

Anion-Specific Binding to *n*-Hexadecyl Phosphorylcholine MicellesJacks P. Priebe,[†] Bruno S. Souza,[†] Gustavo A. Micke,[†] Ana C. O. Costa,[†] Haidi D. Fiedler,[†]
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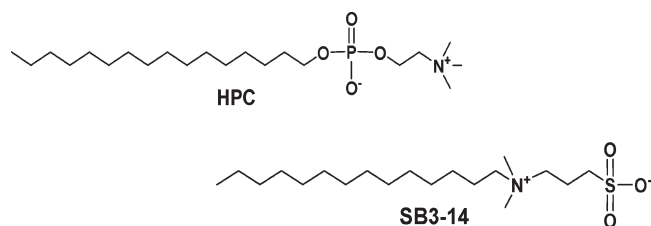
Hexadecyl phosphorylcholine (HPC) micelles incorporate anions rather than cations in the interfacial region, giving an anionoid micelle with a negative zeta potential. Hydronium ion incorporation in the micellar pseudophase parallels the increase in the negative zeta potential, and salts increase the rate of A1 hydrolysis of 2-(*p*-heptyloxyphenyl)-1,3-dioxolane in micellized HPC and inhibit the reaction of OH⁻ with naphthoic anhydride. The kinetic effects are larger with NaClO₄ than with NaCl. The increased micellar negative charge with added salts increases the repulsion between headgroups and decreases the aggregation number. These observations are relevant to understanding the behaviors of biological phosphorylcholine amphiphiles.

Introduction

The interaction of ions with micelles of aqueous ionic surfactants is generally described in terms of electrostatic and ion-specific nonelectrostatic interactions.¹ Anions rather than cations bind to zwitterionic sulfobetaine micelles, and binding increases with soft anions (Pearson definition) following the Hofmeister series.^{2–8} Less-hydrophilic anions (e.g., ClO₄⁻) bind much more strongly than halide ions that follow the sequence I⁻ > Br⁻ > Cl⁻ and OH⁻ and are only weakly bound.^{7–9} The softer, less-hydrophilic anions can enter the headgroup region and interact with the quaternary ammonium ion, whereas the sulfonate ion should be strongly hydrated and should not interact strongly with cations. Anion addition makes the sulfobetaine micelle anionoid with increasing negative surface charge, as given by zeta potentials, following the Hofmeister series, and the micelle then takes up cations (e.g., H₃O⁺). Anion binding, estimated by various methods, is much weaker than with cationic micelles but follows the same ion order in dilute salt.^{3–10}

The ion-headgroup sequence in *n*-hexadecylphosphorylcholine, HPC, micelles is opposite to that in sulfobetaine, SB3-14, micelles, and at the simplest level, the binding of cations should be

preferred over that of anions. Dediazonization trapping of Cl⁻ and Br⁻, examined at high salt concentration with both headgroup sequences, shows that these ions are incorporated into both sulfobetaine and phosphorylcholine micelles with a cation dependence, although the effects on micellar morphology were not considered.¹⁰ In view of the importance of understanding ion interactions with phosphorylcholine amphiphiles in biological systems, we examined salt effects on zeta potentials, aggregation numbers, and rates of hydroxide ion and hydrogen ion-mediated hydrolyses of micelle-bound substrates as physical models of ion-specific interactions at biological interfaces.



Results and Discussion

Salt Effects on the Aggregation Number of HPC. For zwitterionic sulfobetaine surfactants (SB3-*n*), the aggregation number, N_{agg} , is only slightly sensitive to 0.01–0.05 M salts.^{8,11,12} We measured N_{agg} of HPC micelles without and with the salts, which have significant electrophoretic effects on SB3-*n* micelles.^{6–9}

The inset of Figure 1 shows a typical anion effect upon changes in fluorescence intensity against quencher concentrations, according to eq 1,¹³

$$\ln\left(\frac{I_0}{I}\right) = \frac{[\text{DPC}]N_{\text{agg}}}{[\text{HPC}] - \text{cmc}} \quad (1)$$

