

A Theoretical Treatment of Charge-Transfer Interaction in an Aqueous Solution of Polyelectrolyte

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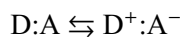
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ABSTRACT: Molecular orbital theory was adopted to explain theoretically the charge-transfer (CT) complexation of aromatic ions (donors) with 9,10-anthraquinone-2-sulfonate (acceptor) in an aqueous solution of polyelectrolyte. By the approximation of the theory, a distinct linear relation between the energies of the CT absorption band and ionization potentials of the donor molecules has been derived although the stoichiometric ratios of CT complexes which formed around the polyion were different.

KEY WORDS Charge-Transfer / Molecular Orbital Method / Polyelectrolyte / Counterion Binding /

Theoretical researches of molecular complexes have become active since Mulliken combined the old concepts of molecular compound and established a new theory.¹ Prior to his research Weiss had pointed out that molecular complexes have an ionic structure D^+A^- , so that the lower the ionization potential for an electron donor is, and the higher the electron affinity for an electron acceptor is, the more easily the molecular complex is formed.² Brackmann regarded the structure of complex as a resonance hybrid to which no-bond and dative structures contribute.³



Based upon these concepts, Mulliken presented a quantum mechanical theory on the charge-transfer (CT) spectra of molecular complex.¹ Recently, CT interaction between aromatic compounds in aqueous media is of interest in connection with studies for host-guest chemistry, enzyme-coenzyme reactions, protein stability, and occurrence of functionality in biological systems. However, most experimental studies of CT complexes so far have been made in organic solution, reports in aqueous solution are relatively rare,⁴ due to low solubility of aromatic compounds to an aqueous solution.

In the previous works,^{5–7} by utilizing the counterion binding of polycations we have succeeded in studying the CT interactions between some aromatic counterions (donors) with 9,10-anthraquinone-2-sulfonate (2-AQS⁻) (acceptor) in the presence of poly(allylammonium chloride) (PAAH⁺Cl⁻). The donors used in these studies were 9,10-dimethoxyanthracene-2-sulfonate (DMACS⁻), 1-pyrenesulfonate (PyS⁻), anthracene-2-sulfonate (ACS⁻), and indoxyl sulfate (InS⁻).

In general, CT interaction occurs through partial electron transfer from the highest occupied molecular orbital of donor molecule to lowest unoccupied molecular orbital of acceptor molecule. So, quantum chemistry theory may make possible to explain theoretically our studies on CT interaction between these aromatic counterions in aqueous solution.

The purpose of this paper is to present a regularity which is useful for predicting empirically the wavelengths and designing novel type CT complexes. From quantum chemistry treatment, it has become feasible to explain a linear relation between the energy of the observed CT band and the calculated ionization potentials of donors although stoichiometric ratios of the CT complexes formed around the polyion were different in the four donor systems.

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EXPERIMENTAL

Materials

Samples used in this study were poly(allylammonium chloride) (PAAH⁺Cl⁻), sodium 9,10-dimethoxyanthracene-2-sulfonate (Na⁺DMACS⁻: donor), sodium anthracene-2-sulfonate (Na⁺ACS⁻: donor), sodium 1-pyrenesulfonate (Na⁺PyS⁻: donor), potassium indoxyl sulfate (3-indolyl hydrogen sulfate) (K⁺InS⁻: donor), and sodium 9,10-anthraquinone-2-sulfonate (Na⁺2-AQS⁻: acceptor). Sample solutions for the absorption spectroscopic measurements were prepared by the method as described previously.⁵⁻⁷ Deionized and distilled water was used as a solvent. Concentrations were expressed as the residue molar concentration (3.0×10^{-4} M) for the polymers and as molar concentration (1.0×10^{-4} M) for counterions (1 M = 1 mol dm⁻³).

Measurements

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

Molecular orbital (MO) calculations were performed on DMACS⁻, ACS⁻, PyS⁻, and InS⁻ using the semi-empirical MO calculation program of MOPAC 97⁸ with COSMO (Conductor-like Screening Model) method.⁹ The ionization potentials of the four molecules were calculated using the fully optimized structures with the PM3 Hamiltonian.

