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Stacking Interaction of Naphthalenesulfonate Ions around Poly(allylammonium) Cation

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ABSTRACT: The viscosity and solubility behavior of poly(allylammonium) chloride ($PAAH^+Cl^-$) in aqueous solutions of sodium 1- and 2-naphthalenesulfonate (Na^+-1-NpS^- and Na^+-2-NpS^-) and the stacking interaction of 1-NpS^-'s and 2-NpS^-'s around $PAAH^+$ were investigated through viscosity, the solubility diagram, and spectroscopic methods (absorption, fluorescence, and ^1H NMR spectroscopy). In both Na^+-1-NpS^- and Na^+-2-NpS^- solutions, the viscosity behavior of $PAAH^+Cl^-$ was clearly different from that of typical polyelectrolyte/added-salt systems; that is, even at salt concentrations as low as $(1–5) \times 10^{-3}$ M, the reduced viscosity η_{sp}/c rapidly decreased and polymer precipitation took place upon dilution. The phase diagram revealed that 2-NpS^- precipitated $PAAH^+Cl^-$ more readily than 1-NpS^-. In the presence of $PAAH^+Cl^-$, the spectra of 2-NpS^- exhibited hypochromism, excimer emission, and a large ring current effect. These results indicate that 2-NpS^-'s associate with each other around $PAAH^+$ due to the stacking interaction of the Np rings. On the other hand, 1-NpS^- hardly showed signs of such an association. This suggests that the orientational state of NpS^- (the distance and angle between Np rings and/or sulfonate groups) around the polyion plays an important role in the stacking interaction between Np rings. The hydrophobic character and the above-mentioned association of NpS^-'s affect both the viscosity and the solubility of the polymer.

Introduction

One of the most characteristic properties of polyelectrolytes in aqueous solution is the counterion binding by the polyion, which is mainly due to the high electrostatic potentials of the polyion.[1-3] As a result of the counterion binding, a layer of highly concentrated counterions is formed around the polyion surface.[4] Therefore, the solution properties of polyelectrolytes should depend upon the nature of this counterion layer. If the counterion has a hydrophobic moiety, the counterion binding will be influenced by its hydrophobicity, chemical structure, bulkiness, and so on.[5,6] In addition, the hydrophobic counterions can associate with each other through hydrophobic and/or van der Waals interactions around the polyion. Thus, the interaction between the polyion and the hydrophobic counterions should result from a combination of two types of processes: one is the electrostatic interaction between a polyion and counterions, and the other is the hydrophobic interaction between the hydrophobic counterions themselves.

A number of studies on the solution properties of polyelectrolyte/hydrophobic dye systems have been carried out in connection with the interaction between polyions and hydrophobic counterions.[7-12] It is well known that the dyes are electrostatically bound to ionic sites of the polyelectrolyte and undergo effective aggregation, resulting from either hydrophobic interaction or some other dye–dye interaction. In addition, it has been established that the binding of dyes to a polyion leads to a decrease in its solution viscosity.[4] Nevertheless, details of these interactions between dyes are not clear-cut because of their complicated structure. To elucidate the binding of hydrophobic counterions to the polyion and the interaction between hydrophobic counterions around it, it could be helpful to use simple aromatic counterions such as benzenesulfonate and naphthalenesulfonate ions. However, few studies have been reported on the interaction between simple aromatic counterions in the presence of a polyion.[13,14] Moreover, the effect of the interaction among hydrophobic counterions on the solution properties of the polyion has not yet been investigated in detail.

We previously examined the association behavior of several hydrophobic counterions, *i.e.*, benzenesulfonate (BS^-), *p*-methylbenzenesulfonate (MBS^-), *p*-ethylbenzenesulfonate (EBS^-), and *p*-propylbenzenesulfonate (PBS^-), around the poly(allylammonium) cation ($PAAH^+$) using viscosity and ^1H NMR spectroscopic methods.[15-17] It was revealed that EBS^-'s, and PBS^-'s, accumulated electrostatically around the polyion, can associate with each other through their hydrophobic interaction. However, BS^- and MBS^-, which are slightly less hydrophobic than EBS^-, did not show any sign of such hydrophobic association. These results indicate that the hydrophobicity of the counterions plays an important role in the association of counterions around the polyion. Since naphthalenesulfonate ions are more hydrophobic than BS^-, association of the ions around the polyion can be anticipated. Moreover, the planarity of the Np ring would be expected to promote the association through a stacking interaction. Differently substituted Np rings (1-NpS^- and 2-NpS^-) may associate with each other in a different manner depending upon their chemical structures. Having a clear understanding of the stacking interaction of two isomers would be very advantageous in elucidating the nature of the interactions between aromatic rings in host–guest chemistry[18] and protein stability.[19] Here, we report on the spectroscopically explored association behavior (stacking interaction) of aromatic 1-NpS^-'s and 2-NpS^-'s around $PAAH^+$ in relation to the abnormal viscosity and solubility behavior of $PAAH^+Cl^-$ observed in their sodium salt solutions.