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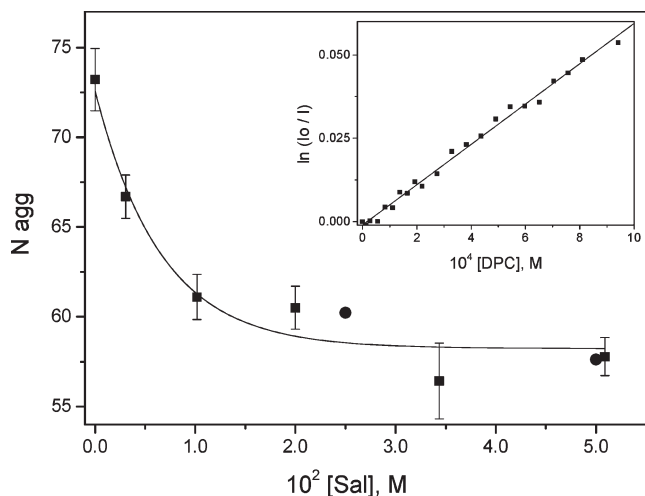


Figure 1. Variation of N_{agg} of HPC with NaClO_4 (■) and 0.05 M NaCl (●) at $25.0 \text{ }^\circ\text{C}$ in 0.05 M HPC . The inset shows the fluorescence quenching of micellized pyrene by added DPC at $25 \text{ }^\circ\text{C}$ in 0.05 M HPC .

where DPC is the 4-carboxy-1-*n*-dodecylpyridinium quencher and the cmc of HPC is $1.2 \times 10^{-5} \text{ M}$.¹⁴ Because $[\text{HPC}] \gg \text{cmc}$, although the cmc of HPC may be sensitive to added salt, its effect on the fluorescence data is very small (i.e., the denominator on the right-hand side of eq 1 is essentially constant).¹³ Anion effects upon N_{agg} calculated from changes in the fluorescence intensity of pyrene as a function of the concentration of the 4-carboxy-1-*n*-dodecylpyridinium ion, DPC, as the quencher are shown in Figure 1.

Without salt (Figure 1), N_{agg} of HPC, ca. 74, is similar to those of similar chain-length zwitterionic spherical micelles, and it decreases to 60 on addition of NaCl or NaClO_4 , a small but unexpected effect because added salts increase N_{agg} of ionic micelles but have little effect on sulfobetaine micelles. The decrease in N_{agg} indicates a small change in micellar volume, and the cubic dependence of the volume on the spherical radius, assuming no change in surfactant packing, should correspond to a decrease of approximately 6% in the micellar radius. On the basis of molecular modeling,^{3b,7} the radius R_m of the zwitterionic HPC micelle is ca. 24 \AA ; therefore, the radius is expected to be slightly lower than ca. 23 \AA in 0.05 M salt. However, added salts may affect surfactant packing so that the change in R_m would be even less than expected from this simple geometrical model; we consider this possibility later.

Capillary Electrophoresis. As with SB3-*n* surfactants, ion incorporation into the micelles can be monitored by following the electrophoretic micellar mobility, and with a low zeta potential, ξ , Henry's equation (eq 2) relates the zeta potential of the micelle (ξ_m) to its mobility¹⁵

$$\xi_m = \frac{\mu\eta}{\epsilon_0\epsilon} f(\kappa R_m) \quad (2)$$

where η is the viscosity of the medium, $f(\kappa R_m)$ corresponds to Henry's function, κ is the Debye–Hückel shielding parameter (m^{-1}), R_m is the radius of the spherical HPC micelle, and ϵ_0 and ϵ correspond to vacuum permittivity and the relative solvent permittivity, respectively. In the binding experiments, ionic strengths were in the range of $0.002\text{--}0.04 \text{ M}$; therefore, κ values

