Charge-Transfer Complexation in an Aqueous Polyelectrolyte Solution. III. Complexation between Pyrenesulfonate or Anthracenesulfonate and Anthraquinonesulfonate Ions

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Charge-transfer (CT) complexations between 1-pyrenesulfonate ion (PyS^-; donor) and 9,10-anthraquinone-2-sulfonate ion (2-AQS^-; acceptor), and between anthracene-2-sulfonate ion (ACS^-; donor) and 2-AQS^- ion around the cationic polymers were studied by means of absorption and fluorescence spectroscopies as well as molecular-orbital calculations. The cationic polymers used in this study were poly(allylammonium) ($PAAH^+$) and poly(1,1-dimethyl-3,5-dimethylenepiperidinium) ($PDDP^+$). When solutions included only donor and acceptor molecules at low concentration, such as solutions of PyS^- (1×10^{-4} M)/2-AQS^- (1×10^{-4} M) and ACS^- (1×10^{-4} M)/2-AQS^- (1×10^{-4} M), they did not show any CT complex formation. However, the addition of polymers to these solutions exhibited charge-transfer absorption bands (CT band). A continuous variation method for CT bands of Na^+PyS^-/Na^+2-AQS^- in both $PAAH^+Cl^-$ and $PDDP^+Cl^-$ systems showed that a 1 : 1 type (PyS^- : 2-AQS^-) complex preferentially formed in the vicinity of these polyions. On the other hand, in the Na^+ACS^-/Na^+2-AQS^- system, a 1 : 2-type (ACS^- : 2-AQS^-) complex preferentially formed around $PAAH^+$ and a 1 : 1-type complex formed around $PDDP^+$. By comparing these results with our previous study between 9,10-dimethoxyanthracene-2-sulfonate and 2-AQS^- in aqueous solution with the same polymers, it has become clear that the stoichiometries of the CT complexes and the peak positions of the observed CT bands are dependent upon the varieties of donor molecules. Molecular-orbital calculations have shown that there is a linear relationship between the calculated energy levels of the highest occupied molecular orbital (HOMO) of the donor molecules and the energies of the observed CT bands; that is, the donor molecule with a higher HOMO energy has the lower energy of the CT band.

The physico-chemical properties of dilute polyelectrolyte solutions are mainly governed by an interaction between charged groups fixed on the side chains of a polymer and their counterions. This interaction is known to be counterion binding, which is one of the characteristic properties of polyelectrolyte solutions.[1] Extensive studies have been reported concerning this phenomenon using a variety of counterions and various polyions.[2—6] Counterion binding gives rise to an interesting behavior, not only to the polymers, whose charges are screened by the counterions, but also to the counterions themselves. Because counterions are concentrated around the polyion moiety as a result of counterion binding, some interesting phenomena occur in aqueous polyelectrolyte solutions, i.e., quenching of fluorescent counterions by metal ions bound to a polyion[7,8] and an energy transfer between counterions.[9]

In our previous papers[10—12], the association behavior of simple aromatic counterions, i.e., *p*-ethylbenzenesulfonate (EBS^-) and 2-naphthalenesulfonate (2-NpS^-), around poly(allylammonium) cation ($PAAH^+$) has been reported. In these studies it was found that EBS^- and 2-NpS^- are bound to $PAAH^+$, and are associated with each other through hydrophobic and/or stacking interactions. In the above circumstances, when an electron donative (donor) ion and an electron acceptive (acceptor) ion are added as counterions in an aqueous polyelectrolyte solution, a charge-transfer (CT) interaction is expected to occur between them, which are bound to a polyion through counterion binding. Generally, the CT interaction is an important intermolecular interaction which can be seen in various fields, especially in the in vivo reactions of biomolecular systems. In these systems, macromolecules have been considered to play an important role to produce a special environment for CT molecules. However, few studies have been reported on these interactions in aqueous media,[13] especially with the presence of a polyion. We have studied the effect of the presence of a

polyion on the CT interaction, and reported that a CT complex was formed between 9,10-dimethoxyanthracene-2-sulfonate ion (DMACS$^-$) and 9,10-anthraquinone-2-sulfonate ion (2-AQS$^-$) in aqueous polymer solutions of poly(allylammonium chloride) (PAAH$^+$Cl$^-$) and poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) (PDDP$^+$Cl$^-$).[14,15] Interestingly, stoichiometric studies of these complexes showed that the type of CT complex was different in each polymer solution. One of the CT complexes of DMACS$^-$ and 2-AQS$^-$ was a 1 : 2 type, which was formed in a PAAH$^+$Cl$^-$ solution; the other was a 1 : 1-type complex, which was formed in a PDDP$^+$Cl$^-$ polymer solution. However, the precise condition and/or the mechanism for the formation of these different types of complexes has not yet been clarified.

