whose NMR spectrum was identical with that described in Method I.

Registry No. 1a, 41625-65-4; **1b**, 54275-93-3; **1c**, 77646-76-5; **2**, 19617-43-7; **3a**, 77589-57-2; **3b**, 77589-58-3; **3c**, 77589-59-4; **4a**, 77589-60-7; **4b**, 77589-61-8; **5a**, 77589-62-9; **5b**, 77589-63-0; **6**, 77589-64-1.

Supplementary Material Available: Atomic coordinate and numbering for the crystallographic analysis and a table of mass spectral data of compounds **3b** and **4b** (8 pages). Ordering information is given on any current masthead page.

Properties of Phenolic and Thiophenolic Surfactant Micelles

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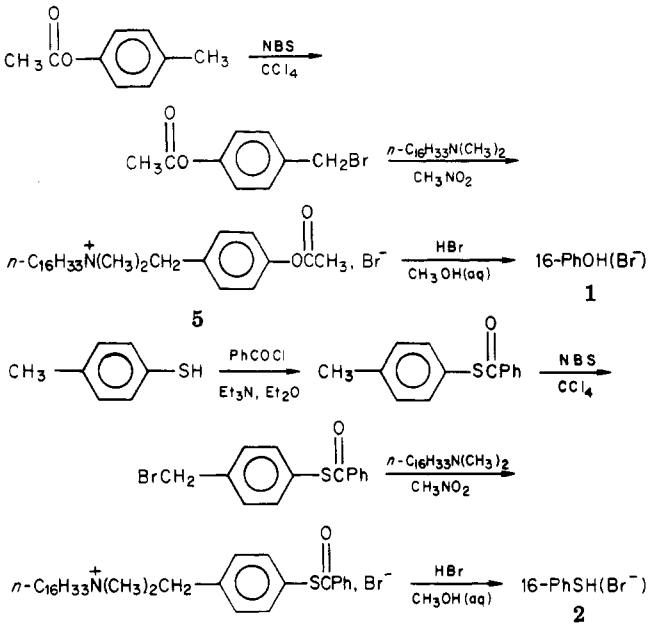
The phenol and thiophenol functionalized surfactants *N*-*n*-cetyl-*N*,*N*-dimethyl-*N*-(*p*-hydroxy[or *p*-mercapto]benzyl)ammonium bromide (**1** and **2**) were synthesized. Under micellar conditions at pH 8, 1.0×10^{-2} M **1**, comicellized with equimolar cetyltrimethylammonium bromide (CTABr), cleaved 2×10^{-5} M *p*-nitrophenyl acetate (PNPA) with $k_\psi = 0.0123$ s^{-1}, whereas 7.5×10^{-3} M **2**, comicellized with 1.33 equiv of CTABr, cleaved PNPA with $k_\psi = 0.034$ s^{-1}. Relative to suitable model reactions with nonmicellar Me_3N^+ analogues of **1** and **2**, micellar enhancements of 27 and 65, respectively, were observed for **1** and **2**. The origins of these factors are discussed, and the esterolytic reactivities of **1** and **2** are compared to related micellar reagents.

Several years ago, Inoue et al. studied the esterolytic cleavage of *p*-nitrophenyl acetate (PNPA) by various lauroylamino acids solubilized in micellar cetyltrimethylammonium bromide (CTABr).[1] They reported the phenolic amino acid derivative *N*-lauroyltyrosine to be a somewhat more efficient reagent for the cleavage of PNPA than the imidazolyl derivative, *N*-lauroylhistidine. For example, in 0.05 M Tris buffer (pH 8.7, 25 °C) with the [lauroylamino acid]/[CTABr] ratio fixed at 0.125 and [PNPA] = 1×10^{-5} M, rate constant vs. [lauroylamino acid] + [CTABr] profiles gave data from which the pseudo-first-order rate constants for PNPA cleavage by the micelle-solubilized lauroylamino acids were calculated to be 0.168 and 0.26 s^{-1}, respectively, for the histidine and tyrosine systems.[1]

The prevailing interest in the remarkable esterolytic properties of imidazolyl surfactant systems[2] prompted us to take a closer look at the comparative reactivities of phenolic and imidazolyl micellar reagents toward PNPA. In this paper, we report the syntheses and comparative esterolytic kinetic properties of phenolic, thiophenolic, and imidazolyl micellar surfactants and appropriate model compounds.

Scheme I



Results

Synthesis. The surfactants of interest were **1** (16-PhOH) and **2** (16-PhSH); these targets also required the corresponding model compounds **3** (1-PhOH) and **4** (1-PhSH). The syntheses of 16-PhOH and 16-PhSH are outlined in Scheme I.

Commercially available *p*-methylphenyl acetate was brominated with NBS, affording the *p*-bromomethyl derivative. This was used to quaternize *N*,*N*-dimethylcetylamine, affording salt **5**, a protected form of the desired surfactant. Deprotection with aqueous methanolic HBr afforded 16-PhOH,Br$^-$ in a 25% overall yield for the three steps. The surfactant was characterized by NMR and

(1) T. Inoue, K. Nomura, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **49**, 719 (1976).

(2) The imidazole moiety can be supplied as an hydrophobic acylhistidine or benzimidazole solubilized by a "carrier" micelle (e.g., CTABr): (a) A. Ochoa-Solano, G. Romero, and C. Gitler, *Science*, **156**, 1243 (1967); (b) C. Gitler and A. Ochoa-Solano, *J. Am. Chem. Soc.*, **90**, 5004 (1968); (c) P. Heitmann, R. Husung-Bublitz, and H. J. Zunft, *Tetrahedron*, **30**, 4137 (1974); (d) A. P. Osipov, K. Martinek, A. K. Yatsimirski, and I. V. Berezin, *Dokl. Akad. Nauk SSSR*, **215**, 914 (1974); (e) K. Martinek, A. P. Osipov, A. K. Yatsimirski, V. A. Dadali, and I. V. Berezin, *Tetrahedron Lett.*, 1279 (1975); (f) K. Martinek, A. P. Osipov, A. K. Yatsimirski, and I. V. Berezin, *Tetrahedron*, **31**, 709 (1975). Or, the imidazole moiety can be part of the surfactant itself: (g) W. Tagaki, M. Chigira, T. Ameda, and Y. Yano, *J. Chem. Soc., Chem. Commun.*, 219 (1972); (h) J. M. Brown and C. A. Bunton, *ibid.*, 969 (1974); (i) J. M. Brown, C. A. Bunton, and S. Diaz, *ibid.*, 971 (1974); (j) D. G. Oakenfull and D. E. Fenwick, *Aust. J. Chem.*, **27**, 2149 (1974); (k) R. A. Moss, R. C. Nahas, S. Ramaswami, and W. J. Sanders, *Tetrahedron Lett.*, 3379 (1975); (l) U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 771 (1976); (m) R. A. Moss, R. C. Nahas, and S. Ramaswami, *J. Am. Chem. Soc.*, **99**, 627 (1977); (n) W. Tagaki, S. Kobayashi, and D. Fukushima, *Chem. Commun.*, 29 (1977); (o) U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 821 (1977); (p) R. A. Moss, T. J. Lukas, and R. C. Nahas, *Tetrahedron Lett.*, 3851 (1977); (q) W. Tagaki, D. Fukushima, T. Eiki, and Y. Yano, *J. Org. Chem.*, **44**, 555 (1979); (r) J. M. Brown, P. A. Chaloner, and A. Colens, *J. Chem. Soc., Perkin Trans. 2*, 71 (1979).

