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Charge-Transfer Complexation in Aqueous Polyelectrolyte Solution. I. Complexation between Dimethoxyanthracenesulfonate Ion and Anthraquinonesulfonate Ion

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Absorption and fluorescence spectroscopic studies on the charge-transfer (CT) complexation between 9,10-dimethoxyanthracene-2-sulfonate ion (DMACS$^-$) and 9,10-anthraquinone-2-sulfonate ion (AQS$^-$) in aqueous solution were performed in the presence of poly(allylammonium chloride) (PAAH$^+$Cl$^-$), as well as in its absence. No spectroscopic indication of the CT complex was recognized by mixing Na$^+$DMACS$^-$ (1×10^{-4} M) with Na$^+$AQS$^-$ (1×10^{-4} M), but the addition of PAAH$^+$Cl$^-$ to the mixed solution brought about the CT complexation. On the other hand, in the absence of PAAH$^+$Cl$^-$, DMACS$^-$ and AQS$^-$ also form the CT complex when their concentrations become ca. 1×10^{-3} M. Therefore, the CT complexation between DMACS$^-$ and AQS$^-$ in PAAH$^+$Cl$^-$ solution can be attributed to a close proximity of DMACS$^-$–AQS$^-$ pairs, which results from the electrostatic binding of them by the polyions. The continuous variation method for the CT band indicated that a 1 : 2 (DMACS$^-$: AQS$^-$) complex and a 1 : 1 complex were preferentially formed in the presence and absence of PAAH$^+$Cl$^-$, respectively. The above results show that the high electrostatic potential of PAAH$^+$ affects the complexation, especially the stoichiometry.

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 potential of the polyion.[1—3] As a result of the counterion binding, a layer of highly concentrated counterions is formed near the polyion surface.[4] Thus, if the counterion has a hydrophobic moiety, the counterions can associate with each other through hydrophobic and/or van der Waals interactions around the polyion.

Many studies on the aggregation of hydrophobic dyes on the polyion have already been reported.[5—8] The dyes are electrostatically bound to the charged groups (ionic sites) of the polyion and undergo effective aggregation, resulting from either hydrophobic interaction or some other dye–dye interaction. Nevertheless, details of these interactions between dyes are not clear because of their complicated chemical structure. In order to elucidate the binding of hydrophobic counterions to the polyion and the interaction between hydrophobic counterions around it, it could be helpful to use more structurally simple counterions. So far we have revealed the association behavior of simple aromatic counterions such as alkylbenzenesulfonate ions and naphthalenesulfonate ions through their hydrophobic and stacking interactions in aqueous solution of poly(allylammonium chloride) (PAAH$^+$Cl$^-$).[9—11] Similarly, it can be expected that the π-electron donative and acceptant counterions bound to the polyion associate with each other through CT interaction.

Several complexations of biochemical interest can be well explained by the occurrence of charge-transfer between reacting species.[12] However, few studies have been reported on the charge-transfer interaction in aqueous media.[13] In addition, very little is known about the charge-transfer (CT) complexation between π-electron donative and acceptant counterions in the electrostatic field created by polyelectrolytes.

In this study we report the CT complexation between 9,10-dimethoxyanthracene-2-sulfonate ion (DMACS$^-$, donor) and 9,10-anthraquinone-2-sulfonate ion (AQS$^-$, acceptor) in aqueous solution in the presence and absence of poly(allylammonium chloride) (PAAH$^+$Cl$^-$). And we clarify the effect of PAAH$^+$Cl$^-$ on the CT complexation.

Experimental

Materials. Poly(allylammonium chloride) (PAAH$^+$Cl$^-$) used in this study was supplied by Nitto Boseki Co., Ltd. It was purified by the previously described method.[14] 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, and hence its degree of polymerization is roughly 1.1×10^3. Both sodium 9,10-dimethoxyanthracene-2-sulfonate (Na$^+$DMACS$^-$) and 9,10-anthraquinone-2-sulfonate (Na$^+$AQS$^-$) of analytical grade were purchased from Tokyo Kasei Co., Ltd., and used without further purification. The molecular structures of PAAH$^+$Cl$^-$, DMACS$^-$, AQS$^-$ are shown in Chart 1. Deionized and doubly distilled water was used as the solvent. Concentrations were expressed in residue molar concentration (M) for polymer and in molar

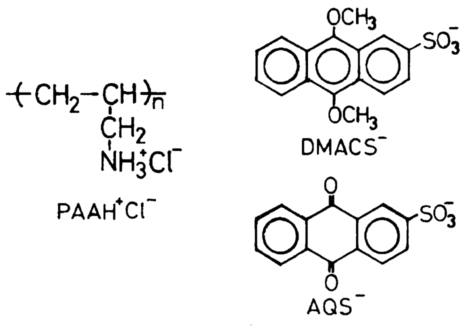

Chart 1.

concentration (M) for salts (1 M=1 mol dm^{-3}).