In the present study we investigated the CT complexation between 1-pyrenesulfonate (PyS$^-$) and 2-AQS$^-$, and between anthracene-2-sulfonate (ACS$^-$) and 2-AQS$^-$ in the same polymer solutions of PAAH$^+$Cl$^-$and PDDP$^+$Cl$^-$, and compared them with the previous results. A stoichiometric study of the newly found complexes showed that they also divided into two types of CT complexes, as were found in previous studies. By comparing these results with those obtained in previous papers, the effects of the charge density of the polyion and the bulkiness of the donor molecules on the types of CT complex were elucidated. We also performed a molecular-orbital calculation in order to quantitatively analyze the observed CT bands of these three donor molecules (DMACS$^-$, PyS$^-$, ACS$^-$). This calculation showed a clear relationship between the observed CT band energies and the calculated highest occupied molecular orbitals (HOMO).

Experimental

Materials. Poly(allylammonium chloride) (PAAH$^+$Cl$^-$) was kindly donated by Nitto Boseki Co. Ltd., and poly(1,1-dimethyl-3, 5-dimethylenepiperidinium chloride) (PDDP$^+$Cl$^-$) was purchased from Aldrich Chemical Co., Inc., respectively. These polymers were purified by reprecipitation (described previously[15,16]). The weight-average molecular weights of the polymers were determined by light scattering to be 1.0×10^5 for both polymers in a 0.2 M NaCl solution, and their degrees of polymerization were 1.1×10^3 and 6.2×10^2, respectively.

Sodium 1-pyrenesulfonate (Na$^+$PyS$^-$) (Molecular Probes, Inc.), and sodium 9,10-anthraquinone-2-sulfonate (Na$^+$2-AQS$^-$) (Tokyo Kasei Co.,Ltd.), were of analytical grade and used without further purification. Sodium anthracene-2-sulfonate (Na$^+$ACS$^-$) was prepared by reducing Na$^+$2-AQS$^-$ with activated Zn powder and 20% NH_4OH for 3 h.[17] The product was treated with activated charcoal to remove any trace of Na$^+$2-AQS$^-$ and other impurities, and was recrystallized from water. The identification of Na$^+$ACS$^-$ was performed by means of infrared and ^{1}H NMR spectroscopies. The molecular structures of PAAH$^+$Cl$^-$, PDDP$^+$Cl$^-$, PyS$^-$, ACS$^-$, and 2-AQS$^-$ are shown in Chart 1.

Deionized and distilled water was used as a solvent. The concentrations were expressed as the residue molar concentration (M) for polymers and in molar concentration (M) for salts (1 M = 1 mol dm^{-3}).

Measurements. The absorption spectra were recorded at 25 °C on a Shimadzu 265FW spectrophotometer equipped with a thermostated cell compartment. Quartz cells with path lengths of 2 mm and 10 mm were used.

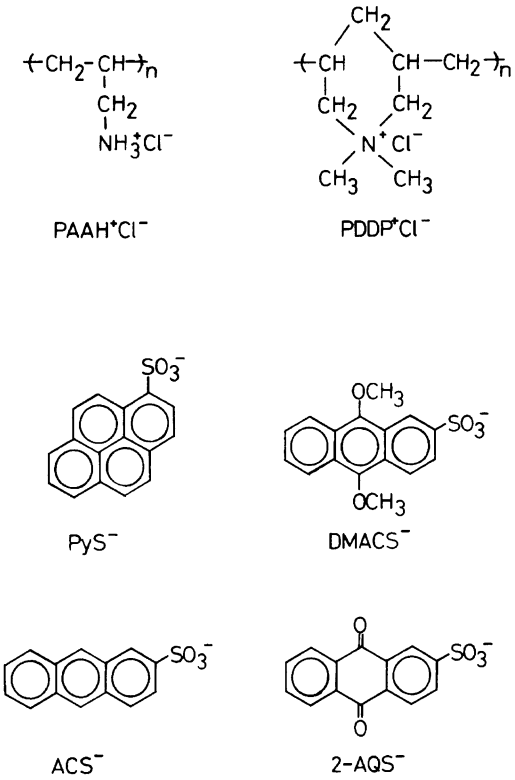

Chart 1. The Chemical structures of PAAH$^+$Cl$^-$, PDDP$^+$Cl$^-$, PyS$^-$, DMACS$^-$, ACS$^-$, and 2-AQS$^-$.

The steady-state fluorescence spectra of both Na$^+$PyS$^-$ and Na$^+$ACS$^-$ were measured on a JASCO FP-777 fluorescence spectrometer at room temperature. Excitation of both Na$^+$PyS$^-$ and Na$^+$ACS$^-$ was done at 365 nm.

Molecular-orbital calculations of PyS$^-$, ACS$^-$, and DMACS$^-$ were performed using a semi-empirical molecular-orbital calculation program of MOPAC[18] ver. 6.01 with the PM3[19] method. The energies of HOMO for all of the donors were calculated using the fully optimized structures with the PM3 Hamiltonian.

