also on the relative amounts of the two species present.

## **Experimental Section**

2-Naphthoic acid was obtained from Aldrich Chemical Co. at a purity of 99%. Material used in the fluorescence decay measurements was recrystallized from a 50% ethanol solution. Absolute ethanol (U.S. Industrial Chemical Corp.) and distilled water were used without further purification. All other chemicals were of reagent grade quality (Mallinckrodt Chemical Co.) and were used without further purification.

Solutions were deaerated with nitrogen prior to spectral or decay measurements. Emission spectra were obtained with a Baird Atomic Model SF-1 fluorescence spectrometer. Quantum efficiency measurements were made with 2-naphthol as a standard for the free 2-naphthoic acid emission and quinine sulfate as a standard for the protonated acid emission.

Decay curves were obtained by the time-correlated single-photon method. The technique and the apparatus employed have been discussed elsewhere.<sup>14,15</sup> A 360-nm interference filter (Corion Instrument Corp.) was used to isolate the free acid emission and a 460-nm filter was used for the protonated acid emission. Excitation was achieved by isolating the deuterium continum of the nanosecond flashlamp with a 0.25-m Jarrell-Ash Ebert monochromator having a band pass of 3.2 nm. The decay curves were analyzed by a reiterative convolution method and a dedicated laboratory computer.

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# Ion Exchange in Micellar Solutions. 7.<sup>1</sup> Effect of Detergent Structure on the Binding and Reactivity of OH<sup>-</sup> in Cationic Micellar Solutions

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Ion-exchange selectivity coefficients for the binding of  $OH^-$  to a series of homologous alkyltrimethylammonium bromides and chlorides and to hexadecylpyridinium chloride (HPCl) and bromide are reported. The magnitude of these selectivity coefficients is determined principally by the nature of the detergent counterion (Cl<sup>-</sup> or Br<sup>-</sup>). Although there appear to be secondary contributions from the head group type, variations in the detergent alkyl chain length (tetradecyl to octadecyl) have little or no effect on the observed  $OH^-$  binding affinity. Quantitative analysis of kinetic data for a series of alkaline hydrolysis reactions in micellar HPCl provides intrinsic reactivity parameters in the micellar pseudophase which are in all cases comparable to those in micellar hexadecyltrimethylammonium bromide (CTAB). It is concluded that the factors which contribute to the binding and to the reactivity of  $OH^-$  at the cationic micellar surface are distinct and that the intrinsic effects of nonfunctionalized cationic detergents on reactivity and equilibria are quite similar (as opposed to being highly surfactant specific).

# Introduction

In the first paper of this series,<sup>2</sup> we outlined an ion-exchange formalism for the quantitative analysis of chemical reactivity and equilibria in micellar solutions of ionic detergents. In subsequent work, this model was applied to experimental data for (a) the binding of the hydroxide ion to cationic micelles,<sup>3</sup> (b) the photohydrolysis of 3,5-dinitroanisole,<sup>4</sup> (c) the alkaline hydrolysis of *p*-nitrophenyl esters in buffered micellar solution,<sup>5</sup> and (d) micellar effects on the dissociation (apparent pK) and reactivity of weak-acid-derived nucleophiles.<sup>6</sup>

In these previous studies, two cationic detergents were employed, CTAB and TTACl. In the present work, we

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Scheme I



extend the data for the binding of  $OH^-$  to cationic micelles to include TTAB, CTACl, STACl, HPCl, and HPBr. In

CH <sub>3</sub> (CH <sub>2</sub> ) <sub>0</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> X <sup>-</sup>	CH3(CH2)15 +N X-
TTAB: $n = 13$ , $X = Br$ CTAB: $n = 15$ , $X = Br$ TTACI: $n = 13$ , $X = CI$ CTACI: $n = 15$ , $X = CI$ STACI: $n = 17$ , $X = CI$	HPCI: $X = CI$ HPBr: $X = Br$

addition, rate data for a series of alkaline hydrolysis reactions (Scheme I) in micellar HPCl are analyzed within the framework of the ion-exchange formalism.<sup>2,6</sup> Comparison with data in CTAB indicates that the factors which contribute to the observed selectivity in OH<sup>-</sup> binding to the micelle are not reflected in the intrinsic reactivity of OH<sup>-</sup> at the cationic micellar surface.

### **Experimental Section**

Materials. N-Methyl-4-cyanopyridinium chloride (MCP) and *p*-nitrophenyl octanoate (NPO) were available from a prior study.<sup>5</sup> Tris(bipyridine)ruthenium(II) dichloride hexahydrate (Ru(bpy)<sub>3</sub><sup>2+</sup>, G. Frederick Smith), p-nitrophenylacetate (NPA, Sigma Chemical Co.), 4-1pyrene)butyric acid (Eastman Kodak), and sodium hydroxide (Merck Titrisol) were used as received. N-Methyl-4-carboxamidopyridinium chloride (MAP) was prepared from the corresponding iodide salt<sup>7</sup> as described previously<sup>5</sup> for MCP. N-Dodecyl- (DoCP) and N-decyl-4-cyanopyridinium bromide (DeCP) were prepared by the procedure of Landquist<sup>8</sup> and purified by recrystallization from acetonitrile-benzene. N-Dodecyl- (DoAP, mp 239-42 °C) and N-decyl-4-carboxamidopyridinium bromide (DeAP, mp 239-41 °C) were prepared by refluxing equimolar quantities of alkyl bromide (Aldrich) and isonicotinamide<sup>9</sup> overnight in acetonitrile, followed by two recrystallizations from acetone-methanol. The purity of all of these pyridinium substrates was verified by halide ion titration<sup>10</sup> and absorption spectroscopy (comparison of molar extinction coefficients with those of the N-methyl analogues<sup>7</sup>). TTAB (Aldrich 99%), CTACl (Herga Indústrias Quimicas, Rio de Janeiro), and STACl (K & K Labs.) were purified by vacuum drying, Soxhlet extraction with dry peroxide-free ether, several recrystallizations from

