Charge-Transfer Complexation in Aqueous Polyelectrolyte Solution. II. Interaction between Polycations and CT Complexes

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(Received January 21, 1994)

The CT complexation between 9,10-dimethoxyanthracene-2-sulfonate ion ($DMACS^-$; donor) and 9,10-anthraquinone-2-sulfonate ion (AQS^-; acceptor) has been studied in aqueous solution of poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) ($PDDP^+Cl^-$). In aqueous $PDDP^+Cl^-$ solution, both $DMACS^-$ and AQS^- are electrostatically bound to the polyion and the CT complex between them is formed around the polyion due to the close proximity of $DMACS^-$–AQS^- pairs. By comparing the CT complexation in aqueous $PDDP^+Cl^-$ solution with that in aqueous poly(allylammonium chloride) ($PAAH^+Cl^-$) solution studied previously, the effects of the charge density of the polyion, the structure of charged groups on the polyion and the local conformation of the polyion upon the CT complexation have been clarified. A plausible structure of the CT complex has been determined so as to satisfy the symmetry-allowed interaction between the HOMO of $DMACS^-$ and the LUMO of AQS^-. The CT complex interacts more strongly with the polyion than Cl^- and the decrease in the viscosity of the polymer (the contraction of the polymer chain) is more effectively caused by the CT complexation. Moreover, the strength of the association (stacking interaction) of aromatic counterions ($DMACS^-$, AQS^-) including the CT complexation affects the binding of these counterions to the polyion.

The properties of polyelectrolyte solutions strongly depend on the electrostatic interactions among charges fixed along the polymer backbone. These interactions are very sensitive to the counterions which coexist. The addition of electrolyte to the medium screens out the repulsive interaction among charges through the counterion binding and/or condensation to the polyion with a high electrostatic potential. This counterion binding is an important feature of polyelectrolyte solutions.[1] When hydrophobic salt is used as an added electrolyte, the hydrophobic counterion may have an influence upon the properties of polyelectrolyte solutions.[2,3] Interactions between hydrophobic counterions bound to the polyion must be taken into careful account.[4]

It is well-known that hydrophobic 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.[5—9] And, it has been established that the binding of dyes to a polyion leads to a decrease in its solution viscosity.[6] Nevertheless, details of these interactions between dyes are not clear-cut because of their complicated structure. In addition, the mutual relation of the electrostatic binding of hydrophobic dyes to the polyion and the hydrophobic interaction between dyes has not been clarified in detail yet. In order to elucidate these problems, it could be helpful to use more simple aromatic counterions. Under these circumstances, we have already studied the hydrophobic (stacking) interaction of alkylbenzenesulfonate ions[10—12] and naphthalenesulfonate ions,[13] and the charge-transfer interaction between dimethoxyanthracenesulfonate ion ($DMACS^-$) and anthraquinonesulfonate ion (AQS^-)[14] in aqueous solutions of poly(allylammonium chloride) ($PAAH^+Cl^-$).

In this study, we present the CT complexation between $DMACS^-$ and AQS^- in aqueous solutions of poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) ($PDDP^+Cl^-$) and compare the complexation with that in aqueous $PAAH^+Cl^-$ solutions examined previously;[14] the chemical structures of these polyelectrolytes are shown in Chart 1. By comparing the CT complexation in two polyelectrolytes solution, the effects of the charge density and of the local conformation of the polyion are clarified. We also performed ^1H NMR and viscosity measurements on the $PDDP^+Cl^-/Na^+DMACS^-$, $PDDP^+Cl^-/Na^+AQS^-$ and $PDDP^+Cl^-/Na^+DMACS^-/Na^+AQS^-$ systems in order to elucidate the mutual relation of the interactions between aromatic counterions, including the CT interaction and the binding of the aromatic counterions to the polyion. A plausible structure of the CT complex was determined so as to satisfy the symmetry-allowed interaction between the HOMO of $DMACS^-$ and the LUMO of AQS^-.

Experimental

Materials. Poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) ($PDDP^+Cl^-$) used in this study was purchased from Aldrich Chemical Co., Inc. It was purified by the following method. The polymer was precipitated from a 5% aqueous solution of the polymer with dioxane.