Experimental Section

Materials. Poly(allylammonium) chloride ($PAAH^+Cl^-$) used in this study was supplied by Nitto Boseki Co. Ltd. It was purified by a previously described method.[20] The weight-average molecular weight of $PAAH^+Cl^-$ was determined by light scattering to be 1.0×10^5 in 0.2 M NaCl. Both Na^+-1-NpS^- and Na^+-2-NpS^- (Tokyo Kasei Co.) were recrystallized from *ca.* 50 vol % aqueous methanol and dried *in vacuo*. Deionized and doubly distilled water was used as the solvent.

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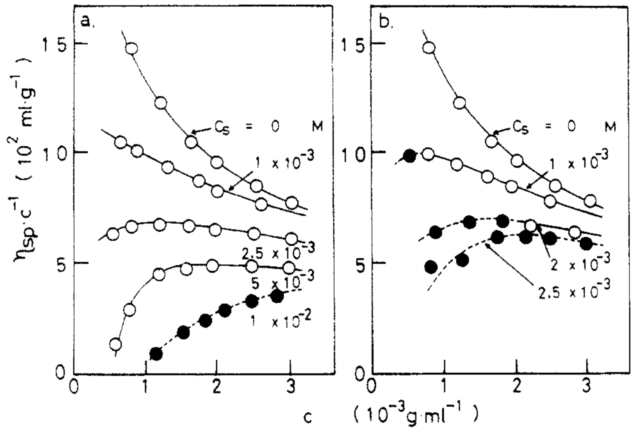


Figure 1. Viscosity plots of PAAH$^+$Cl$^-$ in Na$^+$-1-NpS$^-$ (a) and Na$^+$-2-NpS$^-$ (b) solutions. The solid symbols indicate turbid solution or precipitation of the polymer.

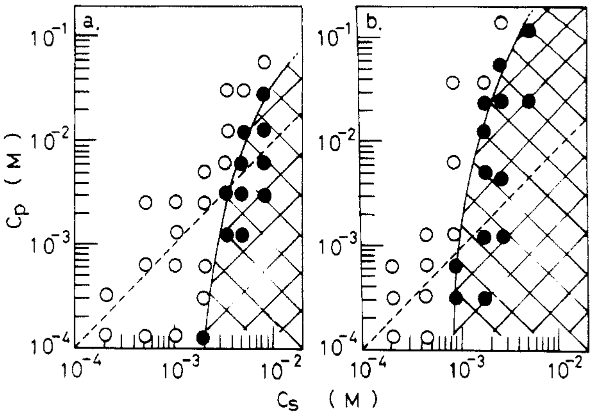


Figure 2. Solubility diagrams of PAAH$^+$Cl$^-$ in aqueous Na$^+$-1-NpS$^-$ (a) and Na$^+$-2-NpS$^-$ (b) systems. The solid symbols indicate turbid solution or precipitation of the polymer.

Measurements. Absorption spectra were recorded at 25 °C on a Shimadzu 265FW spectrophotometer equipped with a thermostated cell compartment.

Steady-state fluorescence spectra were run on a JASCO FP-777 fluorescence spectrometer at a scan rate of 100 nm min^{-1}. The temperature of the water-jacketed cell holder was controlled with a circulating bath. Nitrogen gas was bubbled through the sample solutions for 15 min before measurement.

^{1}H NMR experiments were performed at 500 MHz on a JEOL GSX500 spectrometer (Instrument Center for Chemical Analysis, Hiroshima University). Measurements were carried out at 27 ± 1 °C in D_2O (99.9%). Chemical shifts are given in ppm relative to the external tetramethylsilane standard.

Viscosity was measured with a modified Ubbelohde capillary viscometer at 25 ± 0.01 °C. All the polymer and salt solutions were filtered through a JIS No. 4 sintered glass filter prior to viscosity measurements.

Solubility studies were performed as follows. Na$^+$NpS$^-$ concentrates were added to polymer concentrates in small vials, to which an appropriate amount of water had been added. These were shaken by hand and set aside for 1 day. The presence of precipitation was judged visually. The tests were conducted at room temperature (25 ± 2 °C).

