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SHORT COMMUNICATION

SYNTHESIS AND PROPERTIES OF 4-CYANO-1-(7-CARBOXYHEPTADECYL)PYRIDINIUM BROMIDE: A PROBE OF THE IONIC COMPOSITION NEAR THE SURFACE OF POSITIVELY CHARGED MICELLES

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4-Cyano-1-(7-carboxyheptadecyl)pyridinium bromide (CCHP) was synthesized using standard procedures. The rates and product distribution of the reaction between OH^- ion and CCHP are very similar to those previously obtained with alkyl-substituted 4-cyanopyridinium ions. The effect of hexadecyltrimethylammonium bromide micelles on the rate and product distribution of CCHP indicated that the cyanopyridinium ring of this compound is distal to the surface of the micelle. CCHP constitutes a probe for ionic composition in the vicinity of positively charged micelles.

The structural and functional properties of micellar solutions depend critically on the ionic distribution near the micelle–water interface (Scheme 1).[1] There are several theoretical models that describe ion distribution in micellar solutions.[2] However, the experimental data available concern either the Stern layer[3] or the intermicellar aqueous space,[1a,4] with little or no experimental information on the ion distribution in the region surrounding the micelle. Here we report the synthesis of a probe for ionic distribution at sites distal to the micellar frontier (PMF). We also present preliminary results on the use of a PMF to investigate the distribution of OH^- in micelles of hexadecyltrimethylammonium (cetyltrimethylammonium) bromide (CTAB).

RESULTS AND DISCUSSION

The PMF synthesized (Scheme 2) was 4-cyano-1-(7-carboxyheptadecyl)pyridinium bromide (CCHP) (m.p. 138–140 °C). Analysis of CCHP (Central Analitica do Instituto de Química, USP): calculated for $C_{24}H_{39}BrN_2$, C 61·66, H 8·4, N 5·99; found, C 62·21, H 8·37, N, 6·06%. The NMR, UV and IR spectra were consistent with the structure.

The favourable hydrophobic contribution[1a,5] of the hexadecyl chain together with the (favourable) electrostatic[1a,5,6] interaction of the 7-carboxylate group with the alkylammonium moiety of CTAB and the repulsion of the positively charged surface[1] for the pyridinium ring are likely to lead to the conformation of micellar-incorporated CCHP shown schematically in Scheme 1.

N-Alkyl-4-cyanopyridinium (RCP) ions react with OH^- to yield two products, namely the corresponding carboxamidopyridinium (A) and pyridone (P), which can be conveniently measured by absorption spectra or by CN^- ion determination (Scheme 3).[7] The P/A ratio in solution increases to a plateau with increasing pH (the maximum P/A ratio is about 2).[7] Studies of the alkaline hydrolysis of RCP have been useful in the description of several micellar,[8] intermicellar[3] and vesicular[9] properties. In particular, incorporation of *N*-dodecyl-4-cyanopyridinium ion (DCP) in CTAB

