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Interaction of Polyelectrolyte with a Cationic Surfactant with an ω-Hydroxyl Group

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Synopsis. The sodium salt of poly(styrenesulfonate) interacts with the 12-hydroxydodecyltrimethylammonium cation anticooperatively. A data analysis of the dependence of the anticooperative binding constant on the NaCl concentration indicates an exchange reaction of the surfactant ion with the sodium ion.

Ionic surfactants strongly interact with polyions of opposite charge, and induce precipitation at the high degree of binding due to the increasing hydrophobic properties of the complex.[1—4] The interaction is highly cooperative due to the hydrophobic interaction between bound surfactant tails.[2] Surfactants with a hydrophilic group at the ω-position show different behaviors from normal surfactants: A very high critical micellization concentration or no micelle formation, and weak solubilization power at an equal chain length.[5—8] When such an ionic surfactant interacts with a polyion of the opposite charge, no precipitation is expected due to the surrounding hydrophilic property of the complex. Still, cooperative binding exists through a lateral hydrophobic interaction between the hydrocarbon chains of bound surfactant ions. We examined the binding of 12-hydroxydodecyltrimethylammonium bromide (HDTAB) to an anionic polymer poly(styrenesulfonic acid) (PSS).

Experimental

Materials. A commercial sodium salt of PSS (Chemicals from Polyscience) was dissolved in 0.1 mol dm^{-3} NaOH and dialyzed extensively against water. The concentration was determined by colloid titration with poly(vinyl sulfate) (Wako Pure Chemicals, specific grade for colloid titration) after the addition of a known amount of poly(diallyldimethylammonium chloride) (Wako Pure Chemicals, specific grade for colloid titration).

HDTAB was synthesized by the alkylation of trimethylamine with 12-bromo-1-dodecanol as follows. Trimethylamine gas generated by the addition of 15 mol dm^{-3} NaOH into trimethylamine hydrochloride was introduced into a 60 ml ethanol solution including 0.04 mol 12-bromo-1-dodecanol under refluxing. After refluxing for 3 h, the reaction mixture was kept in a freezer at −18 °C for one day. The resulting white flakes were recrystallized from ethanol and purified from unreacted materials by ether extraction. Recrystallization was again carried out from acetone including a small amount of water. The yield was 62%. The concentration was determined by weighing the amount of white crystals in water.

Measurements. The binding of HDTAB was determined potentiometrically by the use of an HDTA$^+$ ion-selective electrode.[9] A functional poly(vinyl chloride) (PVC) gel membrane was prepared from 0.4 g PVC, a 10 mg carrier complex of HDTA$^+$ with dodecyl sulfate anion and 1.1 g tris(methylphenyl) phosphate used as a plasticizer. The membrane potential was measured with the following concentration cell assembly, which was illustrated previously:[10]

Ag–AgCl electrode	Reference solution	PVC gel membrance	Test solution	Ag–AgCl electrode

In the above, the reference solution was 1 mmol dm^{-3} HDTAB containing 0.05 mol dm^{-3} NaCl as a buffer of ionic strength. The emf of this cell system was given as

$$E = s \log [\mathrm{HDTA}^+] + \text{constant}, \qquad (1)$$

where s is the experimental slope for an emf versus log [HDTAB] plot and shown a Nernst slope (2.303 RT/F. 59.2 mV at 25 °C) in the case of an ideal response. The observed slope was in a range of 56.5 to 59.7 mV for an HDTAB solution in the presence of NaCl; this cell system thus showed a nearly Nernstian response. The absorption and emission spectra were measured using a Hitachi 228 spectrophotometer and a Shimadzu RF 5000 spectrofluorometer, respectively.