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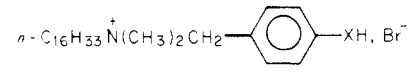
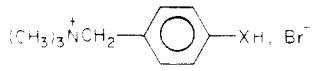


1 (16-PhOH), X = O
2 (16-PhSH), X = S



3 (1-PhOH), X = O
4 (1-PhSH), X = S

elemental analysis. Model compound 1-PhOH was prepared in a similar manner by substituting trimethylamine for *N*,*N*-dimethylcetylamine in the quaternization step.

p-Methylphenyl thioacetate was not a satisfactory starting material for the synthesis of 16-PhSH because NBS partially brominated the acetyl methyl group as well as the *p*-methyl group. Therefore, *p*-methylthiophenol was benzoylated, and the *S*-benzoyl derivative was brominated to afford *p*-(bromomethyl)-*S*-benzoylthiophenol. Reaction of the latter with *N*,*N*-dimethylcetylamine gave the quaternary salt, which afforded 16-PhSH (25% overall yield) upon debenzoylation with aqueous methanolic HBr. Model compound 1-PhSH was analogously prepared by using trimethylamine in the quaternization step. Both thio compounds were characterized by NMR spectroscopy and elemental analysis.

Critical Micelle Concentrations and pK_a Values. Surfactants 16-PhOH and 16-PhSH were of relatively limited solubility in 0.02 M phosphate buffer (pH 8, μ = 0.05, KCl), our usual esterolytic medium, necessitating comicellization with CTABr. We therefore determined the critical micell concentration (cmc) of each surfactant in an appropriate admixture with CTABr, so as to parallel the comicellar systems subsequently used for the kinetic studies.

Cmc's were determined by the surface tension method. For 16-PhOH, the initial solution contained 5.0×10^{-4} M 16-PhOH and 5.0×10^{-4} M CTABr in pH 8.0, 0.02 M phosphate buffer (μ = 0.05, KCl, 25 °C). This solution was successively diluted by addition of buffer, and the surface tension was measured after each dilution with a Fisher Tensiomat. A plot of observed surface tension (γ) vs. log [total surfactant] afforded the apparent or systemic log cmc as the "break point" of the γ vs. concentration correlation; cf. Figure 1. The precision of the surface tension measurements was $<\pm 0.3$ dyn/cm, and the observed cmc of the equimolar 16-PhOH/CTABr comicellar system was 2.25×10^{-4} M.

For 16-PhSH, the initial solution contained 7.5×10^{-4} M 16-PhSH and 1.0×10^{-3} M CTABr in the identical buffer (see above). The observed cmc of the 3:4 16-PhSH/CTABr comicellar system was 8.47×10^{-5} M; cf. Figure 2.

It was necessary to determine pK_a values for compounds 1–4 under appropriate conditions. For surfactant 1, this was done by means of a pH–rate profile, whereas the pK_a's of surfactant 2 and model compounds 3 and 4 were determined spectroscopically.

Pseudo-first-order rate constants for the cleavage of 2.0×10^{-5} M PNPA by equimolar (5.0×10^{-3} M) 16-PhOH/CTABr were determined at various pH's by spectroscopically monitoring the release of *p*-nitrophenoxide ion at 400 nm. Data are summarized in Table I, a log k_ψ vs. pH plot is rendered in Figure 3, and the pK_a (8.04) is taken as the intersection point of the two (least-squares) correlation lines.

The pK_a value of model compound 3 (1-PhOH) was determined spectrophotometrically. Solutions containing

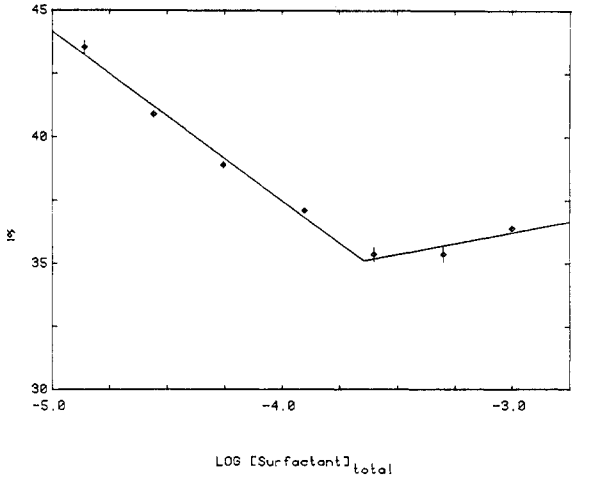


Figure 1. Observed surface tension (γ, dyn/cm) of 1:1 16-PhOH/CTABr in 0.02 M pH 8 phosphate buffer [μ = 0.05 (KCl), 25 °C] vs. log [total surfactant]. The break point occurs at log [surfactant] = −3.648; the *systemic* cmc is 2.25×10^{-4} M.

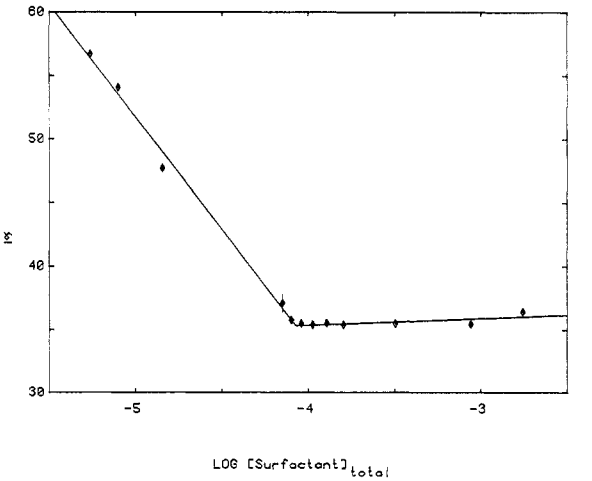


Figure 2. Observed surface tension (γ, dyn/cm) of 3:4 16-PhSH/CTABr (conditions as in Figure 1) vs. log [total surfactant]. The breakpoint occurs at log [surfactant] = −4.072; the *systemic* cmc is 8.47×10^{-5} M.

Table I. pH Dependence of the 16-PhOH/CTABr-PNPA Reactions[a]

pH	buffer (concn, M)	k_ψ, s^{-1} [b]
7.0	phosphate (0.02)	$0.000525 \pm 0.000002_2$
7.5	phosphate (0.02)	$0.00180 \pm 0.00002_2$
8.0	phosphate (0.02)	$0.0074 \pm 0.0003_2$
9.0	borate (0.05)	$0.0213 \pm 0.0004_3$
9.5	borate (0.05)	$0.0335 \pm 0.0002_2$
10.0	borate (0.05)	$0.088 \pm 0.002_3$
11.0	carbonate (0.05)	$0.171 \pm 0.0035_4$ [c]

[a] Buffer ionic strengths were μ = 0.05 (KCl added if necessary). For other conditions, see the text. [b] Errors are average deviations from the mean value of *n* runs. [c] Obtained by stopped-flow spectroscopy.

