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MICELLAR CATALYSIS OF ORGANIC REACTIONS. PART 35. KINETIC DETERMINATION OF THE CRITICAL MICELLE CONCENTRATION OF CATIONIC MICELLES IN THE PRESENCE OF ADDITIVES

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The critical micelle concentration of solutions of cetyltrimethylammonium bromide and of tetradecyltrimethylammonium bromides were determined by a kinetic method. This involved the determination of the rates of the hydroxydehalogenation of some activated aromatic substrates over a wide range of detergent concentrations. Measurements were made in solutions containing significant quantities of added hydroxyl ion and substrates which were themselves amphiphilic. Conventional methods cannot be applied with confidence to such systems. The effects of changing hydroxyl ion concentrations, added sodium bromide, changing the nature of the aromatic substrate (whether neutral or charged), the identity of the micellar counterion and the temperature were investigated. It was wound that added bromide or hydroxyl ions resulted in a lower CMC whereas increased temperature led to an increase in the CMC. The nature of the micellar counterion (Br, F, OH, SO_4) had little effect on the CMC. The presence of a charged aromatic substrate led to a considerable lowering of the CMC, whereas the neutral aromatic substrate used showed very little effect.

INTRODUCTION

The concentration at which micelles begin to form is known as the critical micelle concentration (CMC).[1] Many methods exist to determine this concentration, the most commonly used being conductance, viscosity and surface tension measurements.[1] A plot of any of these values against the detergent concentration shows a marked change in gradient at the onset of micelle formation. These techniques are most useful to determine the CMC of pure micellar solutions and such values are available in the literature.[1] However, the application of such CMC values to real reaction situations is highly questionable. It has long been known that for cationic detergents there is a strong dependence of CMC on the ionic strength. In particular, Bunton and Robinson[2] have shown that the CMC of the cationic detergent cetyltrimethylammonium bromide (CTAB) is decreased from 0·9 mM in pure water to 0·32 mM in the presence of 0·05 M hydroxide ion. This would correspond to a typical added hydroxide concentration used in kinetic studies of hydroxydehalogenation reactions. Simulations of the observed rate of reaction as a function of the detergent concentration by means of the pseudophase ion-exchange model (PPIE) of micellar catalysis depend on the input of an accurate CMC appropriate to the actual reaction conditions. In recent investigations of several nucleophilic aromatic substitution reactions (S_NAr) of hydroxyl ion, better correlations between experimental and calculated rates have been obtained when CMC values lower than those determined in the absence of any additives were used in the simulation.[3]

A kinetic method for determination of the CMC has recently been suggested.[3] Rate constants for a reaction are determined at a range of concentrations both above and below the accepted CMC. For example, in the case of CTAB, plots of rate versus CTAB concentration are obtained which show a sudden change of gradient at about 0·3 mM. Linear sections of the plot at concentrations below and just above this value are extended to produce a point of intersection which is taken as the CMC value. The value obtained by this method is one directly applicable to reaction conditions (in terms of temperature and the presence of substrate and nucleophile). We now report the application of this method to determine the effects of various changes to the solutions in the neighbourhood of these reaction conditions.

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RESULTS AND DISCUSSION

Second-order rate constants for the hydroxydehalogenation of 1-chloro-2,4-dinitrobenzene (**1**), sodium 4-chloro-3,5-dinitrobenzoate (**2**) and sodium 2-chloro-3,5-dinitrobenzoate (**3**) are given in Tables 1–4. The derived CMC values are also included in these tables and the values obtained are summarized in Table 5.

Table 1. Second-order rate constants [$10^3 \times k_2$ (l mol^{-1} s^{-1})] for the hydroxydehalogenation of substrate **1** at 30·7 °C (40 mM hydroxide)

[CTAB] (mM)	k_2 (Br)	[CTAF] (mM)	k_2 (F)
0	0·255	0	0·255
0·1	0·298	0·191	0·344
0·2	0·36	0·334	0·744
0·3	0·59	0·381	1·10
0·4	1·19	0·477	1·69
0·5	2·25	0·596	3·11
0·6	3·10	0·667	3·99
0·7	4·15	0·715	4·53
0·8	4·99	0·953	7·57
0·9	6·20	1·191	10·6
1	7		
2	14·0		
4	21·6		
10	26·4		
12	24·9		
Calculated CMC (mM)	0·32		0·38

Effects of added NaOH and NaBr

From the reactions of substrate **2**, it can be seen in Table 2 that the CMC of CTAB is 0·14 mM in the presence of this substrate and 20 mM hydroxide ion and that it falls to 0·12 mM if the hydroxide concentration is increased to 40 mM. These values should be compared with the accepted literature value of 0·9 mM in the absence of substrate and hydroxide ion.