acetone or acetone-methanol, and exhaustive vacuum drying to remove residual solvent. Apparent molecular weights (determined by potentiometric halide titration)<sup>11</sup> and homologue compositions (determined by Hofmann degradation<sup>3,4,12</sup> of the corresponding hydroxide salts) were as follows: TTAB, 336 g/mol (calcd 336 g/mol), 0.2%  $C_{12}$ , 99.2% C<sub>14</sub>, 0.6% C<sub>16</sub>; CTACl, 323 g/mol (calcd 320 g/mol), 1% C<sub>14</sub>, 97% C<sub>16</sub>, 2% C<sub>18</sub>; STACl, 353 g/mol (calcd 348 g/mol), 4% C<sub>16</sub>, 93% C<sub>18</sub>; 3% C<sub>20</sub>. HPCl (BDH) and HPBr (from dry pyridine and Merck puris. 1-bromohexadecane) were recrystallized six times from acetone (charcoal) and vacuum dried; both analyzed satisfactorily (C, H, N, halide) as the monohydrate. None of these detergents gave evidence of a surface tension minimum in the cmc determinations. All other reagents were analytical grade or superior and all solutions were prepared in freshly boiled deionized water, doubly distilled in glass, which had been allowed to cool under an argon atmosphere.

Critical micelle concentrations (cmc) were determined at 30 °C in the usual manner from plots of conductivity vs. detergent concentration or of apparent surface tension vs. log detergent concentration. Conductivity measurements were performed with a dipping cell and a Metrohm Herisau Model E 365 B conductimeter or a Beckman RC 18A conductivity bridge. Apparent surface tensions were determined under an argon blanket by the ring method with a Fisher Model 20 surface tensiometer.

Incorporation of DoAP and DeAP in HPCl. The emission spectrum of a solution (3.00 mL) of  $Ru(bpy)_3^{2+}$  $(3.5 \times 10^{-5} \text{ M})$  in 0.020 M sodium borate buffer, pH 9.8, was recorded. Successive aliquots (10  $\mu$ L) of a concentrated stock solution of quencher (0.16 M DoAP or 0.17 M DeAP) in the same buffer (containing  $\operatorname{Ru}(\operatorname{bpy})_{3}^{2+}$ ) were added, followed by successive aliquots of HPCl in Ru- $(bpy)_3^{2+}$  containing buffer; the emission spectrum was recorded after each addition. After correction of the total quencher and detergent concentrations for dilution, the initial emission intensity data (addition of quencher alone) were plotted in Stern-Volmer fashion to determine the values of  $K_{SV}$  for quenching in the absence of detergent  $(375 \text{ M}^{-1} \text{ for DoAP and } 385 \text{ M}^{-1} \text{ for DeAP})$ . These values were then employed to calculate the effective intermicellar quencher concentration from the emission intensity ratios in the presence of HPCl. The incorporation constants were determined as the slope of plots of  $[S_T]/[S_f]$  vs.  $[HPCl_T]$ +  $[S_h]$  (passing through the point (1.0, cmc)), in accord with the expression

$$K_{\rm s} = \frac{[{\rm S}_{\rm b}]}{[{\rm S}_{\rm f}](C_{\rm D} + [{\rm S}_{\rm b}])}$$
(1)

for the incorporation constant of an amphiphilic (pseudo-monomer) substrate (S = DoAP or DeAP) of the same charge as the detergent monomer.<sup>14</sup>

Kinetic Measurements. Detergent stock solutions were prepared by weight and the concentration was checked by halide ion titration.<sup>10</sup> Concentrations of the stock solutions of the 4-cyano- and 4-carboxamidopyridinium substrates and quenchers were checked by absorption spectroscopy. All kinetic measurements were performed at 30 °C. The alkaline hydrolysis of MCP in the presence of TTAB, CTACl, and STACl was followed by absorption at 260 nm on a Perkin-Elmer Model 575 spectrophotometer as previously described;<sup>3</sup> pyridone/amide product ratios were

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estimated as before<sup>3,13</sup> from the absorption spectrum following complete reaction. Alkaline hydrolysis of NPA and NPO was followed<sup>5</sup> by monitoring the appearance of the *p*-nitrophenoxide ion at 405 nm with a Beckman M-25 kinetic system. Rate constants were calculated from log  $(A_{\infty} - A_t)$  vs. time plots in the usual manner.<sup>5</sup>

The alkaline hydrolyses of MCP, DoCP, and DeCP in micellar HPCl and of MCP in micellar HPBr were followed indirectly by monitoring the temporal increase in the emission intensity of the  $Ru(bpy)_3^{2+}$  ion at 606 nm (450-nm excitation). Besides being excluded from cationic micelles,<sup>5</sup> the  $Ru(bpy)_3^{2+}$  ion absorbs and emits in the visible and its absorption and emission spectra and emission yield are unaffected by addition of HPCl or HPBr. Furthermore, the emission intensity of the  $Ru(bpy)_3^{2+}$  ion was invariant with time prior to or after complete reaction, indicating the absence of undesirable thermal or photoinduced decomposition of the probe on the time scale of the kinetic measurements. Under pseudo-first-order conditions (excess OH<sup>-</sup>), the derivation of the relationship between  $k_{\Psi}$ for alkaline hydrolysis of these substrates and the temporal variation of the probe emission intensity is straightforward, the desired final expression being

$$\ln \left[ (I_{\infty}/I_t) - 1 \right] = \ln \left[ (I_{\infty}/I_0) - 1 \right] - k_{\Psi} t \tag{2}$$

where  $I_0$ ,  $I_t$ , and  $I_{\infty}$  are the probe emission intensities prior to (t = 0), during (t = t), and after  $(t = \infty)$  complete reaction.<sup>15</sup> Emission measurements were performed on air-equilibrated samples contained in 1-cm path length Teflon stoppered quartz fluorescence cells (Hellma) with a Hitachi-Perkin-Elmer MPF-4 spectrofluorimeter operated in the ratio mode. The general procedure with MCP as substrate was as follows: After recording the initial emission spectrum (intensity  $I_0$  at 606 nm) of an aqueous solution of  $\text{Ru(bpy)}_{3}^{2+}$  (2.95 mL,  $3.5 \times 10^{-5}$  M) in HPCl or HPBr of the desired final concentration, successive  $10-\mu L$  alignots of a 0.16 M stock solution of MCP containing  $3.5 \times 10^{-5}$  M Ru(bpy)<sub>3</sub><sup>2+</sup> (total addition 50  $\mu$ L or  $2.65 \times 10^{-3}$  M final) were added; the emission spectrum was recorded after each addition. Subsequently, 30  $\mu$ L of 1.00 M NaOH was rapidly added and the temporal variation of the emission intensity followed at 606 nm. Rate constants were calculated from the first half-life of plots of  $\ln \left[\Delta I_t / (I_{\infty} - \Delta I_t)\right]$  vs. time, where  $\Delta I_t = I_{\infty} - I_t$  (see eq 2). The initial experiments designed to demonstrate the validity of this approach in the absence of detergent were