Results and Discussion

We first discuss the association behavior of PyS$^-$ and ACS$^-$ around PAAH$^+$ before mentioning the CT complex formation with an acceptor molecule of 2-AQS$^-$. Since 2-AQS$^-$ associates with each other in the vicinity of PAAH$^+$ (as described previously[14]), its association behavior is not discussed in this paper.

Figure 1a shows the absorption spectra of Na$^+$PyS$^-$ in aqueous solution in both the presence and absence of PAAH$^+$Cl$^-$. As the concentration of PAAH$^+$Cl$^-$ increases, the absorption spectra of Na$^+$PyS$^-$ exhibit a significant hypochromic effect and a red shift. These results indicate that there is a strong stacking interaction between PyS$^-$ molecules at the pyrene rings in the presence of PAAH$^+$Cl$^-$. The stacking interaction of PyS$^-$'s can be attributed to an increase in their high local concentration, which was caused by an electrostatic accumulation of the counterions in the vicinity of PAAH$^+$. Figure 1a shows the isosbestic points at 305 and 355 nm. It is an indication of the presence of

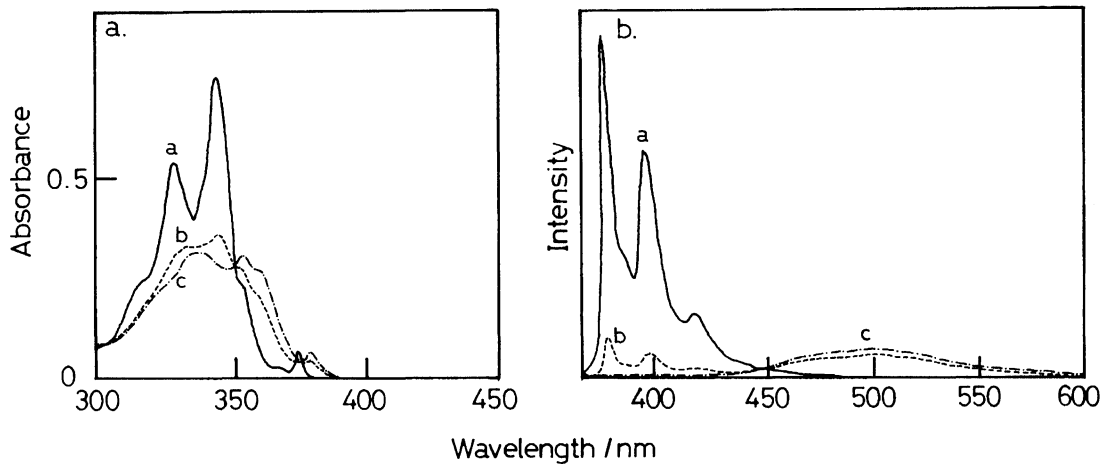

Fig. 1. Absorption spectra (a) and fluorescence spectra (b) of aqueous solutions of Na^+PyS^- in the presence and the absence of $PAAH^+Cl^-$. Cell with a light path of 2 mm was used. The fluorescence spectra were obtained by excitation at 365 nm. $[Na^+PyS^-] = 1.10\times10^{-4}$ M: (a) $[PAAH^+Cl^-] = 0$ M; (b) 5.50×10^{-5} M; (c) 1.10×10^{-4} M.

an aggregation process in this solution. Figure 1b shows the fluorescence spectra of Na^+PyS^- in aqueous solution in both the presence and absence of $PAAH^+Cl^-$. The stacking interaction of PyS^- 's in an aqueous $PAAH^+Cl^-$ solution is more clearly reflected. In the absence of $PAAH^+Cl^-$, PyS^- exhibits a characteristic spectrum of the monomeric pyrene chromophores to emissions at 380, 400, and 420 nm. These monomeric emissions are quenched by the addition of $PAAH^+Cl^-$, and a new broad excimer emission with a maximum near 500 nm appears with the polymer concentration increased.

The excitation spectra obtained for emissions monitored at 400 (monomer) and 530 nm (excimer) for the $PAAH^+Cl^-/Na^+PyS^-$ system are compared in Fig. 2. The excitation spectrum of the $PAAH^+Cl^-/Na^+PyS^-$ system monitored at 400 nm is essentially identical in both spectral shape and peak wavelength with that of Na^+PyS^- in the absence of $PAAH^+Cl^-$ monitored at the same wavelength. However, the excitation spectrum of the $PAAH^+Cl^-/Na^+PyS^-$ system monitored at 530 nm exhibits a red shift from that of Na^+PyS^- in the absence of $PAAH^+Cl^-$ monitored at 400 nm. This implies that the light-absorbing species for the excimer appearing at 530 nm is not for the monomeric pyrene chromophore. Instead, two distinct absorbing species exist[20] and the excimer is formed by excitation of a ground-state dimer.[21] The presence of the ground-state dimers of PyS^- is in agreement with the result of the absorption spectra for the $PAAH^+Cl^-/Na^+PyS^-$ system.