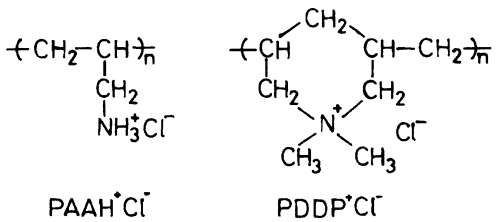


Chart 1. The chemical structures of $PAAH^+Cl^-$ and $PDDP^+Cl^-$.

Upon standing still overnight, the turbid solution separated into two liquid phases, the supernatant solution and the coacervate. The coacervate was dissolved in a small amount of methanol and the solution thus formed was added dropwise to excess dioxane with vigorous stirring. The precipitated polymer was dried under reduced pressure for one week. The weight-average molecular weight of $PDDP^+Cl^-$ was determined by light scattering to be 1.0×10^5 in 0.2 M NaCl solution. Sodium 9,10-dimethoxyanthracene-2-sulfonate (Na^+DMACS^-) and sodium 9,10-anthraquinone-2-sulfonate (Na^+AQS^-) of analytical grade were purchased from Tokyo Kasei Co., Ltd.; these were used without further purification. Deionized and doubly distilled water was used as solvent. Concentrations were expressed in residue molar concentration (M) for polymer and in molar concentration (M) for salts (1 M=1 mol dm^{-3}).

Measurements. Absorption spectra were recorded at 25 °C on a Shimadzu 265 FW spectrophotometer equipped with a thermostated cell compartment. Quartz cells of 2 or 10 mm in path length were used. Unless otherwise noted in captions of figures, a cell of 10 mm in path length was used.

Steady-state fluorescence spectra of Na^+DMACS^- were recorded on a JASCO FP-777 fluorescence spectrometer at room temperature. Excitation was done at 410 nm, which preferentially excites Na^+DMACS^-.

^1H NMR experiments were performed at 270 MHz on a JEOL GSX270 spectrometer (Instrument Center for Chemical Analysis, Hiroshima University). Measurements were carried out in D_2O (99.9%). The chemical shifts were given in ppm relative to the external tetramethylsilane standard.

Viscosity was measured with a modified Ubbelhode 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.

The molecular orbital coefficients of the HOMO of $DMACS^-$ and the LUMO of AQS^- was determined by calculation with the MOPAC 3.00 program using the MNDO option.[15,16]

Results and Discussion

CT Complexation between $DMACS^-$ and AQS^- in Aqueous Solutions of Cationic Polyelectrolytes. Both $DMACS^-$ and AQS^- associate with each other around $PDDP^+$, in analogy with other polyelectrolyte/hydrophobic counterion systems. Detailed descriptions of these association behavior are presented in the latter section. First, we discuss the CT complexation between $DMACS^-$ and AQS^- in the presence of $PDDP^+$. Figure 1 shows the absorption spectra of the $PDDP^+Cl^-/Na^+DMACS^-$, $PDDP^+Cl^-/Na^+AQS^-$, $PDDP^+Cl^-/Na^+DMACS^-/Na^+AQS^-$ systems. In the $PDDP^+Cl^-/Na^+DMACS^-/Na^+AQS^-$ system, a new absorption band with a maximum near 480 nm appeared; this band is attributed to the CT complexation between $DMACS^-$ and AQS^-. The CT complexation exhibited an orange-color solution. Since the CT band does not appear without $PDDP^+$ under the same conditions, we conclude that the CT complexation is achieved by the close proximity of $DMACS^-$–AQS^- pairs on the polyion due to the counterion binding. In this system, $DMACS^-$ and AQS^- electrostatically interact with the polyion directing their aromatic moieties to the opposite sides of the polymer backbone. Thus, their aromatic moieties can easily overlap with each other through CT interaction. In order to determine the stoichiometry of the CT complex between $DMACS^-$ and AQS^- in aqueous $PDDP^+Cl^-$ solution, a continuous variation method (Job plot)[17] was employed for the CT band. The Job plot is shown in Fig. 2. The maximum was observed at $X=0.5$, where $X=[DMACS^-]/([DMACS^-]+[AQS^-])$. It can be concluded, therefore, that a 1 : 1 CT complex is dominantly formed.