(15) At all times t, the Stern-Volmer relationship for the emission intensities in the absence  $(I^0)$  and presence  $(I_t)$  of quencher species (substrate and/or product) is

 $I^{0}/I_{t} = 1 + K_{SV}[MCP]_{t} + K_{SV}'[MAP]_{t} + K''_{SV}[MP]_{t}$ 

where  $K_{\rm SV}$ ,  $K_{\rm SV}'$ , and  $K_{\rm SV}''$  are the respective (apparent) Stern-Volmer quenching constants. Equation 2 thus follows from the integrated form of the rate law under pseudo-first-order conditions:  $\ln ([MCP]_t/[MCP]_0) = -k_{\psi t}$ , using the condition of mass balance  $([MCP]_0 = [MCP]_t + [MAP]_t = [MAP]_{\infty} + [MP]_{\infty})$  and the constancy of the product ratio with time  $([MP]_t/[MAP]_t = [MP]_{\infty}/[MAP]_{\infty})$ . In principle, eq 2 should hold in any situation in which (a) first- or pseudo-first-order chemical reaction of the substrate in the ground state is accompanied by a difference in the efficiencies of quenching of the probe emission by substrate and reaction products; (b) linear Stern-Volmer quenching kinetics are obeyed; (c) probe emission intensities are directly relatable to the corresponding quantum yields. performed in similar fashion, with both sodium 4-(1-pyrene)butyrate (PBA,  $1.0 \times 10^{-5}$  M; 340-nm excitation, 396-nm emission) and Ru(bpy)<sub>3</sub><sup>2+</sup> as emissive probes and 0.10 M NaCl as swamping electrolyte. Alkaline hydrolysis of DoCP and DeCP was followed in analogous fashion, the reaction being initiated by addition of an appropriate aliquot of an 0.50 M stock solution of HPCl in 0.020 M sodium borate buffer, pH 9.8 (containing Ru(bpy)<sub>3</sub><sup>2+</sup>) to a freshly prepared solution of Ru(bpy)<sub>3</sub><sup>2+</sup> (3.5 × 10<sup>-5</sup> M) and substrate (5.0 × 10<sup>-4</sup> M) in the same buffer.

When allowed to stand, micellar solutions of HPCl and HPBr containing 0.010 M NaOH gradually develop absorption band(s) in the visible (perhaps reflecting OH<sup>-</sup> addition to the pyridinium ring followed by ring opening);<sup>16</sup> however, it was found that this process is too slow to interfere significantly with the present kinetic results. It is noteworthy that no such absorption changes were observed at lower pHs (specifically in borate buffer, pH  $\leq$  9.8, or tris-HCl, pH 9.0), even after prolonged storage of the detergent solutions.

Pyridone/amide product ratios following complete alkaline hydrolysis of MCP, DeCP, and DoCP were estimated from the emission intensity ratio  $I^0/I_{\infty}$  assuming that the pyridone product is a nonquencher, i.e., that

$$I_0/I_{\infty} = 1 + K_{\rm SV} [\rm RAP_f]_{\infty} \tag{3}$$

where  $[RAP_f]_{\infty}$  is the concentration of the carboxamidopyridinium product free in the intermicellar aqueous phase after complete reaction. The total concentration of RAP formed is then given by

$$[\operatorname{RAP}_{\mathrm{T}}]_{\infty} = [\operatorname{RAP}_{\mathrm{f}}]_{\infty} \left[ 1 + \frac{K_{\mathrm{s}}C_{\mathrm{D}}}{1 - K_{\mathrm{s}}[\operatorname{RAP}_{\mathrm{f}}]_{\infty}} \right]$$
(4)

a relationship readily derived from eq 1 and the condition of mass balance:  $[RAP_T]_{\infty} = [RAP_f]_{\infty} + [RAP_b]_{\infty}$ . For DeAP and DoAP, the independently determined values of  $K_{SV}'$  and  $K_s$  (vide supra) were employed. For the cationic micelle excluded MAP ion,  $[MAP_f]_{\infty} = [MAP_T]_{\infty}$  in eq 3. In this case, the apparent Stern-Volmer constants for quenching by MAP ( $K_{SV}'$ ) were determined directly by adding aliquots of a MAP stock solution (0.16 M containing Ru(bpy)<sub>3</sub><sup>2+</sup>) to solutions containing Ru(bpy)<sub>2</sub><sup>+</sup> and HPBr at the final concentrations employed in the kinetic runs or by adding MAP to the HPCl reaction mixtures following complete hydrolysis of MCP. In the latter case, it can be readily demonstrated that

$$\frac{I_0}{I_{\infty}} = \left[\frac{I_{\infty}}{I'} - 1\right] = K_{\rm SV}'[\rm MAP]_{ad}$$
(5)

where I' is the resultant emission intensity upon addition of a concentration  $[MAP]_{ad}$  of quencher.

## Results

Alkaline Hydrolysis of MCP in Micellar TTAB, CTACl, and STACl. In addition to being excluded from the micellar phase of cationic detergents,<sup>5</sup> MCP suffers alkaline hydrolysis<sup>3,5,7</sup> to give two products, MAP and MP (Scheme I). The pseudo-first-order rate constaats  $(k_{\Psi})$  for this reaction were determined by plotting absorption (appearance of MP at 260 nm)<sup>3</sup> as a function of concentration of the three quaternary ammonium detergents at a total OH<sup>-</sup> concentration of  $[OH_T] = 0.020$  M (Figure 1). As with CTAB and TTACl,<sup>3</sup> addition of detergent inhibits the alkaline hydrolysis of MCP without affecting the MP/

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<sup>(14)</sup> The molar incorporation constant  $K_s$  is related to the thermodynamic partitioning coefficient  $K_p$ , defined on a mole fraction basis, via  $K_p = \chi_{mic}/\chi_{aq} = 55.5K_s$ . In the present case of a cationic amphiphilic substrate in a cationic micellar solution, the micelle-bound substrate S<sub>b</sub> is necessarily a true component of a micellar pseudophase, i.e.,  $\chi_{mic} = [S_b]/(C_D + [S_b])$ . Indeed, incorporation of a substrate of this type may be viewed as a comicellization phenomenon.