RESULTS AND DISCUSSION

Charge-transfer (CT) complex formation between electron-donors and electron-acceptors is often accompanied by a visual color change of the solution, and appearance of broad absorption band (CT band) not found in either the donors or acceptors alone. As reported in the previous papers,⁵⁻⁷ we also observed the color changes and the CT bands in the Na⁺DMACS⁻/Na⁺2-AQS⁻/PAAH⁺Cl⁻ (orange), Na⁺ACS⁻/Na⁺2-AQS⁻/PAAH⁺Cl⁻ (pale orange), Na⁺PyS⁻/Na⁺2-AQS⁻/PAAH⁺Cl⁻ (deep yellow), and K⁺InS⁻/Na⁺2-AQS⁻/PAAH⁺Cl⁻ (pale yellow) systems, respectively. These phenomena are attributed to the formation of CT complexes between donors and 2-AQS⁻ which are accumulated around PAAH⁺. However, in the absence of PAAH⁺Cl⁻, these changes were not detected in the condition of [donors] = [acceptor] = 1.0×10^{-4} M. Especially, poly-electrolyte seems to play an important role to produce a

Table I. Maxima of charge-transfer bands for complexes of aromatic ions with 9,10-anthraquinone-2-sulfonate ion in the aqueous solution of poly(allylammonium chloride)

Donor	Maximum of CT band		Ionization potential, eV
	λ_{CT} , nm	$h\nu_{CT}$, eV	
DMACS ⁻	480	2.58	8.06
ACS ⁻	460	2.70	8.56
PyS ⁻	450	2.76	8.64
InS ⁻	410	3.02	9.20

special environment for CT complexation in the condition for the above low concentration. In our studies, the aromatic counterions 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.

By the approximation of Mulliken theory,¹ the parabolic or linear relation between the energy of the CT band ($h\nu_{CT}$) and the ionization potential of the donor (I_p) has been derived and experimentally confirmed.¹⁰⁻¹²

$$h\nu_{CT} = aI_p + b \quad (1)$$

Here, a , b , are assumed to be characteristic constants for the CT complexes of any one acceptor. Eq 1 is less strictly than Mulliken's theory, however, for weak complexes formed around the polyion in our studies, this equation can be a sufficient approximation.

If the coefficients in this equation are known for complexes of various acceptors, the positions of the CT bands in the absorption spectra of the complexes can be predicted from the ionization potentials of the donors. Therefore, it is desirable to obtain these relations in many series of complexes. Thus far these relations were confirmed for the various CT complexes in organic solutions,¹³ and the above equation so far reported is only applicable to the 1:1 type CT complexation. However, none of studies have been reported on these relations in aqueous solution. The observed results are summarized in Table I, along with the ionization potentials of the DMACS⁻, ACS⁻, PyS⁻, and InS⁻, which were calculated by MOPAC COSMO method. Using these values, we obtained the following relation for the CT complexes of the aromatic ions with 2-AQS⁻ in Table I.

$$h\nu_{CT} = 0.390I_p - 0.593 \quad eV \quad (2)$$

Figure 1 shows a distinct linear relation between the energies of the observed CT bands and the calculated ionization potentials of them. DMACS⁻, having the lowest ionization potential, indicated the lowest energy of CT band, whereas, InS⁻, having the highest ionization potential, indicated the highest CT band energy.