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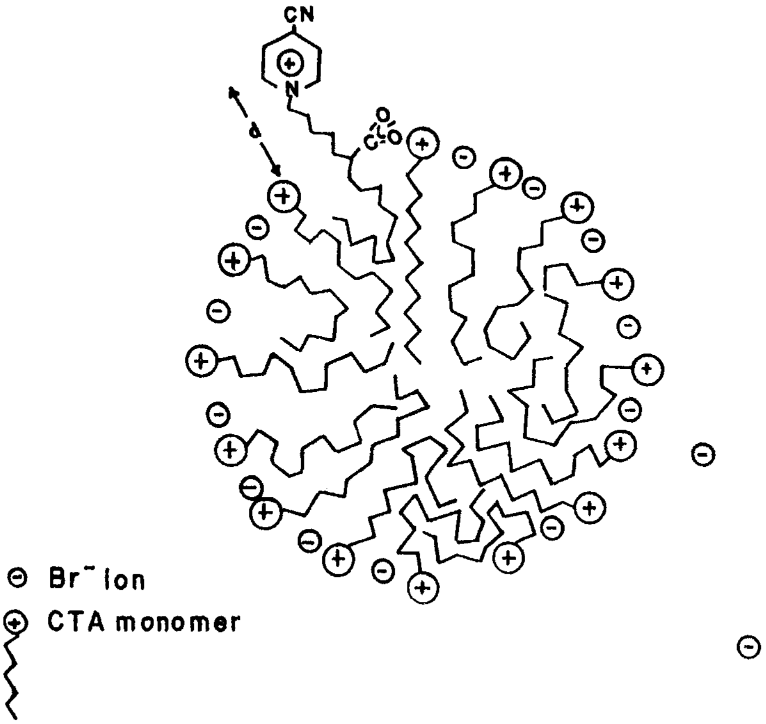
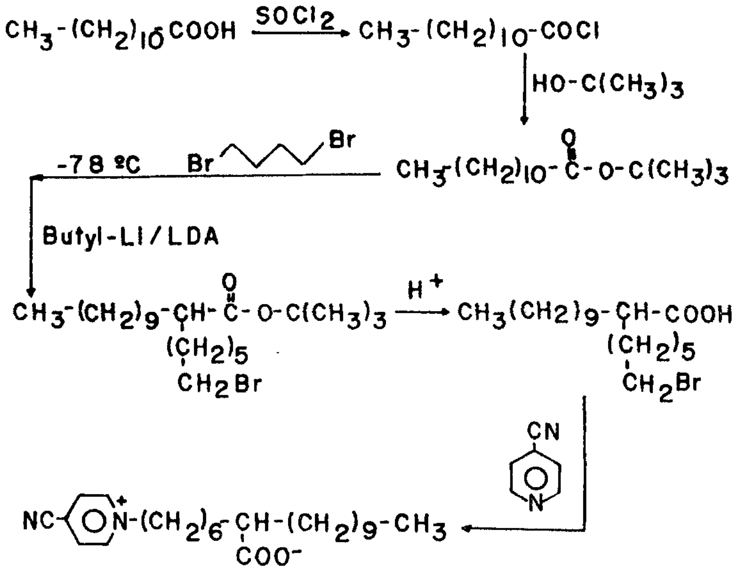
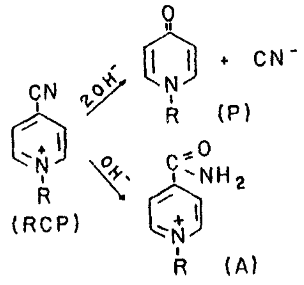


Scheme 1



Scheme 2



Scheme 3

micelles results in rate enhancement and the quantitative formation of pyridone on reaction with OH^- ion.[7b] The effect of CTAB on the DCP product distribution ratio was attributed to the low effective dielectric constant at the reaction site, i.e. the Stern layer.[7b] According to Scheme 1, the reaction site for micellar-incorporated CCHP is not the Stern layer but is separated by a distance *d*. Therefore, reaction of OH^- ion with CTAB-incorporated CCHP should result in a lower percentage of pyridone, a lower rate enhancement and lower ion selectivity in the inhibition produced by salts.

The effect of pH on the observed rate constants (k_ψ) and P/A ratios for reaction (1) obtained with CCHP in aqueous solution are presented in Table 1. The observed rate constants (k_ψ), the dependence of k_ψ on pH and P/A ratios obtained with CCHP and DCP were very similar. The results shown in Table 1 agree with previous data showing that k_ψ and P/A are independent of the length of the alkyl chain for a series of monomeric RCPs.[7b] As found previously with DCP, added salts produced a modest inhibition of the rate of alkaline hydrolysis of CCHP without changing the P/A ratio, within experimental error (not shown). The similarity of the kinetic results obtained with DCP and CCHP strongly suggests no intramolecular ion pair formation in CCHP in solution.

Table 1. Effect of pH on the rate and product composition in the hydrolysis of DCP and CCHP[a]

	k_ψ ($s^{-1} \times 10^3$)		P/A	
pH[b]	DCP[c]	CCHP	DCP[c]	CCHP
10·62	1·14		0·306	
10·72		1·2		0·22
11·12	3·4	3·13	0·603	0·27
11·42		6·78		0·60
11·52	11·2		0·95	
11·6		10·30		0·95
11·82		20·20		1·08
11·85	20·79		1·53	

[a] Rates and product composition were determined as described previously for DCP.[7b]

[b] 0·020 M phosphate buffer.

[c] Data from Ref. 7b.