Measurements. Absorption spectra were recorded at 25 °C on a Shimadzu 265FW spectrophotometer equipped with a thermostated cell compartment. Quartz cells with the path length of 2 mm or 10 mm were used.

Steady-state fluoresence spectra of Na$^+$DMACS$^-$ were recorded on a JASCO FP-777 fluorescence spectrometer at 25 °C. The temperature of the water-jacketed cell holder was controlled with circulating water. Excitation was done at 380 nm for PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$ system and at 410 nm for the PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$/Na$^+$AQS$^-$ system, which preferentially excites Na$^+$DMACS$^-$. All measurements were carried out under aerobic conditions.

Results and Discussion

Complexation between DMACS$^-$ and AQS$^-$ in Aqueous PAAH$^+$Cl$^-$ Solution. Initially, we briefly discuss the association of both DMACS$^-$ and AQS$^-$ around PAAH$^+$ before the description of the CT complexation between DMACS$^-$ and AQS$^-$ in aqueous PAAH$^+$Cl$^-$ solution. Figures 1 and 2 show the absorption (a) and fluorescence (b) spectra of Na$^+$DMACS$^-$, and the absorption spectra of Na$^+$AQS$^-$ in aqueous solution in the presence and absence of PAAH$^+$Cl$^-$, respectively. The emission intensity of Na$^+$AQS$^-$ is much lower than that of Na$^+$DMACS$^-$ and is not appropriate for examination of the intensity change. As the concentration of PAAH$^+$Cl$^-$ is increased, the fraction of the bound DMACS$^-$ or AQS$^-$ to the polyion becomes dominant. Under these conditions, both DMACS$^-$ and AQS$^-$ undergo extensive aggregation around the polyion due to their high local concentration; their absorption spectra are largely changed and the emission intensity of DMACS$^-$ is diminished.

We will now describe the CT complexation between DMACS$^-$ and AQS$^-$ in aqueous PAAH$^+$Cl$^-$ solution in detail. The CT complex formation, in many cases, is attended with a color change of the system. In the present system, although the color change was not observed by mixing Na$^+$DMACS$^-$ (1×10^{-4} M, yellow) with Na$^+$AQS$^-$ (1×10^{-4} M, colorless), the addition of PAAH$^+$Cl$^-$ to the mixed solution produced an orange color. This suggests that DMACS$^-$ and AQS$^-$ form a CT complex in the presence of PAAH$^+$Cl$^-$.

Figure 3 shows the absorption spectra of the PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$, PAAH$^+$Cl$^-$/Na$^+$AQS$^-$, and PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$/Na$^+$AQS$^-$ systems. In the PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$/Na$^+$AQS$^-$ system, a new absorption band with a maximum near 480 nm appeared, which is attributed to the CT complex formation. Since the CT band never appeared without PAAH$^+$Cl$^-$ at the concentration examined, we conclude that the CT complex is produced by a close proximity of DMACS$^-$–AQS$^-$ pairs around PAAH$^+$ caused by the counterion binding. In addition, the spectrum of the PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$/Na$^+$AQS$^-$ system does not fit the additivity of two spectra of the PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$ and PAAH$^+$Cl$^-$/Na$^+$AQS$^-$ systems. Particularly, the absorption intensity of Na$^+$DMACS$^-$ in PAAH$^+$Cl$^-$ solution reduces by the addition of Na$^+$AQS$^-$. This indicates that the association state of both DMACS$^-$ and AQS$^-$ changes due to the CT complexation. In this system, DMACS$^-$ and AQS$^-$ electrostatically interact with the ammonium groups on the PAAH$^+$, directing their aromatic moieties to the opposite side of the polymer backbone. Accordingly, their aromatic moieties can easily overlap each other through CT interaction.

