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Complex Formation in Cationic Dye–Organic Anion Systems in Aqueous Solution

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The interaction between a cationic dye, Methylene Blue (MB), and organic anions (1-naphthalenesulfonate, 2-naphthalenesulfonate, 1-naphthaleneacetate, 2-anthracenesulfonate, 2,7-naphthalenedisulfonate, and 1,3,6-naphthalenetrisulfonate) in aqueous solution has been investigated by means of absorption and fluorescence spectra. The red shifts of the absorption and fluorescence spectra of MB caused by the addition of the organic monoanion are attributed to the 1:1 complex formation between MB and the organic anion. The thermodynamic quantities as well as the equilibrium constants for the complex formation have been determined. From the finding that the absorption spectrum of MB is not affected by the addition of ethanesulfonate, it is concluded that the complex formation is due to the interaction between the MB cation and the aromatic ring in the organic anion. The addition of polyanion (*e.g.*, 2,7-naphthalenedisulfonate) in the low-concentration range accelerates the dimerization of MB; whereas, in the high-concentration range, the formation of the 1:1 complex rather than the MB dimer is dominant. Studies on the complex formation with monoanions have also been made for Rhodamine 6G, Pyronine G, Safranin T, and Crystal Violet, and similar results to that for MB have been obtained.

Studies regarding the interaction between organic cations and organic ions are roughly divided into four categories. The first is the area related to the self-association of a dye in aqueous solution.1–7) This association is due to an interaction between the organic ions of the same kind having a positive charge. Since the concentration ratio of the dimer to the monomer of the dye increases with an increase in the dye concentration, the electronic absorption of the dye does not follow the Beer-Lambert law.

The second is that related to the adsorption of a cationic dye on the surface of an anionic micelle, an anionic lipid membrane, or a microemulsion.8–13) This interaction is attributed to the electrostatic attraction between the cationic dye and the anionic micelle, *etc.* Since the adsorption also induces a change in the absorption and/or fluorescence spectrum of the dye, the spectral change can be used for the determination of the critical micelle concentration.8)

The third is related to a phenomenon known as metachromasy which is observed when an anionic polymer is added into a dye solution.14–19) This phenomenon is accompanied by a shift of the first electronic absorption band to shorter wavelengths. Inorganic anions have also been reported to cause metachromasy.20) Metachromasy is mainly elucidated either by the association of dye under the influence of the anionic polymer or by the interaction of dye with added anion.

The fourth is that related to a complex formation between an organic cation and an organic anion. By the addition of *N*-hexadecylpyridinium chloride (below its critical micelle concentration), a solution of 2-naphtholate becomes pale yellow and its fluorescence is quenched.21) Both the appearance of the color and the fluorescence quenching have been explained in terms of complex formation.

Gicquel *et al.* have studied the complex formation of Crystal Violet with sulfonated azo derivatives by means of resonance Raman and electronic absorption spectra.22) They suggested that the blue shift of the absorption band of Crystal Violet is related to the approach of the sulfonate group in the azo dye to the central carbon in Crystal Violet.

Solvent effects on the charge-transfer band energies of organic cation–organic anion complexes have been investigated by Beaumont and Davis.23) Compared with organic cation–iodide complexes, the charge-transfer bands of organic cation–organic anion complexes are notably less solvent sensitive, this insensitivity being particularly marked in cation–neutral molecule complexes.

The pressure effect on the complex formation between 1-methyl-3-(methoxycarbonyl)pyridinium cation and 8-chlorotheophyllinate anion has been studied by Williams.24) The complex formation of methylviologen with a porphyrin derivative has been pointed out.25)

Organic charge-transfer salts composed of an organic cation (pyrylium or thiopyrylium) and an organic anion (1,1,3,3-tetracyanopropenide or tricyanomethanide) have been investigated by means of the absorption spectra.26) The 1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadienide anion is also known to form charge-transfer salts with tropylium, 2,4,6-trimethylpyrylium, *N*-methylpyridinium cations, *etc.*27)

In spite of these studies, there is little information concerning the interaction between organic cations and organic anions. Thus, in selecting cationic dyes as organic cations, we have investigated an interaction between the dyes and the organic anions, naphthalenesulfonates, anthracenesulfonate, *etc.* in aqueous solutions.