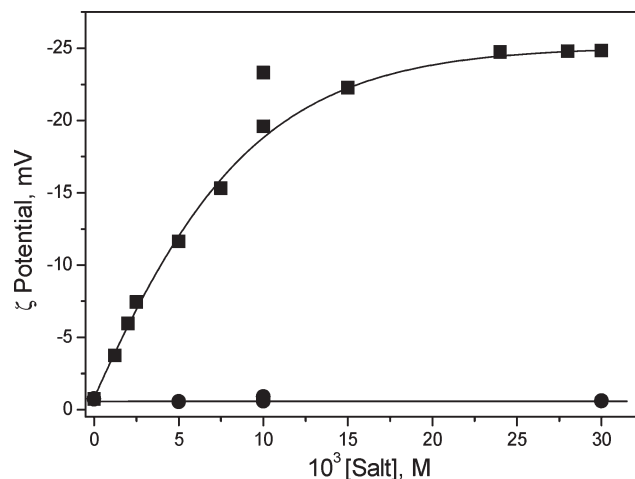
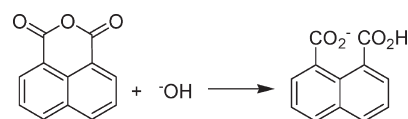


Figure 2. Effects of NaClO_4 (■) and NaCl (●) on zeta potentials of an HPC micelle at $25.0 \text{ }^\circ\text{C}$, 0.05 M HPC , $3 \times 10^{-3} \text{ M}$ sodium tetraborate at pH 9.0.

Scheme 1



were between 1.5×10^8 and $6.6 \times 10^8 \text{ m}^{-1}$. On the basis of R_m of the HPC micelle (vide supra), we calculate $f(\kappa R_m)$ with Ohshima's approximation for a spherical colloidal particle¹⁶ and Henry's function increases by less than 2% (from 0.69 to 0.70) as a function of ionic strength and aggregation number. As shown in Figure 2, the NaCl effect is small, but NaClO_4 significantly increases negative zeta potentials. The calculated values include the small micellar size change effects on Henry's function.

The dependence of the negative zeta potential, ξ , on $[\text{NaClO}_4]$ shows that HPC micelles incorporate the anion more than the cation, although ion-headgroup sequences are opposite to those in sulfobetaine micelles. The negative micellar charge follows the anion concentration, tending to saturation. These results (Figure 2) are qualitatively similar to those on SB3-*n* surfactants in that the maximum zeta potential is strongly anion-specific and anion binding follows the Hofmeister series.^{3–9} The effects were significantly higher for SB micelles as noted later.

Anion Effects on the Reaction with OH^- and H^+ . The anionoid nature of HPC micelles in the presence of added salts should promote cation incorporation (e.g., of H_3O^+) and decrease the concentration of OH^- in the micellar pseudophase.^{7–9} To test this hypothesis, we examined the reaction of naphthoic anhydride, NAn, with OH^- in water, which is first order with respect to the substrate and OH^- ^{17,18} (Scheme 1) and is a useful probe for examining anion-specific effects in micelles.

NAn is sparingly water-soluble and should be fully micellar-bound in 0.05 M HPC at $25.0 \text{ }^\circ\text{C}$. Hydrolysis of $5.0 \times 10^{-5} \text{ M}$ NAn was followed at pH 9.0 (0.005 M borate buffer) by the decreasing absorbance at 340 nm , and first-order rate constants, k_{obs} , decrease with added NaClO_4 and NaCl (Figure 3). Even very dilute ClO_4^- is much more effective than Cl^- at inhibiting the reaction by decreasing the micellar incorporation of OH^- .