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**Figure 1.** Effect of TTAB, CTACI, and STACI on the rate of alkaline hydrolysis of the *N*-methyl-4-cyanopyridinium ion (MCP). Curves are calculated (see text) with  $[OH_T] = 0.020 \text{ M}$ ,  $k_{\Psi}^{0} = 0.0985 \text{ s}^{-1}$ , B = 1.50,  $\alpha = 0.20$ , and the cmc data of Table I. For TTAB, the solid curve and upper and lower dashed curves are calculated for  $K_{OH/BT}$  values of 0.06, 0.04, and 0.08, respectively. For the corresponding curves of CTACI and STACI, the  $K_{OH/CI}$  values are 0.13, 0.11, and 0.15, respectively. For  $\alpha = 0.25$ , the solid curves can be reproduced with  $K_{OH/BT} = 0.08 (TTAB)$  or  $K_{OH/CI} = 0.15 (CTACI, STACI)$  and for  $\alpha = 0.15$  with  $K_{OH/BT} = 0.04 (TTAB)$  or  $K_{OH/CI} = 0.11 (CTACI, STACI)$ .

MAP product ratio, consistent with exclusive localization and reaction of MCP with free hydroxide ion  $([OH_f])$  in the intermicellar aqueous phase.

Alkaline Hydrolysis of MCP in Micellar HPCl and HPBr. Due to the strong ultraviolet absorption of the pyridinium chromophore of HPCl and HPBr, the alkaline hydrolysis of MCP could not be followed directly by absorption. Among the possible alternative approaches for following this reaction, that which appeared to be most adequate (permitting both determination of  $k_{\Psi}$  and of the MP/MAP product ratio), was an indirect method based on the temporal variation of the emission intensity of the  $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$  ion during reaction of MCP with OH<sup>-</sup> (see Experimental Section). The resultant rate data for the effect of HPBr and HPCl on the alkaline hydrolysis of MCP are presented in Figure 2. As in the case of the quaternary ammonium detergents (vide supra), addition of HPCl or HPBr inhibits the alkaline hydrolysis of MCP without significantly affecting the MP/MAP product ratio.

The experimental validity of this approach for determining  $k_{\Psi}$  was verified in the absence of detergent with two structurally distinct emissive probes, i.e., sodium 4-(1-pyrene)butyrate (PBA) and Ru(bpy)<sub>3</sub><sup>2+</sup>, with 0.10 M NaCl as the swamping electrolyte. The fluorescence of PBA ( $\tau_f^0 = 95 \text{ ns}$ )<sup>17</sup> is quenched by both MCP and MAP at the diffusion-limited rate ( $k_q = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), while Ru(bpy)<sub>3</sub><sup>2+</sup> ( $\tau_{em}^0 = 430 \text{ ns}$ )<sup>18</sup> is quenched slightly better by MCP ( $k_q = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) than by MAP ( $k^{q'} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ); the dominant quenching mechanism is presumably electron transfer to the pyridinium ion in all

TABLE I: Critical Micelle Concentrations (cmc) at 30 °C

		10 <sup>3</sup> (cmc), M			
detergent	H <sub>2</sub> O <sup>a</sup>	H <sub>2</sub> O <sup>b</sup>	0.020 M NaOH <sup>a</sup>	0.010 M NaOH <sup>a</sup>	
TTAB	3.47 (3.51) <sup>c</sup>	3.57	1.79		
CTACl	1.28	$1.38~(1.3)^d$	0.22		
STACI	0.33	$0.38 \\ (0.3, 0.4)^d$	0.022		
HPCl	1.0	$1.0(0.9)^{e}$		0.17	
HPBr	0.64	$0.71 \\ (0.705)^{f}$		0.16	

<sup>a</sup> Surface tension. <sup>b</sup> Conductivity. <sup>c</sup> Venable, R. L.; Nauman, R. V. J. Phys. Chem. **1964**, 68, 3498-503. <sup>d</sup> Ralston, A. W.; Eggenberger, D. W.; Harwood, H. J.; DuBrow, P. L. J. Am. Chem. Soc. **1947**, 69, 2095-7. <sup>e</sup> At 25 °C: Malsch, J.; Hartley, G. S. Z. Phys. Chem. (Leipzig) **1934**, A170, 321-36. <sup>f</sup> Hoffman, H.; Nagel, R.; Platz, G.; Ulbricht, W. Colloid Polym. Sci. **1976**, 254, 812-34.

 TABLE II:
 Selectivity Coefficients for Hydroxide Ion

 Exchange in Cationic Micellar Solution (30 °C)

detergent	K <sub>OH/Cl</sub>	detergent	$K_{\rm OH/Br}$
TTACI CTACI STACI HPCI	$\begin{array}{c} 0.14 \pm 0.02^a \\ 0.13 \pm 0.02 \\ 0.13 \pm 0.02 \\ 0.18 \pm 0.04 \end{array}$	TTAB CTAB HPBr	$\begin{array}{c} 0.06 \pm 0.02 \\ 0.08 \pm 0.02^{a} \\ 0.09 \pm 0.02 \end{array}$

<sup>a</sup> Reference 3.

cases.<sup>19,20</sup> Although addition of NaOH (0.010 M) to either probe alone had no effect on the emission intensity, analogous addition of NaOH to solutions containing MCP  $(2.65 \times 10^{-3} \text{ M})$  as quencher resulted in a gradual increase in the probe emission intensity, reaching a stable plateau value (below that in the absence of quencher) after several minutes. Plotting the emission intensity data in accord with eq 2 provided  $k_{\Psi}$  values of 0.020 and 0.021 s<sup>-1</sup>, respectively, with PBA and  $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$  as probes. Product ratios of  $[\operatorname{MP}]_{\infty}/[\operatorname{MAP}]_{\infty} = 1.4$  (with PBA) and 1.0 (with  $\operatorname{Ru}(\operatorname{bpy})_{3}^{2+}$ ) were estimated from the emission intensity ratio  $I_0/I_{\infty}$  (see Experimental Section). Similar measurements in the absence of added NaCl, with  $Ru(bpy)_3^{2+}$  as a probe, gave  $k_{\Psi} = 0.030 \pm 0.002 \text{ s}^{-1}$  and a product ratio of  $1.0 \pm 0.1$ . These kinetic parameters compare quite well with  $k_{\Psi}$  values of 0.030 ± 0.001 and 0.022 ± 0.001 s<sup>-1</sup> in the absence and presence of 0.10 M NaCl and a (salt-insensitive) product ratio of  $1.0 \pm 0.1$  determined by the absorption method<sup>3</sup> at  $[OH_T] = 0.010$  M in the absence of the probes.

