Aggregation of polycation and surfactant anion studied by energy transfer from 2-naphthalenesulfonate ion to 1-pyrenesulfonate ion

Tomoyuki Itaya, Hiroshi Ochiai*, Kazuyoshi Ueda and Akira Imamura
Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 724, Japan
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Aggregation of poly(allylammonium) chloride ($PAAH^+Cl^-$) and sodium 1-octanesulfonate (Na^+OcS^-) has been examined by the energy transfer from 2-naphthalenesulfonate ion (2-NpS^-) to 1-pyrenesulfonate ion (1-PyS^-) using steady-state fluorescence spectroscopy. In aqueous $PAAH^+Cl^-$ solution without Na^+OcS^-, both 2-NpS^- and 1-PyS^- are in an isolated state around the polyion under the conditions studied, indicating no energy transfer between them. In the presence of Na^+OcS^-, on the other hand, efficient energy transfer takes place between 2-NpS^- and 1-PyS^-. In such a system, the aggregate of $PAAH^+$ and OcS^- is formed owing to the electrostatic interaction between $PAAH^+$ and OcS^- and the hydrophobic interaction among OcS^- ions bound to the polyion. Both 2-NpS^- and 1-PyS^- are incorporated in close proximity in the hydrophobic domain of the aggregate, which leads to energy transfer between them. The concentration at which the aggregation of $PAAH^+$ and OcS^- occurs was about three orders of magnitude lower than the critical micelle concentration of OcS^- alone. The fluorescence probe technique using pyrene has also been employed to monitor the aggregation.

(Keywords: poly(allylammonium) chloride; sodium 1-octanesulfonate; aggregate)

Introduction

Because of the intrinsic interest in polymer–surfactant solutions and the importance of these systems in a variety of applications, considerable attention has been paid to the interactions between polyion and surfactant in the solution phase[1–4]. Surfactant-selective electrodes have frequently been used in these studies, and the approach has revealed that the aggregate of polyelectrolyte and surfactant is formed through a contribution of electrostatic binding of the surfactant to the polyion and cooperative hydrophobic effects among bound surfactant ions[5–8].

The nature of the aggregate has, however, been the subject of only limited study. In order to elucidate the nature of polyelectrolyte–surfactant aggregate, it would be helpful to use photochemical techniques[9,10]. The photochemical study by Abuin and Scaiano[10] has demonstrated that the aggregate provides a hydrophobic domain and can control the photochemical behaviour of various substrates. This suggests that the hydrophobic domain of polyelectrolyte–surfactant aggregates can be utilized as a reaction field involving solubilization. It is therefore of interest to examine the energy transfer between chromophores incorporated into polyelectrolyte–surfactant aggregate[11]. However, such behaviour has not been reported for the cationic polyelectrolyte–anionic surfactant system. Here we present a preliminary experiment on the energy transfer from 2-naphthalenesulfonate ion to 1-pyrenesulfonate ion in the aggregate of poly(allylammonium) chloride ($PAAH^+Cl^-$) and sodium 1-octanesulfonate (Na^+OcS^-); the results are also useful as a measure of aggregate formation between the polyion and the surfactant.

Experimental

Poly(allylammonium) chloride ($PAAH^+Cl^-$) used in this study was supplied by Nitto Boseki Co. Ltd. It was purified by a method described previously[12]. The weight-average molecular weight of $PAAH^+Cl^-$ was determined by light scattering to be 1.0×10^5 in 0.2 M NaCl solution. Sodium 2-naphthalenesulfonate (Na^+2-NpS^-, Tokyo Kasei), sodium 1-pyrenesulfonate (Na^+1-PyS^-, Molecular Probes) and sodium 1-octanesulfonate (Na^+OcS^-, Tokyo Kasei) were used without further purification. Pyrene (Tokyo Kasei), used as the fluorescence probe, was purified by recrystallization from ethanol. Deionized and doubly distilled water was used as the solvent.