1-PhOH (1.0×10^{-4} M) and $Me_4N^+Br^-$ (1.0×10^{-4} M) were prepared at pH 1.8, 7.8 (0.02 M PO_4^-), and 11.7. Absorptions were measured for each solution at 5-nm intervals over the range 225–290 nm, and the ratio $(A_{7.8} - A_{1.8})/(A_{11.7} - A_{7.8})$, taken as $[A^-]/[HA]$, was computed for each solution at each wavelength. The average value of $[A^-]/[HA]$ was thus determined to be $0.234 \pm 0.024_{12}$, so that pK_a = 7.8 − log 0.234 = 8.43 ± 0.05.

The pK_a's of thiols 2 (16-PhSH) and 4 (1-PhSH) were determined spectroscopically by using Jencks's method,[3]

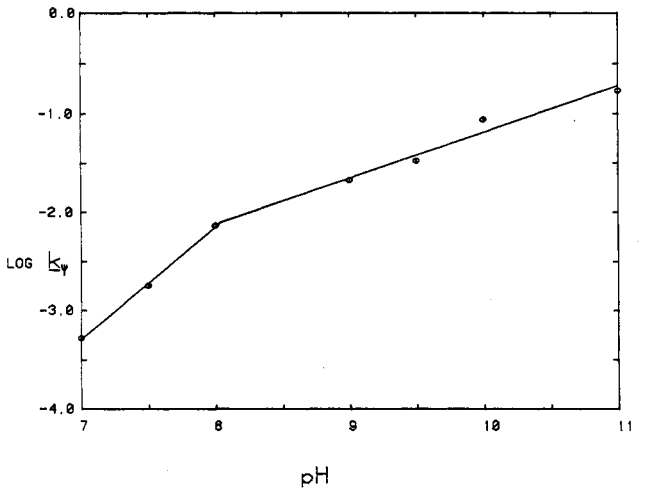


Figure 3. Logarithms of pseudo-first-order rate constants (s^{-1}) for the cleavage of 2×10^{-5} M PNPA by 5×10^{-3} M 16-PhOH + 5×10^{-3} M CTABr vs. pH. The discontinuity at pH 8.04 is taken as the pK_a of 16-PhOH under these comicellar conditions.

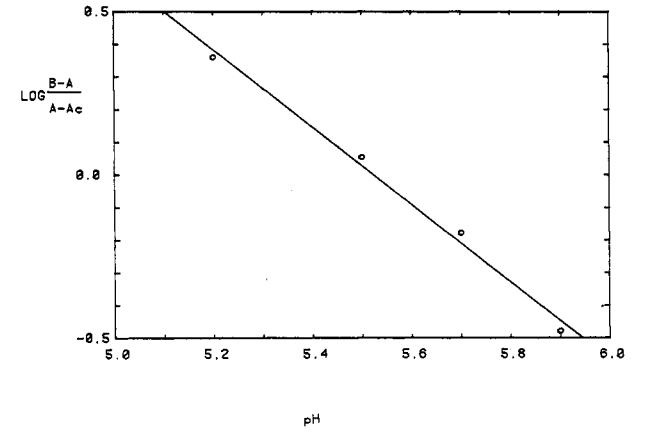


Figure 4. Determination of the pK_a of comicellar 7.5×10^{-4} M 16-PhSH + 1.0×10^{-4} M CTABr in acetate buffer solutions (μ = 0.05). For a discussion, see the text.

in which a series of four or five different buffer ratios was chosen to span the ionization range of the thiol. The thiolate ion absorption was then measured at its λ_{max} after addition of a constant amount of thiol to each buffer solution. The absorbances were also measured in pH 2.5 HCl solution (fully protonated thiol) and in pH 12.0 NaOH solution (thiolate anion). The logarithms of the ratio $(B - A)/(A - A_c)$, in which A is the observed absorbance in a given buffer solution and B and A_c are the absorbances of the basic and acidic forms of the thiol, respectively, were plotted against the observed pH of the buffer solutions at 25 °C. The pK_a was taken as the pH corresponding to log $(B - A)/(A - A_c) = 0$. Using four different acetate buffers (μ = 0.05) and [16-PhSH] = 7.5×10^{-5} M with [CTABr] = 1.0×10^{-4} M, we obtained the data which is graphically displayed in Figure 4. The monitoring λ = 285 nm. The pK_a of micellar (systemic cmc $\sim 8.5 \times 10^{-5}$ M) 16-PhSH was thus determined to be 5.52.

A similar treatment of 7.5×10^{-5} M 1-PhSH in five acetate buffers, monitored at 280 nm, gave pK_a = 6.08. A summary of the pK_a values determined for compounds 1–4, as well as literature values for PhOH and PhSH, appears in Table II.

Relative to PhOH, introduction of the *p*-$Me_3N^+CH_2$ substituent (1-PhOH) induces an acid-strengthening effect

(3) W. P. Jencks and K. Salvesen, *J. Am. Chem. Soc.*, **93**, 4433 (1971).

Table II. pK_a Values

compd	conditions (25 °C, μ = 0.05)	pK_a
PhOH	H_2O,[a] H_2O (μ = 1.0)[b]	9.99,[a] 9.86[b]
1-PhOH	1×10^{-4} M 1-PhOH, equimolar $Me_4N^+Br^-$	8.43
16-PhOH	5×10^{-3} M 16-PhOH, equimolar CTABr	8.04[c]
PhSH	H_2O,[d] H_2O (μ = 0.05)[e]	6.8,[d] 6.8[e]
1-PhSH	7.5×10^{-5} M 1-PhSH	6.08
16-PhSH	7.5×10^{-5} M 16-PhSH, 1.0×10^{-4} M CTABr	5.52[c]

[a] C. H. Rochester, "The Chemistry of the Hydroxyl Group", S. Patai, Ed., Wiley-Interscience, New York, 1971, Part 1, p 327. [b] W. P. Jencks and M. Gilchrist, *J. Am. Chem. Soc.*, **90**, 2622 (1968). [c] Micellar solution. [d] Reference 4. [e] This study, with the method of ref 3.

Table III. Cleavage of PNPA by 16-PhOH/CTABr[a] at 25 °C

10^2[16-PhOH], M[b]	k_ψ, s^{-1} [c]
1.0	0.012 3 ± 0.000 3$_4$
0.75	0.012 0 ± 0.000 2$_4$
0.50	0.007 6 ± 0.000 1$_3$
0.25	0.004 65 ± 0.000 05$_2$
0.10	0.002 45 ± 0.000 04$_2$
0.075	0.002 04 ± 0.000 04$_2$
0.050	0.001 30 ± 0.000 01$_2$
0.025	0.000 64 ± 0.000 01$_2$
0.010	0.000 29 ± 0.000 02$_3$

[a] Solutions were prepared at 70 °C in 0.02 M phosphate buffer, μ = 0.05 (KCl), followed by cooling to 25 °C; [PNPA] = 2.0×10^{-5} M. [b] An equimolar quantity of CTABr was present in each case. [c] Errors are average deviations from the mean of n runs.

(ΔpK_a) of ~1.5 pK units. Micellization (i.e., 16-PhOH vs. 1-PhOH) brings about an additional acidity enhancement of ~0.4 pK unit. Parallel behavior is seen in the thiophenol series: $\Delta pK_a \approx 0.7$ for conversion of PhSH to *p*-$Me_3N^+CH_2PhSH$ (1-PhSH), and micellization (16-PhSH) vs. 1-PhSH) lowers the pK_a by an additional ~0.6 unit.