Selectivity Coefficients for  $OH^-$  Ion Exchange. As in the previous work with CTAB and TTACl,<sup>3</sup> the values of  $K_{OH/Br}$  or  $K_{OH/Cl}$  for the detergents investigated here were obtained by fitting the relationship

$$k_{\Psi,\text{calcd}} = k_{\Psi}'([\text{OH}_{\text{f}}]/[\text{OH}_{\text{T}}]) \tag{6}$$

to the experimental data of Figures 1 and 2. The correction of the second-order rate constant  $(k_2' = k_{\Psi'}/[OH_T])$  for effective intermicellar ionic strength and the calculation of  $[OH_f]$  from the ion-exchange formalism have been described in detail.<sup>3</sup> In the calculations, zero ionic strength rate constants of  $k_{\Psi}^0 = 0.0985 \text{ s}^{-1}$  ( $[OH_T] = 0.020 \text{ M}$ )<sup>3</sup> and  $k_{\Psi}^0 = 0.0360 \text{ s}^{-1}$  ( $[OH_T] = 0.10 \text{ M}$ ), an apparent degree of

<sup>(17)</sup> Quina, F. H.; Toscano, V. G. J. Phys. Chem. 1977, 81, 1750-4.
(18) Estimated from the data in Bensasson, R.; Salel, C.; Balzani, V. J. Am. Chem. Soc. 1976, 98, 3722-4. See also Juris, A.; Gandolfi, M. T.; Manfrin, M. F.; Balzani, V. Ibid. 1976, 98, 1047-8.

<sup>(19)</sup> See, in this regard, footnote 13 of Quina, F. H.; Hamlet, Z.; Carroll, F. A. J. Am. Chem. Soc. 1977, 99, 2240-5.

<sup>(20) (</sup>a) Bock, C. R. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 1974. (b) Nagle, J. K.; Dressick, W. J.; Meyer, T. J. J. Am. Chem. Soc. 1979, 101, 3993-5.



**Figure 2.** Effect of HPBr and HPCI on the rate of alkaline hydrolysis of MCP. Curves are calculated (see text) with  $OH_{T} = 0.010 \text{ M}$ ,  $k_{\Psi}^{0} = 0.036 \text{ s}^{-1}$ , B = 1.50,  $\alpha = 0.20$ , and the cmc data of Table I. For HPBr, the solid and upper and lower dashed curves are calculated for  $K_{OH/Br}$  values of 0.09, 0.07, and 0.11, respectively. For the corresponding curves of HPCI, the  $K_{OH/CI}$  values are 0.18, 0.14, and 0.22, respectively. For  $\alpha = 0.25$ , the solid curves can be reproduced with  $K_{OH/Br} = 0.11$  (HPBr) or  $K_{OH/CI} = 0.22$  (HPCI) and for  $\alpha = 0.15$  with  $K_{OH/Br} = 0.07$  (HPBr) or  $K_{OH/CI} = 0.14$  (HPCI).



**Figure 3.** Effect of HPCI on the alkaline hydrolysis of NPO (6.6 × 10<sup>-6</sup> M) and NPA (8.3 × 10<sup>-6</sup> M) in buffered solution. Curves are calculated (see text). For NPO and NPA in 0.020 M borate buffer, pH 9.5 (O), the following parameters were employed:  $\alpha = 0.20$ ,  $K_{OH/CI} = 0.18$ , cmc (surface tension) =  $0.2 \times 10^{-3}$  M,  $K_s$ (NPO) =  $1.5 \times 10^4$  M<sup>-1</sup>,  $K_{\psi}^0$ (NPO) =  $6.5 \times 10^{-4}$  s<sup>-1</sup>,  $k_{\psi}^0$ (NPA) =  $7.0 \times 10^{-4}$  s<sup>-1</sup>. Best-fit values were  $K_{OH/B} = 1.25$  and  $k_{2m}/(k_2^0 \bar{V}) = 0.65$  M (NPO) or 1.24 M (NPA). For the hydrolysis of NPO in 0.020 M tris-HCI buffer, pH 9.0 ( $\oplus$ ),  $k_{\psi}^0 = 1.7 \times 10^{-4}$  s<sup>-1</sup>, cmc =  $5 \times 10^{-4}$  M, [Cl<sub>ad</sub>] =  $2.2 \times 10^{-3}$  M, and  $k_{2m}/(k_2^0 \bar{V}) = 0.81$  M.

micelle dissociation of  $\alpha = 0.020 \pm 0.05$ ,<sup>3</sup> and the appropriate cmc data of Table I were employed. The resultant selectivity coefficients are collected in Table II.