In Fig. 4, the absorbance of the CT band (480 nm) was plotted against the polymer concentration. It increased gradually with the polymer concentration up to [PAAH$^+$Cl$^-$]=3×10^{-4} M and then saturated. This experimental result indicates that the greater the amounts of bound DMACS$^-$ and AQS$^-$, the more CT complexation is produced. And, at [PAAH$^+$Cl$^-$]=3×10^{-4} M and above, almost all DMACS$^-$ and AQS$^-$ would be bound to PAAH$^+$ and a maximal complexation is achieved.

In order to determine the stoichiometry of the CT complex between DMACS$^-$ and AQS$^-$ in aqueous PAAH$^+$Cl$^-$ solution, a continuous variation method (Job plot[15]) was employed for the CT band. The total concentration of DMACS$^-$ and AQS$^-$ was adjusted to 2×10^{-4} M in a constant concentration of PAAH$^+$Cl$^-$ (3.20×10^{-4} M) solution. Since the interacting sites (ammonium groups) on PAAH$^+$ exist in excess, almost all DMACS$^-$ and AQS$^-$ would be electrostatically bound to the polyion (Fig. 4). The Job plot is shown in Fig. 5. The absorption maximum was observed at X=0.34, where X=[DMACS$^-$]/([DMACS$^-$]+[AQS$^-$]). It can be concluded, therefore, that the 1 : 2 (DMACS$^-$: AQS$^-$) CT complex is preferentially formed. However, the presence of the 1 : 1 CT complex can not be denied from the Job plot (Fig. 6). It is very difficult to interpret why the 1 : 2 complex is preferentially formed. The most reasonable explanation will be discussed below.

Figures 6a and 6b show the change of the absorbance at 480 nm (CT band) and of the emission intensity of Na$^+$DMACS$^-$ at maximum wavelength (460nm) on addition of Na$^+$AQS$^-$ to the PAAH$^+$Cl$^-$/Na$^+$DMACS$^-$ systems, respectively. In Fig. 6b, the observed emission intensity (I) is normalized with that ($I_\circ$) without PAAH$^+$Cl$^-$. These changes depend on the polymer concentration, and can be interpreted in terms of both the CT complexation between DMACS$^-$ and AQS$^-$ and the dissociation of bound DMACS$^-$ from the polyion. As is shown in Fig. 6a, the CT band continuously becomes larger with the concentration of Na$^+$AQS$^-$ in all systems. At lower Na$^+$AQS$^-$ concentrations, the 1 : 1 CT complex may be formed predominantly. When the concentration of Na$^+$AQS$^-$ becomes 1×10^{-4} M and above, an additional AQS$^-$ can be bound to the 1 : 1 complex to form the 1 : 2 complex, which corresponds to the result of Job plot (Fig. 5). On the basis of Fig. 6a, the change of the emission intensity

