Tetrahedron Vol. 43, No. 2, pp. 345 to 350, 1987
Printed in Great Britain.

0040-4020/87 $5.00+.00

REACTIONS OF BETAINE ESTERS WITH HYDROXIDE ION IN REACTIVE AND UNREACTIVE COUNTERION SURFACTANT

HAMAD A.AL-LOHEDAN

Dept. of Chemistry, King Saud University, P.O.Box 2455,
Riyadh-11451, Saudi Arabia.

(*Received in UK* 24 *September* 1986)

Abstract - The reaction of hydroxide ion with methyl N-alkyl-N,N-dimethylglycinate(1) is catalysed by cationic micelles. The variation of the first-order constant, k_ψ, with the concentration of CTACl can be fitted to the pseudophase ion-exchange model, but this model fails when the counterion of the surfactant is OH^-. The variations of k_ψ with counterion of CTAOH fit a kinetic model in which the distribution of the OH^- between the aqueous and micellar pseudophase depends upon $[OH^-]$. The value for the second-order rate constant in the micellar pseudophase predicted by both models is similar and it is smaller than the second-order rate constants in water.

Micellar effects upon the reactions of nucleophiles with carboxylic esters have extensively studied[1-3]. Rate surfactant profiles have been interpreted quantitatively in terms of the concentrations of the two reactants in the Stern layer,and the second-order rate constant in that layer[3-6]. This pseudophase model suggests that second-order rate constants in the micellar pseudophase are similar to those in water.

The concentration of hydrophobic reactant in the micellar pseudophase can often be estimated directly by solubility measurements, ultrafiltration, gel filtration or spectrophotometrically[2], but the problem is more difficult with hydrophilic ions. A very useful and widely used approach is to assume that counterions compete for ionic sites on the micellar surface and that the fraction β of these sites which are neutralized by counterions is approximately constant[7]. This general approach has been applied successfully to rate and equilibrium constant of many reactions in aqueous micelles[8-11]. However, the treatment involves several parameters, e.g. β , whose values are not known with certainty. In addition, interionic competition between, for example, an inert anion Cl^- and a nucleophile OH^- may not be described accurately in terms of an ion-exchange model (Scheme 1 where subscripts W and M denote aqueous and micellar pseudophase respectively).

Scheme 1

$$OH^-_M + Cl^-_W \rightleftharpoons OH^-_W + Cl^-_M$$

$$K^{OH}_{Cl} = [OH^-_W][Cl^-_M] / [OH^-_M][Cl^-_W] \quad ...... \quad 1$$

The problem of interionic competition can be eliminated by using a reactive-ion surfactant in which ionic reagent is the micellar counterion[12-14] such as CTAOH. Therefore its concentration in the micellar pseudophase should be constant, provided that β is constant and the first-order rate constant, k_ψ, for the overall reaction, should increases with increasing [surfactant] and become constant once substrate is fully micellar bound. This behaviour has been observed for reactions involving hydrogen ions[12] in micellized alkanesulfonic acids and of N-alkylpyridinium ion in micellized CTACN[13] and for substitution by Br^- [15,16]. Nucleophilic reaction in CTAOH and CTAF do not fit this pattern[12,14,17] and it appears that here the concentration of micellar bound OH^- or F^- increases with increasing total concentration. We were interested, therefore, in studying reactions of other substrates such as betaine esters (1) in micellized reactive-ion surfactant where the nucleophile was OH^- and in CTACl Scheme 2.

Scheme 2

$$R\overset{+}{N}Me_2CH_2CO\text{-}OMe \;+\; OH^- \longrightarrow R\overset{+}{N}Me_2CH_2CO_2^- \;+\; MeOH$$

1

1_a R = $C_{10}H_{21}$

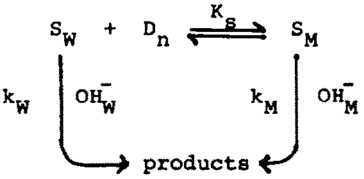
1_a R = $C_{12}H_{25}$

1_c R = $C_{14}H_{29}$

RESULT AND DISCUSSION

The second-order rate constant, k_ψ, for aqueous basic hydrolysis of the hydrophobic betaine esters (1) is 79 $M^{-1}s^{-1}$. The variation of the observed first-order rate constants, k_ψ, with [CTACl] follows a typical pattern, i.e. they goes through maxima with increasing surfactant concentration at constant $[OH^-]$ (figure 2) but in case of reactive-ion surfactant, such as CTAOH, the observed first-order rate constants, k_ψ, increase with increasing [CTAOH] or $[OH^-]$ (figure 1)

Scheme 3



The relation between rate and surfactant concentration can be written in terms of scheme 3 for reactions of anions[19].