We have already examined the CT complexation between $DMACS^-$ and AQS^- in aqueous solutions of poly(allylammonium chloride) ($PAAH^+Cl^-$).[14] The comparison between the CT band in $PAAH^+Cl^-$ solution and that in $PDDP^+Cl^-$ solution under the same conditions is shown in Fig. 3. The intensity of the CT band of the $PAAH^+Cl^-$ system is stronger than that of the $PDDP^+Cl^-$ system. In aqueous $PAAH^+Cl^-$ solution, in addition, a 1 : 2 ($[DMACS^-]:[AQS^-]$) complex is preferentially formed.[14] It is important to emphasize that this stoichiometry is different from that of the $PDDP^+Cl^-$ system.

Since the CT complexation is achieved by the counterion binding to the polyion, it should be influenced by the charge density of the polyion and the species of the charged groups on the polyion. $PAAH^+$ is a cationic polyelectrolyte with primary ammonium groups and the axial charge spacing on the polyion is ca. 2.5 Å. On the other hand, $PDDP^+$ is a cationic polyelectrolyte with quaternary ammonium groups and the axial charge spacing on the polyion is ca. 4.9 Å. This means that the charge density of $PDDP^+$ is lower than that of $PAAH^+$. Apparently, $PDDP^+$ can not bind the counterions more strongly than $PAAH^+$ and, consequently, the CT complexation around $PDDP^+$ is not so effective as that around $PAAH^+$. In addition, two methyl groups attached to charged nitrogen atom (quaternary ammonium group) on the $PDDP^+$ prevent the counterions from approaching the charges on the polymer. This effect may also be unfavorable to the CT complexation. It is concluded, therefore, that the CT complexation between aromatic counterions in polyelectrolyte solution mainly depends on the ability of the polyion to attract the counterions.

The difference in the stoichiometry of the complexes formed in two cationic polyelectrolyte solutions may thus be interpreted in terms of the local conformation of the polymer. When the 1 : 2 complex is formed on the polyion, the successive three charged groups on the polyion should face to the sulfonate groups of the complex. $PAAH^+$ may take on such a local conformation without difficulty. However, $PDDP^+$ seems not to take on such a local conformation because of the steric hindrance among its piperidinium rings. As mentioned

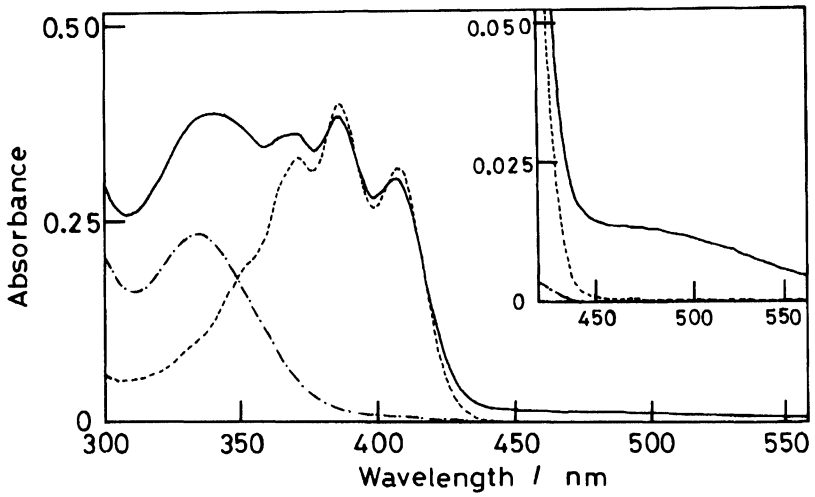


Fig. 1. Absorption spectra of the $PDDP^+Cl^-/Na^+DMACS^-$ (---), $PDDP^+Cl^-/Na^+AQS^-$ (-·-), and $PDDP^+Cl^-/Na^+DMACS^-/Na^+AQS^-$ (—) systems. Quartz cell of 2 mm in path length was used. $[Na^+DMACS^-]=4.00\times10^{-4}$ M, $[Na^+AQS^-]=4.00\times10^{-4}$ M, $[PDDP^+Cl^-]=1.06\times10^{-3}$ M.