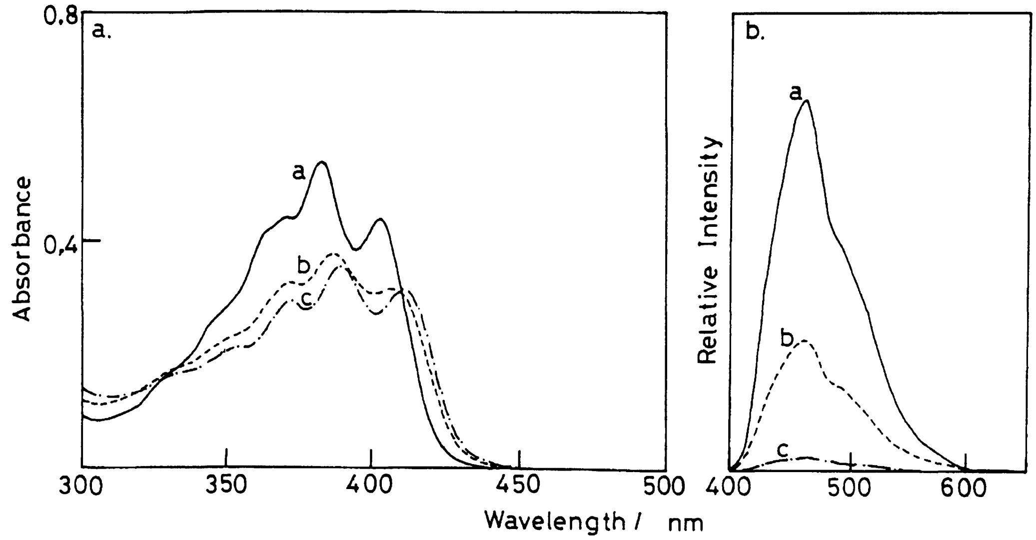

Fig. 1. Absorption spectra (a) and fluorescence spectra (b) of aqueous solutions of Na^+DMACS^- in the presence and absence of $PAAH^+Cl^-$. Cells with a light pass of 10 mm were used. The fluorescence spectra are obtained by excitation at 380 nm. $[Na^+DMACS^-]=1.03\times10^{-4}$ M: a, $[PAAH^+Cl^-]=0$ M; b, 6.40×10^{-5} M; c, 1.07×10^{-4} M.

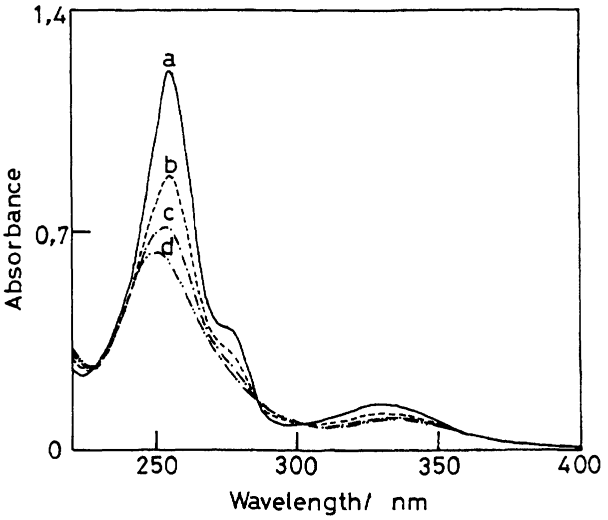

Fig. 2. Absorption spectra of aqueous solutions of Na^+AQS^- in the presence and absence of $PAAH^+Cl^-$. Cells with a light pass of 2 mm were used. $[Na^+DMACS^-]=1.03\times10^{-4}$ M: a, $[PAAH^+Cl^-]=0$ M; b, 6.40×10^{-5} M; c, 1.07×10^{-4} M; d, 1.49×10^{-4} M.

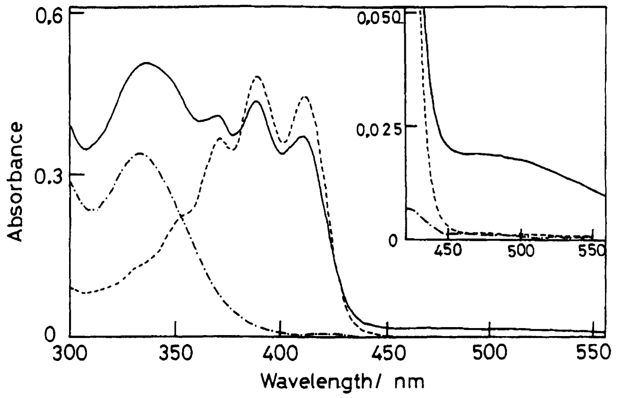

Fig. 3. Absorption spectra of the $Na^+DMACS^-/PAAH^+Cl^-$ (---), $Na^+AQS^-/PAAH^+Cl^-$ (-·-), and $Na^+DMACS^-/Na^+AQS^-/PAAH^+Cl^-$ (—) systems. Cells with a light pass of 10 mm were used. $[Na^+DMACS^-]=1.03\times10^{-4}$ M, $[Na^+AQS^-]=1.03\times10^{-4}$ M, $[PAAH^+Cl^-]=2.13\times10^{-4}$ M.

of Na^+DMACS^- (Fig. 6b) can be explained reasonably as follows.