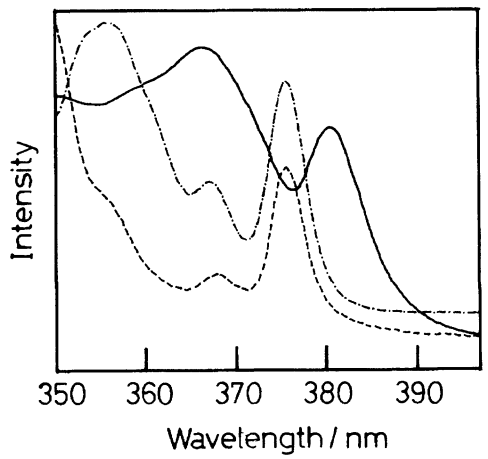

Fig. 2. Excitation spectra of aqueous solutions of Na^+PyS^- in the presence and the absence of $PAAH^+Cl^-$. Na^+PyS^- monitored at 400 nm (- - -); $Na^+PyS^-/PAAH^+Cl^-$ system monitored at 400 nm (–·–) $Na^+PyS^-/PAAH^+Cl^-$ system monitored at 530 nm (——). $[Na^+PyS^-] = 1.10\times10^{-4}$ M: $[PAAH^+Cl^-] = 2.20\times10^{-4}$ M.

Figures 3a and 3b show the absorption and fluorescence spectra of Na^+ACS^- in an aqueous solution in both the presence and absence of $PAAH^+Cl^-$. As the concentration of $PAAH^+Cl^-$ increases, the absorption spectra of Na^+ACS^- exhibit a significant hypochromic effect, a red shift and an isosbestic point (ca. 370 nm); also, the emission intensity of Na^+ACS^- decreases. These results indicate an aggregation between the ACS^- molecules in the presence of $PAAH^+Cl^-$. When $PDDP^+Cl^{-1}$ was used as a polymer in both Na^+PyS^- and Na^+ACS^- solutions, similar spectral changes were obtained, which indicate that the association of PyS^-'s and ACS^- 's occurred in the presence of $PDDP^+Cl^-$.

In general, CT complexation between electron-donor and electron-acceptor molecules in solution is accompanied by a visual color change of solutions. The solutions of Na^+PyS^- (1×10^{-4} M)/$PAAH^+Cl^-$, Na^+ACS^-(1×10^{-4} M)/$PAAH^+Cl^-$, and Na^+2-AQS^- (1×10^{-4} M)/$PAAH^+Cl^-$ used in this study were colorless. However, the addition of $PAAH^+Cl^-$ to solutions containing both Na^+PyS^- and Na^+2-AQS^-, and to that containing both Na^+ACS^- and Na^+2-AQS^- turned the color of the solutions yellow and pale orange, respectively. Figure 4 shows the absorption spectra of the $Na^+PyS^-/PAAH^+Cl^-$, Na^+2-$AQS^-/PAAH^+Cl^-$, and Na^+PyS^-/Na^+2-$AQS^-/PAAH^+Cl^-$ systems. Figure 5 also shows the absorption spectra of the $Na^+ACS^-/PAAH^+Cl^-$, Na^+2-$AQS^-/PAAH^+Cl^-$,