Results and Discussion

Viscosity and Solubility Behavior of PAAH$^+$ in Na$^+$NpS$^-$ Solutions. Figure 1 shows the viscosity plots of PAAH$^+$ in Na$^+$-1-NpS$^-$ (a) and Na$^+$-2-NpS$^-$ (b) solutions. In Na$^+$-1-NpS$^-$ systems, the viscosity plots are abnormal (the viscosity behavior is different from a typical polyelectrolyte/added-salt system). The reduced viscosity η_{sp}/c rapidly decreased at lower polymer concentration when the solution was diluted with a 5 × 10^{-3} M salt solution, and the polymer precipitated with a 1 × 10^{-2} M salt solution. In Na$^+$-2-NpS$^-$ systems, polymer precipitation even occurred at a salt concentration as low as 1 × 10^{-3} M. A similar abnormal viscosity behavior along with precipitation have previously been observed in dilute sodium *p*-ethylbenzenesulfonate (Na$^+$EBS$^-$)/PAAH$^+$Cl$^-$ systems.[15] Judging from the fact that PAAH$^+$Cl$^-$ does not precipitate in aqueous 3 M NaCl solution,[21] it seems that hydrophobic ions such as NpS$^-$ and EBS$^-$ precipitate the polyion more readily than simple hydrophilic ions (Cl$^-$). In the present systems, the hydrophilic Cl$^-$ around PAAH$^+$ is exchanged with a second hydrophobic counterion (NpS$^-$) upon dilution with Na$^+$NpS$^-$ solutions. Consequently, the hydration state around PAAH$^+$ acquires a more hydrophobic character, which facilitates effective contraction and precipitation of the polyion coils.

The solubility of PAAH$^+$Cl$^-$ was tested in aqueous Na$^+$-1-NpS$^-$ and Na$^+$-2-NpS$^-$ solutions to clarify the effect of the chemical structure of naphthalenesulfonate ions on the solubility of the polymer. Figure 2 shows the solubility diagrams of PAAH$^+$Cl$^-$ in aqueous Na$^+$-1-NpS$^-$ (a) and Na$^+$-2-NpS$^-$ (b) solutions. The dashed lines represent the equimolar ratio of PAAH$^+$Cl$^-$ (repeating unit) to Na$^+$NpS$^-$. The phase diagram clearly show a difference in the precipitation phenomena of the polymer in Na$^+$-1-NpS$^-$ and Na$^+$-2-NpS$^-$ solutions. The precipitation zone (hatched) of the Na$^+$-2-NpS$^-$ system is spread to a lower salt and/or higher polymer concentration region than that of the Na$^+$-1-NpS$^-$ system, suggesting that the former precipitates more readily than the latter. For example, in a Na$^+$-2-NpS$^-$ solution of 1 × 10^{-3} M, the polymer precipitates readily below a polymer concentration of 1 × 10^{-3} M, while it does not in Na$^+$-1-NpS$^-$ solutions of the same composition.

Generally, precipitation of polyelectrolytes by simple salt addition is consistent with counterion binding and/or ion pair formation.[22] A large excess of the added salt leads to the precipitation of the polyion because the charges on the polyion are neutralized by counterion binding. However, in the PAAH$^+$Cl$^-$/Na$^+$NpS$^-$ systems, it should be noted that the polymer precipitates even when the molar ratio of PAAH$^+$Cl$^-$ (repeating unit) to Na$^+$NpS$^-$ is larger than unity ($C_p > C_s$); that is, the precipitation of PAAH$^+$ does not require an excessive amount of Na$^+$NpS$^-$. Thus, in the present systems, in addition to the charge shielding, the effect of the hydrophobic moiety (Np ring) of the counterion must be taken into consideration for the solubility of the polyion. Moreover, if NpS$^-$'s associate with each other, a stronger interaction with the polyion should be induced, which would lead to the effective reduction of the ionic hydration around PAAH$^+$. In particular, judging from the viscosity measurements and precipitation observations, it seems that 2-NpS$^-$'s associate with each other more effectively than 1-NpS$^-$'s do. The differences in association between aromatic molecules could be expected to be clearly reflected in spectroscopic data. Thus, in accordance with this notion, spectroscopic analyses (absorption, fluorescence, and ^{1}H NMR spectroscopy) were carried out and are described in the following section.

Absorption Spectra. Figure 3 shows the absorption spectra of Na$^+$-1-NpS$^-$ (a) and Na$^+$-2-NpS$^-$ (b) in aqueous solution in the presence and absence of PAAH$^+$Cl$^-$. In the presence of PAAH$^+$Cl$^-$, the absorption spectra of Na$^+$-2-NpS$^-$ exhibit hypochromism with a significant red shift. The hypochromism was most outstanding when PAAH$^+$ (repeating unit, C_p) equimolar to Na$^+$-2-NpS$^-$ was added. On the other hand, the spectra of Na$^+$-1-NpS$^-$ do not exhibit any significant change by the addition of

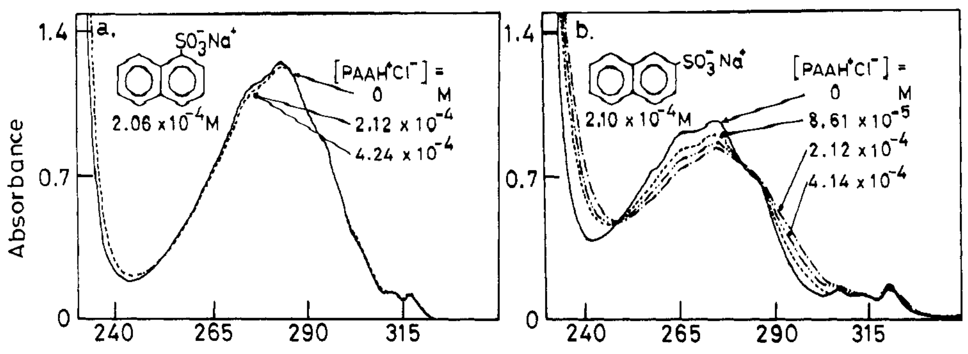


Figure 3. Absorption spectra of Na^+-1-NpS^- (a) and Na^+-2-NpS^- (b) in the presence and absence of $PAAH^+Cl^-$.