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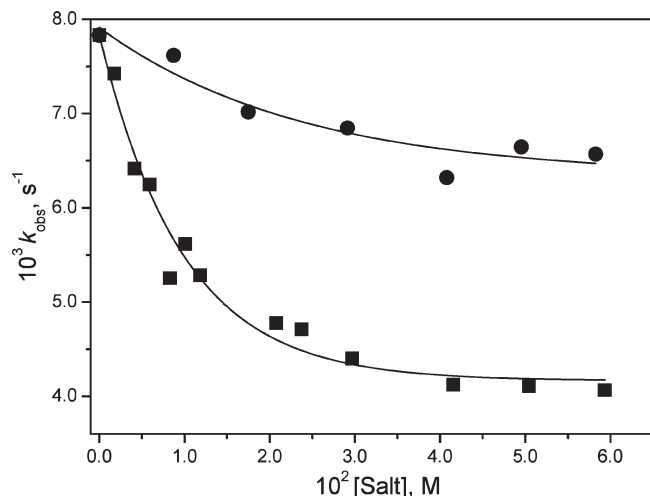
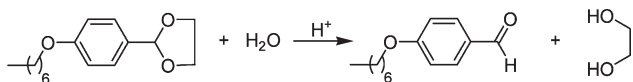


Figure 3. Plot of k_{obs} for the hydrolysis of NAn as a function of [NaCl] (●) or [NaClO₄] (■), at 25.0 °C with 0.05 M HPC at pH 10.0 and 0.005 M borate buffer. The lines are drawn to guide the eye.

Scheme 2



The anion order for salt inhibition of the reaction of OH[−] with NAn (Figure 3) is as expected in terms of the classical ion-exchange model developed to treat reactivities in ionic micelles.¹ However, the situation is more complex in zwitterionic micelles, where the variation of zeta potentials indicates the development of anionoid character, especially upon addition of NaClO₄ and other salts with low-charge-density anions.^{6–9} Inhibition by NaClO₄ (Figure 3) is consistent with a large effect on the zeta potential, but NaCl, which has little effect on the zeta potential, (Figure 2), modestly inhibits the reaction of OH[−], showing that these rate effects are intrinsically related to changes in the zeta potential.

Direct evidence for anion effects in HPC micelles is the acceleration of specific hydrogen ion-catalyzed hydrolysis in HPC micelles by added salt. Anionic micelles effectively incorporate cations (e.g., H₃O⁺) in competition with other cations and with minor anion effects.¹ The zeta potentials of HPC micelles indicate that they should have little affinity for (noncomplexing) cations but with added NaClO₄ they should bind H₃O⁺; with NaCl, for example, there should be a smaller effect.^{5–8}

We tested this hypothesis by examining the acid hydrolysis of 2-(*p*-heptoxyphenyl)-1,3-dioxolane (HPD) in HPC micelles at pH 4.0 with very dilute buffer and added NaCl or NaClO₄ (Scheme 2). The hydrophobic dioxolane was selected because for the specific hydrogen ion catalyzed, A1, hydrolysis is first order with respect to the substrate and dilute strong acid and is accelerated by anionic micelles.^{9,10}

Added electrolytes increase the protonation power of moderately concentrated acids (>1 M) beyond the range of the pH scale, where Hammett's acidity scale is applicable, but should have little effect at pH 4, where HPC is zwitterionic. The sparingly soluble dioxolane (1.1×10^{-5} M) should be almost completely micelle-bound. Figure 4 shows first-order rate constants, k_{obs} , with added NaClO₄ and NaCl for the A1 hydrolysis of 1.1×10^{-5} M HPD in micellized HPC. Added NaClO₄ increases the rate constant significantly more than NaCl, showing that ClO₄[−] is