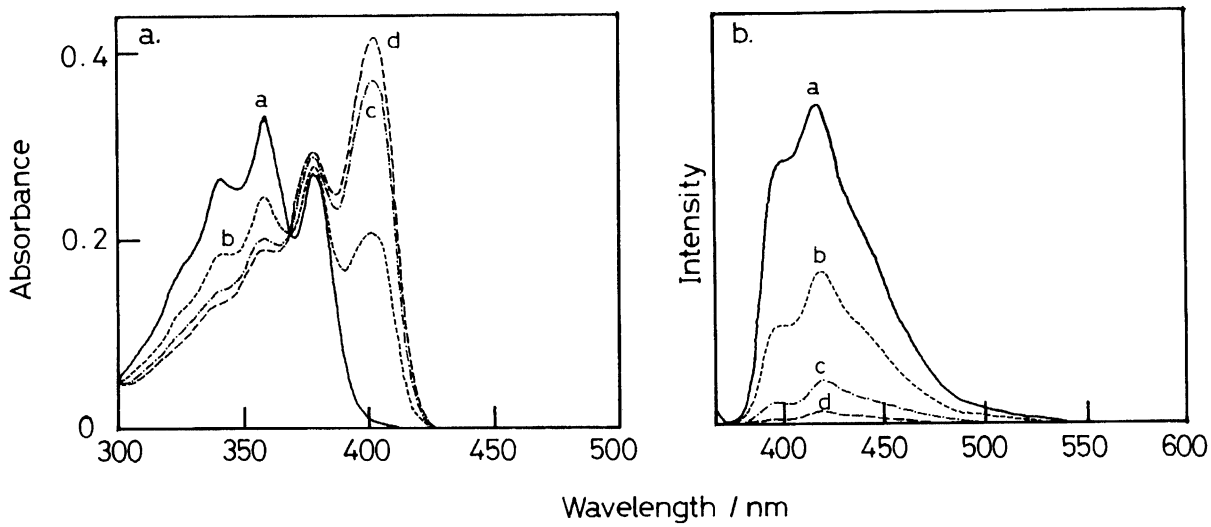

Fig. 3. Absorption spectra (a) and fluorescence spectra (b) of aqueous solutions of Na^+ACS^- in the presence and the absence of $PAAH^+Cl^-$. Cell with a light path of 10 mm was used. The fluorescence spectra were obtained by excitation at 365 nm. $[Na^+ACS^-] = 1.00\times10^{-4}$ M: (a) $[PAAH^+Cl^-] = 0$ M; (b) 5.00×10^{-5} M; (c) 1.00×10^{-4} M; (d) 2.00×10^{-4} M.

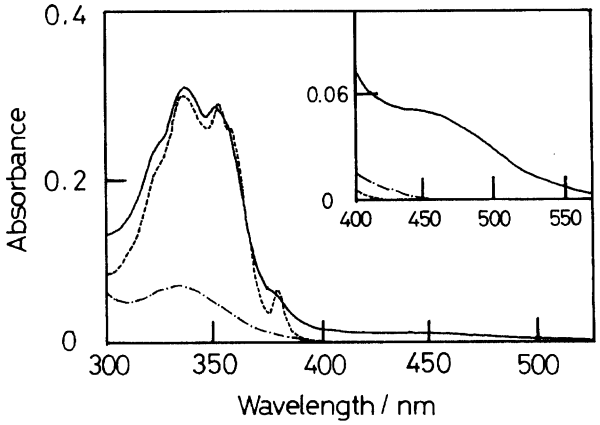

Fig. 4. Absorption spectra of $Na^+PyS^-/PAAH^+Cl^-$ (---), Na^+2-$AQS^-/PAAH^+Cl^-$ (-·-) and Na^+PyS^-/Na^+2-$AQS^-/PAAH^+Cl^-$ (—) systems. Cells with a light path of 2 and 10 mm (for the CT band) were used. $[Na^+PyS^-] = 1.10\times10^{-4}$ M, $[Na^+2\text{-}AQS^-] = 1.10\times10^{-4}$ M, $[PAAH^+Cl^-] = 4.40\times10^{-4}$ M.

and Na^+ACS^-/Na^+2-$AQS^-/PAAH^+Cl^-$ systems. In Na^+PyS^-/Na^+2-$AQS^-/PAAH^+Cl^-$, new broad absorption bands (CT band) with a maximum near 450 nm is observed. The Na^+ACS^-/Na^+2-$AQS^-/PAAH^+Cl^-$ system also shows a new broad CT band near to 460 nm. These bands correspond to the observed color changes of these solutions. Since these CT bands never appeared in the absence of $PAAH^+Cl^-$ at this concentration of donors and acceptors ($[Na^+PyS^-] = [Na^+2\text{-}AQS^-]$, and $[Na^+ACS^-] = [Na^+2\text{-}AQS^-] = 1\times10^{-4}$ M), the CT bands can be attributed to the formation of CT complexation between 2-AQS^-, and PyS^- or/and ACS^- which are bound to $PAAH^+$ through counterion binding; that is, PyS^-, ACS^-, and 2-AQS^- are electrostatically accumulated in the vicinity of the polyion, and approach each other enough to produce CT complexation. In the present system, PyS^-, ACS^- and 2-AQS^- should be bound to $PAAH^+$, facing their charged groups ($-SO_3^-$) to the cationic charged sites ($-NH_3^+$) on $PAAH^+$. In this case, their aromatic parts can easily overlap with each other, which may cause the CT interaction.

In order to determine the stoichiometries of the CT complexes between PyS^-/2-AQS^- and ACS^-/2-AQS^- in two aqueous polymer solutions ($PAAH^+Cl^-$ and $PDDP^+Cl^-$), a continuous variation method (Job Plot[22]) was employed for the CT bands. The results are shown in Figs. 6 and 7 for both the Na^+PyS^-/Na^+2-AQS^-/polymers and the Na^+ACS^-/Na^+2-AQS^-/polymers systems, respectively.