In 1.06×10^{-4} M $PAAH^+Cl^-$ solution, the ammonium groups on the polymer are almost occupied by $DMACS^-$ prior to addition of Na^+AQS^-, and $DMACS^-$'s associate each other around the polyion. Accordingly, the emission intensity of $DMACS^-$ is strongly quenched. When Na^+AQS^- is added to the $PAAH^+Cl^-/Na^+DMACS^-$ system, AQS^- is preferentially associated with $DMACS^-$ bound to the polyion to form the CT complex. And AQS^- is bound to the polyion in replacement of $DMACS^-$, which leads to the removal of $DMACS^-$ unformed CT complex from the polyion moieties. Consequently, the emission intensity of Na^+DMACS^- increases (the emission quenching recovers) and approaches the value (I_0) observed in the absence of the polymer. In 2.13×10^{-4} M $PAAH^+Cl^-$ solution, added AQS^- associates with $DMACS^-$ through CT interaction around the polyion until the ammonium groups on the polyion are all occupied by the complex. Then, a further addition of Na^+AQS^- ($[Na^+AQS^-]>1\times10^{-4}$ M) induces the displacement of the $DMACS^-$ from the polyion domain owing to the 1:2 CT complexation around the polyion, which leads to increase the emission intensity of $DMACS^-$ at $[Na^+AQS^-]>1\times10^{-4}$ M. In 4.26×10^{-4}

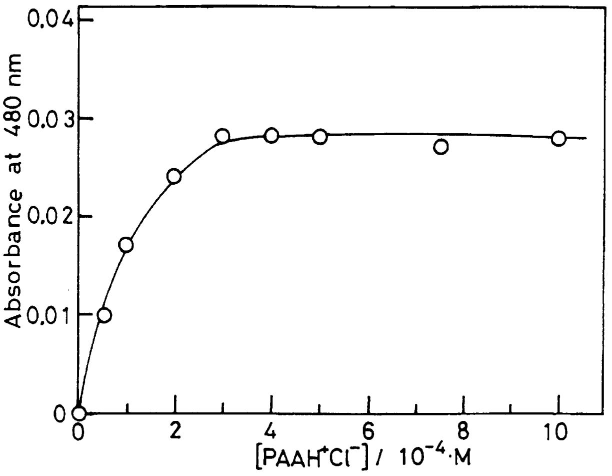

Fig. 4. Dependence of the concentration of PAAH$^+$Cl$^-$ on the absorbance at 480 nm (CT band). [Na$^+$DMACS$^-$]=1.00×10^{-4} M, [Na$^+$AQS$^-$]=1.00×10^{-4} M.

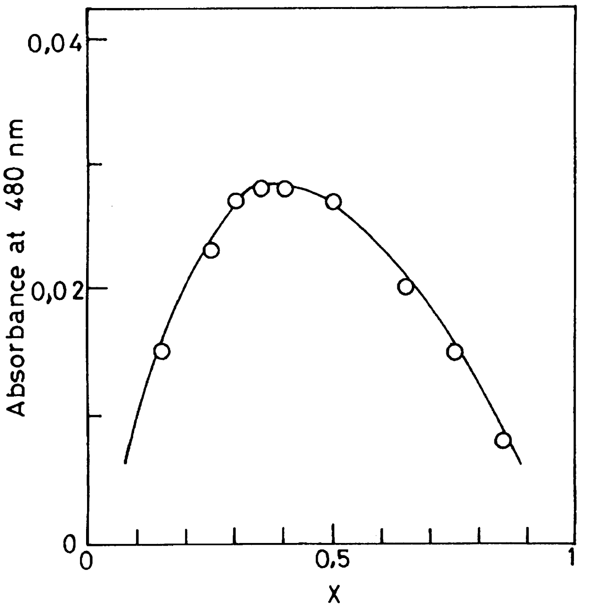

Fig. 5. Continuous variation plot for complexation of DMACS$^-$ with AQS$^-$ in aqueous PAAH$^+$Cl$^-$ solution. The change in the absorbance at 480 nm (CT band) was monitored. The total concentration was adjusted to 2×10^{-4} M in a constant concentration of PAAH$^+$Cl$^-$ solution (3.20×10^{-4} M).