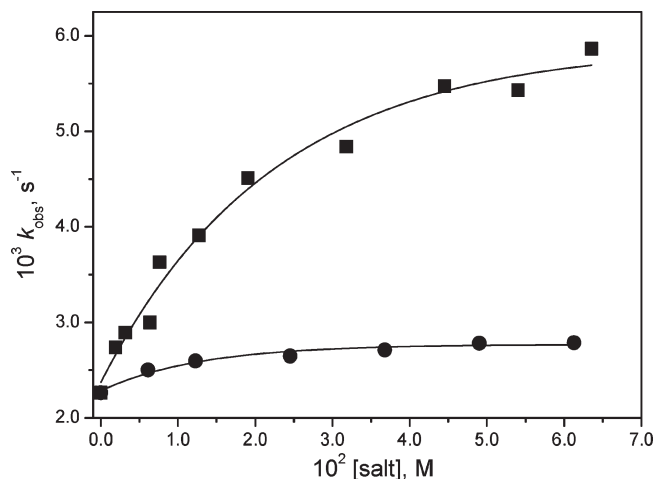


Figure 4. Plot of k_{obs} for the hydrolysis of HPD as a function of [NaCl] (●) or [NaClO₄] (■) at 25.0 °C with 0.05 M HPC at pH 4.0 and 0.005 M acetate buffer.

much more effective than Cl[−] at increasing the micellar incorporation of H₃O⁺,^{7,8} consistent with the significant difference in zeta potentials (Figure 1).

Although sulfobetaine and phosphoryl choline micelles differ in ionic orientations in the headgroup regions, some anions preferentially enter the interfacial regions of both sets of surfactant micelles on the basis of zeta potentials, dediazonization trapping, and kinetic effects.^{5–11} In a sulfobetaine micelle, the hydrophilic headgroup SO₃[−] is at the surface, in close contact with water, whereas the less-hydrophilic quaternary ammonium ion is far from the water and located near the hydrocarbon-like interior (Figure 5).

In HPC micelles, without salt the tether to Me₃N⁺ should be oriented approximately parallel to the micellar surface, as reported for phosphatidylcholine vesicles and other biological assemblies,^{19,20} but this group should extend into the water-rich surface region because of interaction between Me₃N⁺ and an added anion, in particular, ClO₄[−] (Figure 5). The consequent increase in the negative micellar surface charge, due to the extended tether, should increase the repulsion between headgroups with a decrease in N_{agg} , consistent with the difference in the aggregation numbers of ionic and nonionic micelles of similar chain lengths.

In purely electrostatic terms, the estimated zeta potential of HPC with ClO₄[−] (−19 mV) allows the calculation of the free energy for anion transfer, $\Delta G^{\circ}_{\text{tr}} = -3.1 \text{ kJ mole}^{-1}$, calculated from $\Delta G^{\circ}_{\text{tr}} = zF\xi_{\text{max}}$, where z is the ionic charge number and F is Faraday's constant. The strong interaction of ClO₄[−], as compared to halide ions, with the positively charged ammonium moiety of an SB micelle is well established, indicating the relative importance of Coulombic and ion-specific interactions. A comparison of zeta potentials and transfer free energies for the perchlorate anion to HPC micelles with those of SB3-14 (−69.8 mV, $\Delta G^{\circ}_{\text{tr}} = -11.4 \text{ kJ mole}^{-1}$)⁸ shows that the location of ClO₄[−] in the water-rich environment at the surface of an HPC micelle with its penetration opposed by the anionic interior disfavors the transfer energy of the perchlorate anion by 50.8 mV, corresponding to ca. 8.3 kJ mole^{−1}.

The perchlorate ion interacts strongly with the quaternary ammonium ion in sulfobetaine micelles,^{5–9} and in aqueous HPC micelles, its interaction with the surface NMe₃⁺ should promote