Results and Discussion

Figure 1 shows examples of the emf measurement in the absence (solid circles) and in the presence of PSS at 10 mmol dm^{-3} NaCl. The calibration shown by solid circles gives an excellent linear relationship with a 57.2 mV slope down to 6×10^{-5} mol dm^{-3} HDTAB. The plot for PSS/HDTAB mixed system shows a large deviation from the calibration, and tends to converge to the calibration at a high concentration of HDTAB. A good reproducibility was also obtained (compare the circle

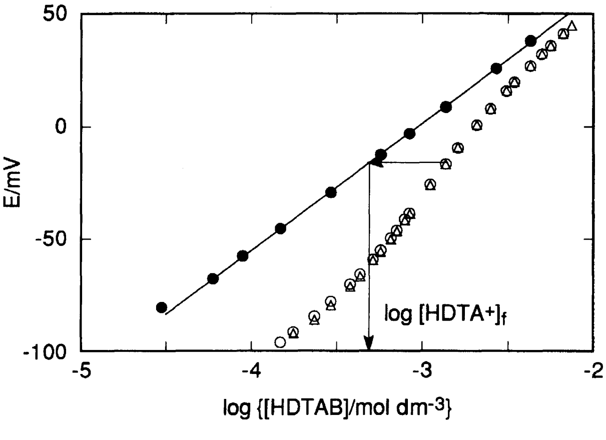

Fig. 1. Emf measurements of HDTAB in the absence (solid circles) and presence (open marks) of PSS. The open marks show the reproducibility.

and triangle).

A comparison of the emf value with the calibration allows us to determine the equilibrium concentration ($\log[\mathrm{HDTA}^+]_\mathrm{f}$ in Fig. 1), and to then calculate the bound quantity of HDTA^+ ions.[9,11] Figure 2 thus shows the constructed binding isotherms of HDTA^+ by PSS in the presence of NaCl, where the degree of binding (x), defined by the ratio of the bound quantity of HDTA^+ to total ionic concentration of polyelectrolyte, is plotted against the equilibrium concentration of HDTA^+.

The Langmuir model could not reproduce these curves, and the linear lattice model that we successfully applied to surfactant binding by polyelectrolyte[11—19] suggested anticooperative binding. Since the origin of anticooperativity for this PSS/HDTAB system is unknown, we took the anticooperativity into account only phenomenologically. For equilibrium 2 of a surfactant (S^+) bound by a polyion, the apparent binding constant (K_app) is presented as Eq. 3:

$$\mathrm{P} + \mathrm{S}^+ \rightleftarrows \mathrm{PS} \tag{2}$$

and

$$K_\mathrm{app} = \frac{[\mathrm{PS}]}{[\mathrm{P}][\mathrm{S}]} = K \exp\left(-\frac{\omega x}{kT}\right). \tag{3}$$

Equation 3 implies that free energy change for equilibrium 2 depends on x. The parameter ω measures the degree of anticooperativity. Table 1 gives the values of parameters K and ω/kT obtained by a best-fit method; the simulated curves are shown by the solid lines in Fig. 2. The binding constant (K) decreases as the NaCl concentration increases, due to a weakened electrostatic interaction of the HDTA^+ cation with the PSS polyanion. The plot of $\ln K$ versus $\ln[\mathrm{Na}^+]_\mathrm{total}$ shows a linear relationship, and the slope is -0.99 (Figure is not shown). This result indicates that the exchange equilibrium of HDTA^+ with Na^+ is as follows:

$$\mathrm{P\text{-}Na} + \mathrm{S}^+ \rightleftarrows \mathrm{P\text{-}S} + \mathrm{Na}^+, \tag{4}$$

where K in Eq. 3 is presented as $K_0/[\mathrm{Na}^+]$. From the calculated K_0 (=56), we obtained the standard free energy change to be $\Delta G^\circ = -11\ \mathrm{kJ\,mol^{-1}}$, where the standard state is a hypothetical state of a molarity (C°) based on infinitive dilution for Na^+ and S^+ ions; it is a state involving a complete binding for the bound P-Na and P-S ions. Because of the exchange reaction, the activity coefficient terms compensate for both sides in reaction 4, and can thus be canceled out.

Table 1. Parameters Used in Simulation by Eq. 3

$[\mathrm{NaCl}]/\mathrm{mol\,dm^{-3}}$	$K/\mathrm{mol^{-1}\,dm^3}$	ω/kT
0.10	540	0.4
0.05	1040	1.3
0.02	2400	1.8
0.01	4500	2.5

PSS: 0.002 $\mathrm{mol\,dm^{-3}}$ of ionic group.