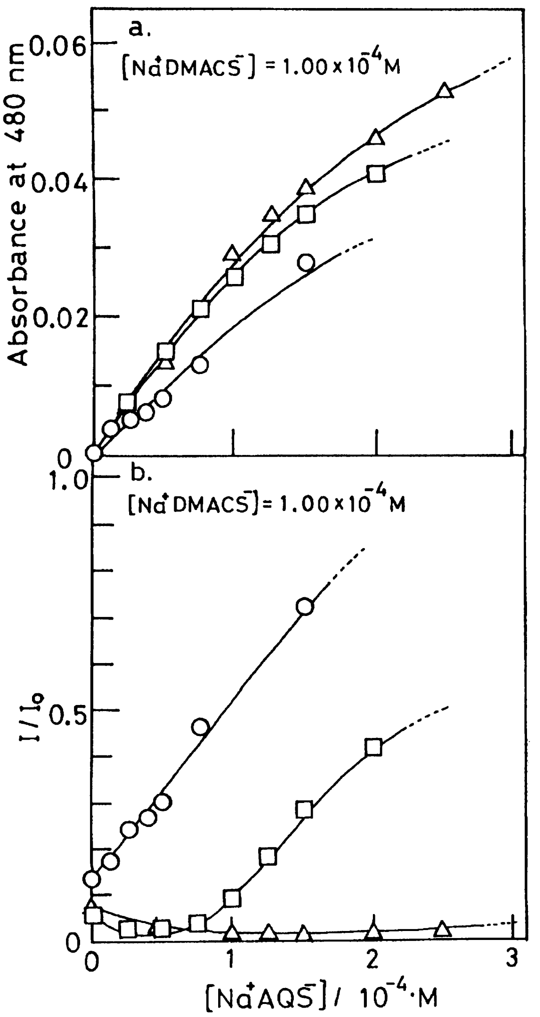

Fig. 6. Change of the absorbance at 480 nm (CT band) (a) and of the emission intensity of Na$^+$DMACS$^-$ at maximum wavelength (b) upon addition of Na$^+$AQS$^-$ to the PAAH$^+$Cl$^-$/ Na$^+$DMACS$^-$ systems. The emission intensity of Na$^+$DMACS$^-$ are measured by excitation at 410 nm. The dotted lines indicate a precipitation of the polymer. [PAAH$^+$Cl$^-$]=1.06×10^{-4} M (○); 2.13×10^{-4} M (△); 4.26×10^{-4} M (□).

M PAAH$^+$Cl$^-$ solution, the ammonium groups on the polyion remain in large excess. Thus, all of the added AQS$^-$ are bound to PAAH$^+$ and associate with DMACS$^-$ to form the CT complex. Thus, a significant quenching of the emission of DMACS$^-$ is observed in the entire concentration range of Na$^+$AQS$^-$ examined. At present, further detailed analysis of CT complexation in polyelectrolyte system is very difficult because the CT band between the 1:1 complex and the 1:2 complex is indistinguishable. The dotted lines in Fig. 6 represent the precipitation of the polyion. The CT complex strongly interacts with the polyion, which may lead to the precipitation of the polyion.

Complexation between DMACS$^-$ and AQS$^-$ in Pure Water Solution. In this section, we discuss the complexation between DMACS$^-$ and AQS$^-$ without PAAH$^+$Cl$^-$. An orange color was produced by mixing Na$^+$DMACS$^-$ (1×10^{-3} M) and AQS$^-$ (1×10^{-3} M) in aqueous solution. This color change was not observed until their concentrations became ca. 1×10^{-3} M.

Figure 7 shows the absorption spectra of Na$^+$DMACS$^-$, Na$^+$AQS$^-$, and the mixture of Na$^+$DMACS$^-$ and Na$^+$AQS$^-$ in aqueous solution. In the mixture solution, a new absorption band with a maximum near 480 nm appeared, which is attributed to the CT complexation.

The stoichiometry of the complex between DMACS$^-$ and AQS$^-$ in pure water was determined by a continuous variation method (Job plot) for the CT band (the absorbance at 480 nm). The total concentration of DMACS$^-$ and AQS$^-$ was adjusted to 2×10^{-3} M. The Job plot is shown in Fig. 8. The maximum was observed at $X=0.5$, where $X=[\text{DMACS}^-]/([\text{DMACS}^-]+[\text{AQS}^-])$. It can be concluded, therefore, that a 1 : 1 (DMACS$^-$: AQS$^-$) complex is formed. It is important to emphasize that this stoichiometry is different from that in the presence of the polymer (Fig. 5).