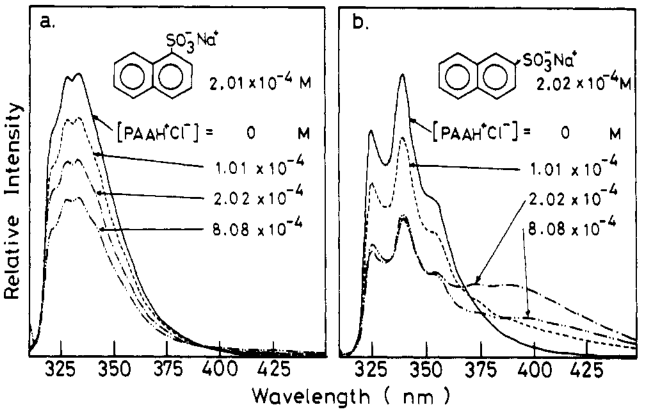


Figure 4. Fluorescence spectra of Na^+-1-NpS^- (a) and Na^+-2-NpS^- (b) in the presence and absence of $PAAH^+Cl^-$ at room temperature. Excitation was at 300 nm for Na^+-1-NpS^- and 290 nm for Na^+-2-NpS^-.

$PAAH^+Cl^-$. These results indicate that there is a strong stacking interaction of 2-NpS^-'s at the Np rings in the presence of $PAAH^+Cl^-$. The stacking interaction of 2-NpS^-'s can be attributed to an increase in their local concentration, which results from an electrostatic accumulation of counterions caused by the positively charged polyion.

Figure 3 also shows that two isosbestic points (*ca.* 250 nm and *ca.* 280 nm) exist in the $PAAH^+Cl^-/Na^+$-2-NpS^- system. A definite isosbestic point is associated with the aggregation process. Ford and Kamat[23] reported that the dimer of 2-anthracenesulfonate ion is preferentially formed on SiO_2/Al_2O_3 particles. In addition, Menger and Whitesell[24] observed that the aggregation of 1-pyrenesulfonate ion in water stops at the dimer level. Such an effect may be important in the present $PAAH^+Cl^-/Na^+$-2-NpS^- system as well. Thus, it seems that the dimer is the predominant form of aggregate of 2-NpS^- formed around $PAAH^+$.

Fluorescence Spectra. Figure 4 shows the fluorescence spectra of Na^+-1-NpS^- (a) and Na^+-2-NpS^- (b) in aqueous solution in the presence and absence of $PAAH^+Cl^-$. The stacking interaction of NpS^-'s in aqueous $PAAH^+Cl^-$ solution is more clearly reflected. In the absence of $PAAH^+Cl^-$, both 1-NpS^- and 2-NpS^- exhibit a structured spectrum characteristic to the emission of locally isolated monomeric Np chromophores peaking at 333 nm for 1-NpS^- and 338 nm for 2-NpS^-. The monomer emission intensity decreased by the addition of $PAAH^+Cl^-$ in both systems. In addition, in the $PAAH^+Cl^-/Na^+$-2-NpS^- system, a broad excimer emission with a maximum at 400 nm appeared in the presence of $PAAH^+Cl^-$. However, in the $PAAH^+Cl^-/Na^+$-1-NpS^- system, such an excimer emission was not observed.

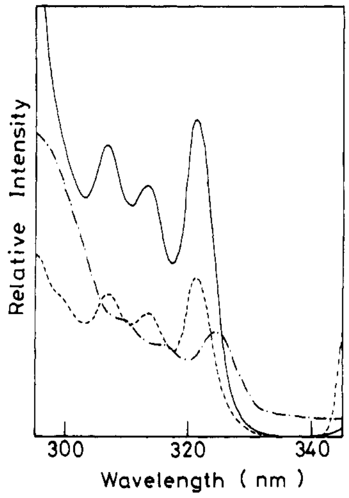


Figure 5. Excitation spectra of Na^+-2-NpS^- in the presence and absence of $PAAH^+Cl^-$ at room temperature: (—) Na^+-2-NpS^- monitored at 345 nm; (- - -) Na^+-2-$NpS^-/PAAH^+Cl^-$ system monitored at 345 nm; (-·-) Na^+-2-$NpS^-/PAAH^+Cl^-$ system monitored at 400 nm.