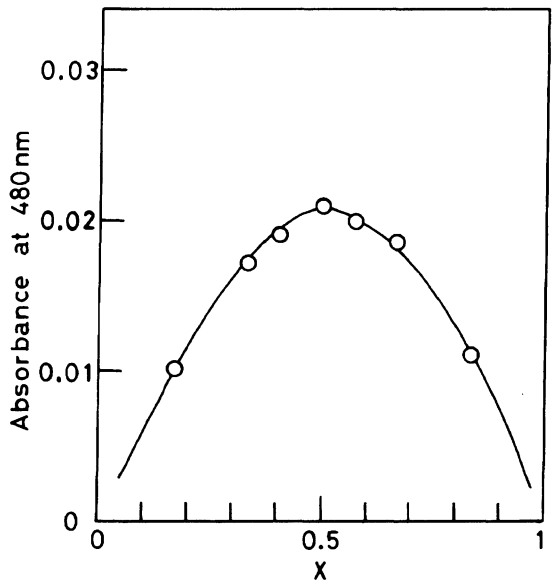


Fig. 2. Continuous variation plot for the CT complexation between $DMACS^-$ and AQS^- in aqueous solution of 5.40×10^{-4} M $PDDP^+Cl^-$. $X=[Na^+DMACS^-]/([Na^+DMACS^-]+[Na^+AQS^-])$ $[Na^+DMACS^-]+[Na^+AQS^-]=3.00\times10^{-4}$ M.

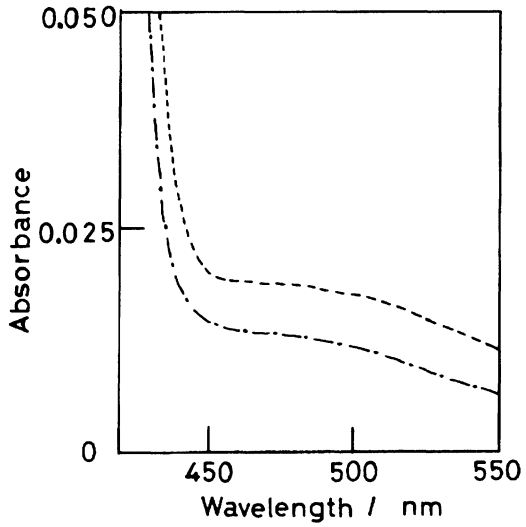


Fig. 3. Comparison between the CT band (---) in the $PAAH^+Cl^-$ solution and that (-·-) in the $PDDP^+Cl^-$ solution. $[Na^+DMACS^-]=1.00\times10^{-4}$ M, $[Na^+AQS^-]=1.00\times10^{-4}$ M, [polymer]$=2.13\times10^{-4}$ M.

above, $PDDP^+$ can not condense the counterions more strongly than $PAAH^+$. Therefore, $PDDP^+$ can not satisfy the requirement of the 1 : 2 complexation. In aqueous solution of $PDDP^+Cl^-$, consequently, the 1 : 1 CT complex alone is formed.

Effect of Added Salt (NaCl) on the CT Complexation. Figure 4 shows the effect of added NaCl on the CT complexation between $DMACS^-$ and AQS^- in aqueous solution of $PDDP^+Cl^-$. The changes of the absorbance at 480 nm (CT band) and the emission intensity at 460 nm (maximum wavelength) of Na^+DMACS^- are plotted in Fig. 4(a) and 4(b), respectively. The emission of $DMACS^-$ reflects the binding of it to the polyion and the observed emission intensity (I) is represented as a value relative to that of $DMACS^-$ (I_0) without $PDDP^+Cl^-$. The CT band is not influenced by the addition of NaCl up to $[NaCl]=1\times10^{-3}$ M. However, further addition of NaCl leads to a decrease in the CT band and the CT band finally disappears. The emission of Na^+DMACS^- is strongly quenched by the CT complexation around $PDDP^+$ prior to the addition of NaCl. The emission intensity does not also change by the addition of NaCl up to $[NaCl]=1\times10^{-3}$ M. However, further addition of NaCl leads to an increase in the emission intensity of Na^+DMACS^- and the emission intensity finally increases to that in the absence of