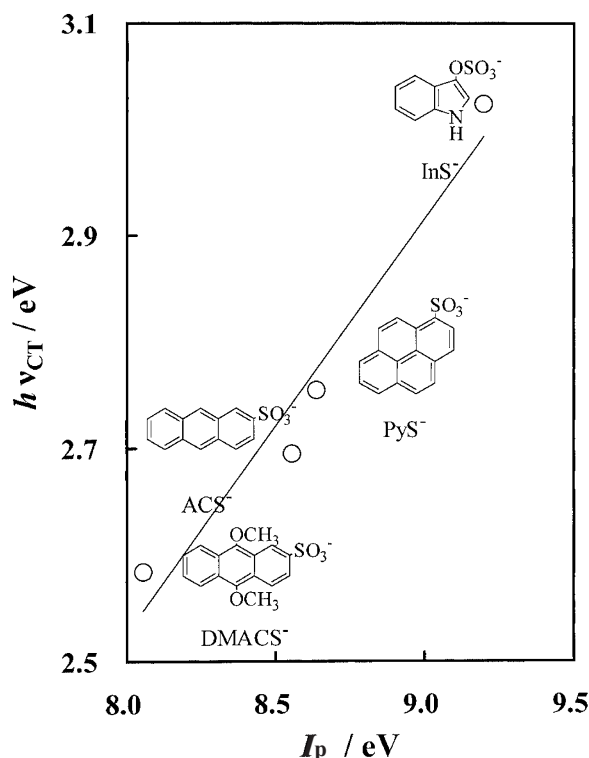


Figure 1. Plot of energy of charge-transfer absorption band vs. ionization potential. DMACS⁻: dimethoxyanthracenesulfonate, ACS⁻: anthracenesulfonate, PyS⁻: pyrenesulfonate, InS⁻: indoxyl sulfate.

Table II. Types (donor: acceptor) of charge-transfer complexes with 2-AQS⁻ (acceptor)

DMACS ^{-a}	1:2
ACS ^{-b}	1:2
PyS ^{-b}	1:1
InS ^{-c}	2:1

^aData from ref 5. ^bData from ref 6. ^cData from ref 7.

In the previous papers,⁵⁻⁷ we determined the stoichiometry of the CT complexes by means of a continuous variation method as shown in Table II. It is interesting that in our studies the stoichiometries of the complexes of not one to one but one-to-two (asymmetric type), two-to-one (sandwich type) were observed. That is, the 1:2-type CT complexes (DMACS⁻: 2-AQS⁻, ACS⁻: 2-AQS⁻), the 1:1-type (PyS⁻: 2-AQS⁻), and the 2:1-type (InS⁻: 2-AQS⁻) was preferentially formed, respectively. In the case of the former 1:2-type, donor and acceptor were observed as an aggregate of D-A-A and thus the contribution from the acceptor molecule apart from the donor molecule could be neglected. This enabled us to treat the 1:2-type CT complexes by the same manner as the case for 1:1-type and therefore the HOMO energies of these two types of complexes could be related to the ν_{CT} in a same plot.

On the other hand, for the 2:1-type in the InS⁻/2-

AQS⁻/PAAH⁺ system, the two donor molecules are considered to be combined symmetrically in the both sides of the acceptor molecule, which is in D-A-D arrangement. Therefore, it seems to be difficult to apply the same elucidation as that done by the 1:1(D-A) or 1:2(D-A-A) formation to the 2:1(D-A-D) case, since the magnitude of the CT interaction in D-A-D complex can roughly be considered about two times that of the D-A complex. This makes it difficult to compare the relation between the energies of the observed CT band ($h\nu_{CT}$) and the calculated ionization potentials (I_p) by utilizing the same plots as those obtained in the D-A and D-A-A systems.

However, it was derived from quantum chemical treatment that these three types of arrangements, D-A, D-A-A, and D-A-D CT complexes, can approximately be compared between the $h\nu_{CT}$ and the I_p of donor molecules under the condition that the acceptor molecule is the same for all the cases as follows.

For the 1:2-type (D-A-A) CT complex, the reason for the neglect ion of the effect from remote acceptor molecule can easily be understood by utilizing the matrix expression between non-interacting state and charge-transfer state. That is, the wave function including CT interaction can be expressed by

$$\psi = a\psi(D \cdot A \cdot A) + b\psi(D^+ \cdot A^- \cdot A) + c\psi(D^+ \cdot A \cdot A^-) + \dots \quad (3)$$

Neglecting the higher order terms in the expansion, the secular equation to determine the coefficients a , b , and c can be expressed by