The total concentration of Na^+PyS^- and Na^+2-AQS^- ($[Na^+PyS^-] + [Na^+2\text{-}AQS^-]$) was adjusted to 2.20×10^{-4} M in a constant concentration of polymer solutions of $PAAH^+Cl^-$ and $PDDP^+Cl^-$ (4.40×10^{-4} M), and that of Na^+ACS^- and Na^+2-AQS^- ($[Na^+ACS^-] + [Na^+2\text{-}AQS^-]$) was adjusted to 2.00×10^{-4} M in an aqueous solution of 3.00×10^{-4} M $PAAH^+Cl^-$ and in 4.40×10^{-4} M $PDDP^+Cl^-$, respectively. Maxima were observed at $X = 0.5$ ($X = [\text{donor}]/[\text{donor}] + [\text{acceptor}]$) for the Na^+PyS^-/Na^+2-$AQS^-/PAAH^+Cl^-$, the Na^+PyS^-/Na^+2-$AQS^-/PDDP^+Cl^-$, and the Na^+ACS^-/Na^+2-$AQS^-/PDDP^+Cl^-$ systems. On the other hand, in the case of the Na^+ACS^-/Na^+2-$AQS^-/PAAH^+Cl^-$ system, a maximum was observed at $X = 0.34$. It shows a 1 : 1-type CT complex formed in the former three systems, and a 1 : 2 (ACS^- : 2-AQS^-)-type CT complex formed for the latter system in the presence of the polyion, respectively.

In previous papers[14,15] we reported on CT complexation between 9,10-dimethoxyanthracene-2-sulfonate ($DMACS^-$) and 2-AQS^- in aqueous $PAAH^+Cl^-$ solution; stoichiometric studies of these complexes showed that the type of CT complex was different in each polymer solution. A continuous variation method indicated that a 1 : 2 ($DMACS^-$: 2-AQS^-)-type CT complex was preferentially formed in the presence of $PAAH^+Cl^-$. On the other hand, a 1 : 1 ($DMACS^-$: 2AQS^-)-

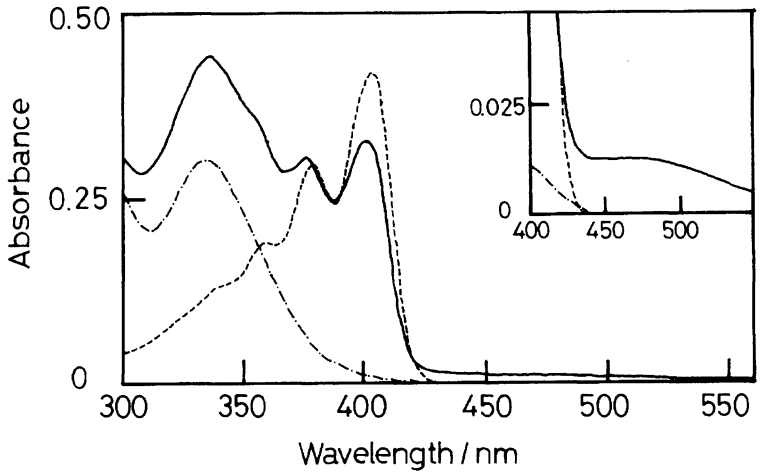

Fig. 5. Absorption spectra of $Na^+ACS^-/PAAH^+Cl^-$ (- - -), $Na^+2\text{-}AQS^-/PAAH^+Cl^-$ (– • –) and/$Na^+ACS^-/Na^+2\text{-}AQS^-/PAAH^+Cl^-$ (—) systems. Cell with a light path of 10 mm was used. $[Na^+ACS^-] = 1.00\times10^{-4}$ M, $[Na^+2\text{-}AQS^-] = 1.00\times10^{-4}$ M, $[PAAH^+Cl^-] = 3.00\times10^{-4}$ M.

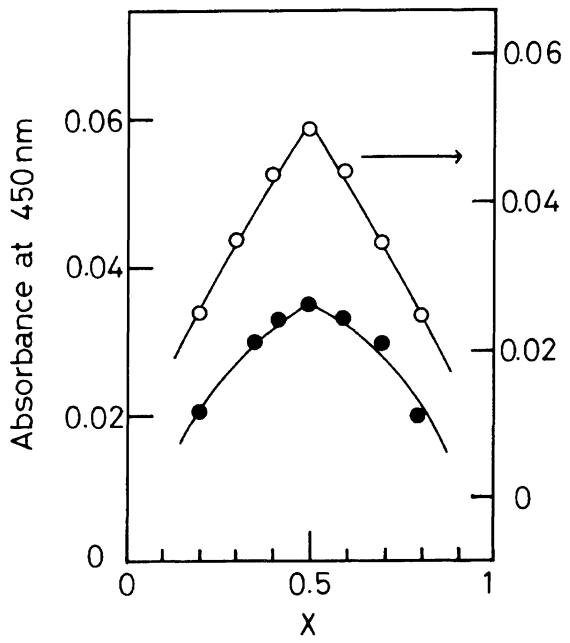

Fig. 6. Continuous variation plots for the CT complexation between PyS^- and $2\text{-}AQS^-$ in aqueous solution of 4.40×10^{-4} M $PAAH^+Cl^-$ (○), and $PDDP^+Cl^-$ (●) systems. $X = [Na^+PyS^-]/([Na^+PyS^-] + [Na^+2\text{-}AQS^-])$. $[Na^+PyS^-] + [Na^+2\text{-}AQS^-] = 2.20\times10^{-4}$ M. The absorbance was measured at 450 nm.