Steady-state fluorescence studies were carried out with a Jasco FP-777 fluorescence spectrophotometer at room temperature, with excitation at 290 nm. Since the absorbance at 290 nm of 2-NpS^- is about 30 times greater than that of 1-PyS^- under the conditions examined, one can selectively excite the Np chromophores at this wavelength. The energy-transfer efficiency was characterized by the ratio of the emission intensity of 2-NpS^- at 340 nm and 1-PyS^- at 396 nm.

The fluorescence emission spectra of pyrene were recorded at an excitation wavelength of 340 nm. The ratio of the intensities of the third and first vibrational bands of the pyrene molecule (I_3/I_1) was used as a monitor for the formation of hydrophobic microdomain in polyelectrolyte–surfactant aggregate.

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* To whom correspondence should be addressed

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Results and discussion

Figure 1 shows the fluorescence spectra of $Na^+2\text{-}NpS^-$, $Na^+1\text{-}PyS^-$, and a mixture of both at the same concentrations in aqueous $PAAH^+Cl^-$ solution. The emission at 325, 340 and 354 nm is the monomer fluorescence of the Np chromophore, and the emission at 377 and 396 nm is the monomer fluorescence of the Py chromophore. None of the spectra shows specific chromophore interaction, such as excimer formation. Moreover, the emission spectrum of their mixture seems to hold approximately the additivity of each spectrum of $Na^+2\text{-}NpS^-$ and $Na^+1\text{-}PyS^-$. These results indicate that both $2\text{-}NpS^-$ and $1\text{-}PyS^-$ are in an isolated state around $PAAH^+$.

As shown in *Figure 1*, because of overlap of the emission spectra of $2\text{-}NpS^-$ and $1\text{-}PyS^-$, the absolute energy-transfer efficiency was difficult to measure. The extent of energy transfer was conveniently estimated in terms of the ratio of the emission intensity of $1\text{-}PyS^-$ at 396 nm to that of $2\text{-}NpS^-$ at 340 nm (I_{Py}/I_{Np}); the larger value of I_{Py}/I_{Np} indicates a relatively higher energy-transfer efficiency.

Figure 2 shows the influence of addition of $Na^+1\text{-}OcS^-$ on the fluorescence spectra obtained by excitation at 290 nm of the $PAAH^+Cl^-/Na^+2\text{-}NpS^-/Na^+1\text{-}PyS^-$ system. In the presence of Na^+OcS^-, a significant quenching of the Np emission and a dramatic enhancement of the Py emission are observed. This result documents a typical characteristic of efficient energy transfer between Np and Py[13]. In the presence of Na^+OcS^-, the interactions of $PAAH^+$ with OcS^- bring about their aggregation. The aggregates are supposed to consist of clusters of surfactants bound on the polyion chain[14,15]. Thus, both $2\text{-}NpS^-$ and $1\text{-}PyS^-$ may be incorporated in close proximity in the hydrophobic domain of the aggregates, which leads to a high efficiency of energy transfer between $2\text{-}NpS^-$ and $1\text{-}PyS^-$.

Figure 3a shows the variation of I_{Py}/I_{Np} in aqueous $PAAH^+Cl^-$ solution as a function of the surfactant concentration. The ratio I_{Py}/I_{Np} is almost constant up to $[Na^+OcS^-] = 3 \times 10^{-4}$ M, which indicates no energy transfer from $2\text{-}NpS^-$ to $1\text{-}PyS^-$. However, a sharp increase in the ratio I_{Py}/I_{Np} is observed at $[Na^+OcS^-] > 3 \times 10^{-4}$ M, and a maximal value is obtained at $[Na^+OcS^-] = 1.5 \times 10^{-3}$ M. The increased ratio I_{Py}/I_{Np} at $[Na^+OcS^-] > 3 \times 10^{-4}$ M is explained by the aggregation of the polyion and the surfactant, leading to the incorporation of $2\text{-}NpS^-$ and $1\text{-}PyS^-$ into the aggregates and the close proximity of Np–Py pairs. Consequently, high efficiency of the energy transfer is achieved. Increasing the concentration of Na^+OcS^-