Alkaline Hydrolysis of NPO and NPA in Buffered Micellar HPCl. Experimental data for the effect of HPCl on  $k_{\Psi}$  for alkaline hydrolysis of NPO and NPA (Scheme I) in buffered solution are presented in Figure 3. The curves were calculated from the equation<sup>5,6</sup>

$$k_{\Psi} = k_{\Psi}^{0} [k_{2m}/(k_{2}^{0}\bar{V})] K_{s} K_{OH/Cl} [Cl_{b}] / [Cl_{f}] + 1 | / (1 + K_{s}C_{D})$$
(7)

TABLE III: Best-Fit Parameters for Alkaline Hydrolysis Reactions in Micellar HPCl (Scheme I) and CTAB at 30  $^\circ {\rm C}^a$ 

parameter	substrate	HPCl	CTAB
77	Monh	0.10 0.04	
KOH/Cl	MCP	$0.18 \pm 0.04$	
K <sub>OH/Br</sub>	MCP <sup>b</sup>		$0.08 \pm 0.02^{c}$
$K_{OH/B}^{d}$	NPO/NPA	1.25	$2.3^{e}$
$k_{\rm m}/k_{\rm o}^{\rm o}$	NPA	0.46	$0.37^{e}$
$k_{\rm m}/k_{\rm o}^{0}$	NPO	0.24	$0.29^{e}$
$k_{\rm m}/k_{\rm o}^{\rm o}$	NPO <sup>f</sup>	0.30	$0.40^{g}$
$k_{\rm m}/k_2^{\circ}$	DoCP	10	$10,^{h} 11^{g}$
$k_{2m}/k_{2}^{0}$	DeCP	9	$10^{h}$

<sup>a</sup> 0.020 M sodium borate buffer, pH 9.5-9.8 (except as noted). <sup>b</sup> Unbuffered (NaOH). <sup>c</sup> Reference 3. <sup>d</sup> Selectivity coefficient for OH<sup>-</sup>/B(OH)<sub>4</sub><sup>-</sup> ion exchange. <sup>e</sup> Reference 5. <sup>f</sup> 0.020 M tris-HCl, pH 9.0 (HPCl), or 0.010 M tris-HBr, pH 8.8 (CTAB). <sup>g</sup> Zanette, D. Doctoral Thesis, Instituto de Química, Universidade de São Paulo, São Paulo, 1981. <sup>h</sup> Reference 21.

where  $k_{\Psi}^{0}$  is the pseudo-first-order rate constant in the absence of detergent ( $6.5 \times 10^{-4} \text{ s}^{-1}$  for NPO and  $7.0 \times 10^{-4}$ s<sup>-1</sup> for NPA in 0.020 M borate buffer, pH 9.5;  $1.7 \times 10^{-4}$ s<sup>-1</sup> for NPO in 0.020 M tris-HCl buffer, pH 9.0),  $k_{2m}$  and  $k_2^0$  are the respective second-order rate constants for reaction in the micellar and aqueous phases,  $\bar{V}$  is the effective reaction volume (per mole of micellized detergent) at the micellar surface, and  $K_s$  is the substrate incorporation coefficient (the following values in CTAB<sup>5</sup> were employed:  $1.5 \times 10^4$  M<sup>-1</sup> for NPO and 54 M<sup>-1</sup> for NPA). The bound–free counterion ratio  $[\rm Cl_b]/[\rm Cl_f]$  was calculated from the appropriate expressions  $^{5,6}$  of the ion-exchange formalism for either ideal (tris-HCl) or nonideal (borate) buffer. With  $\alpha = 0.20$ ,  $K_{OH/Cl} = 0.18$  (Table II), and the appropriate cmc values (legend Figure 3), the curves were adjusted to the experimental rate data either by varying the intrinsic reactivity parameter  $k_{2m}/(k_2^{0}V)$  alone (tris-HCl buffer) or by simultaneous variation of both  $k_{2m}$  $(k_2^0 \bar{V})$  and  $K_{\rm OH/B}$  for hydroxide-borate ion-exchange (borate buffer).<sup>5</sup> In Table III, the resultant best-fit values are compared with data for these same reactions in buffered (borate or tris-HBr) CTAB. In both cases, the intrinsic reactivity ratio  $k_{2m}/k_2^0$  was obtained by multiplication of  $k_{2m}/(k_2^0 V)$  by the common values of  $\bar{V} = 0.37 \text{ M}^{-1}$ employed previously for CTAB.5,6

Alkaline Hydrolysis of DoCP and DeCP in Buffered *Micellar HPCl.* The effect of HPCl on the rate of alkaline hydrolysis of the N-dodecyl- (DoCP) and N-decyl-4cyanopyridinium (DeCP) ions was investigated in 0.020 M borate buffer, pH 9.8. As in the case of MCP, the pseudo-first-order rate constants were obtained from the temporal variation of the emission intensity of the  $Ru(bpy)_3^{2+}$ ion. The experimental rate data for hydrolysis of DoCP and DeCP (Figure 4) were simulated via eq 7. The value of  $k_{\Psi}^{0}$  (1.54 × 10<sup>-4</sup> s<sup>-1</sup>) was extrapolated from data at higher  $pH^{21}$  and the  $K_s$  values for DoCP and DeCP were taken to be equal to those determined experimentally for the corresponding amides ( $45 \pm 5 \text{ M}^{-1}$  for DoAP and  $3 \pm 1 \text{ M}^{-1}$ for DeAP); the remaining parameter values were the same as those utilized to simulate the alkaline hydrolysis of NPO and NPA in borate buffer. The best-fit values are compared in Table III with data for alkaline hydrolysis of DoCP and DeCP in micellar CTAB.<sup>13,21</sup>

The values of the pyridone/amide product ratio estimated from the emission intensity data proved to be rather imprecise (due to the proximity of  $I_0/I_{\infty}$  to unity in eq 3).

<sup>(21)</sup> Politi, M. J. Master's Dissertation, Instituto de Quimica, Universidade de São Paulo, São Paulo, 1980. The alkaline hydrolysis of *N*-alkyl-4-cyanopyridinium ions in the presence and absence of CTAB will be discussed in detail elsewhere.



Figure 4. Effect of HPCI on the rate of alkaline hydrolysis of DoCP (O) and DeCP (●) in 0.020 M borate buffer, pH 9.8. The curves are calculated (see text) with common parameters  $\alpha = 0.20$ ,  $K_{OH/CI} = 0.18$ ,  $K_{OH/B} = 1.25$ , cmc (surface tension) =  $0.2 \times 10^{-3}$  M, and  $k_{\Psi}^{0} = 1.54 \times 10^{-4} \text{ s}^{-1}$ . The values of  $K_s$  and  $k_{2m}/(k_2^{0}\bar{V})$  are, respectively, 45 M<sup>-1</sup> and 27 M for DoCP and 3 M<sup>-1</sup> and 24.3 M for DeCP. Neglect of the salt dependence of  $K_s$  for these substrates<sup>32</sup> contributes to the deviations at the lower detergent concentrations.