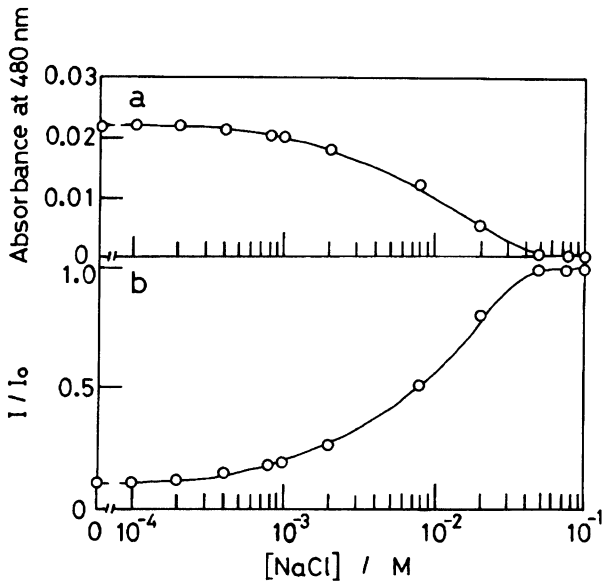


Fig. 4. Effect of added NaCl on the absorbance at 480 nm (CT band) (a) and the emission intensity at 460 nm of Na^+DMACS^- (b) in aqueous solutions of 5.40×10^{-4} M $PDDP^+Cl^-$. $[Na^+DMACS^-]=1.50\times10^{-4}$ M, $[Na^+AQS^-]=1.50\times10^{-4}$ M.

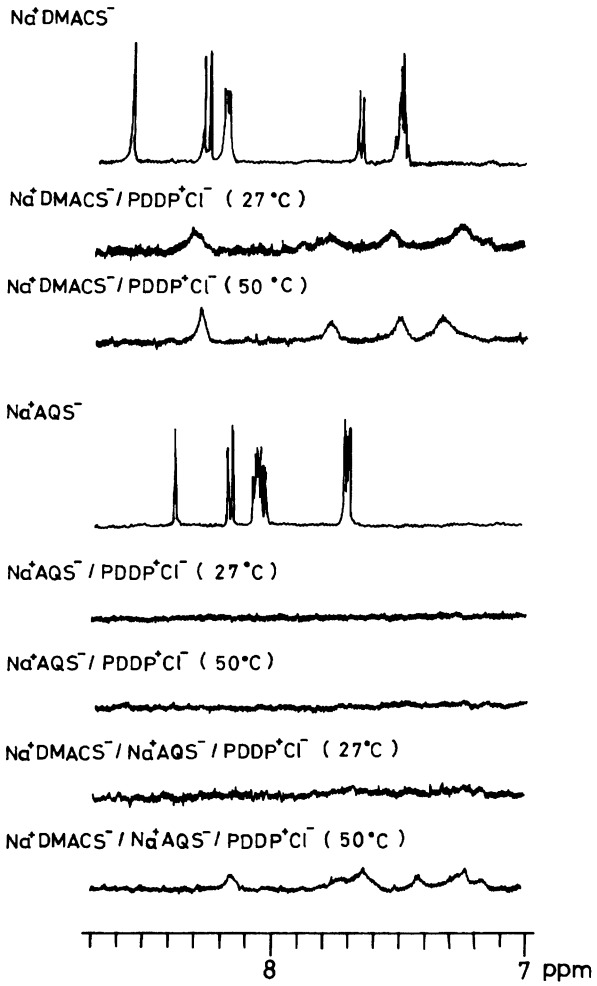


Fig. 5. ^1H NMR spectra of Na^+DMACS^- and Na^+AQS^- in D_2O solution in the presence and absence of $PDDP^+Cl^-$. $[Na^+DMACS^-]=3.34\times10^{-4}$ M, $[Na^+AQS^-]=3.36\times10^{-4}$ M, $[PDDP^+Cl^-]=8.67\times10^{-4}$ M.

the polymer. The above results can be explained reasonably as follows. The CT complex strongly interacts with the polyion because of the CT interaction between $DMACS^-$ and AQS^- on the polyion. Thus, the binding of the CT complex to the polyion is not influenced by the addition of small amounts of NaCl (ca. 1×10^{-3} M) is added to the system, the charges on the polyion are shielded by an excess of NaCl condensed around it. As a result of the shielding of charges on the polyion, both $DMACS^-$ and AQS^- are preferentially removed from the polyion moieties. Concurrently, the CT complexation is also prevented by the separation of $DMACS^-$–AQS^- pairs.