It has already been reported that AQS$^-$ is dimerized in aqueous solution.[13] In fact, a plot of absorbance at 370 nm of aqueous Na$^+$AQS$^-$ solution vs. concentration (not shown here) deviated from linearity above 5×10^{-4} M Na$^+$AQS$^-$. This deviation from the Beer's law as the concentration increases has been observed in the various dyes[16,17] or 1-pyrenesulfonate[18] systems. The deviation may arise from a dimer or aggregate formation. In the case of Na$^+$DMACS$^-$, on the other hand, the plot of the absorbance at 420 nm vs. the concentration obeyed the Beer's law up to 2×10^{-3} M examined. Therefore, at 1×10^{-3} M, AQS$^-$ forms a dimer, but DMACS$^-$ does not form a dimer. In aqueous mixture solution of Na$^+$DMACS$^-$ (1×10^{-3} M) and Na$^+$AQS$^-$ (1×10^{-3} M), both the CT complex and the dimer of AQS$^-$ would coexist.

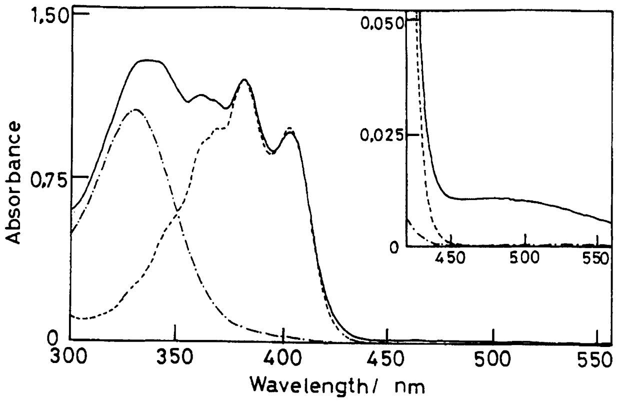

Fig. 7. Absorption spectra of aqueous Na$^+$DMACS$^-$ (---), Na$^+$AQS$^-$ (-•-), and Na$^+$DMACS$^-$/Na$^+$AQS$^-$ (—) solutions. Cells with a light pass of 2 mm were used. $[\text{Na}^+\text{DMACS}^-]=1.00\times10^{-3}$ M, $[\text{Na}^+\text{AQS}^-]=1.00\times10^{-3}$ M.

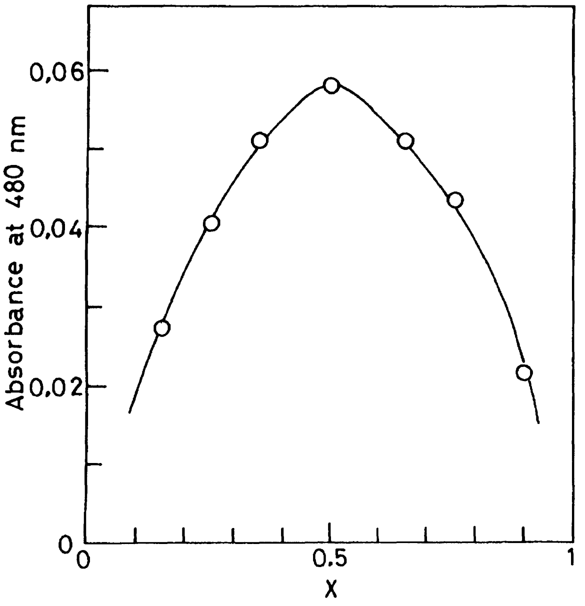

Fig. 8. Continuous variation plot for complexation between DMACS$^-$ and AQS$^-$ in pure water. $[\text{Na}^+\text{DMACS}^-]+[\text{Na}^+\text{AQS}^-]=2.00\times10^{-3}$ M. Cells with a light pass of 10 mm were used for monitoring the CT band.

Figure 9 shows the effect of NaCl on the CT complexation in pure water. This result clearly indicates that NaCl promotes the complexation between DMACS$^-$ and AQS$^-$. Since both DMACS$^-$ and AQS$^-$ have a sulfonate group ($-SO_3^-$), the electrostatic repulsion between their sulfonate groups prohibits the complexation. In aqueous solution of NaCl, the negative charges of the sulfonate anions may be neutralized by the Na$^+$ of added NaCl to result in an increase of the CT interaction.