Experimental

Methylene Blue (MB), purchased from Wako, was recrystallized twice from water.[28] Rhodamine 6G obtained from Tokyo Kasei, Pyronine G from Chroma, and Safranin T from Tokyo Kasei were recrystallized twice from ethanol. Crystal Violet from Tokyo Kasei was recrystallized twice from water. Sodium 1-naphthalenesulfonate (1NS) from Tokyo Kasei and sodium 2-naphthalenesulfonate (2NS) from Wako were recrystallized twice from a water–ethanol mixture. Sodium 1-naphthaleneacetate (1NA) from Wako was recrystallized twice from a 1-butanol–hexane mixture. Sodium 2-anthracenesulfonate (2AS) was synthesized from sodium anthraquinone-2-sulfonate,[29] and recrystallized three times from water. Disodium 2,7-naphthalenedisulfonate (NDS) and trisodium 1,3,6-naphthalenetrisulfonate (NTS) were purchased from Tokyo kasei, and recrystallized twice from a water–ethanol mixture.

Absorption spectra were measured with a Hitachi 124 or a Shimadzu 260 spectrophotometer. The fluorescence spectra were recorded on a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier. The spectral response of the spectrofluorometer was determined by the previous method.[30] Measurements were made at 25 °C unless otherwise stated. In order to avoid the concentration change of a dye caused by adsorption on a glass surface, all the glass wares (volumetric flasks, pipets, *etc.*) used for sample preparations were soaked with a dye solution, and then rinsed with water immediately before use.

Results and Discussion

Complex Formation of Methylene Blue (MB) with Sodium 2-Naphthalenesulfonate (2NS). Figure 1 shows the absorption spectra of 10^{-5} M (1 M= 1 mol dm^{-3}) aqueous solutions of MB with varying concentrations of 2NS. The absorption maximum of MB shifted to the red as the concentration of 2NS increased. Below a 2NS concentration of 5×10^{-3} M, an isosbestic point is observed at 680 nm. The spectral change presented in Fig. 1 is attributed to the 1:1 complex formation between MB and 2NS. The possibility that such a spectral change is caused by a change in pH or ionic strengths of the sample solutions can be ruled out from the findings that nearly the same spectral change was observed for buffered solutions at a pH 6.7 (0.033 M potassium dihydrogenphosphate–0.033 M disodium hydrogenphosphate) or solutions containing 0.1 M NaCl. Although the MB dimer exists even at a concentration as low as 10^{-5} M, the concentration ratio of the MB dimer to the MB monomer is calculated to be only 1.5% from the data of the equilibrium constant for the dimerization of MB.[3] Therefore, the effect of the MB dimer on the concentrations of the MB monomer and the complex can be neglected under the conditions of the low concentration of the complex. This explains the appearance of the isosbestic point in the absorption spectra of the MB solutions containing 2NS below 5×10^{-3} M.

The absorption spectrum of MB did not change by the addition of sodium ethanesulfonate up to 0.1 M. This indicates that the interaction between MB and 2NS to form the complex is that between an MB cation and a naphthalene ring in 2NS rather than that between an MB cation and a sulfonate group in