Nonetheless, the product ratio in the presence of HPCl (ca. 4) is significantly higher than the limiting ratio  $(1.75)^{7,21}$ at high pH in the absence of micelles, in agreement with data in micellar CTAB<sup>13,21</sup> which indicate preferential formation of the pyridone product in the micellar phase.

## Discussion

If we assume a Langmuir-Stern isotherm, the ratio between the fractional coverage ( $\theta_{\rm X} = [{\rm X}_{\rm b}]/C_{\rm D}$ ) of the micelle surface by the monovalent  $(z_X = \pm 1)$  counterion X and the analytical concentration of free counterion  $([X_f])$  is given by<sup>6</sup>

$$\theta_{\rm X}/[{\rm X}_{\rm f}] = \beta_0(1-\theta) \exp(\Phi_{\rm X}/RT) \exp(-z_{\rm X}F\Psi_0/RT) \quad (8)$$

The proportionality constant  $\beta_0$  may include activity coefficients but is otherwise independent of the nature of the counterion;  $\theta = \sum \theta_i$  represents the total counterion coverage in the Stern region. The overall counterion adsorption potential  $(\Phi_X - z_X F \Psi_0)$  is presumed (somewhat artificially) to be separable into a purely electrostatic (point charge) component, which depends only on the counterion charge and the micellar surface potential,  $\Psi_0$ , and a specific adsorption potential,  $\Phi_X$ , which incorporates all additional factors not directly identifiable with the point charge character of the counterion. Thus,  $\Phi_X$  encompasses such factors as hydrated ion size effects (e.g., on the distribution and magnitude of the surface charge density, on the structure of the inner regions of the diffuse double layer, and on image charge interactions), partial outer-sphere desolvation, hydrophobic contributions (especially important for organic counterions), polarizability, and specific counterion-head group interactions (e.g., charge transfer). For a micellar solution containing movovalent counterions X and Y, division of eq 8 by an equivalent expression for Y gives

$$K_{\mathrm{X/Y}} = \frac{\theta_{\mathrm{X}}[\mathrm{Y}_{\mathrm{f}}]}{\theta_{\mathrm{Y}}[\mathrm{X}_{\mathrm{f}}]} = \frac{[\mathrm{X}_{\mathrm{b}}][\mathrm{Y}_{\mathrm{f}}]}{[\mathrm{X}_{\mathrm{f}}][\mathrm{Y}_{\mathrm{b}}]} = \exp[(\Phi_{\mathrm{X}} - \Phi_{\mathrm{Y}})RT]$$

where  $K_{X/Y}$  is the ion-exchange selectivity coefficient. Formulated in this manner, the selectivity is attributed to differences in the specific adsorption potentials of the X/Y counterion pair.<sup>6</sup>

Under any given (fixed) set of conditions,  $K_{X/Y}$  should thus be independent of  $\theta$  as long as there is ideal (statis-

tical) mixing of the counterions on the micelle surface.<sup>22</sup> In applying ion-exchange formalisms to experimental data, it is customary to assume in addition that  $\theta$  is constant and equal to  $1 - \alpha$  over the usual range ( $\leq 0.1$  M) of detergent and added salt concentrations. In this regard, the validity of the use of a common value of  $\theta = 1 - \alpha = 0.80$ throughout in the present work depends on the extent to which  $\theta$  varies with detergent and counterion type and concentration. Theoretical treatments<sup>23</sup> indicate that the local counterion concentration in the vicinity of a highly charged (micellar or polyelectrolyte) surface is largely determined by the primary surface charge density, with only secondary contributions due to variations in the radius of curvature, increasing amphiphile and external electrolyte concentration, and site binding. On the experirmental side, recent data<sup>24</sup> for alkyltrimethylammonium bromides imply that an increase in the alkyl chain length is accompanied by a slight decrease in the apparent degree of micellar dissociation; however, the net variation is within the range utilized of  $\alpha = 0.20 \pm 0.05$  (see captions to Figures 1 and 2). Moreover, the available experimental evidence<sup>25,26</sup> for alkyltrimethylammonium detergents in the presence of hydrophilic counterions such as  $Br^{-}$ ,  $NO_{3}^{-}$ ,  $CN^{-}$ , and (presumably)  $Cl^{-}$  are consistent with relative insensitivity of  $\theta$  to detergent and added salt concentrations ( $\leq 0.1$  M). On the other hand, this does not appear to be the case for reactive counterion surfactants with highly hydrophilic counterions, in particular F<sup>-</sup> and OH<sup>-</sup>. Nonetheless, as Bunton et al.<sup>25</sup> have pointed out, one may reasonably expect  $\theta$  to be constant at low coverages of OH<sup>-</sup> in the presence of much more strongly bound counterions such as Br.<sup>27</sup> In this context, we note that the data simulations in Figures 1 and 2 are inherently biased in favor of the data at the higher detergent concentrations  $(\theta_{\rm OH} \le 0.1 \text{ for } C_{\rm T} \ge 0.05 \text{ M in all cases})$ . In any event, the fact that a single value of  $K_{\rm OH/Br}$  adequately reproduced the experimental data for hydrolysis of MCP in micellar CTAB at two quite different total OH<sup>-</sup> concentrations (0.001 and 0.020 M) in our earlier study<sup>3</sup> indicates that there is no marked dependence on  $\theta_{OH}$ .

The data of Table II for the alkyltrimethylammonium detergents indicate that the selectivity for OH<sup>-</sup> at the micelle surface is relatively insensitive to an increase in the length of the surfactant alkyl chain from tetradecyl to hexadecyl to octadecyl, in accord with the results of ion-exchange analysis<sup>26</sup> of kinetic data in TTACl and CTACl. Indeed, the magnitudes of the selectivity coefficients  $K_{OH/Cl}$  and  $K_{OH/Br}$  appear to be determined largely by the nature of the counterion alone. In this respect, it should be noted that, since  $K_{Br/Cl} > 1$  (ca. 5 for CTAB),<sup>28</sup> any variation in the net degree of counterion binding upon changing the detergent counterion from Br<sup>-</sup> to Cl<sup>-</sup> would

<sup>(22)</sup> A counterexample is provided by the peculiar properties of CTAB-CTACl mixtures in the absence of added electrolyte. Almgren, M.; Löfroth, J.-E.; Rydholm, R. Chem. Phys. Lett. 1979, 63, 265-8, and references cited therein.