The excitation spectra obtained for emissions monitored at 345 (monomer) and 400 nm (excimer) for the $PAAH^+Cl^-/Na^+$-2-NpS^- system are compared in Figure 5. The excitation spectrum of the $PAAH^+Cl^-/Na^+$-2-NpS^- system monitored at 345 nm is essentially identical with that of Na^+-2-NpS^- without $PAAH^+Cl^-$ monitored at 345 nm in both spectral shape and peak wavelength. However, the excitation spectrum of the Na^+-2-$NpS^-/PAAH^+Cl^-$ system monitored at 400 nm exhibits a red shift from that of Na^+-2-NpS^- without $PAAH^+Cl^-$ monitored at 345 nm. This implies that the light-absorbing species for the excimer appearing at 400 nm is not the monomeric Np chromophore. Instead, two distinct absorbing species exist[25] and the excimer is formed by excitation of a ground-state dimer (as opposed to a collision between a ground-state monomeric species with an excited-state monomeric species). The presence of the ground-state dimers of 2-NpS^- is in agreement with the result of absorption spectra for the $PAAH^+Cl^-/Na^+$-2-NpS^- system.

Figure 6 shows the dependence of the monomer and excimer emission intensities for the $PAAH^+Cl^-/Na^+$-1-NpS^- and $PAAH^+Cl^-/Na^+$-2-NpS^- systems upon the molar ratio of $PAAH^+$ (repeating unit, C_p) to Na^+NpS^-, defined as C_p/C_s. The observed emission intensity (I) is represented as a relative value to that of the monomer (I_0) without $PAAH^+Cl^-$. The monomer emission for both the $PAAH^+Cl^-/Na^+$-1-NpS^- and $PAAH^+Cl^-/Na^+$-2-NpS^- systems exhibits self-quenching in the presence of $PAAH^+Cl^-$. The self-quenching originates from the electronic perturbation in the π-system of NpS^-'s electrostatically accumulated around $PAAH^+$.[26] The degree of self-

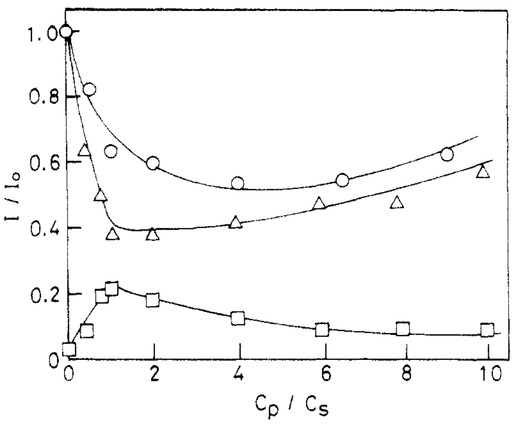


Figure 6. Change of the fluorescence intensity of Na$^+$-1-NpS$^-$ (2.01 × 10^{-4} M) and Na$^+$-2-NpS$^-$ (2.02 × 10^{-4} M) in aqueous PAAH$^+$Cl$^-$ (2.02 × 10^{-4} M) solution as a function of the molar ratio of PAAH$^+$Cl$^-$ (repeating unit) to Na$^+$NpS$^-$, C_p/C_s: (○) Na$^+$-1-NpS$^-$ (monomer); (△) Na$^+$-2-NpS$^-$ (monomer); (□) Na$^+$-2-NpS$^-$ (excimer).

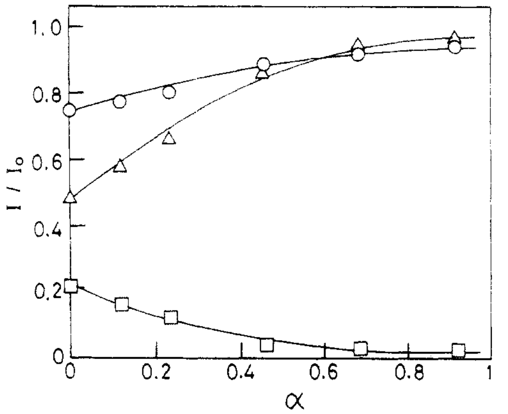


Figure 7. Dependence of the fluorescence intensity of Na$^+$-1-NpS$^-$ (2.01 × 10^{-4} M) and Na$^+$-2-NpS$^-$ (2.02 × 10^{-4} M) in aqueous PAAH$^+$Cl$^-$ (2.02 × 10^{-4} M) solution on the charge density of PAAH$^+$, α: (○) Na$^+$-1-NpS$^-$ (monomer); (△) Na$^+$-2-NpS$^-$ (monomer); (□) Na$^+$-2-NpS$^-$ (excimer).

quenching for the PAAH$^+$Cl$^-$/Na$^+$-2-NpS$^-$ system is greater than that for the PAAH$^+$Cl$^-$/Na$^+$-1-NpS$^-$ system. This suggests that the stacking interaction between 2-NpS$^-$'s is much stronger than that between 1-NpS$^-$'s. The excimer emission intensity for the PAAH$^+$Cl$^-$/Na$^+$-2-NpS$^-$ system is the largest when an equimolar amount of PAAH$^+$ to 2-NpS$^-$ is added (at $C_p/C_s = 1$). This means that the highest local concentration of 2-NpS$^-$ around PAAH$^+$ is attained at $C_p/C_s = 1$.