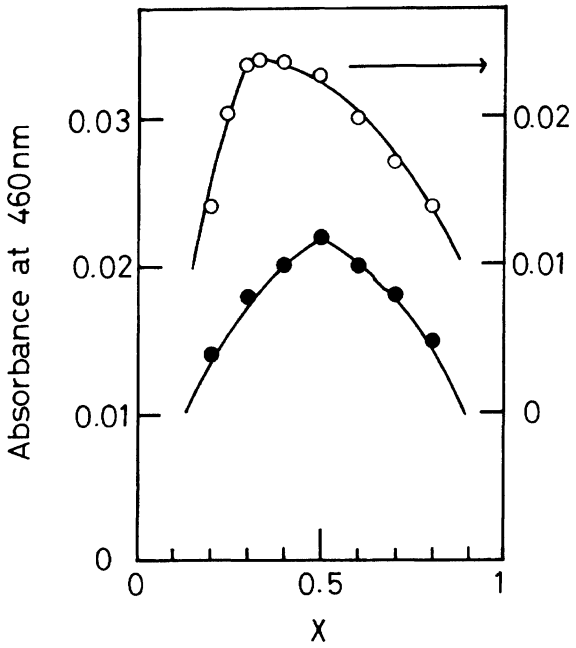

Fig. 7. Continuous variation plots for the CT complexation between ACS^- and $2\text{-}AQS^-$ in aqueous solution of 3.00×10^{-4} M $PAAH^+Cl^-$ (○), and 4.40×10^{-4} M $PDDP^+Cl^-$ (●) systems. $X = [Na^+ACS^-]/([Na^+ACS^-] + [Na^+2\text{-}AQS^-])$. $[Na^+ACS^-] + [Na^+2\text{-}AQS^-] = 2.00\times10^{-4}$ M. The absorbance was measured at 460 nm.

type CT complex was formed in the presence of $PDDP^+Cl^-$. The types of CT complexes obtained in the previous and present studies are summarized in Table 1. From this table we can mention two points. The first is that the CT complexes were always the 1 : 1-type when $PDDP^+$ was used as a polymer component of the system. The second is that although in the case of $PAAH^+$ it would prefer the 1 : 2-type complexes, the 1 : 1-type was formed when the PyS^- was used as a donor molecule. These points indicate the importance of the effects of the charge density of the polyion and the bulkiness of the donor molecules on the types of CT complex. Since both the donor and acceptor molecules must be attracted to the polyion by the electrostatic interaction in order to make a complex, the charge density of the polyion should play an important role in the formation of the CT complex. The $PDDP^+$ has a lower charge density than does that of $PAAH^+$ along the polyion chain; also, its charged group is bulky. This implies that the $PDDP^+$ could not attract the $2\text{-}AQS^-$ molecules so close as to induce their dimerization, as was shown in the $PAAH^+$ solution.

On the other hand, for the $PAAH^+Cl^-$ system, $Na^+2\text{-}AQS^-$ molecules can be attracted close to the polyion. Since

Table 1. Summary of the Types of Charge Transfer Complexes

System	Donor	Acceptor	Polymer	Type
1[a)]	$DMACS^-$	AQS^-	$PAAH^+$	1 : 2
2[b)]	$DMACS^-$	AQS^-	$PDDP^+$	1 : 1
3[c)]	PyS^-	AQS^-	$PAAH^+$	1 : 1
4[c)]	PyS^-	AQS^-	$PDDP^+$	1 : 1
5[c)]	ACS^-	AQS^-	$PAAH^+$	1 : 2
6[c)]	ACS^-	AQS^-	$PDDP^+$	1 : 1

a) Data from Ref. 14. b) Data from Ref. 15. c) Data of this work.

