ a second-order rate constant for this reaction is obtained by dividing the first-order rate constant by the concentration of hydrogen ions per unit concentration of hydrogen ions in the micelles. We cannot conveniently use molarity, and therefore we use unit molality, i.e., the number of hydrogen ions per micelle.

It is generally assumed that the concentration of micelles, $C_{\text{m}}$, is given by[6,27,36]

$$C_{\text{m}} = (C_{\text{D}} - \text{cmc})/N \qquad (1)$$

(where $N$ is the aggregation number).

The concentration of bound hydrogen ions/mol of micelle is given by

$$m^{\text{m}}_{\text{H}^+} = C^{\text{m}}_{\text{H}^+}N/(C_{\text{D}} - \text{cmc})$$

(29) M. J. Minch, unpublished results.

(30) W. K. Mathews, J. W. Larsen, and M. J. Pikal, *Tetrahedron Lett.*, 513 (1972), and references cited therein.

(31) M. E. Feinstein and H. I. Rosano, *J. Colloid Interface Sci.*, 24, 73 (1967).

(32) T. Ingram and M. N. Jones, *Trans. Faraday Soc.*, 65, 297 (1969).

(33) C. A. Bunton and R. H. DeWolfe, *J. Org. Chem.*, 30, 1371 (1965); T. H. Fife, *Accounts Chem. Res.*, 5, 264 (1972).

(34) R. B. Dunlap and E. H. Cordes, *J. Amer. Chem. Soc.*, 90, 4395 (1968); L. R. Romsted and E. H. Cordes, *ibid.*, 90, 4404 (1968).

(35) For general consideration of the incorporation of substrates into micelles, see ref 3–6.

(36) The assumptions involved in eq 1 have been discussed extensively. The most serious ones in our treatment are that $N$ and the structure of the micelle are independent of the reactants and that the cmc is independent of the (low) concentration of substrate.

**Table VII.** Kinetic Treatment of the Micellar Catalyzed Reaction in HCl

| | $C_{H^+}$, M | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1.0 × 10⁻³ | | | 3.16 × 10⁻³ | | | 1.0 × 10⁻² | | | 3.0 × 10⁻² | | |
| $10^2 C_{NaLS}$ | $10^3 C^w_{H^+}$ | $m^m_{H^+}$ | $10^3 k_\psi/m^m_{H^+}$ | $10^3 C^w_{H^+}$ | $m^m_{H^+}$ | $10^3 k_\psi/m^m_{H^+}$ | $10^3 C^w_{H^+}$ | $m^m_{H^+}$ | $10^3 k_\psi/m^m_{H^+}$ | $10^3 C^w_{H^+}$ | $m^m_{H^+}$ | $10^3 k_\psi/m^m_{H^+}$ |
| 1.8 | 0.41 | 2.64 | 1.18 | 1.55 | 5.45 | 1.64 | 5.75 | 13.3 | 1.82 | 17.8 | 42.9 | 0.88 |
| 2.4 | | | | 1.32 | 4.55 | 1.76 | 4.57 | 13.0 | 1.34 | | | |
| 3.6 | 0.24 | 1.48 | 1.26 | 1.15 | 3.19 | 2.05 | 3.98 | 9.45 | 1.54 | 14.5 | 26.6 | 1.19 |
| 6.0 | 0.16 | 1.24 | 1.34 | 0.16 | 2.26 | 1.96 | 3.09 | 6.45 | 2.05 | 11.7 | 18.7 | 1.43 |
| 8.4 | | | | 0.66 | 1.66 | 1.87 | | | | | | |

and the second-order rate constant is simply $k_\psi/m^m_{H^+}$. The units of this rate constant are sec⁻¹, and it can be compared with the usual second-order rate constant for an acid catalyzed reaction in water by dividing the latter by 55.5 (if the solution is dilute so that 1000 ml of it contain 55.5 mol of water). In this approach we are comparing the rates of reaction in the micelles and in the water in terms of reactant concentration/mol of water or of micelle. In order to make this comparison, we use a value of $N = 62$ for NaLS.[37] This value of $N$ is an arbitrary one, because it was determined in the absence of added electrolyte, and $N$ probably increases as electrolyte is added. Our general conclusions are not affected by the value assigned to $N$, and we could just as well calculate a second-order rate constant, $k_\psi/m^s_{H^+}$, in terms of concentration/mol of micellized surfactant, where $m^s_{H^+}$ is the concentration of bound hydrogen ions/mol of micellized surfactant, i.e.