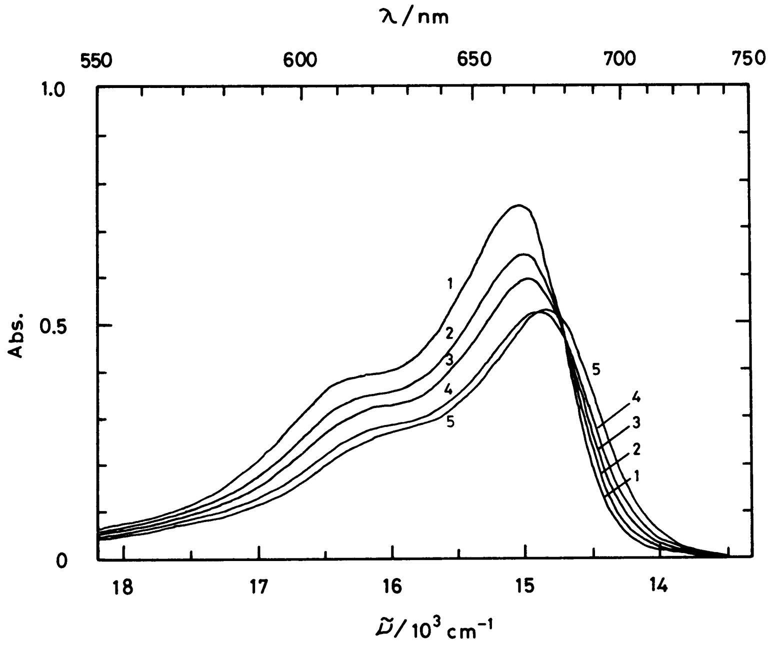

Fig. 1. Absorption spectra of MB (10^{-5} M) in aqueous solution in the presence of 2NS. Concentration of 2NS: 1, 0 M; 2, 10^{-3} M; 3, 2×10^{-3} M; 4, 5×10^{-3} M; 5, 10^{-2} M.

2NS although the attractive force between an MB cation and a sulfonate group may play an important role in the early stage of the complexation. On the other hand, for the complexes formed between Crystal Violet and sulfonated azo derivatives, it has been suggested that the central carbon in Crystal Violet interacts with the sulfonate group in the azo dye.[22] As mentioned above, the maximum of the absorption spectrum of Crystal Violet is shifted to the blue region in contrast to the red shift of the absorption maximum in the MB-2NS system.

When the existence of the dimer of MB is ignored, the absorption-spectrum change can be analyzed by the following equation:[31]

$$\frac{[\mathrm{MB}]_0}{A-A_0}=\frac{1}{\varepsilon_1-\varepsilon_0}+\frac{1}{(\varepsilon_1-\varepsilon_0)K'}\frac{1}{[\mathrm{2NS}]}, \tag{1}$$

where A and A_0 are the absorbances in the presence and absence of 2NS, $[\mathrm{MB}]_0$ is the initial concentration of MB, ε_1 and ε_0 are the molar absorption coefficients of the 1:1 complex, MNS, and MB, K' is the equilibrium constant for the formation of MNS under the assumption of neglecting the MB dimer, and [2NS] is the initial concentration of 2NS. A plot of $[\mathrm{MB}]_0/(A-A_0)$ *vs.* 1/[2NS] at 660 nm is shown in Fig. 2 (line (a)). A straight line is obtained with the equilibrium constant K'=340 M^{-1}. In order to evaluate the more precise value of the equilibrium constant, we must take into account the existence of the MB dimer. When such a consideration is made, Eq. 1 becomes

$$\frac{[\mathrm{MB}]+[\mathrm{MNS}]}{A-A_0'}=\frac{1}{\varepsilon_1-\varepsilon_0}+\frac{1}{(\varepsilon_1-\varepsilon_0)K}\frac{1}{[\mathrm{2NS}]}, \tag{2}$$

where [MB] and [MNS] are the concentrations of the MB monomer and MNS, A_0' is the calculated absorbance of [2NS] under the assumption that MNS thoroughly dissociates to MB and 2NS without a variation of the concentration of the MB dimer, and K is the equilibrium constant for the formation of MNS. A_0', [MB], and [MNS] were calculated using the K' value estimated from a plot of Eq. 1 and the literature value of the equilibrium constant for the dimerization of MB.[3] A plot of ([MB]+[MNS])/$(A-A_0')$ *vs.* 1/[2NS] at 660 nm is shown in Fig. 2 (line (b)). The plot for Eq.2 also yields a good straight line. From the intercept and the slope, K was determined to be 400 M^{-1}, about 15% larger than K' (=340 M^{-1}). Furthermore, we tried to construct a plot for Eq. 2 using K in place of K' for the calculations of A_0', [MB], and [MNS]. However, the new value of K, thus obtained, was identical with the previous value of K obtained by the use of K'.