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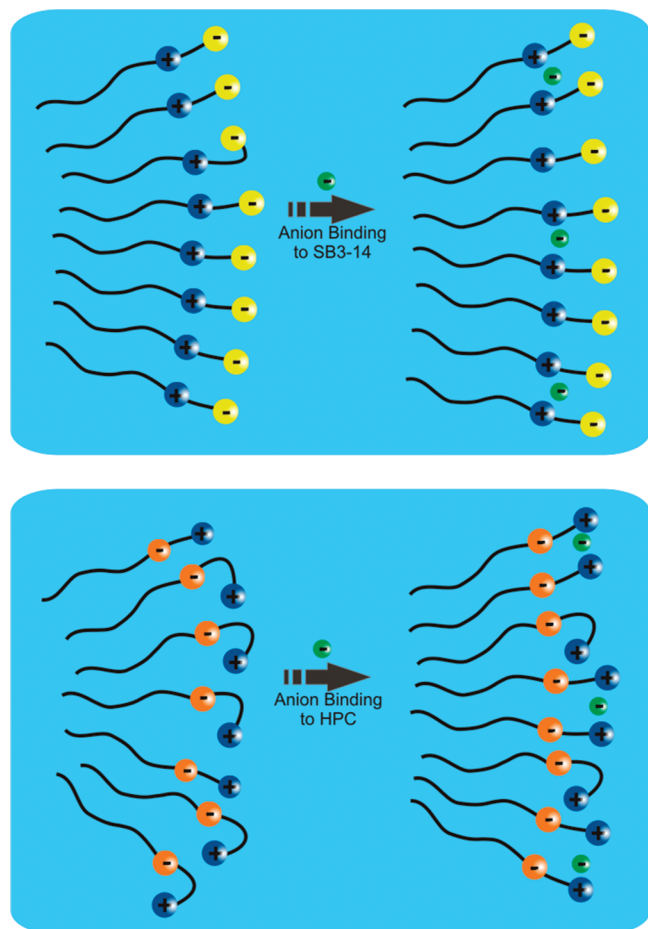


Figure 5. Cartoon model of anion binding to SB3-14 and HPC micelles.

tether group extension (i.e., salts would move the headgroup in these micelles toward the water-rich environment). Because the micellar size and shape are governed, in part, by headgroup and hydrocarbon tail structures, the micellar aggregation numbers, conformations, and surfactant packing could be unusually sensitive to added salts with anion specificity. The decrease in micellar size, as shown by salt effects on N_{agg} (Figure 1), is probably related to these ionic effects on headgroup structure.

In this and earlier work on kinetic salt effects, we showed that in zwitterionic micelles Na^+ does not compete effectively with H_3O^+ , although these ions have similar affinities for anionic dodecyl sulfate micelles.¹ Electrostatic interactions of anionic micelles with hydrated spherical anions (e.g., Na^+) should be of major importance but are less important in zwitterionic micelles, where ion specificity plays a relatively larger role and ion binding is much weaker. The nonspherical hydrated hydronium ion (e.g., the eigencation H_9O_4^+),²¹ unlike the spherical Na^+ , has a strong transient dipole that would allow an ion-specific interaction with the dipolar micellar headgroup of a zwitterionic micelle as well as the Coulombic interaction and should be more important than that of a metal monocation, consistent with our conclusions on relative rate effects.^{5–9}

Despite subtle differences in ionic interactions, sulfobetaine and phosphorylcholine micelles preferentially incorporate anions, depending on their location in the Hofmeister series, and anionoid micelles, with negative zeta potentials but to different extents, are

then generated in both types of surfactants. The extent of incorporation of different anions, as in sulfobetaine micelles,^{8,9} follow the Hofmeister series, with large anions showing the stronger effects and small, hydrophilic anions, with larger hydration energies, only weakly incorporated into the micellar pseudo-phase. Interactions of anions with HPC micelles is stronger for readily dehydrated ions than for those with tight solvation shells, and the incorporation of anions changes zwitterionic surfaces, affecting both packing and surface charges, which should modulate the properties of these surfaces and micellar sizes. These observations should be important in understanding the behaviors of biological phosphorylcholine amphiphiles.