A corresponding, although smaller, effect was also observed for tetradecyltrimethylammonium bromide (TTAB) where the CMC for a pure solution of 3·5 mM falls to 1·15 mM in the presence of substrate and 40 mM hydroxide ion and 0·95 mM when 5 mM added bromide is also present.

These effects can be rationalized in terms of increased counterion population in the Stern layer of the micelles arising from the higher ionic concentrations generally. This leads to reduced repulsions between micellar head groups, resulting In greater micelle stability, and hence lower CMC values. Bromide ion, which is much more strongly adsorbed than hydroxide ion in the Stern layer, has a correspondingly greater effect. The increased β

Table 2. Second order rate constants [$10^3 \times k_2$ (l mol^{-1} s^{-1})] for the hydroxydehalogenation of substrate **2** at 30·7 °C

	CTAB			TTAB	
[DET] (mM)	20 mM OH$^-$	40 mM OH$^-$	40 mM OH$^-$, 5 mM Br$^-$	40 mM OH$^-$	40 mM OH$^-$, 5 mM Br$^-$
0	1·13	1·13	1·15	1·13	1·15
0·05	1·14	1·24	1·29		
0·1	1·12	1·23	1·44		
0·15	2·44	2·95	3·55		
0·2	5·44	5·82	5·30		
0·3	14·2	13·0	9·66		
0·4	18·9	19·3	11·9		
0·5	31·6	23·4	15·1	1·12	1·12
0·6	35·1	29·1	15·5		
0·7	42·5	30·5	15·9		
0·8	45·7	32·9	17·0	1·14	1·13
1	47·8	33·1	17·6	1·18	1·9
1·2				2·22	4·03
1·4				4·15	7·01
1·5				5·71	8·03
2				13·4	14·1
2·5				18·7	14·9
3				23·4	15·5
3·5				23·4	16
4				23·6	16·5
Calc. CMC (mM)	0·14	0·12	0·08	1·15	0·95

Table 3. Second-order rate constants [$10^3 \times k_2$ (l mol^{-1} s^{-1})] for the hydroxydehalogenation of substrate **2** at 30·7 °C in micelles with various counterions

[CTA] (mM)	k (F)	[CTA] (mM)	k (OH)	[CTA] (mM)	k (SO$_4$)
0	1·13	0	1·13	0	1·13
0·024	1·29	0·022	1·27	0·04	1·15
0·048	1·13	0·043	1·34	0·08	1·27
0·083	1·17	0·054	1·19	0·10	1·20
0·119	1·40	0·086	1·44	0·12	1·40
0·143	2·63	0·108	2·87	0·14	1·78
0·191	5·72	0·129	4·86	0·16	3·13
0·238	8·57	0·151	6·07	0·18	3·80
0·286	11·6	0·216	13·4	0·20	5·29
0·334	16·5	0·27	19·6	0·24	7·76
0·381	18·8	0·302	23·7	0·30	12·6
0·477	24·9	0·345	28·8	0·36	17·1
0·596	32·9	0·431	40·8	0·40	18·8
0·667	35·9	0·518	48·8	0·60	29·4
0·715	39·2	0·604	52·9	0·80	34·3
0·953	43·0	0·647	59·4	1·0	35·7
1·191	—	0·669	67·2	1·20	35
Calc.CMC (mM)	0·13		0·12		0·14

Table 4. Second-order rate constants [$10^3 \times k_2$ (l mol^{-1} s^{-1})] for the hydroxydehalogenation of substrate **3** as a function of temperature

[CTAB] (mM)	30·7 °C	56·5 °C
0	0·027	0·42
0·04	—	0·45
0·05	0·055	—
0·08	—	0·51
0·1	0·055	—
0·12	—	0·48
0·15	0·082	—
0·16	—	0·46
0·2	0·118	0·70
0·3	0·44	1·01
0·4	1·105	2·5
0·5	1·58	5·18
0·6	2·12	8·71
0·7	2·47	13·5
0·8	2·66	13·7
0·9	—	18·2
1	3·04	18·9
Calc. CMC (mM)	0·24	0·38

value that arises in situations where added ions are present in the reaction solution needs to be taken into account in any simulation (β refers to the fraction of micellar head groups paired with a counterion in the Stern layer).

Effect of temperature

In Table 4, the results of studies of substrate **3** at two different temperatures are shown. The CMC is higher at the higher temperature. This result is not surprising since the micellization process involves an ordering of detergent molecules and would therefore be expected to involve a negative entropy change. An increase in temperature might therefore be expected to shift the equilibrium in favour of breaking up micelles. The prediction of entropy changes is, however, often complicated by solvation effects and the effect of temperature on CMC may not always be in this direction.

Effect of micellar counterion

The effect of the micellar counterion (F, Br, OH and SO$_4$) on the measured CMC in the reaction conditions studied was very small, barely outside experimental error for either of substrates **1** and **2**. This is not surprising in view of the fact that at concentrations around the observed CMC detergent counterions will exchange with swamping concentrations of hydroxide ions. Regardless of the nominal detergent counterion, the micelles are effectively micelles of CTA hydroxide at concentrations around the CMC in reaction conditions.