These acidity enhancements are principally due to electrostatic stabilization of the anionic (conjugate base) forms of compounds 1–4. In the case of compounds 3 and 4, the stabilizations, relative to PhOH and PhSH, are due to the introduction of the cationic *p*-$Me_3N^+CH_2$ substituent. For micellar 16-PhOH and 16-PhSH, the additional stabilization of the cationic CTABr/16-PhXH comicelle buttresses the stabilizing effect of the para cationic substituent. Very similar micellar effects attend the solubilizations of thiophenol in CTABr ($\Delta pK_a \approx 0.6$)[4] and of phenol in CTABr ($\Delta pK_a \approx 0.4$–0.5).[5]

Kinetic Studies with Phenolic Reagents. The cleavage of PNPA by excess micellar 16-PhOH was followed spectrophotometrically at 400 nm in pH 8 buffer. Pseudo-first-order rate constants as a function of [16-PhOH] appear in Table III, and a rate constant/[surfactant] profile, constructed from Table III, appears in Figure 5. k_ψ^{max} for 10^{-2} M 16-PhOH, comicellized with 10^{-2} M CTABr, was 0.0123 s^{-1}.

A second rate constant/[16-PhOH] profile (not shown) was determined under identical buffer conditions, but with the maximum concentration of 16-PhOH = 7.5×10^{-3} M

(4) I. M. Cuccovia, E. H. Schröter, P. M. Monteiro, and H. Chaimovich, *J. Org. Chem.*, **43**, 2248 (1978).
(5) H. Chaimovich, A. Blanco, L. Chayet, L. M. Costa, P. M. Monteiro, C. A. Bunton, and C. Paik, *Tetrahedron*, **31**, 1139 (1975).

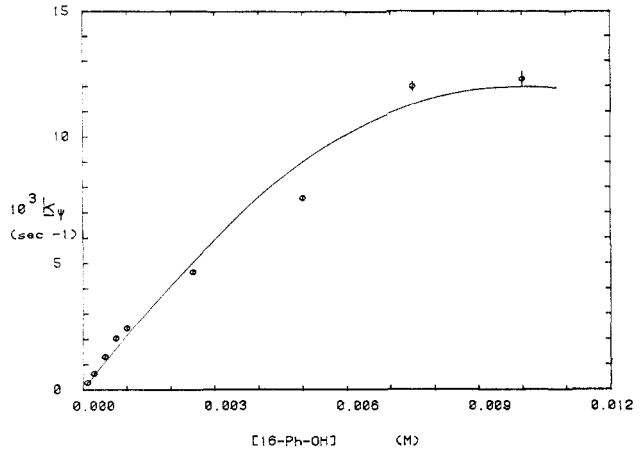


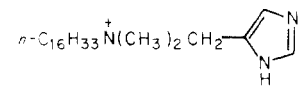
Figure 5. Pseudo-first-order rate constants (s^{-1}) for the pH 8 cleavage of PNPA by comicellar (1:1) 16-PhOH/CTABr vs. [16-PhOH]. See the text and Table III.

(in 1.0×10^{-2} M CTABr; [16-PhSH]/[CTABr] = 0.75). The graphical form of this profile was quite similar to that of Figure 5 and gave $k_\psi^{max} = 0.006\,35\ s^{-1}$.

For comparison, model phenol **3** was used to cleave PNPA. With [**3**] = 1×10^{-2} M and [$Me_4N^+Br^-$] = 1×10^{-2} M in 0.02 M phosphate (μ = 0.05 (KCl)), $k_\psi = 0.000\,45 \pm 0.000\,01_2\ s^{-1}$.

The reaction product of 16-PhOH and PNPA is 16-PhOAc (**5**, Scheme I), so that 16-PhOH turnover in the presence of excess PNPA would be controlled by the O-deacetylation of 16-PhOAc. The latter reaction is quite slow at pH 8, but we did study it briefly at pH 9. The deacetylation was followed by the appearance of 16-PhO^- at 280 nm (λ_{max} = 272 nm for 10^{-4} M 16-PhOH in 10^{-4} M CTABr at pH 9), produced by the cleavage of 16-PhOAc (λ_{max} = 260 nm for 10^{-3} M 16-PhOAc in 10^{-3} M CTABr at pH 7).

In 0.05 M, pH 9 borate buffer, k_ψ for 16-PhOAc → 16-PhOH was $0.000\,54 \pm 0.000\,01_2\ s^{-1}$ (5×10^{-4} M 16-PhOAc in 9.5×10^{-3} M CTABr). Repetition of this experiment with 9.5×10^{-3} M 16-Im (**6**)[2g,k] as the comicellar surfactant



6 (16-Im)

gave $k_\psi = 0.098 \pm 0.008_3$ (stopped-flow spectroscopy). We thus observed a 181-fold enhancement in the micellar deacetylation of 16-PhOAc by 16-Im, relative to CTABr. This is most probably due to acetyl transfer from 16-PhOAc to 16-Im, followed by rapid deacetylation of MeC(O)-16-Im.[2m] Analogous experiments with nonmicellar 1-PhOAc gave $k_{deacet} = 0.000\,27 \pm 0.000\,01_4\ s^{-1}$ at pH 9 (only 2 times slower than its 16-PhOAc micellar analogue). Significant enhancement of this deacetylation could not be elicited upon addition of 16-Im ($k_{deacet} = 0.000\,36 \pm 0.000\,01_3\ s^{-1}$ with 9.5×10^{-3} M 16-Im). Apparently, hydrophilic cationic 1-PhOAc is excluded from cationic 16-Im micelles.

Note, finally, that the deacetylation of 16-PhOAc at pH 9 is considerably slower than the 16-PhOH cleavage of PNPA at pH 8, so that micellar 16-PhOH would turn over only very slowly in the PNPA cleavage reaction.

Kinetic Studies with Thiophenolic Reagents. Due to its low pK_a (~5.5), 16-PhSH is >99% ionized in CTABr comicellar solution at pH 8. The solubility of the resulting zwitterionic 16-PhS^- is lower than that of the corresponding less ionized (~50%) 16-PhOH/16-PhO^- system, so that pH 8 comicellar solutions of 16-PhSH in CTABr are preparable only with lower ratios of functional to nonfunctional surfactant and at a lower maximum concentration of the functional reagent. Our most concentrated solution, 7.5×10^{-3} M 16-PhSH in 1.0×10^{-2} M CTABr, was prepared by vigorously stirring the thiol surfactant in CTABr solution for 1–3 h; dissolution times varied with [16-PhSH] and pH. Final solutions were without noticeable Tyndall effect.

Table IV. Cleavage of PNPA by 16-PhSH/CTABr at 25 °C[a]

10^3[16-PhSH], M	10^3[16-PhSH + CTABr], M[b]	k_ψ, s^{-1} [c]
7.5	17.5	$0.034 \pm 0.001_2$
6.0	14.0	$0.0268 \pm 0.0006_3$
4.5	10.5	$0.022 \pm 0.001_3$
3.0	7.0	$0.0145 \pm 0.0004_2$
2.25	5.25	$0.0080 \pm 0.0002_2$
1.5	3.5	$0.0028 \pm 0.0001_2$
0.75	1.75	$0.0016 \pm 0.0001_2$

[a] Conditions: 0.02 M phosphate buffer, μ = 0.05 (KCl), pH 8, [PNPA] = 2×10^{-5} M. [b] 1.33 equiv of CTABr was present in each case. [c] Errors are average deviations from the mean of n runs.