The effect of CTAB on the rate of reaction of CCHP with OH^- ion is shown in Figure 1. The maximum value of the P/A ratio found for CCHP in CTABr at pH 9·6 was 4·5 (Table 2). As previously found with DCP,[7b] the P/A ratio for CCHP was constant above 0·003 M CTAB. The effect of CTAB was quantitatively analysed using the formalism of the pseudo-phase model with explicit consideration of ion exchange (PPIE).[10] For CCHP, the appropriate expression describing the effect of a positively charged detergent on the rate of this reaction is[10,11]

$$k_\psi = \frac{OH_f k_{2w}[(k_{2m}/k_{2w})K_s K_{OH/Br}(Br_b/Br_f) + 1]}{1 + K_s C_d} \qquad (1)$$

OH_f, the concentration of intermicellar OH^- ion, was calculated from the pH; k_{2m} and k_{2w} are the second-order rate constants in water and micelle, respectively, K_s is the substrate distribution constant, $K_{OH/Br}$ is the OH^-/Br^- ion-exchange constant, C_d is the concentration of micellized detergent and Br_f and Br_b are the concentrations of bound and free Br^- ion, respectively. The use of this formalism, fitting procedures and computing techniques has been described extensively.[10,11] From the effect of salts on the micellar-modified

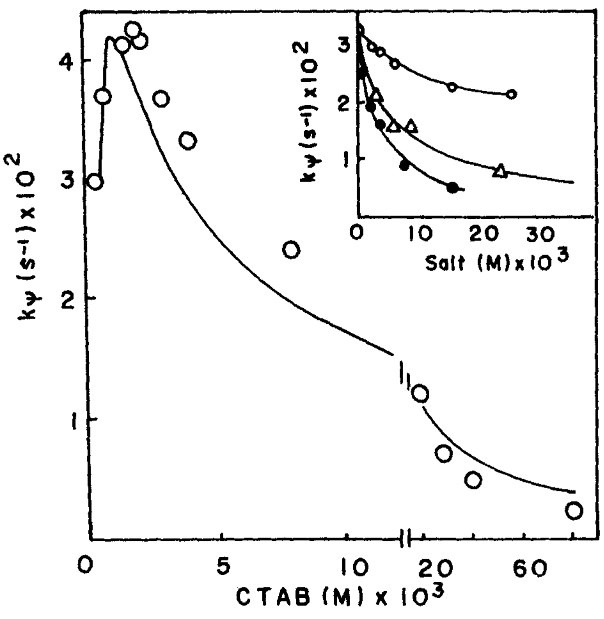


Figure 1. Effect of CTAB on the rate of hydrolysis of CCHP. Borate buffer, 0·02 M, pH 9·60; [CCHP] = $3 \cdot 0 \times 10^{-5}$ M. Inset shows effect of salts in the presence of 4·0 mM CTAB: (●) NaBr; (△) NaCl; (○) NaF. All curves are calculated (see text)

Table 2. Parameters obtained from the analysis of the effect of CTAB on the rate and product composition in the hydrolysis of DCP and CCHP

Substrate	k_{2m} (l mol^{-1} s^{-1})[a]	P/A[b]	$K_{OH/Br}$	K_{OH}/Cl	K_{OH}/F
DCP[c]	26·4	>25	0·08	0·13	0·3
CCHP	6·8	4·5	0·14	0·45	1·4

[a] Best fit parameter calculated assuming a partial molar volume of 0·37 l mol^{-1}.[1,7b]

[b] Pyridone/amide ratio measured after complete reaction (ten half-lives) with 0·005 M CTAB; above this detergent concentration the P/A ratio is constant.

[c] Data obtained from Ref. 7b, except for the chloride and fluoride ion selectivity coefficients. Ion selectivity coefficients calculated from the effect of salt on the rate in the presence of CTAB.

reaction (Figure 1, inset) and from the results presented in Figure 1, we calculated[10,11] the parameters given in Table 2.

The decrease in the yield of pyridone and ion selectivity obtained with micelle-incorporated CCHP (Table 2) and the failure to fit perfectly the kinetic data with the PPIE model (Figure 1) are consistent with the initial proposal. In the proposal (Scheme 1), the position of the pyridinium ring of CCHP, at a distance *d* from the micellar surface, should result in kinetics and product compositions intermediate between those obtained for CCHP in water and those with DCP in micelles (compare Tables 1 and 2).

In conclusion, we have synthesized a probe that reacts with OH$^-$ ion at a distance of the amphiphilic micellar region. Structural data on this system, calculations of OH$^-$ ion distribution and extensions of the PMF rationale to other systems are under investigation.

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