$$m^s_{H^+} = C^m_{H^+}/(C_D - \text{cmc})$$

The values of $k_\psi/m^m_{H^+}$ are given in Table VII, and multiplying them by $N = 62$ gives the values of $k_\psi/C^s_{H^+}$. Bearing in mind the uncertainties involved in rate and especially in pH measurement these values are as good as can be expected, and they account for the variations in the rate constants with concentration of dilute acid. They do not decrease at high surfactant concentrations, as do the values of $k_2^c$ and $k_2^a$ (Figures 1–3), suggesting that this rate fall off is indeed associated with a "dilution" of the hydrogen ions on addition of micelles.[7,10] This treatment is least satisfactory for the highest concentration of HCl, which is to be expected because our assumptions about micellar structure fail when large numbers of hydrogen ions are interacting strongly with the anionic micelle and displacing sodium ions from its Stern layer. Our assumption that the rate of reaction in the micellar pseudophase will be proportional to the number of hydrogen ions in the micelle may be unsatisfactory if the number of hydrogen ions/micelle becomes very high especially if some of them are in a second sphere or bound covalently to the lauryl sulfate ion, i.e., if lauryl sulfuric acid in micelles of NaLS is not strong[38] (the increase of the rate constants with increasing NaLS concentration in 0.03 $M$ HCl (Table VII) could be explained in these terms). There are also problems for the most dilute solutions of HCl, not so much because of perturbations of micellar structure, but because of the experimental errors in estimating the number of hydrogen ions/micelle and the inherent uncertainties of pH measurement and the fact that in very dilute HCl most of the hydrogen ions are taken up by the anionic micelle.

(37) K. J. Mysels and L. H. Princen, *J. Phys. Chem.*, **63**, 1696 (1959).
(38) The acid hydrolysis of micellized alkyl sulfates shows that the undissociated acid is formed,[20] but only at relatively high acidities.

**Table VIII.** Treatment of Kinetics in Terms of Molality per Micellized Surfactant Ion[a]

| $10^2 C_{NaLS}$ | $10^3 C_{H^+}$ | | | |
|---|---|---|---|---|
| | 1.00 | 3.16 | 10.0 | 30.0 |
| 1.8 | 7.4 | 10.2 | 11.3 | 5.5 |
| 2.4 | | 10.9 | 8.3 | |
| 3.6 | 7.8 | 12.7 | 9.6 | 7.5 |
| 6.0 | 8.3 | 12.2 | 12.7 | 8.9 |
| 8.4 | | 11.6 | | |

[a] Values of $10^2 k_\psi/m^s_{H^+}$.

In calculating the second-order rate constants in terms of hydrogen ions/micelle (Table VII) we ignore the increasing aggregation number of the micelle with increasing electrolyte concentration[39] (for example, $N = 72$ for NaLS in 0.03 $M$ NaCl[37]). Allowance for this increase would slightly increase the rate constants in 10⁻³ $M$ HCl, relative to the others, but the overall uncertainties in our treatment are greater than this correction, so we have not made it, and we have no information on the aggregation number of the lauryl sulfate ion in the presence of relatively high concentrations of hydrogen ions.

The mean value of the second-order rate constants, $k_\psi/m^m_{H^+}$, for reactions in the micelle is 1.65 × 10⁻³ sec⁻¹, with the concentration expressed in unit molality; it can be compared with that of 1.02 × 10⁻¹ sec⁻¹ for the mean value of $k_\psi/m^s_{H^+}$ (Table VIII) and 0.287 × 55.5 = 15.9 for the mean second-order rate constant calculated in terms of the unit molality of hydrogen ions in water for reaction in water in the absence of micelles, expressed in terms of the unit molality of HCl in water. Paradoxically, the second-order rate constants for reaction in the micelles expressed either in terms of concentration per micelle or surfactant are very much smaller than that in water. Incorporation of the substrate and the hydrogen ions into the anionic micelle will stabilize them relative to solution in water, and this stabilization is apparently only partially offset by micellar stabilization of the transition state. Much of the rate enhancement of this bimolecular reaction is therefore caused by the bringing together of the reagents by the micelle, in other words by a proximity effect.