The substrate S and hydroxide ion (OH^-) will be distributed between aqueous and micellar pseudophases, denoted by the subscripts W and M, respectively, with reaction occurring in either pseudophase, D_n the micellized surfactant and K_s the binding constant is given by

$$K_s = [S_M]/[S_W]\,([D] - CMc) \quad \dots\dots\dots\dots\dots\dots \quad 2$$

Reactive-ion Surfactant: Scheme 3 leads to eq. 3, where the bracketed quantities represent concentrations in moles per liter of solution and m_{OH}^{s} is the mole ratio of bound OH^- to micellized surfactant, and k_M (s^{-1}) the related second-order rate constant[3,14,20]

$$\text{rate} = k_W[S_W][OH_W^-] + k_M[S_M]\,m_{OH}^{s} \quad \dots\dots\dots\dots\dots\dots \quad 3$$

where

$$m^{s}_{OH} = [OH^{-}_{M}] / [D_{n}] \qquad \ldots\ldots\ldots\ldots\ 4$$

The observed first-order rate constant with respect to S is given by

$$k_{\psi} = \frac{k_{W}[OH^{-}_{W}] + k_{M}K_{s}\, m^{s}_{OH}\,([D] - CMc)}{1 + K_{s}\,([D] - CMc)} \qquad \ldots\ldots\ldots\ldots\ 5$$

If OH^{-} is the only counterion in solutions[12,13,17]

$$m^{s}_{OH} = \beta \qquad \ldots\ldots\ldots\ldots\ 6$$

and with fully bound substrate

$$k = \beta\, k_{M} \qquad \ldots\ldots\ldots\ldots\ 7$$

i.e., k_{ψ} should then reach a constant value. This behaviour is found for reactions in some reactive ion surfactant, e.g. CTACN[13], CTABr[15,16] and some sulfonic acids[12]. However, it is convenient to write eq.5 in the form

$$k_{\psi} = \frac{k_{W}[OH^{-}_{W}] + k_{M}K_{s}\,[OH^{-}_{M}]}{1 + K_{s}\,([D] - CMc)} \qquad \ldots\ldots\ldots\ldots\ 8$$

We assume that the distribution of a counterion OH^{-} between the aqueous and micellar pseudophases follows eq. 9, where, K'_{OH}

$$K'_{OH} = [OH^{-}_{M}]/[OH^{-}_{W}]\,([D_{n}] - [OH^{-}_{M}]) \qquad \ldots\ldots\ldots\ldots\ 9$$

can be regarded as a binding constant assumed to be independent of the concentration of counterions in the aqueous and micellar pseudophases.

Our approach is to use eq. 8 and 9 to simulate the variation of k_{ψ} (eq.8) with concentration of surfactant or added nucleophile. The second-order rate constant k_{W}, are measured directly and k_{M}, K_{s} and K'_{OH} are treated as adjustable parameters. However, for basic hydrolysis of 2-naphthyl acetate in CTAOH, $K_{OH} = 60\ M^{-1}$ [18,22], and we use this value here. The critical micelle concentration, CMC is also treated as an adjustable parameter. Variations in the CMC, k_{W} and K_{s} have little effect on most of our simulated rate-surfactant profiles because most of our experiments were done at relatively high [surfactant] especially with the more hydrophobic substrate. The CMC was taken to be 8×10^{-4} for CTAOH and 4×10^{-4} for CTACl and K_{s} are relatively unimportant but we take $K_{s} = 30$, 62, 275 for decyl, dodecyl and tetradecyl derivatives respectively. This general model is described in detail in ref. 8 and 18

The treatment can also be applied to experiments with add OH^{-}. The ion binding parameters were $K'_{OH} = 60\ M^{-1}$, under all conditions. Our estimates of k_{M} are in Table 1.

Reaction in CTACl: The rate-surfactant profile can be treated quantitatively by using the pseudophase ion-exchange model based on eq. 1, with the concentration of micellar-bound OH^{-} calculated by using the ion-exchange equilibrium 1[7]. The values of ion-exchange constants have been estimated by several methods such as electrochemistry[23,24] or an indicator such as arenesulfonate ion[25] or ultrafiltration.