Stacking Interaction between Aromatic Counterions around the Polyion. The NMR technique is suitable for clarifying the stacking interaction (including the CT interaction) of aromatic counterions around the polyion.[10,12,13] When aromatic counterion associate with each other around the polyion, an intermolecular ring current shift should be observed in the counterion signals. The ^1H NMR spectra of Na^+DMACS^-, Na^+AQS^-, and the mixture of Na^+DMACS^- and Na^+AQS^- in D_2O solution in the presence and absence of $PDDP^+Cl^-$ are shown in Fig. 5. In the presence of $PDDP^+Cl^-$, the ^1H signals of $DMACS^-$ exhibit a ring current shift with a line broadening. And the line broadening of the ^1H signals of Na^+AQS^- and the mixture of Na^+DMACS^- and Na^+AQS^- in $PDDP^+Cl^-$ solution are significant, they disappear at room temperature. These results suggest that both $DMACS^-$ and AQS^- stack with each other on the polyion and that the CT complex between $DMACS^-$ and AQS^- is formed when they coexist in the polymer solution. In addition, if we judge from the marked broadening of the aromatic proton signals, the motion of the aromatic counterions is highly restricted due to the strong stacking interaction between the counterions bound to the polyion electrostatically. The stronger the interaction between aromatic counterions bound to the polyion is, the more remarkable the broadening of the ^1H signals of the aromatic counterions is. As is shown in Fig. 5, even at 50 °C the ^1H signals of Na^+AQS^- in the presence of $PDDP^+Cl^-$ did not appear, indicating the stable stacking interaction between AQS^- 's bound to the polyion. On the other hand, in the $PDDP^+Cl^-/Na^+DMACS^-/Na^+AQS^-$ system, the marked broadening of ^1H signals of the aromatic counterions is slightly dissolved at 50 °C. These results show that the strength of the interaction between aromatic counterions in $PDDP^+Cl^-$ solution is in this order; the interaction between AQS^- 's > the interaction between $DMACS^-$ and AQS^- (CT interaction)

> the interaction between $DMACS^-$'s. The carbonyl groups at the 9- and 10-positions of AQS^- have a permanent dipole because of their mesomeric effect. The interaction between AQS^- 's, therefore, seems to be stabilized via dipole–dipole and/or dipole-induced dipole interactions.[18] Thus, it may be concluded that in $PAAH^+Cl^-$ solution, $DMACS^-$ can be bound to the aggregate of AQS^- through CT interaction to form the 1:2 CT complex. However, in aqueous solution of $PDDP^+Cl^-$, the 1:1 CT complex alone is formed because the polyion can not take on a suitable local conformation for 1:2 complexation, as described previously.

Structure of the CT Complex between $DMACS^-$ and AQS^- around $PDDP^+$. As is shown in Fig. 5, in the $PDDP^+Cl^-/Na^+DMACS^-/Na^+AQS^-$ system, a marked broadening of ^1H signals of the aromatic counterions is observed. Thus, it is not possible to determine the structure of the CT complex between $DMACS^-$ and AQS^- around $PDDP^+$ on the basis of the ^1H NMR data. We tried to infer the structure of the CT complex with the aid of the symmetry of the HOMO of $DMACS^-$ and the LUMO of AQS^-. Generally, the stabilization of CT interactions depends on the overlap between the occupied orbitals of donor molecules and the unoccupied orbitals of acceptor molecules. The CT interaction is most outstanding when the overlap of the orbitals of donor and acceptor molecules is greatest. This means that CT interactions are sensitive to the relative orientation of donor and acceptor molecules.[19,20] Here, we consider the overlap of the HOMO of $DMACS^-$ (donor) and the LUMO of AQS^- (acceptor), which most strongly contribute to the stabilization of the CT complexation. The molecular orbital coefficients of the HOMO of $DMACS^-$ and the LUMO of AQS^- calculated by MNDO method[15,16] are schematically depicted in Fig. 6. Taking into consideration the facts that the interaction between $PDDP^+$ and aromatic counterions ($DMACS^-$, AQS^-) is essentially electrostatic and that the complexation between $DMACS^-$ and AQS^- possessing the same charge ($-SO_3^-$) is interfered with to some extent by the electrostatic repulsion, we propose in Scheme 1 a plausible structure for the CT complex between $DMACS^-$ and AQS^- around $PDDP^+$. In this model, the aromatic rings of $DMACS^-$ and AQS^- are fully overlapped with