The effects of the charge density of the polyion (Figure 7) and the added salt, NaCl (Figure 8), upon the fluorescence spectra of the PAAH$^+$Cl$^-$/Na$^+$NpS$^-$ systems at $C_p/C_s = 1$ are summarized as relative intensity change. The abscissa in Figure 7 represents the degree of neutralization (deprotonation) α of PAAH$^+$ ($-NH_3^+ \rightarrow NH_2 + H^+$). As the charge density of the polyion decreases (α increases), the monomer emission for both the PAAH$^+$Cl$^-$/Na$^+$-1-NpS$^-$ and PAAH$^+$Cl$^-$/Na$^+$-2-NpS$^-$ systems increases to the original intensity observed in the absence of PAAH$^+$Cl$^-$. On the other hand, the excimer emission for the PAAH$^+$Cl$^-$/Na$^+$-2-NpS$^-$ system decreases with the decrease of the charge density of the polyion. The suppression of the charge effect of the polyion by neutralization lowers the accumulation of 2-NpS$^-$'s around PAAH$^+$, and the stacking interaction between 2-NpS$^-$'s becomes weaker. A similar result is also observed by addition of NaCl (Figure 8). The decrease of the excimer emission for the PAAH$^+$Cl$^-$/Na$^+$-2-NpS$^-$ system by the addition of NaCl can be ascribed to the dissociation of 2-NpS$^-$ bound around PAAH$^+$ due to the competitive binding with Cl$^-$. Figure 9 shows the fluorescence spectrum of the PAAH$^+$/Cl$^-$/Na$^+$-2-NpS$^-$ system measured at different temperatures. The excimer emission decreases with increasing temperature, which indicates that the stacking interaction of 2-NpS$^-$'s becomes weak. Thus, the association (stacking interaction) of 2-NpS$^-$'s around PAAH$^+$ depends on the charge density of the polyion, the coexistence of added salt (NaCl), and the temperature in the same manner as in polyelectrolyte/triphenylmethane dye systems.[27]

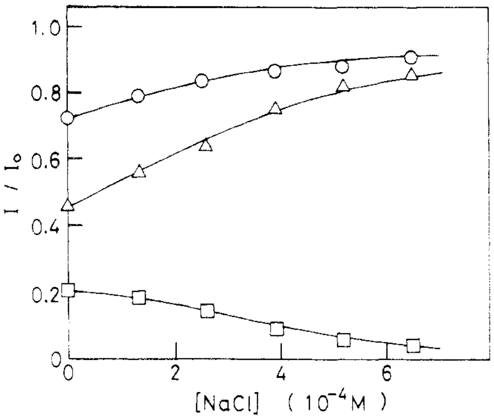


Figure 8. Dependence of the fluorescence intensity of Na$^+$-1-NpS$^-$ (2.01 × 10^{-4} M) and Na$^+$-2-NpS$^-$ (2.02 × 10^{-4} M) in aqueous PAAH$^+$Cl$^-$ (2.02 × 10^{-4} M) solution on added NaCl concentration: (○) Na$^+$-1-NpS$^-$ (monomer); (△) Na$^+$-2-NpS$^-$ (monomer); (□) Na$^+$-2-NpS$^-$ (excimer).

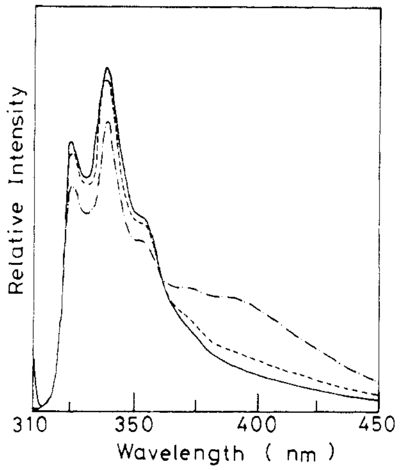


Figure 9. Fluorescence spectrum of Na$^+$-2-NpS$^-$ (2.02 × 10^{-4} M) in aqueous PAAH$^+$Cl$^-$ (2.02 × 10^{-4} M) solution at different temperatures: (—) 50 °C; (- - -) 35 °C; (-·-) 20 °C.

^{1}H NMR Spectra. The NMR method is suitable for clarifying the association behavior of the hydrophobic counterions around the polyion. In particular, if aromatic counterions associate with each other around PAAH$^+$, an intermolecular ring current shift should be observed in the counterion signals. The stacking interaction of the aromatic rings induces an upfield shift of the ring proton signals due to an increased magnetic shielding. The ^{1}H NMR spectra of the PAAH$^+$Cl$^-$/Na$^+$-1-NpS$^-$ and PAAH$^+$Cl$^-$/Na$^+$-2-NpS$^-$ systems are shown in Figure 10. Standard decoupling techniques, NOE differential spectra, and 2D NMR spectra (COSY and NOESY) were used for the ^{1}H signal assignment of both salts (the results are now shown here). Distinct assignments between protons e and g for 1-NpS$^-$ and between protons a and e and between protons b and c for 2-NpS$^-$ were not possible.