The other general approach is to simulate the variation of rate or equilibrium constant with [surfactant] by taking the ion-exchange constant as an adjustable parameter[7,8,11,24]. These various methods predict values of K^{OH}_{Br} of 10-20[8,14,22] and K^{OH}_{Cl} 3-6[8]. This treatment has a fundamental problem which is that the treatment contain a variety of adjustable parameters and the data can often be fitted by various combination of these parameters[8]. The general approach in fitting the variation of k_ψ with [surfactant] or salt is to use eq. 1 and the mass balance relation with assumed values of K_{Cl}^{OH} to calculate $[OH_M^-]$ and $[OH_W^-]$, to insert these values into the rate equation, using assumed values of k_M and K_s and measured k_W and to simulate the variation of k_ψ with [CTACl] for example.

Our data could be fitted by taking $K_{Cl}^{OH} = 4\ M^{-1}$ and $\beta = 0.75$ (cf. ref.7,8 and 26). We assumed that K_s are similar to those which we use for reaction in CTAOH(fig.2) i.e.,30, 62, 275 M^{-1} for substrate (1a-c) respectively. Variations in the CMC or K_s had no effect on the predicted rate-surfactant profiles except in very dilute surfactant. The estimates of k_M (s^{-1}) are given in Table 1.

Table 1. Values of k_M[a]

substrate[b]	conditions[c]		
	1	2	3
$C_{10}H_{21}\overset{+}{N}Me_2Y$	150	144	140
$C_{12}H_{25}\overset{+}{N}Me_2Y$	140	140	130
$C_{14}H_{29}N\ Me\ Y$	135	133	125

[a] values of k_M in reciprocal seconds at 25°C

[b] $Y = CH_2CO_2Me$

[c] 1 , in CTAOH ; 2. in CTAOH + OH^- ; 3, in CTACl .

<u>Rate Constants in the Micellar and Aqueous Pseudophase</u>: Rate constants in the micellar pseudophase, k_M cannot be compared directly with second-order rate constant in water k_W. The comparison can be made considering that the volume of Stern layer of micelles, 0.14 L mol^{-1} is the volume element of reaction in the micellar pseudophase[3,14,15] so that the second-order rate constant k_M in terms of moles of reagent in 1 L of Stern layer is

$$k_2^m = 0.14\ k_M \qquad \text{.............} \quad 10$$

When we calculate the second-order k_2^m using eq. 10 for various esters in micellar pseudophase it appears that k_2^m is 17-22 $M^{-1}\ s^{-1}$ and is smaller than k_W in water which is 79 $M^{-1}\ s^{-1}$ for reactions of (1 a-c). These differences are not unexpected because there is a negative salt effect on reactions of OH^- with betaine esters in water[27], and the high ionic concentration in the Stern layer should inhibit reactions. However, all the treatments suggest that concentration of reactants into a small volume at the micelle-water interface is the main factor in rate enhancements of bimolecular reactions.

EXPERIMENTAL

The preparation or purification of N-alkyl-N,N-dimethylglycinate and CTACl follows standard methods[8,12]. The surfactant CTAOH was prepared from CTABr by treating it with Ag_2SO_4 and the product $(CTA)_2SO_4$ was treated with $Ba(OH)_2$[18] .The CTAOH was prepared and stored in a refrigerator, although we saw no evidence of decomposition when they were left for several days at room temperature under N_2. The absence of Br^-, Ba^{2+}, SO_4^{2-} in CTAOH was tested by standard methods.

All the reaction were followed spectrophotometrically at 215 nm in water at 25.0°C. The change in absorbance during reaction was small and we were restricted as to the range of reactant concentration. We used 0.002 M ester and 0.02 M NaOH, so that the individual runs were first-order for most of the reactions. The first-order rate constants, k_ψ are expressed in reciprocal seconds. The inert counter-ion was Cl^- in all the experiments because absorbance by Br^- causes problem at these low wavelength.

Acknowledgement : Support of this work by the Research Center, College of Science, King Saud University is greatly acknowledged.