Pseudo-first-order rate constants for cleavage of PNPA were determined as a function of [16-PhSH] at pH 8.0 and 25 °C and are summarized in Table IV. k_ψ for 7.5×10^{-3} M 16-PhSH/1.0×10^{-2} M CTABr was 0.034 s^{-1}. Note, however, that the low solubility of 16-PhS^- limits the obtainable k_ψ. The data suggest that higher values of k_ψ could be obtained if it were possible to study higher concentrations of 16-PhSH.

A second k_ψ/[16-PhSH] profile was determined under identical buffer conditions, but with the maximum concentration of 16-PhSH being 5.0×10^{-3} M (in 1.0×10^{-2} M CTABr). k_ψ^{max} was $0.019 \pm 0.001_5\ s^{-1}$, but this value was clearly a point on a still-rising, nearly linear correlation.

For comparison, model thiophenol **4** was used to cleave PNPA. With [**4**] = 7.5×10^{-3} M and [$Me_4N^+Br^-$] = 1.0×10^{-2} M in 0.02 M pH 8 phosphate buffer (μ = 0.05 (KCl)), $k_\psi = 0.000\,52 \pm 0.000\,01_2\ s^{-1}$.

The cleavage product expected from 16-PhSH and PNPA is 16-PhSAc, which was independently prepared by isopropenyl acetate acylation of 16-PhSH (see Experimental Section). Deacetylation of 16-PhSAc (Cl^- form) was followed at pH 8 via the appearance of 16-PhS^- at 290 nm (λ_{max} = 268 nm for 1.0×10^{-4} M 16-PhSH/1.25×10^{-4} M CTABr at pH 8.0), produced by the cleavage of 16-PhSAc (λ_{max} = 252 nm for 1.5×10^{-4} M 16-PhSAc in 2×10^{-4} M CTABr at pH 6). In 0.02 M pH 8 phosphate buffer (μ = 0.05 (KCl)), k_ψ for 16-PhSAc → 16-PhSH was $0.000\,30 \pm 0.000\,01_2\ s^{-1}$ (5.0×10^{-4} M 16-PhSAc, Cl^- in 9.5×10^{-3} M CTABr).[6] Repetition of this experiment with 9.5×10^{-3} M 16-Im (**6**) as the comicellar surfactant gave $k_\psi^{deacet} = 0.062 \pm 0.001_3\ s^{-1}$, a 207-fold enhancement in the micellar deacetylation of 16-PhSAc by 16-Im, relative to CTABr.

Comparison of k_ψ^{deacet} for 16-PhSAc in CTABr at pH 8 ($0.000\,30\ s^{-1}$) with k_ψ^{max} for PNPA cleavage by 16-SH/CTABr at pH 8 ($0.034\ s^{-1}$) shows that turnover of the thiophenolic micellar reagent would be slow and rate-controlling under conditions of excess substrate. It is conceivable, however, that comicellar 16-PhSH/16-Im would form a practical cleavage/turnover system, although

(6) Under comparable conditions, deacetylation of comicellar 16-PhOAc/CTABr gave $k_\psi = 0.000\,12\ s^{-1}$, so that the ratio of psuedo-first-order micellar deacetylation rate constants was ~2.5 for 16-PhSAc vs. 16-PhOAc at pH 8.

Table V. Cleavage of PNPA by Selected Comicellar Reagents[a]

entry	surfactant	concn, M	[CTABr], M	k_ψ, s^{-1}
1	16-OH (7)	0.010	0.010	0.001 30
2	16-PhOH (1)	0.010	0.010	0.012 3
3	16-PhOH (1)	0.0075	0.010	0.006 35
4	16-PhSH (2)	0.0075	0.010	0.034
5	16-Im (6)	0.0075	0.010	0.041 4
6	1-PhOH (3)[b]	0.010	[c]	0.000 45
7	1-PhSH (4)[b]	0.0075	[c]	0.000 52

[a] Conditions: pH 8.0, 0.02 M phosphate buffer, μ = 0.05 (KCl), 25 °C, [PNPA] = 2×10^{-5} M. [b] Nonmicellar reaction. [c] 0.010 M added $Me_4N^+Br^-$.

it would be difficult to disentangle the several competitive acylations and deacylations which would occur simultaneously.

Miscellaneous Rate Constants. For comparative purposes, several PNPA cleavage reactions were studied with imidazole surfactant 16-Im (**6**) and choline surfactant 16-OH (**7**). In pH 8.0, 0.02 M phosphate buffer (μ = 0.05

$$n\text{-}C_{16}H_{33}N^+(CH_3)_2CH_2CH_2OH,Br^-$$
7 (16-OH)

(KCl), 25 °C), $k_\psi = 0.0414 \pm 0.0000_2$ s^{-1} for cleavage of 2×10^{-5} M PNPA by 7.5×10^{-3} M 16-Im in 1.0×10^{-2} M CTABr. Under similar conditions, $k_\psi = 0.001\,30 \pm 0.000\,02_2$ s^{-1} for PNPA cleavage by equimolar (1×10^{-2} M) 16-OH/CTABr.

Discussion

One purpose of this work was to determine the comparative micellar kinetic efficiencies of imidazolyl and phenolic surfactant systems in PNPA esterolysis. Table V collects appropriate rate constants. In all cases, the functional surfactants were examined in comicellar solution with CTABr. Comparison of entries 3 and 5 make it clear that the imidazole residue of 16-Im, separated by a methylene group from the quaternary nitrogen of the micellized surfactant, is a significantly more effective nucleophile (by a factor of 6.5) toward PNPA than the comparably situated phenol residue of 16-PhOH under analogous reaction conditions. This result is the reverse of that obtained by Inoue et al.[1] in their comparison of the amino acid nucleophiles *N*-lauroylhistidine and *N*-lauroyltyrosine, each solubilized in micellar CTABr.

Although a definitive reason for the opposed outcomes of the present and earlier investigations is lacking, we suspect that the principal factor is that the active nucleophilic form of the imidazole residue in the acylhistidine case is the neutral imidazole,[1] whereas in the (present) example of 16-Im, it is the much more nucleophilic imidazole anion.[2g,k,l,p] The effective reactivities, relative to phenol/phenoxide micellar reagents at pH 8–9, are such that the holomicellar 16-Im reagent is more reactive toward PNPA, whereas the micelle-solubilized acylhistidine reagent is less reactive.