<sup>(23)</sup> Manning, G. S. Q. Rev. Biophys. 1978, 11, 179-246. Stigter, D. Prog. Colloid. Polym. Sci. 1978, 65, 45-52. Weisbuch, G.; Guéron, M. J. Phys. Chem. 1981, 85, 517-25. Gunnarsson, G.; Jönsson, B.; Wennerström, H. Ibid. 1980, 84, 3114-21. Linse, P.; Gunnarsson, G.; Jönsson, B. Ibid. 1982, 86, 413-21.

<sup>(24)</sup> Zana, R. J. Colloid. Interface Sci. 1980, 78, 330-7.

<sup>(25)</sup> Banton, C. A.; Gan, L.-H.; Moffatt, J. R.; Romsted, L. S.; Savelli,
G. J. Phys. Chem. 1981, 85, 4118-25, and references cited therein.
(26) Al-Lohedan, H.; Bunton, C. A.; Romsted, L. S. J. Phys. Chem.
1981, 85, 2123-9. This work also makes a critical comparison of the

various methods which have been employed to determine selectivity coefficients for OH<sup>-</sup> binding to cationic micelles.

<sup>(27)</sup> See in this regard Larsen, J. W.; Magid, L. J. J. Am. Chem. Soc. 1974, 96, 5774-82

<sup>(28)</sup> Bartet, D.; Gamboa, C.; Sepúlveda, L. J. Phys. Chem. 1980, 84, 272-5.

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presumably<sup>25</sup> be in the direction of a (slight) decrase in  $\theta$ , i.e., in a direction which would tend to *increase* the differences between the values of  $K_{OH/Cl}$  and  $K_{OH/Br}$  relative to those in Table II. Although the values of  $K_{OH/Br}$  for HPBr and CTAB are quite similar, the  $K_{OH/Cl}$  values for HPCl and CTACl are consistent with a modest detergent head group effect on the OH/Cl selectivity. A lower degree of selectivity at the HPCl micellar surface may also be noted in the values of  $K_{OH/B}$  for hydroxide/borate exchange at the HPCl and CTAB micellar surfaces (Table III). The apparent lack of a head group effect in the case of HPBr can be nicely rationalized in terms of slightly enhanced Br<sup>-</sup> binding to HPBr as a consequence of an additional charge transfer contribution<sup>29</sup> to the Br<sup>-</sup> specific adsorption potential (vide supra, eq 8).

The most important feature of the parameters in Table III is the marked similarity of the intrinsic reactivity ratios  $k_{2m}/k_2^0$  in micellar HPCl and CTAB. Since the  $k_2^0$  values in the aqueous phase are necessarily identical for each reaction, the similarity in these ratios is tantamount to similar  $k_{2m}$  values in the micellar pseudophase.

As previously found for the alkaline hydrolysis of NPO and NPA in buffered micellar CTAB,<sup>5</sup> there also appears to be a slight reduction in the intrinsic reactivity of OH<sup>-</sup> at the HPCl micellar surface  $(k_{2m}/k_2^0 < 1)$ . However, upon going from an aqueous to a micellar reaction environment, the overall decrease in OH<sup>-</sup> reactivity is rather slight (2– 4-fold). Hence, it is probably naive to expect that the rate constant for alkaline hydrolysis of NPO or NPA would exhibit pronounced sensitivity to the (presumably) more subtle variations in microenvironment associated with a change in the nature of the detergent head group and counterion. Indeed, this relative insensitivity is borne out by the data of Table III for these substrates.

In contrast, data for the alkaline hydrolysis of DoCP and DeCP in micellar CTAB imply the existence of a true micellar effect on both intrinsic reactivity  $(k_{2m}/k_2^0 \text{ ca. } 10)$ and the pyridone/amide product ratio (predominant pyridone formation).<sup>13,21</sup> In principle, these effects may be ascribed to a change in local medium properties (e.g., a lower effective dielectric constant in the micellar pseudophase), to an electrostatic influence of the micellar surface charge on the relative activation energies for OH<sup>-</sup> attack at the nitrile (to give amide) or on the cyanopyridinium ring (to give pyridone), or to a combination of both factors,<sup>13,21</sup> It is therefore quite significant that, even for these substrates, the intrinsic rate accelerations in HPCl are virtually identical with those in CTAB (Table III).

## Conclusions

For a given head group (trimethylammonium), the OH<sup>-</sup> ion-exchange selectivity coefficient is found to be rather insensitive to the alkyl chain length of the detergent, being determined essentially by the nature of the counterion. Moreover, the quantitative differences in the observed rate constants for a series of alkaline hydrolysis reactions in micellar CTAB and HPCl are attributable almost exclusively to the somewhat more favorable OH<sup>-</sup> binding at the HPCl micellar surface (reflecting the change in both the detergent head group and counterion). Although somewhat limited in scope, the present results point to two important general conclusions: (1) the factors which contribute to the binding and to the intrinsic reactivity of OH<sup>-</sup> at the cationic micellar surface are distinct; and (2) although only a few detergents (notably CTAB) have been widely employed in ground-state kinetic studies,<sup>30</sup> the resultant intrinsic effects of a detergent such as CTrAB on chemical reactivity and equilibria are probably quite representative for nonfunctionalized cationic detergents in general.

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<sup>(29)</sup> Ray, A.; Mukerjee, P. J. Phys. Chem. 1966, 70, 2138-43. Stigter, D. Ibid. 1974, 78, 2480-5.

<sup>(30)</sup> A case in point is provided by the pyridinium detergents. Micellized pyridinium ions have been widely employed as fluorescence quenchers,<sup>31</sup> as substrates,<sup>13,21,32</sup> and as scavengers of the hydrated electron.<sup>33</sup> In contrast, only a few detailed studies of pyridinium micelle modified reactions have been reported. These include the decomposition of cumene hydroperoxide<sup>24</sup> and of the 6-nitrobenzisoxazole-3-carboxylate ion<sup>35</sup> in micellar HPBr and a study of the catalytic properties of functionalized pyridinium detergents.<sup>36</sup>

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