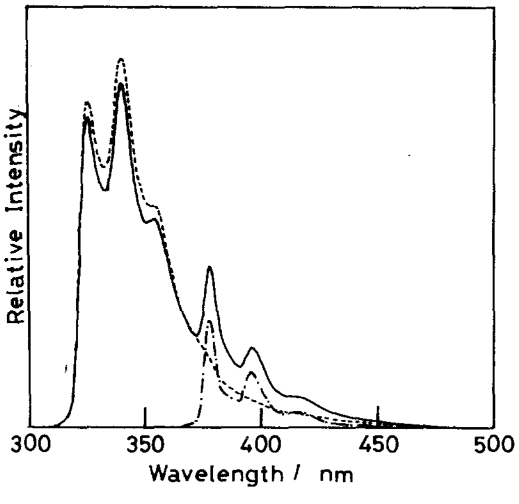

Figure 1 Fluorescence spectra of: ---, $Na^+2\text{-}NpS^-$ (1.0×10^{-4} M); -·-, $Na^+1\text{-}PyS^-$ (3.0×10^{-6} M); ——, a mixture of both at the same concentrations in aqueous $PAAH^+Cl^-$ (1.0×10^{-2} M) solution. Excitation was at 290 nm

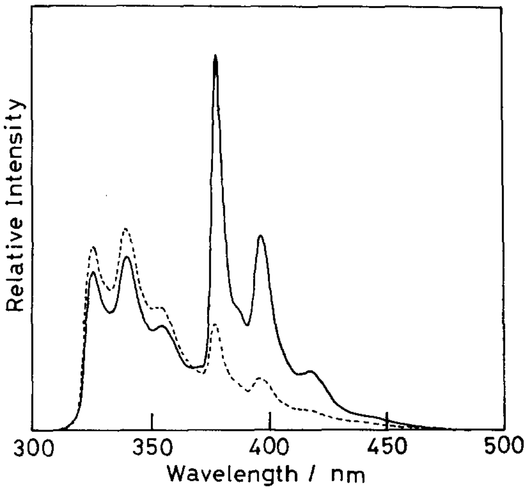

Figure 2 Influence of addition of Na^+OcS^- on the fluorescence spectra of the $PAAH^+Cl^-/Na^+2\text{-}NpS^-/Na^+1\text{-}PyS^-$ system: ---, in the absence of Na^+OcS^-; ——, in the presence of Na^+OcS^-. $[PAAH^+Cl^-] = 1.0 \times 10^{-2}$ M, $[Na^+2\text{-}NpS^-] = 1.0 \times 10^{-4}$ M, $[Na^+1\text{-}PyS^-] = 3.0 \times 10^{-6}$ M, $[Na^+OcS^-] = 1.5 \times 10^{-3}$ M