REFERENCES

1. Martinek,K.; Yatsimirski,A.K.;Levashov,A.V.; Berezine,I.V. "In Micellization, Solubilization and Microemulsions", Mittal,K.L.; Ed., Plenum Press,New York, 1977.
2. Fendler,J.H.; Fendler,E.J., "Catalysis in Micellar and Micromolecular solutions", Academic Press, New York, 1975.
3. Al-Lohedan,H.A., Ph.D.thesis, University of California,Santa barbara,1981.
4. Al-Megren,M.; Rydholm,R., J.Phys.Chem., 1979,83,360.
5. Cucovia,I.M.; Schroter,E.H.; Monterio,P.M.; Chaimovich,H., J.Org.Chem.,1978, 43,2248.
6. Epstein,J.; Kaminski,J.J.; Bodor,N.; Enever,R.; Sowa,J.; Huguchi,T., J.Org. Chem.,1978,43,2816.
7. Romsted,L.S. in ref. 1, p.509.
8. Al-Lohedan,H.; Bunton,C.A.; Romsted,L.S., J.Phys.Chem.,1981,85,2123.
9. Quina,F.H.; Chaimovich,H., J.Phys.Chem., 1979,83,1844.
10. Bunton,C.A.; Romsted,L.S.; Sepulveda,L., J.Phys.Chem., 1980,84,2611.
11. Funasaki,N.; Murata,A., Chem.Pharm.Bull., 1980,28,805.
12. Bunton,C.A.; Romsted,L.S.; Saelli,G., J.Am.Chem.Soc.,1979,101,1253.
13. Bunton,C.A.; Romsted,L.S.; Thamavit,C., J.Am.Chem.Soc.1980,101,3900.
14. Al-Lohedan,H.; Bunton,C.A., J.Org.Chem.,1982,47,1160.
15. Al-Lohedan,H.; Bunton,C.A.; Moffatt,J.R., J.Phys.Chem.,1983,87,332.
16. Bunton,C.A.; Romsted,L.S., In "Solution Behaviour of Surfactants. Theoretical and Applied Aspects",Fendler,E.J.,Mittal,K.L.,Ed. Plenum Press, New York,1982, Vol.2, p.975.
17. Bunton,C.A.; Frankson,J.; Romsted,L.S., J.Phys.Chem.,1980,84,2607.
18. Bunton,C.A.; Gan,L.H.; Moffatt,J.R.; Romsted,L.S.; Savelli,G., J.Phys.Chem., 1981,85,4118.
19. Menger,F.M.; Portnoy,C.F., J.Am.Chem.Soc.,1967,89,4968.
20. Bunton,C.A.; Carrasco,N.; Huang,S.K.; Paik,C.H., J.Am.Chem.Soc.,1978,100,5420.
21. Al-Lohedan,H.; Bunton,C.A.; Romsted,L.S., J.Org.Chem.,1982,47,3528.
22. Vera,S.; Rodenas,E., Tetrahedron,1986,42,143.
23. Larsen,J.W.; Magid,L., J.Am.Chem.Soc.,1974,46,5774.
24. Bunton,C.A.; Ohenzetto,K.; Sepulveda,L., J.Phys.Chem.,1979,81,2000.
25. Bartet,D.; Gamboa,C.; Sepulveda,L., J.Phys.Chem.,1980,84,272.
26. Gunnarson,G.; Jonsson,B.; Wennerstrom,H., J.Phys.Chem.,1980,84,3114.
27. Bell,R.P.; Lindars,F.J., J.Chem.Soc.,1954,4601, Bell,R.P.; Collier,B.A.W., Trans. Faraday Soc.,1964,60,1087.