Effect of the aromatic substrate

The CMC value of 0·32 mM for CTAB in the presence of 40 mM hydroxide ion and neutral substrate **1** can be compared with Bunton and Robinson's value[2] of

Table 5. Comparison of CMC values (mM) at 30·7 °C obtained by different methods

Detergent	Conditions	Conductance	Kinetics
CTAB	Water	0·9	
	40 mM OH^-		
	Subst. **1**		0·32
	Subst. **2**		0·12
	Subst. **3**		0·24
	Subst. **3** at 56·5 °C		0·38
	40 mM OH^- + 5 mM Br^-		
	Subst. **2**		0·08
	20 mM OH^-		
	Subst. **2**		0·14
CTAF	40 mM OH^-		
	Water	0·9	
	Subst. **1**		0·38
	Subst. **2**		0·13
CTAOH	Total OH^- = 40 mM		0·116
CTAS	Water	0·6	
	40 mM OH^-		
	Subst. **2**		0·14
TTAB	Water	3.5	
	40 mM OH^-		
	Subst. **2**		1.15
	40 mM OH^- + 5 mM Br^-		
	Subst. **2**		0·95

0·32 mM for CTAB in the presence of 50 mM hydroxide ion at a slightly different temperature. This is an indication that this substrate itself has little or no effect on the CMC value. The only reservation is that Bunton and Robinson's result depends on a dye incorporation method and the dye itself may have an effect which is not negligible, and similar to that of the substrate.

With the presence of charged substrates, however, much lower values of CMC were observed. There is a strong indication that these anionic species are seeding the formation of micelles at very low concentrations. Substrates **2** and **3** have a geometry which allows for a close association of the anionic part of the substrate with the cationic quaternary ammonium of the CTA ion at the same time as the hydrophobic nitro groups of the substrate are associated with the hydrophobic cetyl section of the CTA ion.

For CTAB in the presence of 40 mM hydroxide ion, the CMC falls from 0·32 mM with substrate **1** to 0·24 mM with substrate **3** and 0·12 mM with substrate **2**. Similar effects are observed with CTAF. With substrate **2** a closer electrostatic interaction is possible than with substrate **3** because of the absence of the bulky chlorine atom *ortho* to the benzoate anion.

EXPERIMENTAL

Materials. Substrates **1**–**3** were available from previous studies.[4] CTAB was purified by the method of Mukerjee and Mysels.[5] TTAB was purified by recrystallization from ethanol as described by Nauman and Venable.[6] CTAF,[7] CTAS[8] and CTAOH[8] were prepared as described previously. Distilled water was further purified with a Millipore Milli-Q system to achieve a resistivity of 16 MΩ cm.

Kinetics. Stock solutions of the substrates (0·01 M in AR acetonitrile), detergents in water, and sodium hydroxide in water were prepared.

CTAF was stored in plastic equipment. Sodium hydroxide was standardized by titration against hydrochloric acid with bromocresol green as indicator. The required amount of detergent solution and sodium hydroxide were pipetted into a cuvette and the solution was allowed to reach thermal equilibrium in the sample compartment of the spectrophotometer. The substrate (18 μl) was then added by microsyringe, the mixture was stirred vigorously and product formation was monitored at 358 nm (**1**), 442 nm (**2**) and 373 nm (**3**) on a Varian DMS 70 UV–visible spectrophotometer. The reactions were followed for 10 half-lives where practical to obtain an experimental infinity measurement. For slow reactions data were collected over at least two half lives. A computer program designed to give the best straight-line fit was used to provide an infinity value by curve fitting. Good agreement was obtained between rate constants obtained by the two methods. Reactions were carried out in a cuvette maintained at constant temperature in the jacketed cell holder of the spectrophotometer.The temperature within the cell was determined with a Jenco Thermistor thermometer. Rate constants were obtained in duplicate and mean values are reported in the tables.

Critical micelle concentrations. (a) Conductivity. The CMC was determined in neutral solution at 30·0 °C, using a jacketed beaker containing purified water (30 ml) and a platinum electrode attached to an Activon PTI-10 conductivity meter. Aliquots (0·5 ml) of detergent solution (0·01 M) were added and the conductivity was measured as a function of detergent concentration.

(b) Kinetics. In the case of CTA-based systems, rates were measured for a series of detergent concentrations between 0 and 1 mM. In each case, a plot of rate constant versus detergent concentration showed two distinct linear sections: a low gradient linear section at very low concentration and a much steeper section at intermediate to high concentration. The CMC for the system was taken as being the concentration corresponding to the point of intersection between the two linear sections of the plot. A similar method was used for TTA-based systems, except that the concentration range was higher, detergent concentrations up to 4 mM being used.

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