It is worthwhile to examine the pH 8, PNPA-based comparative reactivities of 16-PhOH and 16-PhSH against the background of a wider array of functional micellar reagents. From Table V, micellar 16-PhOH is seen to be ~1 order of magnitude more potent than 16-OH (entries 2 vs. 1), whereas the latter is more reactive than nonfunctional CTA by a very similar factor.[2k] Further, 16-PhSH is found to be ~5 times more potent in PNPA esterolysis than 16-PhOH (entries 4 vs. 3), and quite comparable to 16-Im (entry 5). Note, however, that 16-PhSH is less reactive toward PNPA than 16-SH (**8**). Under comparable conditions the latter micellar reagent cleaves PNPA 15–20 times more rapidly.[7]

$$n\text{-}C_{16}H_{33}N^+(CH_3)_2CH_2CH_2SH,Cl^-$$
8 (16-SH)

The comparative reactivities of micellar 16-OH, 16-PhOH, 16-PhSH, and 16-SH are determined by their pK_a values and by the intrinsic reactivities of their reactive conjugate bases. Taking the pK_a of micellar 16-OH as ~12.4,[8] the acidity ordering (pK_a) is as follows: 16-OH (12.4) < 16-PhOH (8.04)[9] < 16-SH (7.32)[7] < 16-PhSH (5.5).[9] At pH 8, the approximate extents of ionization would be as follows: 16-OH, 0.004%; 16-PhOH, 48%; 16-SH, 83%; 16-PhSH, >99%. It is therefore clear that 16-S^- is considerably more reactive toward PNPA than the aromatic thiolate reagent 16-PhS^-; the rate constant advantage of 15–20 for 16-SH vs. 16-PhSH (see above) underestimates the intrinsic reactivity advantage of 16-S^- over 16-PhS^-, due to the greater extent of ionization of 16-PhSH at pH 8. Similarly, 16-O^- must be much more reactive toward PNPA than 16-PhO^-, because, although 16-PhOH cleaves the ester ~10 times more rapidly than 16-OH at pH 8, the former reagent is ~12 000 times more extensively ionized to its reactive anionic form under the reaction conditions. Relative reactivity advantages of ethoxide over phenoxide and of thioethoxide over thiophenoxide have been previously reported for the cleavage of PNPA.[10]

In comparison to their model compounds, 16-PhOH and 16-PhSH are, respectively, 27 (Table V, entries 2 vs. 6) and 65 (entries 4 vs. 7) times more reactive toward PNPA. Corrected for the different extents of ionization of the micellar vs. the nonmicellar models (see above), these kinetic advantages reduce to factors of 14 (16-PhO^-) and 64 (16-PhS^-). Micellization would thus appear to have an intrinsically greater effect on the kinetic potency of the thiophenoxide nucleophile, relative to the phenoxide nucleophile. Recent work with CTA-comicellized phenoxide (reactions with 2,4-dinitrofluorobenzene or *p*-nitrophenyl diphenyl phosphate)[5,11] and thiophenoxide (cleavage of PNPA)[4] suggests that the observed micellar rate enhancements are, in these cases, adequately explained by the effect of concentrating the substrates (and reactants) in the micellar phase. The apparently greater micellar potentiation of 16-PhSH, relative to 16-PhOH, may be due to microscopic differences in the Stern layers of the thiophenolic and phenolic micelles (e.g., Stern layer volume, degree of hydration, extent and strength of ion pairing).

There is also good quantitative agreement between the present and previous studies. The 4.6-fold greater micellar kinetic enhancement of 16-PhS^- vs. 16-PhO^- found in the present study of PNPA cleavage is similar to the 4.8-fold superior potentiation observed with thiophenol/CTA as opposed to phenol/CTA in reactions with 2,4-dinitrofluorobenzene.[5] Additionally, the observed micellar enhancement for 16-PhS^- relative to 1-PhS^- (64-fold) parallels the ~50-fold increase in PNPA thiolysis by thiophenoxide ion elicited by solubilization in CTABr.[4]

Although the forgoing comparisons and mechanistic conclusions appear reasonable and self-consistent, we must

(7) R. A. Moss, G. O. Bizzigotti, and C.-W. Huang, *J. Am. Chem. Soc.*, **102**, 754 (1980).
(8) C. A. Bunton and L. G. Ionescu, *J. Am. Chem. Soc.*, **95**, 2912 (1973); C. A. Bunton, S. Diaz, J. M. Hellyer, Y. Ihara, and L. G. Ionescu, *J. Org. Chem.*, **40**, 2313 (1975).
(9) See Table II.
(10) D. J. Hupe and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 451 (1977). See also G. Guanti, G. Cevasco, S. Thea, C. Dell'Erba, and G. Petrillo, *J. Chem. Soc., Perkin Trans. 2*, 327 (1981).
(11) C. A. Bunton, G. Cerichelli, Y. Ihara, and L. Sepulveda, *J. Am. Chem. Soc.*, **101**, 2429 (1979).

caution that they tacitly assume similar mechanisms for PNPA cleavage by all of the nucleophilic reagents. Actually, the PNPA cleavage reactions pass through tetrahedral intermediates formed by attack of the nucleophiles on the ester.[10] Since the pK_a's of the arene thiol reagents (Table II) are lower than that of PNPA (7.14 in water[10]), it is possible that *expulsion* of p-nitrophenol from the tetrahedral intermediate is rate determining in the reaction of, e.g., 16-PhSH with PNPA,[4,10] whereas *formation* of the tetrahedral intermediate is rate determining in the 16-PhOH (and other) micellar PNPA cleavages. The apparent self-consistency of the data in the light of this potential mechanistic complication deserves further investigation.

Finally, we note that the functional surfactants, 16-PhOH and 16-PhSH, generate micellar reagents which are much easier to study than the corresponding phenol/CTA or thiophenol/CTA systems. The latter require separate examination of phenol or thiophenol binding to the CTA micelles, i.e., of functional reagent partitioning between aqueous and micellar phases. The need for such ancillary studies is obviated by working with the holomicellar 16-PhXH reagents.

Experimental Section

General Methods. Melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 727B spectrometer, UV spectra were determined with a Cary Model 14 instrument, and NMR spectra were measured with a Varian T-60 spectrometer and are reported relative to internal Me_4Si. Microanalyses were performed by Robertson Laboratory.

***p*-(Bromomethyl)phenyl Acetate.** A 250-mL, round-bottomed flask, fitted with a reflux condenser and magnetic stirring bar, was charged with 15.0 g (100 mmol) of *p*-methylphenyl acetate (Pfaltz and Bauer) and 17.8 g (100 mmol) of *N*-bromosuccinimide (recrystallized from water, dried under vacuum) in 40 mL of CCl_4. The mixture was stirred and irradiated at close range with a 250-W GE infrared heating lamp, which initiated reflux. After 4 h of reflux under irradiation, the reaction mixture was cooled, and the solid succinimide (floating atop the solvent) was filtered. A CCl_4 wash of the solid was combined with the filtrate, and the solution was dried over $CaCl_2$. The drying agent was filtered and CCl_4 stripped on the rotary evaporator, affording a residue which was distilled over a short column through an air condenser. Unreacted starting material was recovered at 60–65 °C (0.4 mmHg), and this was followed by 14.3 g (62.4 mmol, 62.4%) of *p*-(bromomethyl)phenyl acetate [bp 100–105 °C (0.4 mmHg)] which solidified upon cooling. Recrystallization from *n*-hexane gave material of melting point 48–50 °C, which was used without further purification: NMR ($CDCl_3$) δ 7.1–7.6 ("q", 4 H, aryl), 4.53 (s, 2 H, $BrCH_2$, 2.33 (s, 3 H, CH_3COO).