Na^+2-AQS^- has two carbonyl groups at the 9- and 10-positions of the anthraquinone ring, it has a permanent dipole; therefore, once the Na^+2-AQS^- molecules are closely bound to the polyion and closely packed with each other, Na^+2-AQS^- molecules seem to be associated so as to make a dimer structure and become stabilized via dipole–dipole and/or dipole–induced dipole interactions.[23] This lead to a 1 : 2-type CT complex with a donor molecule. In the present Na^+ACS^-/Na^+2-AQS^-/$PAAH^+Cl^-$ system, a similar 1 : 2-type (ACS^- : 2-AQS^-) CT complex seems to be formed in a similar manner as that of the Na^+DMACS^-/Na^+2-AQS^-/$PAAH^+Cl^-$ system. However, even if a polymer has a large charge density ($PAAH^+$), the donor and acceptor molecules could not make a 1 : 2 type complex in the case of the Na^+PyS^-/Na^+2-AQS^-/$PAAH^+Cl^-$ system. In this case, the bulky structure of the Na^+PyS^- molecule would prevent the CT complex from approaching very close to the surface of the polyion. This could not allow the acceptor molecules of Na^+2-AQS^- to become a dimer form, because Na^+2-AQS^- molecules must be closely bound to the polyion in order to make a dimer structure.[15] This again indicates the importance of the electrostatic circumstance around the polyion for CT complexation.

Finally, we investigated the relationship between the donor molecules and the peak wavelenghts of their observed CT bands. When Na^+2-AQS^- was used as an acceptor molecule, CT bands were observed at 450 nm for the Na^+PyS^-/Na^+2-AQS^- system, at 460 nm for the Na^+ACS^-/Na^+2-AQS^- system, and at 480 nm for the Na^+DMACS^-/Na^+2-AQS^- system, respectively. Since these systems were too complicate to carry out a theoretical analysis exactly, we simplified the system and tried a semi-empirical molecular-orbital calculation (MOPAC PM3 method) on the wavelength of the CT bands. Generally speaking, CT interaction between a donor and an acceptor molecule occurs effectively when an interaction between an occupied molecular orbital of a donor and an unoccupied molecular orbital of an acceptor is in a same phase[24,25] (symmetry-allowed). In addition, a CT band occurred by electron transitions from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor. In the present study, since 2-AQS^- is a common acceptor in all three donor systems, the difference in the observed CT band may be attributable to the difference in the HOMO's energy levels among these three donors (Na^+PyS^-, Na^+ACS^-, and Na^+DMACS^-). The effect of the counterions of the donor, acceptor and polymers were not taken into account in this study because their effects were the same in all systems, and could be considered to be subtracted as a common factor as a first approximation. The type of complex, that is, a 1 : 1- or 1 : 2-type, was also not considered in the calculation. This was because a donor molecule interacts strongly with one acceptor molecule and weakly with another remote acceptor when acceptor molecules form a dimer. That is, the remote acceptor interacts strongly with the polymer cation to form a kind of dipole moment and this remote dipole moment can reasonably be expected to have a small effect on the donor, and thus this effect can be neglected. Form molecular-orbital calculations, the energy levels of HOMO for the donor molecules are in the following order: $DMACS^- > ACS^- > PyS^-$. Figure 8 shows a distinct relationship between the energies of the observed CT band in three systems and the calculated HOMO's energy levels for donor molecules. Na^+DMACS^-, having the highest energy level of HOMO, indicated the lowest energy of CT band. On the other hand, Na^+PyS^-, having the lowest HOMO's energy, indicated the highest CT band energy. Although this calculation included many simplified rough treatments, it seems to have been reasonable judging from the accordance of the calculated values and the observed ones shown in Fig. 8. The relation between the observed CT band and the energy level of HOMO has been observed in the CT interaction in some organic solvents. From the present study, we obtained a similar tendency on CT complexation between aromatic ions in aqueous media, especially in an electrostatic field formed by a polyion.

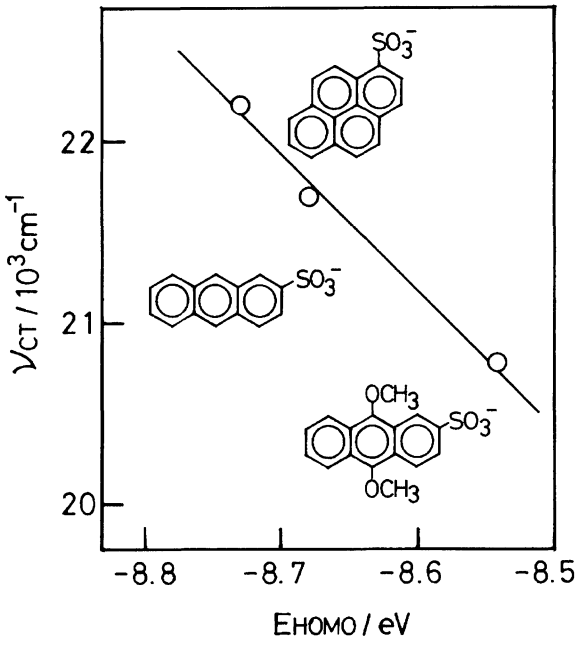

Fig. 8. A relationship between energy levels of highest occupied molecular orbital (E_{HOMO}) of $DMACS^-$, ACS^-, and PyS^- and observed CT band (ν_{CT}) in the three donor systems.

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