The degree of anticooperativity (ω) decreases as the NaCl concentration increases. Though the reason is unclear, we tentatively propose that this may be influenced by a conformational change of the polyelectrolyte. Namely, the compactness of the polyion is more influenced by surfactant binding at a low ionic strength than at a high ionic strength, and the change from an expanded to a compact conformation may induce a free energy loss for surfactant binding. Since the hydrophobic interaction is very weak among HDTA^+ ions, the compact conformation of PSS provides no advantage of binding of the HDTA^+ ion.

The binding isotherms of a regular surfactant dodecyltrimethylammonium ion (DTA^+) to PSS are reproduced from the data in Ref. 11 in Fig. 3. They rise up at a concentration one order lower than those of HDTA^+, and show S-shape curves. These facts indicate a stronger interaction of the DTA^+ ion than the HDTA^+ ion, and the cooperative nature of DTA^+ binding at a degree of binding less than 0.5. A comparison of both results (Figs. 2 and 3) indicates that the introduction of a hydrophilic OH group in a normal surfactant molecule at the ω-position induces a weakened binding and an anticooperative nature in surfactant binding.

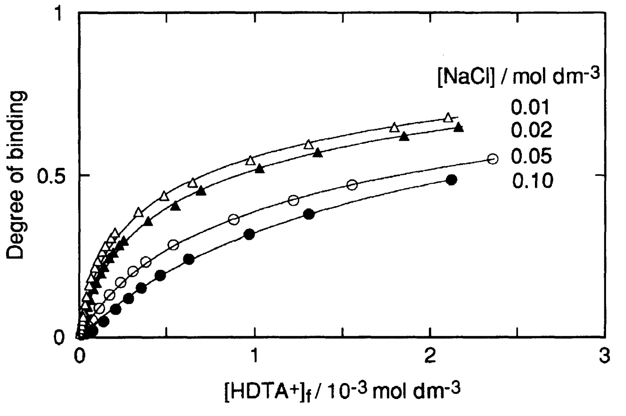

Fig. 2. Binding isotherms of HDTA^+ by PSS in the presence of NaCl.

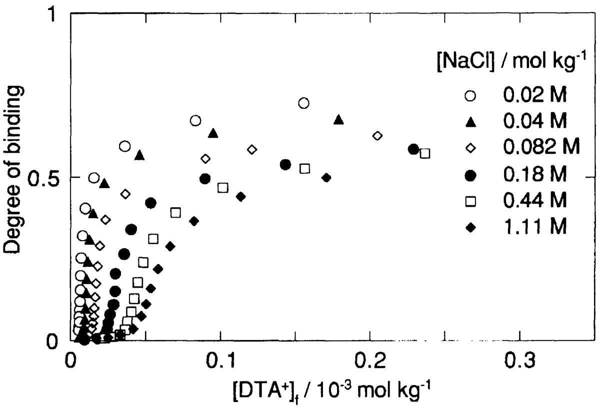

Fig. 3. Binding isotherms of DTA^+ by PSS in the presence of NaCl. The data were obtained form Ref. 11.

Solubilization of pyrene was examined for this PSS/HDTAB complex. The absorbance of pyrene at 339 nm was more intense (0.20) in a mixed solution of 3 mmol dm^{-3} HDTAB and 2 mmol dm^{-3} PSS than in 2 mmol dm^{-3} PSS solution (0.03). The intensity ratio of the first to third vibronic peaks in the pyrene fluorescence spectrum (I_1/I_3) was 1.36 in a PSS/HDTAB mixture at a concentration of pyrene at which the absorbance was 0.05. These facts indicate the solubilization of pyrene into a PSS/HDTAB complex of low polarity. However, this I_1/I_3 ratio is higher than that obtained in a complex of DTA$^+$ with PSS (1.15).[20] This suggests that HDTA$^+$ forms a domain having a larger polarity than that of a regular surfactant DTA$^+$.

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