In order to apply an alternate method which requires no correction for the MB dimer formation, we used a dilute MB solution containing only a negligible amount of the MB dimer, although the experimental error became larger owing to the smaller absorbance of the dilute solution. For a 2×10^{-6} M MB solution, the change in the absorp-

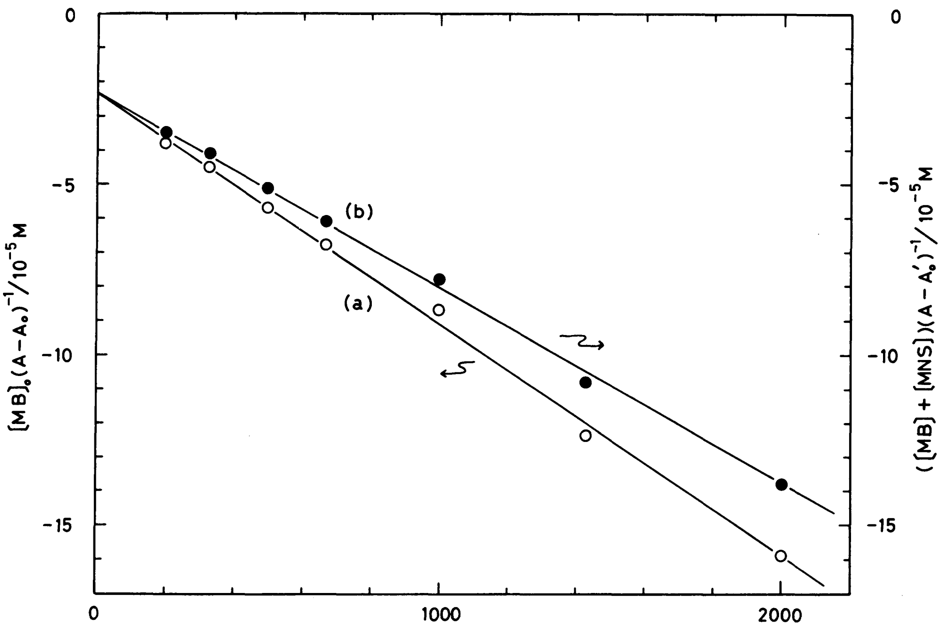

Fig. 2. (a) Plot of $[\mathrm{MB}]_0/(A-A_0)$ *vs.* 1/[2NS] at 660 nm. (b) Plot of ([MB]+[MNS])/$(A-A_0')$ *vs.* 1/[2NS] at 660 nm.

tion spectrum with the addition of 2NS was very similar to that for the 10^{-5} M MB solution. The equilibrium constant (=410 M^{-1}) evaluated from the absorption-spectrum change for the 2×10^{-6} M solutions was in excellent agreement with that of the 10^{-5} M solutions.

For the fluorescence measurements, 2×10^{-6} M solutions of MB were used to eliminate the reabsorption of fluorescence by the dye. Figure 3 shows the fluorescence spectra of MB in the absence and presence of 2NS which are normalized at the intensity maxima. With the increase in the 2NS concentration, the fluorescence intensity decreases accompanied by the red shift of the spectrum. Such changes in the fluorescence spectrum as well as the absorption spectrum are due to the complex formation between MB and 2NS. From the dependence of the fluorescence intensity on the 2NS concentration, the equilibrium constant for the complex formation was estimated by a similar method to that employed in the absorption study.[31] The equilibrium constant thus obtained is 370 M^{-1}, which agrees reasonably well with those obtained from the change in the absorbance both for the 2×10^{-6} and 10^{-5} M MB solutions. The equilibrium constants determined from the measurements of the absorbance and fluorescence intensity correspond to those in the electronic ground state and the excited state of MB, respectively. The good agreement between the equilibrium constants in the ground and excited state arises from the shortness of the fluorescence lifetime of MB.[32]

Temperature Dependence of the Equilibrium Constant. The temperature dependence of the equilibrium constants obtained from the measurements of the absorption and the fluorescence was examined over a temperature range from 3 to 43 °C. These results are shown in Fig. 4. Good straight-line relationships are obtained with the same slope and intercept for both methods. The enthalpy change ΔH and the entropy change ΔS for the complex formation are determined to be -28 kJ mol^{-1} and -46 J K^{-1} mol^{-1}, respectively.