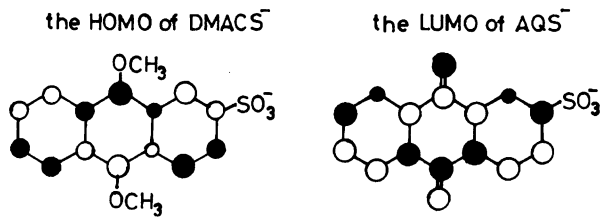
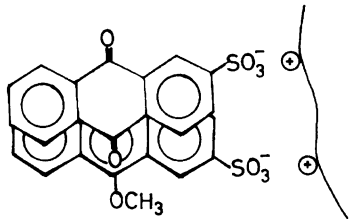


Fig. 6. The molecular orbital coefficients of the HOMO of $DMACS^-$ and the LUMO of AQS^-.



Scheme 1. A plausible structure of the CT complex between $DMACS^-$ and AQS^- around the polycation.

each other at the intermolecular plane-to-plane distance over the range 3.2—3.5 Å,[21] matching the symmetry of the HOMO of $DMACS^-$ and the LUMO of AQS^-. When the aromatic rings of $DMACS^-$ and AQS^- are overlapped with each other as shown in Scheme 1, the symmetry-allowed interaction between the HOMO of $DMACS^-$ and the LOMO of AQS^- is entirely achieved.

Viscosity Behavior of $PDDP^+Cl^-$ in Aromatic Salt Solution. The viscosity of aqueous solutions of polyelectrolytes is strongly dependent upon the conformation of the polymeric chain. This conformation is in turn dependent on the environment (e.g., ionic strength) sensed by the macromolecules.[22,23]

Addition of Na^+DMACS^-/Na^+AQS^- (1:1) to $PDDP^+Cl^-$ solution causes a sharp decrease in viscosity. Figure 7 shows this effect on the reduced viscosity of an aqueous solution of $PDDP^+Cl^-$. The addition of equivalent amounts of NaCl to the $PDDP^+Cl^-$ solution also causes a decrease in the viscosity, but its change is less pronounced than that observed when Na^+DMACS^-/Na^+AQS^- is added. The sharp decrease in viscosity upon addition of Na^+DMACS^-/Na^+AQS^- is attributed to a coiling of the initially more extended polyelectrolyte chain. This indicated that the effect on the viscosity should be interpreted in terms of coiling of the chain that accompanies the CT complexation between $DMACS^-$ and AQS^-

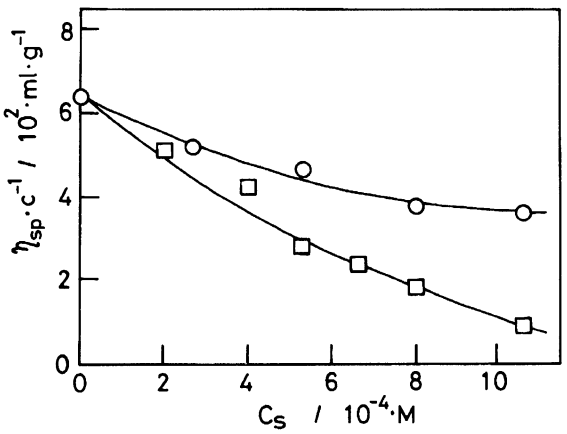


Fig. 7. Effect of the addition of NaCl (○) and Na^+DMACS^-/Na^+AQS^- (1:1) (□) on the reduced viscosity of an aqueous solution of $PDDP^+Cl^-$ (5.457×10^{-4} g ml^{-1}) at 25 °C.