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E & H_{13} - S_{13}E \\ H_{12} - S_{12}E & H_{22} - E & H_{23} - S_{23}E \\ H_{13} - S_{13}E & H_{23} - S_{23}E & H_{33} - E \end{vmatrix} = 0 \quad (4)$$

where, matrix elements are defined as

$$H_{11} = \int \psi^*(D \cdot A \cdot A)H\psi(D \cdot A \cdot A)d\tau \quad (5)$$

$$H_{22} = \int \psi^*(D^+ \cdot A^- \cdot A)H\psi(D^+ \cdot A^- \cdot A)d\tau \quad (6)$$

$$H_{33} = \int \psi^*(D^+ \cdot A \cdot A^-)H\psi(D^+ \cdot A \cdot A^-)d\tau \quad (7)$$

$$H_{12} = \int \psi^*(D \cdot A \cdot A)H\psi(D^+ \cdot A^- \cdot A)d\tau \quad (8)$$

$$H_{13} = \int \psi^*(D \cdot A \cdot A)H\psi(D^+ \cdot A \cdot A^-)d\tau \cong 0 \quad (9)$$

$$H_{23} = \int \psi^*(D^+ \cdot A^- \cdot A)H\psi(D^+ \cdot A \cdot A^-)d\tau \cong 0 \quad (10)$$

The overlap matrices are also expressed in the same manner. In the eqs 5-10, the terms H_{13} and H_{23} as well

as S_{13} and S_{23} can be neglected, because the interaction not only between D and remote A but also between neighboring acceptors can be expected to be very small. Therefore, the matrix of eq 4 can be reduced to two by two as

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E & \cong 0 \\ H_{12} - S_{12}E & H_{22} - E & \cong 0 \\ \cong 0 & \cong 0 & H_{33} - E \end{vmatrix} = 0 \quad (11)$$

By solving the above equation, it can be derived that the energy change in the ground state energy is given by

$$\Delta_N^{DAA} = -\frac{(H_{12} - S_{12}H_{11})^2}{H_{22} - H_{11}} = \Delta_N^{DA} \quad (12)$$

from the completely non-interacting state H_{11} and the excited state is by

$$\Delta_E^{DAA} = \frac{(H_{12} - S_{12}H_{22})^2}{H_{22} - H_{11}} = \Delta_E^{DA} \quad (13)$$

from the charge transfer state H_{22} . These results are the same as those solved for 1:1 (D-A) CT complex and therefore we have discussed in the previous paper⁷ the relationship between the ν_{CT} and the HOMO levels for the 1:1 and 1:2 complexes at a time.

In a similar manner, for the 2:1 (D-A-D) formation of the present case, the wave function for the total system can be given by

$$\begin{aligned} \psi = & a\psi(D \cdot A \cdot D) + b\psi(D^+ \cdot A^- \cdot D) \\ & + c\psi(D \cdot A^- \cdot D^+) + \dots \end{aligned} \quad (14)$$

Neglecting the higher order terms, the secular equation for this wave function is expressed by

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{22} - E & \cong 0 \\ H_{12} - S_{12}E & \cong 0 & H_{22} - E \end{vmatrix} = 0 \quad (15)$$

where the following definitions are used:

$$H_{11} = \int \psi^*(D \cdot A \cdot D)H\psi(D \cdot A \cdot D)d\tau \quad (16)$$

$$H_{22} = \int \psi^*(D^+ \cdot A^- \cdot D)H\psi(D^+ \cdot A^- \cdot D)d\tau \quad (17)$$

$$H_{33} = \int \psi^*(D \cdot A^- \cdot D^+)H\psi(D \cdot A^- \cdot D^+)d\tau = H_{22} \quad (18)$$

$$H_{12} = \int \psi^*(D \cdot A \cdot D)H\psi(D^+ \cdot A^- \cdot D)d\tau = H_{13} \quad (19)$$

$$H_{23} = \int \psi^*(D^+ \cdot A^- \cdot D)H\psi(D \cdot A^- \cdot D^+)d\tau \cong 0 \quad (20)$$