Proximity effects could be important in many systems, for example for reactions in ice[40] and in enzymes.[5] It has been argued that they should be relatively small,[41a]

(39) E. W. Anacker and H. M. Ghose, *J. Phys. Chem.*, **67**, 1713 (1963); *J. Amer. Chem. Soc.*, **90**, 3161 (1968); T. Cohen and T. Vassilliades, *J. Phys. Chem.*, **65**, 1774 (1961).
(40) R. E. Pincock, *Accounts Chem. Res.*, **2**, 97 (1969).
(41) (a) D. R. Storm and D. E. Koshland, *Proc. Nat. Acad. Sci. U. S.*, **66**, 445 (1970); A. Daffron and D. E. Koshland, *ibid.*, **68**, 2463 (1971); (b) M. I. Page and W. P. Jencks, *Proc. Nat. Acad. Sci. U. S.*, **68**, 658 (1971); (c) T. C. Bruice, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 21 (1971); *Nature (London)*, **237**, 335 (1972); T. C. Bruice, A. Brown, and D. O. Harris, *Proc. Nat. Acad. Sci. U. S.*, **68**, 658 (1971).
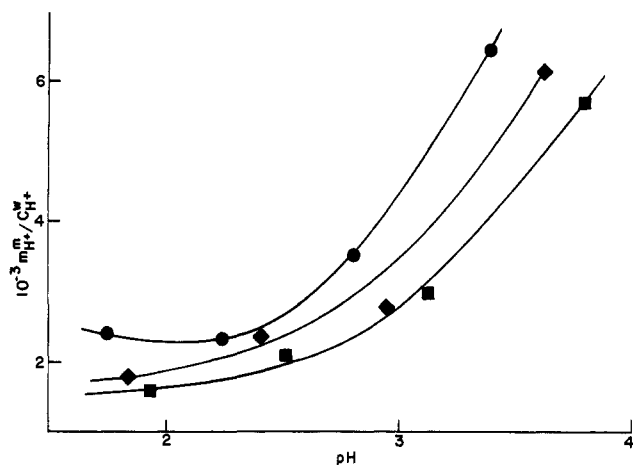
Figure 5. Relationship between "free" and micellar bound hydrogen ions in dilute HCl and pH: (●) 0.018 $M$ NaLS; (◆) 0.036 $M$ NaLS; (■) 0.06 $M$ NaLS.

but this argument assumes no specific interaction between reagents and catalyst (cf. ref 5, 41b,c).

Micellar catalysis, and presumably catalysis by polyelectrolytes[3,42] and liquid crystals,[43] thus depends in a complex way upon proximity and the relative interactions of initial and transition states with an interface, except that for unimolecular micellar catalyzed reactions, proximity effects are absent, and we are concerned only with the interactions of the initial and transition states in the micelle.

The kinetically unfavorable factors of reagent incorporation are offset by favorable micelle–transition state interactions and the fact that entropy of translation (and possibly of other degrees of freedom) of the reactants has been lost in their incorporation into the micelle. We can compare micellar catalysis of bimolecular reactions with intramolecular catalysis, and they have similar rate enhancing factors.[41]

**Treatment of Salt Effects.** Using the pH of dilute HCl in the presence of NaLS and added sodium or tetramethylammonium chloride, we calculated the amounts of free and micellar bound hydrogen ions given in Table IX, and hence the values of the second-

Table IX. Kinetic Treatment of the Kinetic Salt Effects[a]

| Salt | $10^3 C^w_{H^+}$ | $m^s_{H^+}$ | $10^2 k_\psi / m^s_{H^+}$ |
|---|---|---|---|
| 0.05 $M$ NaCl | 6.31 | 0.017 | 5.9 |
| 0.10 $M$ NaCl | 7.24 | 0.011 | 8.3 |
| 0.053 $M$ Me₄NCl | 7.59 | 0.009 | 6.0 |
| 0.105 $M$ Me₄NCl | 7.94 | 0.0067 | 5.3 |

[a] In 0.018 $M$ NaLS and $10^{-2}$ $M$ HCl.

order rate constants, $k_s$, in terms of bound hydrogen ions/micellized surfactant. In calculating the cmc values, we assume the effects of dilute HCl and the salts upon the cmc are additive. The problem in calculating $k_\psi / m_{H^+}$ in the presence of added salts is that the aggregation numbers of NaLS in Me₄NCl have not been measured, although we expect them to be larger than in NaCl.[37,39]

(42) C. G. Overberger and J. C. Salamone, Accounts Chem. Res., 2, 217 (1969).
(43) S. T. Ahmad and S. Friberg, J. Amer. Chem. Soc., 94, 5196 (1972).