Table 1. Reduced Viscosity Values of $PDDP^+Cl^-$ in Na^+DMACS^-/Na^+AQS^- Solutions

X[a)]	η_{sp}/c ($ml\,g^{-1}$)
0	237.9
0.5	275.3
1	338.8

a) $X=[Na^+DMACS^-]/([Na^+DMACS^-]+[Na^+AQS^-])$
$[PDDP^+Cl^-]=5.457\times10^{-4}$ $g\,ml^{-1}$ (3.333×10^{-3} M)
$[Na^+DMACS^-]+[Na^+AQS^-]=5.333\times10^{-4}$ M.

around $PDDP^+$. The CT complex strongly interacts with the polyion, which leads to the coiling of the polymer chain.

Then, to elucidate the mutual relation between the conformation of the polymer chain and the binding of the aromatic counterions to the polyion, we compared the reduced viscosities of $PDDP^+Cl^-$ in aqueous Na^+DMACS^-, Na^+AQS^-, and Na^+DMACS^-/Na^+AQS^- (1:1) solutions. The values are summarized in Table 1. Since the ionic strength is equal in all three systems, the reduced viscosities should reflect the strength of the binding of the aromatic counterions to the polyion. The reduced viscosities decrease in the order of Na^+AQS^- system > Na^+DMACS^-/Na^+AQS^- (1:1) system > Na^+DMACS^- system. This order agrees with that of the strength of the interaction between aromatic counterions bound to the polyion estimated by ^1H NMR (Fig. 5). This shows that the binding of aromatic counterions to the polyion depends on the strength of the association between aromatic counterions bound to the polyion. When the aromatic counterions are bound to the polyion, the stacking interaction between them enhances the counterion binding to the polyion. Therefore, the stacked aromatic counterions strongly interact with the polyion, which leads to the decrease in viscosity of the polyion (the contraction of the polyion chain).

References

1) F. Oosawa, "Polyelectrolyte," Marcel Dekker, New York (1971).
2) S. Miyamoto and N. Imai, *Biophys. Chem.*, **11**, 91 (1980).
3) M. Satoh, E. Yoda, T. Hayashi, and J. Komiyama, *Macromolecules*, **24**, 1123 (1991).
4) W. G. Herkstroeter, P. A. Martic, S. E. Hartman, J. L. R. Williams, and S. Farid, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 2473 (1983).
5) M. K. Pal and S. Basu, *Makromol. Chem.*, **27**, 69 (1958).
6) A. N. Dey and S. R. Palit, *Indian J. Chem.*, **5**, 191 (1967).
7) T. Takagishi, Y. Nakata, and N. Kuroki, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 807 (1974).
8) V. Vilaglina, L. Costanino, and R. Sartorio, *J. Phys. Chem.*, **80**, 959 (1976).
9) K. Yamaoka and M. Takatsuki, *Bull. Chem. Soc. Jpn.*, **51**, 3182 (1978).
10) T. Itaya, K. Ueda, and H. Ochiai, *Polym. J.*, **24**, 539 (1992).
11) T. Itaya, K. Ueda, H. Ochiai, and A. Imamura, *Polym. J.*, **25**, 545 (1993).
12) T. Itaya, H. Ochiai, T. Aoyama, K. Ueda, and A. Imamura, *J. Polym. Sci., Polym. Phys. Ed.*, **32**, 171 (1994).
13) T. Itaya, K. Ueda, H. Ochiai, and A. Imamura, *Macromolecules*, **26**, 6021 (1993).
14) T. Itaya, Y. Kawabata, H. Ochiai, K. Ueda, and A. Imamura, *Bull. Chem. Soc. Jpn.*, **67**, 1538 (1994).
15) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1979).
16) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1979).
17) D. Job, *Ann. Chem. Phys.*, **10**(9), 113 (1928).
18) T. Sato, T. Ogawa, and K. Kano, *J. Phys. Chem.*, **88**, 3678 (1984).
19) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1951).
20) R. S. Mulliken, *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956).
21) C. K. Prout and B. Mayah, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1072 (1972).
22) A. Takahashi, T. Kabo, and M. Nagasawa, *J. Phys. Chem.*, **71**, 2001 (1967).
23) M. Kowblansky and P. Zema, *Macromolecules*, **14**, 1451 (1981).