The determinant of eq 15 is reduced to the two equations

$$H_{22} - E = 0 \quad (21)$$

and

$$\begin{vmatrix} H_{11} - E & \sqrt{2}(H_{12} - S_{12}E) \\ \sqrt{2}(H_{12} - S_{12}E) & H_{22} - E \end{vmatrix} = 0 \quad (22)$$

It can be seen that the eq 22 has the same form as the determinant for 1:1-type (D-A) complex other than that the off-diagonal elements are scaled by $\sqrt{2}$. Thus, the eigenvalues for this determinant can easily be found in the same form as the D-A type and the energy change in the ground state results in

$$\Delta_N^{DAD} = 2\Delta_N^{DA} \quad (23)$$

This means that the energetic change in the ground state for D-A-D type complex can be estimated by two times of those for D-A type complex. The energy in the excited state is given by eq 21 and thus the energy change becomes zero. In general, it is known that the energy changes by the interaction between two molecules of D and A provide very small values for the ground state compared to the difference between H_{11} and H_{22} . That is, the following equation can be applied:

$$h\nu^{DAD} = I_p - E_A + 2\Delta_N^{DA} \quad (24)$$

where I_p means the ionization potential of donor molecule and E_A the electron affinity of acceptor molecule. On the other hand, if $S_{12}H_{11} \cong S_{12}H_{22}$ in eqs 12 and 13, Δ_N^{DA} can be nearly equal to $-\Delta_E^{DA}$ in the

$$h\nu^{DA} = I_p - E_A + \Delta_N^{DA} - \Delta_E^{DA} \quad (25)$$

This may lead to nearly equivalent ν_{CT} for D-A and D-A-D, that is

$$h\nu^{DAD} \cong h\nu^{DA} \quad (26)$$

and therefore can be a reason that Figure 1 gives a linear relation between the observed $h\nu_{CT}$ and the calculated ionization potentials regardless of the kind of donor molecule included. It should be noticed, however, that the vertical transition through D-A-D from symmetric ground state to symmetric excited state is forbidden. From the experimental condition that the complexes are combined irregularly on the polymer chain, we suppose that the molecules in D-A-D are stacked with various orientations and the wave functions for this complex are given anti-symmetrically around the central acceptor molecule, revealing the CT spectrum approximately based on the wave function given by eq 14. At least, it was shown that eq 13 for D-A-A and eq 23 for D-A-D CT complexes, these were predicted from experimental

data, can be also elucidated mathematically under some assumptions.

As a conclusion of our work, it may be possible to predict CT complexation between 2-AQS⁻ by calculating the ionization potential of donor molecules before measurements the absorption spectroscopy or preparations of them, and to apply for the conducting materials correlating with the polymers in the near future.

REFERENCES

1. R. S. Mulliken and W. B. Pearson, "Molecular Complex", Wiley-Interscience, John Wiley & Sons, Inc., New York, N.Y., 1969.
2. J. Weiss, *J. Chem. Soc.*, 245, (1942).
3. W. Brackmann, *Rec. Trav. Chim.*, **68**, 147 (1959).
4. W. R. Gilkerson and A. L. Mixon, *J. Solution Chem.*, **19**, 491 (1990).
5. T. Itaya, Y. Kawabata, H. Ochiai, K. Ueda, and A. Imamura, *Bull. Chem. Soc. Jpn.*, **67**, 1538 (1994).
6. Y. Kawabata, T. Itaya, Y. Sasaki, H. Ochiai, K. Ueda, and A. Imamura, *Bull. Chem. Soc. Jpn.*, **69**, 2453 (1996).
7. Y. Kawabata, T. Itaya, K. Ueda, H. Ochiai, Y. Aoki, and A. Imamura, *Polym. J.*, **35**, 50 (2003).
8. J. J. P. Stewart, Fujitsu Ltd., Tokyo, Japan (1998).
9. A. Klamt and G. Schuurmann, *J. Chem. Soc., Perkin Trans.*, **2**, 799 (1993).
10. S. H. Hasting, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).
11. H. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).
12. R. Foster, *Tetrahedron*, **10**, 96 (1960).
13. M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **35**, 1609 (1962).