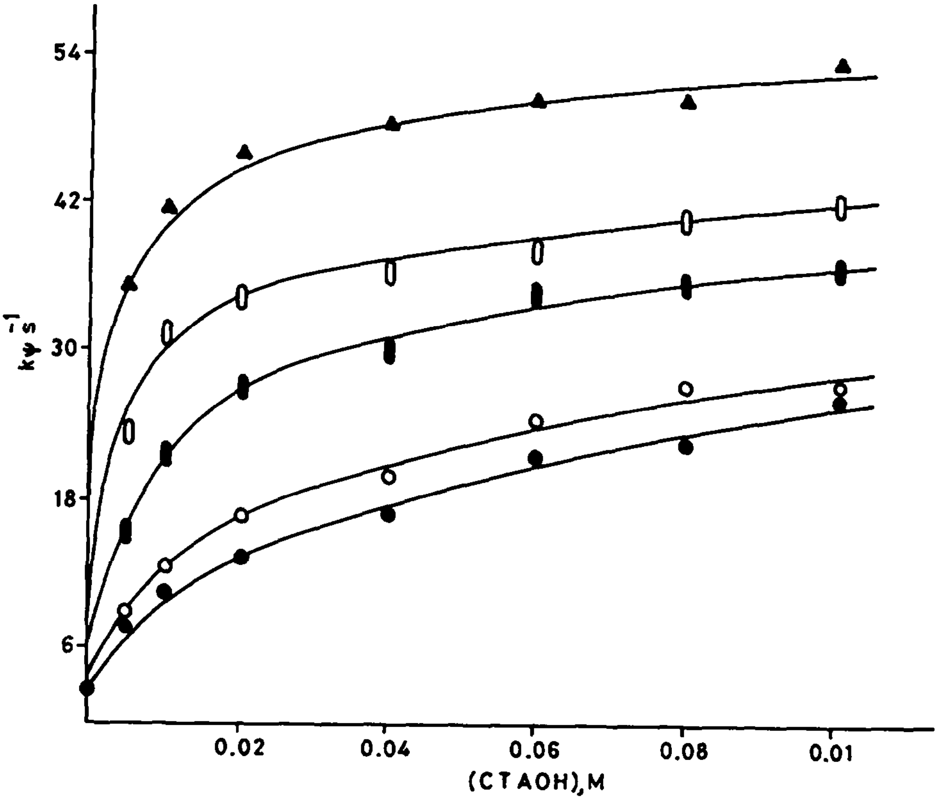


Fig. 1. Reaction of betain esters (1) in CTAOH solid points in CTAOH, open in (CTAOH 0 01 M NaoH); (●,o) $R=C_{10}H_{21}$(▮,0) $R=C_{12}H_{25}$(▲) $R=C_{14}H_{29}$

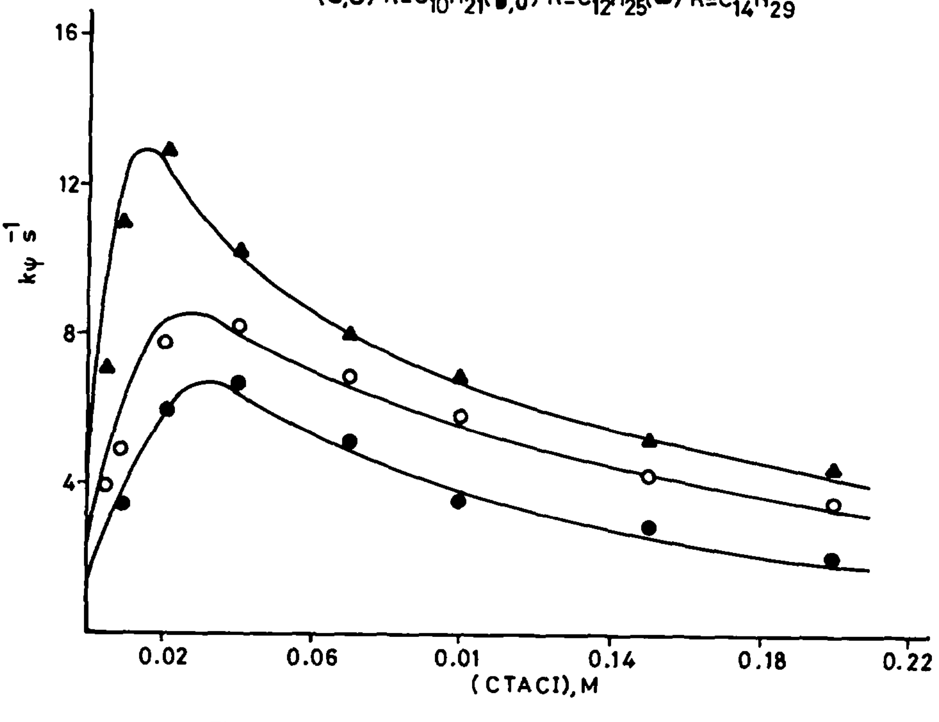


Fig. 2. Reactions of N-decyl, N-dodecyl and N-tetradecyl-N,N-dimethylglycinate with 0 02 M $\bar{O}H$ in CTACl, (O) $R=C_{10}H_{21}$ (●) $R=C_{12}H_{25}$(▲) $R=C_{14}H_{29}$