Comparison of the amounts of "free" and micellar bound hydrogen ions with those in the absence of added salts suggests that part of the negative salt effect is, as predicted, caused by exclusion of the hydrogen ion from the micelle, but the fact that these rate constants (Table IX) are approximately half those calculated for the absence of added salts suggests that other effects, e.g., changes in the structure of the micelles, or in their number, are of importance. Added salts cause micelles to grow and change their shapes from spherical toward spheroidal and eventually to rodlike, and these changes could affect reaction rate at the micellar surface. At the same time the approximations involved in relating the concentration of free hydrogen ions to pH become highly suspect with increasing ionic strength, and the reliability of the second-order rate constants decreases.

**Treatment of the Reaction in Buffered Solutions.** The amounts of "free" and micellar bound hydrogen ions can be calculated from pH measurements of surfactant solutions if the total concentration of hydrogen ions is known, as it is for solutions of dilute HCl,[44] but this treatment cannot be applied to buffered solutions. There should be a relation between the relative amounts of free and micellar bound hydrogen ions and the surfactant concentration, although we would not expect it to be simple. However, we noticed that the values of $m^m_{H^+} / C^w_{H^+}$ (this term is proportional to the concentrations of free and bound hydrogen ions) varied smoothly with pH for a given concentration of surfactant in dilute HCl, except for the lower concentrations of surfactant. These variations are shown in Figure 5. In constructing these plots, we did not use surfactant concentrations below 0.018 $M$ because at these low concentrations the cmc is not small relative to $C_{NaLS}$, and in any event we have restricted our kinetic treatment to surfactant concentrations which are large enough for the bulk of the substrate to be incorporated in the micelle.

If we assume that the relation between free and bound hydrogen ions will be the same in dilute buffer and HCl solutions of the same pH, we can use the curves in Figure 5 to calculate the concentrations of hydrogen ions/ micelle in the buffered solutions. These values of $m^m_{H^+}$ are given in Table X. In calculating them, we assume that the cmc = $10^{-3}$ $M$ for NaLS in all the solutions, on the assumption that chloride and the carboxylate ions will have similar effects upon the cmc. (The error which is introduced by this assumption is much less than those which stem from the experimental and theoretical uncertainties of the pH measurements.) Contrary to our expectations, we found satisfactory agreement between the values of $k_\psi / m^m_{H^+}$ for all except the most concentrated buffer, and even here the value was essentially independent of $C_{NaLS}$, and the agreement between these values of $k_\psi / m^m_{H^+}$ for the various buffers contrasts sharply with the large differences between $k_2^b$ and $k_2^m$ shown in Figure 3. Our treatment should be least satisfactory at relatively high concentrations of HCl or buffers because of electrolyte effects upon the micellar properties and the errors in the pH measurements.

The most unexpected result was the agreement between the values of $k_\psi / m^m_{H^+}$ in the buffers and in dilute

(44) The calculation assumes that there are no covalently bound hydrogen ions in the micelle.

Table X.

**Table X.** Kinetic Treatment of the Micellar Catalyzed Reaction in Buffer

| Buffer[a] | $10^2 C_{NaLS}$ | $10^3 k_\psi$ | $10^3 C^w_{H^+}$ | $m^m_{H^+}/C^w_{H^+}$[b] | $m^m_{H^+}$ | $10^3 k_\psi/m^m_{H^+}$ |
|---|---|---|---|---|---|---|
| A | 1.8 | 12.2 | 2.34 | 2940 | 6.88 | 1.77 |
| A | 3.6 | 8.87 | 1.95 | 2630 | 5.13 | 1.73 |
| A | 6.0 | 7.30 | 1.62 | 2310 | 3.74 | 1.95 |
| B | 1.8 | 8.97 | 1.51 | 3610 | 5.45 | 1.65 |
| B | 3.6 | 6.06 | 1.17 | 3200 | 3.74 | 1.62 |
| B | 6.0 | 5.04 | 1.00 | 2790 | 2.79 | 1.81 |
| C | 1.8 | 13.0 | 3.09 | 2680 | 8.28 | 1.57 |
| C | 3.6 | 9.91 | 2.51 | 2450 | 6.15 | 1.61 |
| C | 6.0 | 8.08 | 2.34 | 2090 | 4.89 | 1.65 |
| D | 1.8 | 7.65 | 3.47 | 2610 | 9.06 | 0.84 |
| D | 3.6 | 7.11 | 3.24 | 2300 | 7.45 | 0.95 |
| D | 6.0 | 6.40 | 3.16 | 1960 | 6.19 | 1.03 |