***N*-*n*-Cetyl-*N*,*N*-dimethyl-*N*-(*p*-acetoxybenzyl)ammonium Bromide (5).** *p*-(Bromomethyl)phenyl acetate (3.44 g, 15 mmol) was magnetically stirred for 60 h at 25 °C with excess *N*,*N*-dimethyl-*N*-*n*-cetylamine[12] (5.00 g, 18.6 mmol) in 40 mL of nitromethane. Excess dry ether was added, the solution was chilled, and the precipitated solid was filtered. Recrystallization (EtOAc) afforded 5.42 g (11 mmol, 73%) of ammonium salt **5**: mp 112–113 °C; NMR ($CDCl_3$) δ 7.2–8.0 ("q", 4 H, aryl), 5.23 (s, 2 H, $ArCH_2$), 3.2–3.7 (m + s, 8 H, $^+N(CH_3)_2CH_2C_{15}$), 2.37 (s, 3 H, CH_3COO); 1.3 ("s", 28 H, $(CH_2)_{14}$), 0.90 (crude t, 3 H, $(CH_2)_{14}CH_3$).

Anal. Calcd for $C_{27}H_{48}BrNO_2$: C, 65.02; H, 9.71; N, 2.81; Br, 16.03. Found: C, 64.88; H, 9.46; N, 2.71; Br, 15.99.

***N*-*n*-Cetyl-*N*,*N*-dimethyl-*N*-(*p*-hydroxybenzyl)ammonium Bromide (1).** The protected surfactant **5** (7.0 g, 14 mmol), 18 mL of 1 N aqueous HBr, and 45 mL of methanol were magnetically stirred at 25 °C for 24 h; a precipitate formed. After neutralization to pH 6–7 with saturated aqueous NaOH, the product was filtered and recrystallized from EtOAc/EtOH (95:5), affording 3.54 g (7.8 mmol, 56%) of **1**: mp 128–130 °C; NMR (Me_2SO-d_6) δ 7.6–6.9 ("q", 4 H, aryl), 4.50 (s, 2 H, $ArCH_2$), 2.97 ("s", 8 H, $(CH_3)_2N^+CH_2C_{15}$), 1.30 ("s", 28 H, $(CH_2)_{14}$), 0.90 (crude t, 3 H, $(CH_2)_{14}CH_3$).

Anal. Calcd for $C_{25}H_{46}BrNO$: C, 65.74; H, 10.16; N, 3.07; Br, 17.51. Found: C, 65.62; H, 10.01; N, 2.92; Br, 17.65.

***N*,*N*,*N*-Trimethyl-*N*-(*p*-acetoxybenzyl)ammonium Bromide.** *p*-(Bromomethyl)phenyl acetate (6.88 g, 30.0 mmol) and trimethylamine (4.2 g, 71 mmol, added as a 33% solution in ethanol) were magnetically stirred at 25 °C for 30 min. Volatiles were stripped off under aspirator vacuum followed by high vacuum overnight. The crude solid was recrystallized from EtOAc/EtOH (95:5), affording 4.78 g (16.6 mmol, 55.3%) of **1-PhOAc**: mp 178–180 °C; NMR ($CDCl_3$) δ 7.1–7.8 ("q", 4 H, aryl), 5.13 (s, 2 H, $ArCH_2$), 3.4 (s, 9 H, $(CH_3)_3N^+$), 2.33 (s, 3 H, CH_3COO).

Anal. Calcd for $C_{12}H_{18}BrNO_2$: C, 49.99; H, 6.30; N, 4.86; Br, 27.74. Found: C, 49.80; H, 6.50; N, 4.62; Br, 27.53.

***N*,*N*,*N*-Trimethyl-*N*-(*p*-hydroxybenzyl)ammonium Bromide (3).** The preceding salt (3.5 g, 12 mmol) was stirred magnetically with 6 mL of 1 N aqueous HBr in 18 mL of methanol (24 h, N_2 blanket). Neutralization to pH 6–7 with saturated aqueous NaOH solution was followed by rotary evaporation and lyophilization. The residual solid was stirred in dry acetone and filtered (to remove NaBr). This procedure was repeated twice. Acetone was stripped from the final filtrate, and the solid was dried under vacuum, affording 1.51 g (6.14 mmol, 51%) of (hygroscopic) **3**: mp 165–166 °C; NMR (Me_2SO-d_6) δ 6.9–7.6 ("q", 4 H, aryl), 4.63 (s, 2 H, $ArCH_2$), 3.10 (s, 9 H, $(CH_3)_3N^+$).

Anal. Calcd for $C_{10}H_{16}BrNO$: C, 48.77; H, 6.55; N, 5.69; Br, 32.47. Found: C, 47.95; H, 6.44; N, 5.49; Br, 33.02.[13]

***p*-Methyl-*S*-benzoylthiophenol.** A 500-mL, round-bottomed flask was fitted with a dropping funnel and magnetic stirring bar and charged with 12.4 g (100 mmol) of *p*-methylthiophenol (Aldrich), 14.05 g (100 mmol) of freshly distilled benzoyl chloride, and 100 mL of dry ether. The mixture was stirred and cooled (ice/water bath), while 13 g (130 mmol) of freshly distilled triethylamine (diluted with an equal volume of ether) was added slowly from the dropping funnel. After 2 h, the reaction mixture was allowed to warm to 25 °C; solid $Et_3NH^+Cl^-$ was filtered and washed with ether. Rotary evaporation of the combined ether fractions afforded 14.6 g (64%) of the desired benzoyl derivative: mp 75–77 °C; NMR ($CDCl_3$) δ 7.1–7.6, 7.9–8.1 (m, 9 H, aryl), 2.4 (s, 3 H, CH_3).

***p*-(Bromomethyl)-*S*-benzoylthiophenol.** By use of the procedure described above for *p*-(bromomethyl)phenyl acetate, 5.85 g (26 mmol) of *p*-methyl-*S*-benzoylthiophenol and 5.54 g (31 mmol) of *N*-bromosuccinimide were reacted in 50 mL of CCl_4 for 90 min. The crude solid product was recrystallized from *n*-hexane, affording 5.64 g (18.4 mmol, 71%) of the title bromo compound: mp 86–88 °C; NMR ($CDCl_3$) δ 7.4–7.8, 8.0–8.2 (m, 9 H, aryl), 4.5 (s, 2 H, CH_2). This material was used without further purification.

***N*-*n*-Cetyl-*N*,*N*-dimethyl-*N*-[*p*-(benzoylthio)benzyl]ammonium Bromide.** The preceding bromo compound (5.0 g, 16 mmol) was stirred vigorously for 16 h with 8.0 g (30 mmol) of *N*,*N*-dimethyl-*N*-*n*-cetylamine[12] in 40 mL of nitromethane. Dry ether was added to the suspension (5 mL), and the solid was filtered and recrystallized from EtOAc/EtOH (95:5), affording 6.2 g (11 mmol, 66%) of the protected surfactant: mp 157–158 °C; NMR ($CDCl_3$) δ 7.4–8.2 (m, 9 H, aryl), 5.4 (s, 2 H, $ArCH_2$), 3.4–3.9 (m + s, 8 H, $(CH_3)_2N^+CH_2C_{15}$), 1.3 (s, 28 H, $(CH_2)_{14}$), 0.90 (crude "t", 3 H, $(CH_2)_{14}CH_3$).

Anal. Calcd for $C_{32}H_{50}BrNOS$: C, 66.62; H, 8.74; S, 5.56. Found: C, 66.64; H, 8.89; S, 5.82.