The positive value of ΔS has been reported for the dimerization of Rhodamine B[33,34] in contrast to the negative value of ΔS usually evaluated for the aggregation of two molecules.[35–37] Generally, ΔS for the complex formation can be divided into two parts, ΔS_c and ΔS_s. Here, ΔS_c is the entropy change for the complexation which does not involve the succeeding reorientation process of solvent molecules, and ΔS_s is the entropy change for the reorientation of solvent molecules immediately after the association between two species. Because an MB cation associates with a negatively-charged 2NS molecule to form a neutral complex MNS, solvating water molecules surrounding an MNS complex may be expected to orient more randomly than those surrounding an uncomplexed, charged MB or 2NS molecule. Such a deduction leads to a positive value of ΔS_s. Our experimental result provides a negative value of ΔS for the complex formation. The implication is that the negative value of ΔS_c may prevail over the positive value of ΔS_s in the MB–2NS system, resulting in a negative value for the net ΔS.

Complex Formation of MB with Other Organic

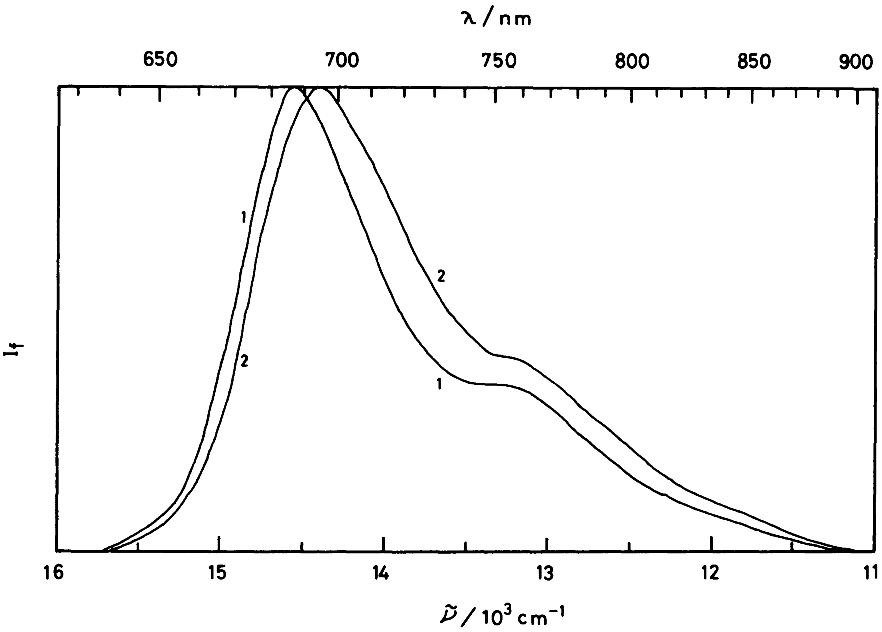

Fig. 3. Normalized fluorescence spectra of MB (2×10^{-6} M) in aqueous solution in the presence of 2NS. Concentration of 2NS: 1, 0 M; 2, 5×10^{-3} M.