[a] Buffers: A, $1.45 \times 10^{-2}$ $M$ $ClCH_2CO_2^-$ + $2 \times 10^{-3}$ $M$ $ClCH_2CO_2Na$; B, $6 \times 10^{-3}$ $M$ $NCCH_2CO_2H$ + $4 \times 10^{-3}$ $M$ $NCCH_2CO_2Na$; C, $1.35 \times 10^{-2}$ $M$ $NCCH_2CO_2H$ + $5 \times 10^{-3}$ $M$ $NCCH_2CO_2Na$; D, $6 \times 10^{-2}$ $M$ $NCCH_2CO_2H$ + $4 \times 10^{-2}$ $M$ $NCCH_2CO_2Na$. [b] Estimated from the data plotted in Figure 5.

HCl. The mean of the values of $k_\psi/m^m_{H^+}$ in HCl is $1.61 \times 10^{-3}$ sec$^{-1}$ (except in 0.03 $M$ HCl where it is $1.74 \times 10^{-3}$ sec$^{-1}$), whereas that for all the buffers except the most concentrated one is $1.73 \times 10^{-3}$ sec$^{-1}$. This agreement leads us to believe that it is possible to treat these reactions by our method irrespective of the source of the hydrogen ions, and that electrolyte effects upon micellar structure are not especially important in these dilute solutions. The values of $k_\psi/m^m_{H^+}$ in buffer are independent of surfactant concentrations for $C_{NaLS} \gg 0.018$ $M$ in agreement with the results for dilute HCl.

## Conclusions

We can draw certain conclusions from these results.

(i) Comparisons of the reactivities of various substrates in bimolecular micellar catalyzed reactions are meaningful only if they are made under identical conditions, and they apply only to these particular conditions.

(ii) The decrease of rate of these reactions with increasing surfactant concentration above that required for incorporation of all the substrate into the micelles can be explained in terms of a dilution of the reagent over an increasing number of micelles. Our results were obtained for a hydrogen ion catalyzed reaction but we expect the same explanation to apply to reactions of anionic reagents.

(iii) Complete interpretation of the relation between reaction rate and surfactant concentration requires the separation of free and micellar bound reagents (the hydrogen ion in the present work). This problem complicates the interpretation of, for example, solvent isotope or temperature effects in micellar catalysis.

(iv) The treatment in principle allows us to isolate electrolyte effects caused by exclusion of the reagent from the micelle provided that micellar properties such as cmc and aggregation number are known under the appropriate conditions.

(v) It will be difficult in most cases to provide complete kinetic interpretations if buffers are used to control hydrogen or hydroxide ion concentration, and therefore it will be difficult to interpret micellar effects upon general acid or base catalyzed reactions.

Many micellar catalyzed reactions are being studied in which it will not be possible to separate the concentrations of "free" and micellar bound reagent, if only because specific electrodes are not available for all ionic reagents and the problem is even worse for uncharged reagents. In these cases it will be wise to specify the reaction conditions in detail, and if several buffers have to be used for a range of substrates of different reactivities it may be possible to relate activities by overlapping the buffers, so that each pair of compounds can be studied under common conditions by an approach similar to that which Hammett used in developing his acidity scale.[45]

We deliberately restricted our study to a hydrogen ion catalyzed reaction in micelles, but the same problems may be present in other systems, for example, in reactions catalyzed by polyelectrolytes, or liquid crystals, or enzymes, where a reagent can be distributed to an unknown extent between the aqueous phase and the pseudophase of the catalyst. In some of these reactions it may also be difficult to decide whether pH can be used to calculate the activity of the hydrogen or hydroxide ions, and to establish the significance of the relative reactivities of various substrates, or of the source of any rate enhancements that may be observed, and we may have to be content with the measurement of gross differences in reaction rates determined under various arbitrary conditions. We do not suggest that discussion of micellar catalysis is unwarranted when the amounts of "free" and micellar bound reagents cannot be estimated, but in these cases it will be difficult to separate the various factors which influence reactivity, just as kinetic solvent effects are often discussed even when the solvent effects upon the free energies of the initial and transition states are not known, although this separation enormously clarifies any discussion. However, the present results suggest that observations on micellar catalyzed bimolecular reactions by ourselves and others may be incomplete in not taking into account the partitioning of a reagent between the solvent and the micelles.

(45) R. H. Boyd in "Solvent Solute Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.