***N*-*n*-Cetyl-*N*,*N*-dimethyl-*N*-(*p*-mercaptobenzyl)ammonium Bromide (2).** The protected surfactant (1.20 g, 2.08 mmol) was stirred and refluxed for 65 h with 8 mL of 48% aqueous HBr diluted with 10 mL of water and 25 mL of methanol. The solution was then cooled and aspirated to afford a precipitate which was filtered and dried under vacuum. IR spectroscopy indicated the absence of carbonyl absorption, and Ellman's assay[14] indicated >93% free SH. Recrystallization from EtOAc/EtOH (95:5) gave

(12) R. C. Nahas, Ph.D. Dissertation, Rutgers University, New Brunswick, NJ, 1978, pp 115–116.

(13) Traces of H_2O or NaBr may have lowered the observed percent of C.

(14) A. F. S. A. Habeeb, *Methods Enzymol.*, **25**, 457 (1972). Our experimental procedure is described in R. A. Moss, T. J. Lukas, and R. C. Nahas, *J. Am. Chem. Soc.*, **100**, 5920 (1978).

0.78 g (1.65 mmol, 79.3%) of thiol surfactant **2**: mp 126–128 °C; NMR ($CDCl_3$) δ 7.8–7.7 ("q", 4 H, aryl), 5.1 (s, 2 H, $ArCH_2$), 4.0 (s, 1 H, SH), 3.3–3.9 (m + s, 8 H, $(CH_3)_2N^+CH_2C_{15}$), 1.27 (s, 28 H, $(CH_2)_{14}$), 0.90 (crude "t", 3 H, $(CH_2)_{14}CH_3$).

Anal. Calcd for $C_{25}H_{46}BrNS$: C, 63.51; H, 9.82; Br, 16.92. Found: C, 62.61; H, 9.55; Br, 17.19.[15]

***N,N,N*-Trimethyl-*N*-[*p*-(benzoylthio)benzyl]ammonium Bromide.** *p*-(Bromomethyl)-*S*-benzoylthiophenol (3.0 g, 9.8 mmol) and trimethylamine 0.57 g (9.7 mmol in a 33% solution in ethanol) were stirred at 25 °C for several minutes. The suspension liquified and then solidified. Ethanol was removed under vacuum, and the residual solid was recrystallized from EtOAc/EtOH (95:5), affording 2.47 g (6.75 mmol, 69%) of the title compound: mp 200–202 °C; NMR ($CDCl_3$) δ 7.4–8.1 (m, 9 H, aryl), 5.27 (s, 2 H, $ArCH_2$), 3.47 (s, 9 H, $(CH_3)_3N^+$).

Anal. Calcd for $C_{17}H_{20}BrNOS$: C, 55.72; H, 5.51; S, 8.76. Found: C, 55.67; H, 5.59; S, 8.82.

***N,N,N*-Trimethyl-*N*-(*p*-mercaptobenzyl)ammonium Bromide (4).** The preceding ammonium salt (1.2 g, 3.3 mmol) was stirred and refluxed for 4 h with 3 mL of 48% aqueous HBr, diluted with 15 mL of water. The solution was cooled and aspirated, and the white precipitate (benzoic acid) was filtered. The residual solution was lyophilized, affording an oily residue which solidified upon trituration with ethyl acetate. The crude solid was recrystallized from EtOAc/EtOH (95:5), affording 0.52 g (2.0 mmol, 61%) of **4**: mp 156–158 °C; NMR (D_2O/DSS) δ 7.0–7.5 ("q", 4 H, aryl), 4.30 (s, 2 H, $ArCH_2$), 3.03 (s, 9 H, $(CH_3)_3N^+$).

Anal. Calcd for $C_{10}H_{16}BrNS$: C, 45.78; H, 6.15; N, 5.35. Found: C, 45.59; H, 6.22; N, 5.32.

***N*-*n*-Cetyl-*N,N*-dimethyl-*N*-[*p*-(acetylthio)benzyl]ammonium Chloride.** Thiosurfactant **2** (0.30 g, 0.64 mmol), 4 mL of isopropenyl acetate (Aldrich), 10 mL of dry CH_2Cl_2, and several drops of benzenesulfonic acid were stirred at 25 °C for 60 h. The solvent was stripped off, and the solid residue was triturated with dry ether. The solid was filtered and dried. NMR spectroscopy indicated that acetylation had occurred but that the original bromide counterion of **2** had been largely replaced by benzenesulfonate. Therefore, the solid was added to 50 mL of water and 5 g of Dowex 1-X8 ion-exchange resin beads (Cl^- form). This mixture was heated to 65 °C with stirring, cooled, and filtered. The filtrate was lyophilized to yield 0.18 g (0.38 mmol, 59%) of 16-PhSAc,Cl. This material was very hygroscopic: NMR ($CDCl_3$) δ 7.3–7.8 ("q", 4 H, aryl), 5.13 (s, 2 H, $ArCH_2$), 3.27 (br s, 8 H, $(CH_3)_2N^+CH_2$), 2.43 (s, 3 H, $SCOCH_3$), 1.27 (s, 28 H, $(CH_2)_{14}$), 0.90 (crude "t", 3 H, $(CH_2)_{14}CH_3$). This material was used for deacetylation experiments without further purification.

Cmc and pK_a Measurements. These are described above in the Results section.

Kinetic Studies. Reactions were generally monitored on a Gilford Model 250 spectrophotometer coupled to a Gilford Model 6051 recorder. A constant-temperature circulating bath maintained the reaction temperature at 25.0 ± 0.02 °C. All buffers were prepared from nitrogen-purged steam-distilled water and were purged again immediately before use. The reactions of 16-PhOAc with 16-Im at pH 9 and of 16-PhOH with PNPA at pH 11 (Table I) were followed by stopped-flow spectroscopy.[16] Details of the kinetics conditions and observed rate constants may be found in the Results section. Rate constants were obtained from computer-generated correlations of log $(A_\infty - A_t)$ with time in the standard way. Reactions were generally followed to >90% completion and showed first-order kinetics with correlation coefficients >0.999.

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Registry No. **1**, 77551-97-4; **2**, 77551-98-5; **3**, 77551-99-6; **4**, 77552-00-2; **5**, 77552-01-3; **6**, 57879-45-5; **7**, 20317-32-2; **8**, 67675-68-7; *p*-(bromomethyl)phenyl acetate, 52727-95-4; *p*-methylphenyl acetate, 140-39-6; *N,N*-dimethyl-*N*-cetylamine, 112-69-6; trimethylamine, 75-50-3; *N,N,N*-trimethyl-*N*-(*p*-acetoxybenzyl)ammonium bromide, 77552-02-4; *p*-methyl-*S*-benzoylthiophenol, 10371-42-3; *p*-methylthiophenol, 106-45-6; benzoyl chloride, 98-88-4; *p*-(bromomethyl)-*S*-benzoylthiophenol, 77552-03-5; *N*-cetyl-*N,N*-dimethyl-*N*-[*p*-(benzoylthio)benzyl]ammonium bromide, 77552-04-6; *N,N,N*-trimethyl-*N*-[*p*-(benzoylthio)benzyl]ammonium bromide, 77552-05-7; *N*-cetyl-*N,N*-dimethyl-*N*-[*p*-(acetylthio)benzyl]ammonium chloride, 77552-06-8; *p*-nitrophenyl acetate, 830-03-5; benzenethiol, 108-98-5.

(15) Several analyses did not improve the carbon value.

(16) For equipment details, see ref 7.