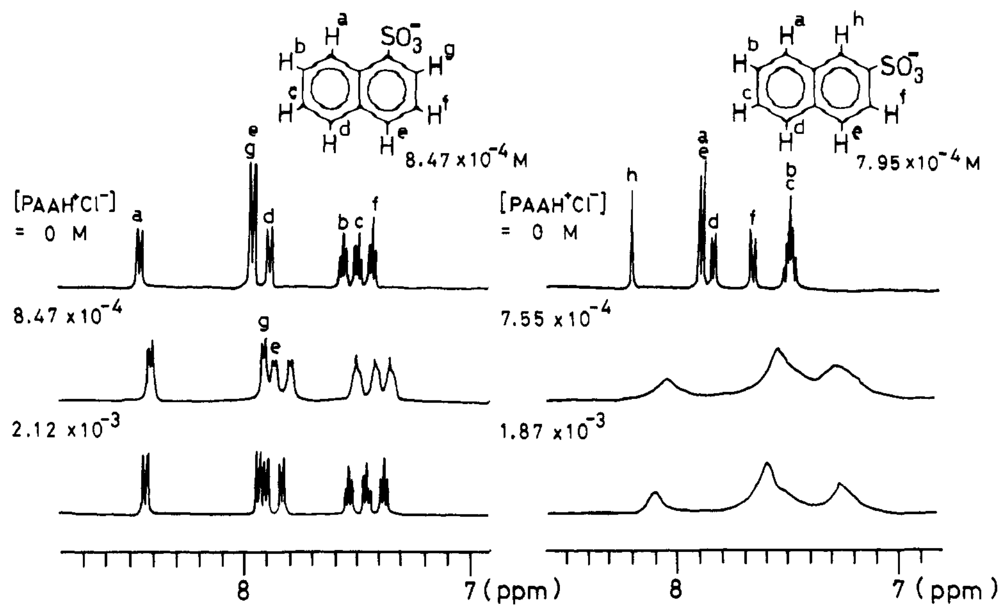


Figure 10. ^1H NMR spectra of Na^+-1-NpS^- (left) and Na^+-2-NpS^- (right) in the presence and absence of $PAAH^+Cl^-$. The small letters indicate each proton of Na^+NpS^-.

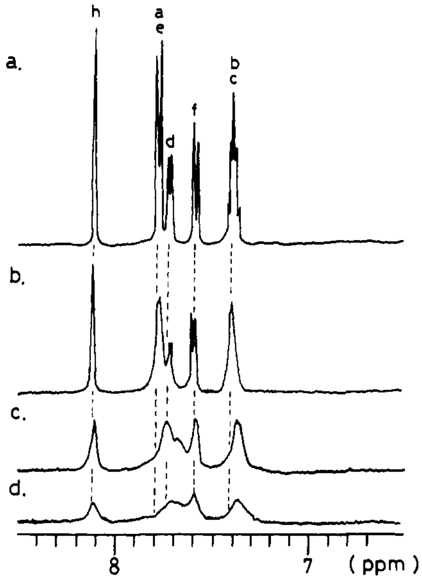
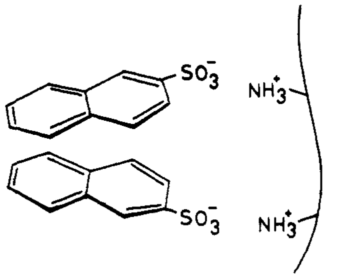


Figure 11. ^1H NMR spectrum of Na^+-2-NpS^- (7.95×10^{-4} M) in D_2O solution containing $PAAH^+Cl^-$ (1.99×10^{-3} M) at different temperatures: (a) 50 °C; (b) 40 °C; (c) 30 °C; (d) 20 °C. The small letters have the same significance as those in Figure 10.

As seen in Figure 10, in the presence of $PAAH^+Cl^-$, ^1H signals of 2-NpS^- exhibit a large ring current shift accompanied by a remarkable line broadening. This result definitely supports the existence of the ground-state aggregate of 2-NpS^-'s (stacking interaction) suggested by the absorption and fluorescence spectra. On the other hand, the upfield shift of the 1-NpS^- signals by the addition of $PAAH^+Cl1-$ is very small as a whole. The overlapped signal of protons e and g in the absence of $PAAH^+Cl^-$, resolved into the respective signals in the presence of $PAAH^+Cl^-$, due to a larger ring current shift of proton e than that of proton g. The line broadening of ^1H signals for 1-NpS^- is not significant as compared with that of 2-NpS^-. This implies that 1-NpS^-'s have much difficulty in associating with each other around $PAAH^+$, though they are densely retained in the polyion atmosphere.