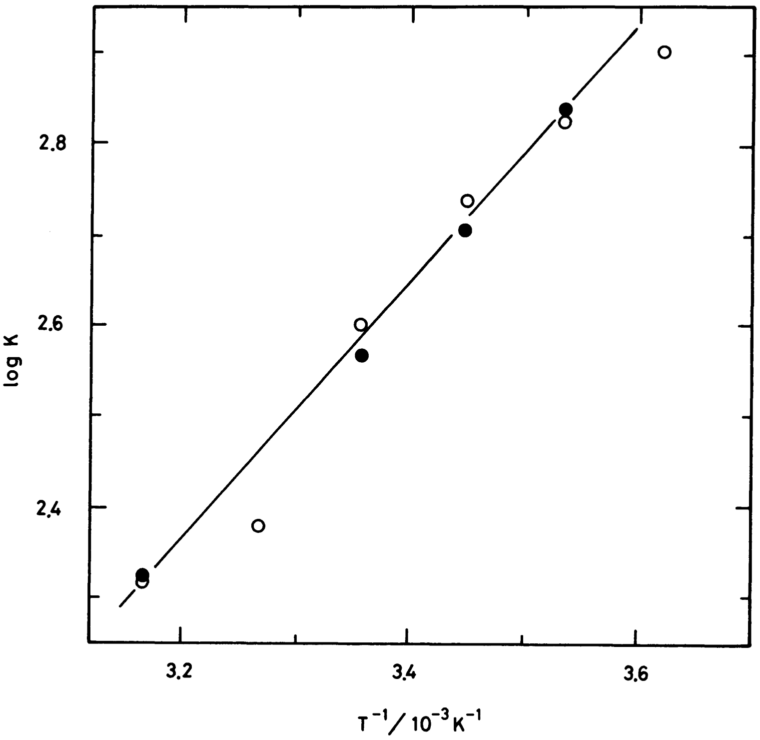

Fig. 4. Temperature dependence of K: (○) data obtained from the absorbance change in the absorption spectra; (●) data obtained from the intensity change in the fluorescence spectra.

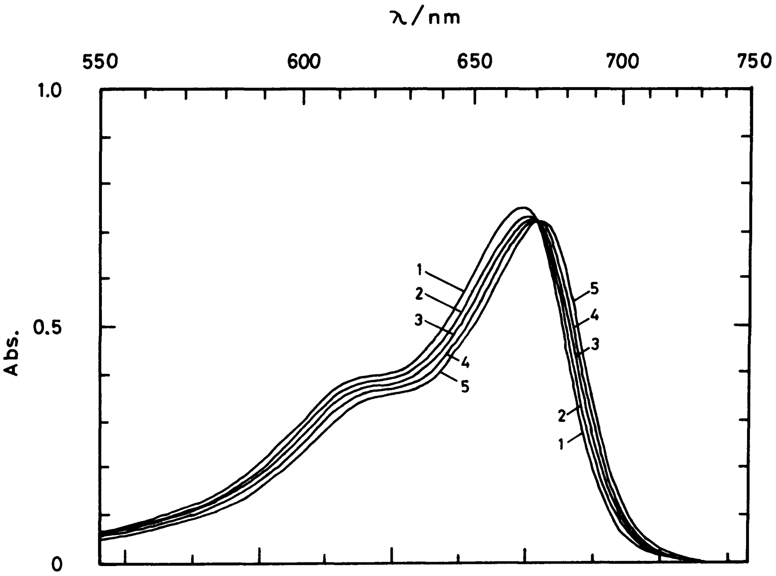

Fig. 5. Absorption spectra of MB (10^{-5} M) in aqueous solution in the presence of 1NS. Concentration of 1NS: 1, 0 M; 2, 2×10^{-3} M; 3, 5×10^{-3} M; 4, 10^{-2} M; 5, 2×10^{-2} M.

Monoanions. In addition to 2NS, the absorption and fluorescence spectra were similarly studied for other organic monoanions, 1-naphthalenesulfonate (1NS), 1-naphthaleneacetate (1NA), and 2-anthracenesulfonate (2AS). Figures 5 and 6 show the absorption spectra of MB solutions containing varying concentrations of 1NS and 2AS, respectively. As in the case for 2NS, both a red shift of an absorption maximum and an isosbestic point are observed on adding the monoanion. The 1:1 complex formation between