Experimental Section

Materials. Hexadecylphosphoryl-*N,N,N*-trimethylethanolamine (HPC) was the surfactant, and pyrene (Aldrich) was the fluorescent probe. Preparation and purification of 2-(*p*-heptoxyphenyl)-1,3-dioxolane (HPD) followed previously described procedures.²² 4-Carboxy-1-*n*-dodecylpyridinium (DPC) was synthesized as described²³ (m.p. 189 °C, dec.), ¹H NMR (CDCl_3 , 400 MHz) δ : 8.61 d (2H), 8.42 d (2H), 4.64 t (2H), 2.04 m (2H), 1.36 m (2H), 1.25 m (16H), 0.88, t (3H). Other reagents and solvents were of analytical grade and were used without further purification.

Capillary Electrophoresis. Capillary electrophoresis was monitored on an Agilent CE^{3D} system with on-column diode-array detection at 25 °C.¹⁶ Borate at pH 9.0 was used to avoid pH effects on electroosmotic flow.^{5,8,9} Samples were introduced by hydrodynamic injection at 50 mbar/5 s. Fused-silica capillaries (Polymicro Technologies) with a total total length of 48.5 cm, an effective length of 40 cm, and 50 μm i.d. were used. The system was operated under normal polarity and 30 kV. The capillary was conditioned by flushes of 1 M NaOH (5 min), deionized water (5 min), and electrolyte solution (10 min.). Between experiments, the capillary was reconditioned by a pressure flush with electrolyte containing 3 mM sodium borate (2 min). The micellar mobility was monitored by following the migration of micelle-bound pyrene (1 μM), acetone (0.1%) was used as an electroosmotic flow marker,¹⁶ and the electrophoretic mobility of the micelle (μ , $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$) was calculated from eq 3

$$\mu = \frac{L_{\text{eff}}}{E} \left(\frac{1}{t_{\text{app}}} - \frac{1}{t_{\text{eo}}} \right) \quad (3)$$

where E is the applied electric field strength (V m^{-1}), L_{eff} is the effective length of the capillary, and t_{app} and t_{eo} are the migration times of the micelle and the electroosmotic flow, respectively.

Kinetics. Reactions with OH^- were monitored spectrophotometrically in aqueous HPC at pH 9.0, sodium borate buffer (0.005 M), and 0–0.54 M electrolyte at 25.0 ± 0.1 °C in a UV–vis spectrophotometer by decreasing absorbance at 340 nm, with the addition of 30 μL of a naphthoic anhydride (NAn) in MeCN to 3 mL of reaction solution so that $[\text{NAn}] = 5.5 \times 10^{-5}$ M. The acid hydrolysis of 2-(*p*-heptoxyphenyl)-1,3-dioxolane (HPD, 1.1×10^{-5} M) in 0.05 M HPC micelles at pH 4.0, sodium acetate buffer (0.005 M), and added NaCl or NaClO_4 at 25.0 ± 0.1 °C were followed by the increasing absorbance at 286 nm. Temperatures in quartz cuvettes were controlled with a thermostatted water-jacketed cell holder. Absorbance versus time data were stored directly on a microcomputer, and first-order rate constants, k_{obs} , were estimated from linear plots of $\ln(A_{\infty} - A_t)$ against time for at

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least 90% reaction by using an iterative least-squares program; correlation coefficients were >0.999 for all kinetic runs.

Fluorescence Measurements. Fluorescence quenching of pyrene by 4-carboxy-1-*n*-dodecylpyridinium (DPC) was monitored on a Varian Cary Eclipse spectrofluorimeter. The probe concentration was low (2×10^{-6} M) to avoid excimer formation, and the quencher concentration was 0 to 7.08×10^{-4} M. The [pyrene]/[micelles] and [quencher]/[micelles] values were low to ensure Poisson distributions.¹⁴ Excitation and emission wavelengths were 337 and 394 nm, respectively. The cmc of HPC is

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very low (0.012 mM),¹⁴ and at 0.05 M, the concentration of micellized surfactant is essentially constant. Higher aggregation numbers (178) measured by light scattering are reported in the Anatrace catalog, and N_{agg} apparently depends on conditions and surfactant concentration because a value of 33 was reported by Reynolds for a solution containing 10^{-4} M surfactant.²⁴

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