Figure 11 shows the dependence of the ^1H NMR spectrum of the $PAAH^+Cl^-/Na^+$-2-NpS^- system upon temperature. When the temperature was raised, the ^1H signals of 2-NpS^- exhibited a downfield shift with signal sharpening. This indicates that the stacking of the Np rings is loosened, and therefore the restriction to motion is relaxed with increasing temperature. Furthermore, the ^1H NMR spectra at higher temperatures permit an estimation of the magnitude of the ring current shift for the protons of 2-NpS^- in the following order: a, d, e > b, c > f, h. It is worth noting that the chemical shift change of protons f and h adjacent to the sulfonate group is smaller than any other proton. Protons f and h are insensitive to the temperature change, as shown in Figure 11.

Scheme I. Model of 2-NpS^-'s Associated around $PAAH^+$



Association Behavior of 2-NpS^-'s around $PAAH^+$. The magnitude and order of the ring current shift are highly dependent on the orientation of the aromatic ring plane of the associated 2-NpS^-'s.[28] The change in the chemical shift and temperature dependence of the ^1H signals for 2-NpS^- (Figures 10 and 11) offer some important information on the structure of associated 2-NpS^-'s. In particular, the smaller change in ring current shift and insensitivity to temperature change of protons f and h may be key points in deducing the association structure. Moreover, the association of 2-NpS^-'s possessing the same charge ($-SO_3^-$) will be interfered with to some extent by the electrostatic repulsion.

Taking into consideration that the interaction between $PAAH^+$ and 2-NpS^- is essentially electrostatic, we propose the structure in Scheme I for the associated state of 2-NpS^-'s around the polyion on the basis of the change in the chemical shift of 2-NpS^-. In this model, the Np rings are not overlapped completely due to the charge repulsion of the sulfonate groups. Consequently, protons f and h do not exist above the Np ring of the other 2-NpS^-, which leads to the smaller charge in chemical shift and the insensitivity to temperature change of protons f and h.

Ford and Kamat[23] have reported that the 2-anthracenesulfonate ion (2-AS$^-$) dimerized upon adsorption from aqueous solution onto positively charged alumina-coated silica particles and that the 1,5-anthracenedisulfonate ion (1,5-AS$^-$) and the 1-anthracenesulfonate ion (1-AS$^-$) also adsorbed to the particles but did not dimerize. They pointed out the importance of a subtle orientational effect controlling the dimer formation from the fact that neither 1,5-As$^-$ nor 1-AS$^-$ dimerizes under similar experimental conditions. Such an orientational effect may be true in the present association of 1-NpS$^-$ and 2-NpS$^-$ around PAAH$^+$. Since 2-NpS$^-$ is substituted by a sulfonate group nearly along the long molecular axis of its Np ring, it can be electrostatically bound to PAAH$^+$ while directing its Np ring outward. Accordingly, an easy overlapping of 2-NpS$^-$'s around PAAH$^+$ may be attained as shown in Scheme I. On the other hand, in the case of 1-NpS$^-$, which is substituted along the short axis, the electrostatic binding of 1-NpS$^-$ to PAAH$^+$ forces its Np ring to come close to the polymer chains. Consequently, the bulkiness of the Np ring exerts a steric hindrance, which causes 1-NpS$^-$'s to have much difficulty in associating. In addition, even if 1-NpS$^-$'s overlap each other in the same manner as 2-NpS$^-$'s do, the average NH_3^+/NH_3^+ distance on the polymer surface is insufficient to reach two sulfonate groups of overlapped 1-NpS$^-$'s. Therefore, the association of the hydrophobic (aromatic) counterions around the polyion depends on the distance and angle between the groups involved (hydrophobic and/or ionic groups). Thus, the difference in the association behavior (stacking interaction) around PAAH$^+$ between two naphthalenesulfonate ions (1-NpS$^-$ and 2-NpS$^-$) has an influence on the solution properties (viscosity and solubility) of the polymer.

Conclusions

Spectroscopic methods (absorption, fluorescence, and ^{1}H NMR spectroscopy) were used to investigate the stacking interaction of 1-NpS$^-$'s and 2-NpS$^-$'s around PAAH$^+$. 2-NpS$^-$'s associate with each other around PAAH$^+$ due to the electrostatic binding of 2-NpS$^-$ to the polyion. On the other hand, 1-NpS$^-$ hardly showed signs of such an association. The fact that 1-NpS$^-$'s do not associate with each other under similar experimental conditions suggests that the orientational state of NpS$^-$ around PAAH$^+$ controls the association. The association of NpS$^-$'s around the polyion depends on the distance and angle between the groups involved (Np rings and ionic groups). The reduction of ionic hydration around PAAH$^+$ due to the hydrophobicity of the naphthalenesulfonate counterions brings about the lowering of its solubility in aqueous solution. In addition, the association of 2-NpS$^-$ also affects both the viscosity and solubility of PAAH$^+$Cl$^-$ in aqueous solution. The associated 2-NpS$^-$'s have the character of divalent counterions and they strongly interact with the polyion, which leads to effective precipitation of it.

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