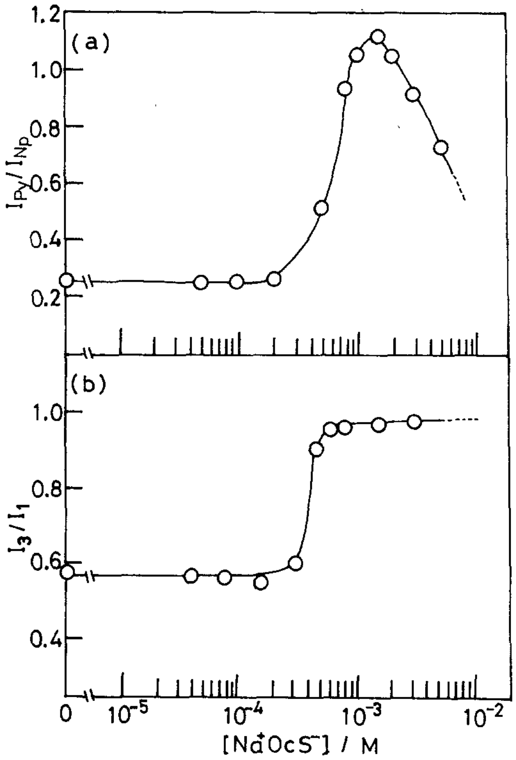

Figure 3 (a) Variation of the ratio (I_{Py}/I_{Np}) of the emission intensity of $1\text{-}PyS^-$ at 396 nm to that of $2\text{-}NpS^-$ at 340 nm in aqueous $PAAH^+Cl^-$ solution as a function of Na^+OcS^- concentration. $[Na^+2\text{-}NpS^-] = 1.0 \times 10^{-4}$ M, $[Na^+1\text{-}PyS^-] = 3.0 \times 10^{-6}$ M, $[PAAH^+Cl^-] = 1.0 \times 10^{-2}$ M. (b) Plot of the ratio (I_3/I_1) of the intensities of the third and first vibrational bands in pyrene (2×10^{-6} M) in aqueous $PAAH^+Cl^-$ solution as a function of Na^+OcS^- concentration. $[PAAH^+Cl^-] = 1.0 \times 10^{-2}$ M. The dotted lines indicate precipitation of the polymer

above 1.5×10^{-3} M reduces the energy-transfer efficiency owing to the separation of Np–Py pairs, which is accompanied by the enlargement of the hydrophobic domain of the polymer–surfactant aggregate. At $[\mathrm{Na^+OcS^-}] > 5 \times 10^{-3}$ M, the polyion precipitates, which may be attributed to the neutralization of charges on the polyion as a result of surfactant binding.

In order to monitor the aggregation of $\mathrm{PAAH^+}$ with $\mathrm{OcS^-}$, the fluorescence probe technique using pyrene has been employed. When $\mathrm{Na^+OcS^-}$ is added to a solution of $\mathrm{PAAH^+Cl^-}$ containing pyrene (2×10^{-6} M) the fluorescence spectrum of pyrene changes at a critical surfactant concentration. The spectrum shows an increase of the band at 384 nm (intensity, I_3) relative to that of the band at 373 nm (I_1). An increase in I_3/I_1 reflects transfer of pyrene from a more polar to a less polar environment[16]. It is well documented that this type of change commonly accompanies micelle formation, in both the absence and the presence of polymer[17]. A plot of I_3/I_1 for pyrene in aqueous $\mathrm{PAAH^+Cl^-}$ solution as a function of the $\mathrm{Na^+OcS^-}$ concentration is shown in *Figure 3b*. The curve shows a sharp increase in I_3/I_1 over a narrow range of the surfactant concentrations. It is noted that the ratio I_3/I_1 in $\mathrm{PAAH^+Cl^-}$–$\mathrm{Na^+OcS^-}$ solutions reaches a steady value (~ 0.95) at a surfactant concentration, suggesting that aggregates are formed. The result clearly indicates that the non-polar environment for pyrene molecules is provided by the polyelectrolyte–surfactant aggregates. The surfactant concentration at which the I_3/I_1 value increases sharply corresponds well to that at which $I_{\mathrm{Py}}/I_{\mathrm{Np}}$ begins to increase (*Figure 3a*). Therefore, the fluorescence probe technique using pyrene confirms the conclusion that the energy transfer of 2-$\mathrm{NpS^-}$ to 1-$\mathrm{PyS^-}$ takes place in the polyion–surfactant aggregate.

Generally, it has been reported that the aggregate of polyion with surfactant is formed at concentrations one or two orders less than the critical micelle concentration (c.m.c.) of the corresponding surfactant[9,18]. However, in this system, the aggregation begins to occur at $[\mathrm{Na^+OcS^-}] = 3 \times 10^{-4}$ M, which is about three orders lower than the c.m.c. (1.5×10^{-1} M) of the $\mathrm{Na^+OcS^-}$ itself[19]. Thus, it seems that this aggregation is assisted by stronger electrostatic forces and more cooperative hydrophobic effects among bound surfactant ions.

This study suggests that the energy transfer experiment is very useful for investigating the aggregation of polyelectrolyte and surfactant. At present, further detailed studies using the energy transfer of 2-$\mathrm{NpS^-}$ to 1-$\mathrm{PyS^-}$ are in progress in order to clarify the effects of the length of the surfactant, the neutralization degree of the polyion and the ionic strength on the aggregation of $\mathrm{PAAH^+}$ and alkanesulfonate ions. We hope that these studies will provide interesting information on the mechanism of aggregation of the cationic polymer and alkanesulfonate ions.

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