Effect of PAAH$^+$Cl$^-$ on the Complexation between DMACS$^-$ and AQS$^-$. Polyions have been shown to have large effects on the rates of ionic reaction.[19,20] If the reaction involves two counterions, considerable enhancement of reaction rates is generally observed, due to electrostatic attraction of ionic reactants by polyion charges.[21] Similarly, PAAH$^+$ is a fully charged vinylic polyelectrolyte and its high charges pro-

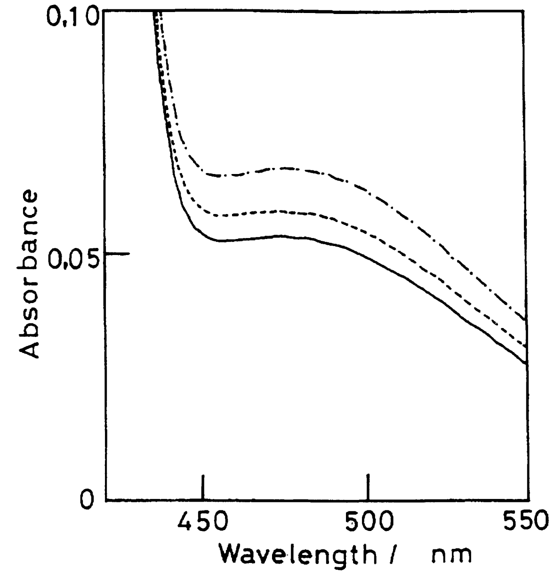

Fig. 9. Absorption spectra of the Na$^+$DMACS$^-$/Na$^+$AQS$^-$ system in aqueous NaCl solutions. [NaCl]=0 M (—); 1×10^{-2} M (---); 1×10^{-1} M (-•-). Cells with a light pass of 10 mm were used.

duce a strong electric field which attracts the counterions. Therefore, $DMACS^-$ and AQS^- are electostatically accumulated around $PAAH^+$, which brings about the complexation between $DMACS^-$ and AQS^- accompanying the CT interaction.

As noted above, both $DMACS^-$ and AQS^- associate with each other around $PAAH^+$. Both $DMACS^-$ and AQS^- are assumed to be amphiphilic molecules, because the negative charge of the sulfonate anion of these compounds is localized. It seems, therefore, that the driving force for the association of both $DMACS^-$ and AQS^- is van der Waals or hydrophobic interaction. However, in the absence of $PAAH^+Cl^-$, AQS^- forms the dimer at 1×10^{-3} M but $DMACS^-$ does not form at the same concentration. This suggests that the interaction between anthraquinone rings is stronger than that between dimethoxyanthracene rings. The carbonyl groups at the 9- and 10-positions of the anthraquinone ring have a permanent dipole because of their mesomeric effect. The dimer of AQS^- (the interaction between AQ rings), therefore, seems to be stabilized via dipole–dipole and/or dipole–induced dipole interactions.[22]

Perhaps, the stable dimer of AQS^- is also formed in the presence of $PAAH^+Cl^-$. In fact, in the poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride)/Na^+DMACS^-/Na^+AQS^- system, we have found that the interaction between AQS^- 's is stronger than that between $DMACS^-$'s, and between $DMACS^-$ and AQS^- (CT interaction) by means of ^{1}H NMR spectra (Because of some technical difficulty, we could not obtain the clear NMR data in the present system).[23] Judging from this result, the most reasonable explanation for the formation of the 1 : 2 complex in aqueous $PAAH^+Cl^-$ solution is as follows: The extremely stable dimer of AQS^- associates with a $DMACS^-$ through the CT interaction to form the 1 : 2 molecular complex. Thus, the 1 : 2 complex in aqueous $PAAH^+Cl^-$ solution may be conceivable to be an asymmetric type complex but not to be a sandwich type one. A high electrostatic potential created by the polyion depresses the charge repulsion among SO_3^- groups in forming the complex, which assists the formation of the 1 : 2 complex. Without $PAAH^+Cl^-$, on the other hand, the formation of the 1 : 2 complex is prevented by the electrostatic repulsion between the AQS^- dimer and $DMACS^-$, and between the 1 : 1 complex and AQS^-. Consequently, the 1 : 1 CT complex alone is formed in pure water.

We do not have any information on the geometrical structure of the complex. At present, further detailed study is in progress in order to clarify its structure formed in the presence and absence of the polymer. The result will be reported in the near future. Moreover, various CT complexations in aqueous polyelectrolyte solution will be systematically investigated from now on.

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