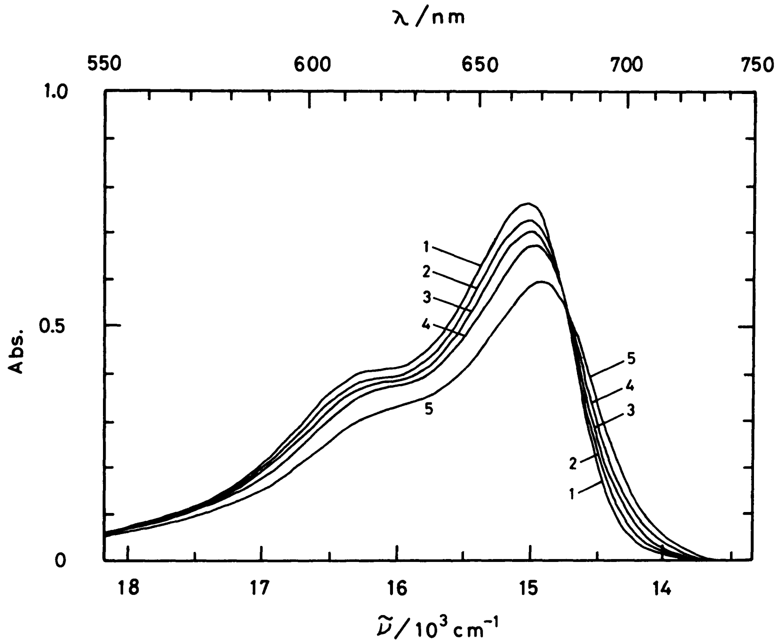

Fig. 6. Absorption spectra of MB (10^{-5} M) in aqueous solution in the presence of 2AS. Concentration of 2AS: 1, 0 M; 2, 2×10^{-5} M; 3, 5×10^{-5} M; 4, 10^{-4} M; 5, 2×10^{-4} M.

MB and the monoanion is responsible for these spectral changes. The equilibrium constants for the complex formation with 1NS, 1NA, and 2AS were determined to be 180, 240, and 7400 M^{-1}, respectively. The markedly large equilibrium constant for 2AS provides evidence that the interaction in the complex formation involves the aromatic ring in the anion.

The fluorescence spectrum of MB in the presence of 1NS is entirely similar to that in the presence of 2NS. In contrast, only the quenching of the MB fluorescence was observed for the MB–2AS system, indicating that the MB–2AS complex is nonfluorescent. The triplet state of the complex, derived primarily from the lowest triplet state of 2AS, may be assumed to lie in energy close to the lowest triplet state of anthracene (14900 cm^{-1}).[38] On the other hand, the energy of the first excited singlet state of the complex is estimated to be ≈14400 cm^{-1} from the maximum positions of the absorption and fluorescence of the complex. Since the maximum position of the complex fluorescence was found to be nearly constant irrespective of the kinds of anions, the peak position of the MB–2NS fluorescence was used in the above estimate. From the relationship between the energy levels of the complex, it is suggested that the nonradiative relaxation occurs with high efficiency through the triplet state derived primarily from 2AS.

The values of ΔH for the complex formation with 1NS, 1NA, and 2AS are determined to be −30, −28, and −49 kJ mol^{-1}, respectively, and the values of ΔS for 1NS, 1NA, and 2AS are −53, −47, and −92 J K^{-1} mol^{-1}, respectively. The absolute values of both thermodynamic quantities for 2AS are about two-fold larger than those for 2NS, 1NS, and 1NA. This finding also confirms a much stronger interaction of MB with 2AS possessing the anthracene ring than that with the anions possessing the naphthalene ring.

The addition of sodium benzenesulfonate to an MB solution results in no change in the absorption spectrum of MB within experimental error. The redox potential of MB in aqueous solution has been reported to be +0.011 V.[39] This value is high enough to form an electron donor-acceptor (EDA) complex with an appropriate electron donor. Whether the organic anions form EDA complexes with electron acceptors (tetracyanoethylene and chloranil) or not was not confirmed owing to the insolubility of these acceptors in water; however, the ionization potentials of the organic anions are probably not too different from the corresponding, unsubstituted aromatics which are known to form EDA complexes. In the complexes between MB and the organic anions, it seems to be reasonable that MB is an electron acceptor and the organic anions are electron donors.

Complex Formation of MB with Di- and Trianions. Spectroscopic studies were also made for a dianion, disodium 2,7-naphthalenedisulfonate (NDS) and a trianion, trisodium 1,3,6-naphthalenetrisulfonate (NTS). The absorption spectra of 10^{-5} M MB solutions with varying concentrations of NTS are

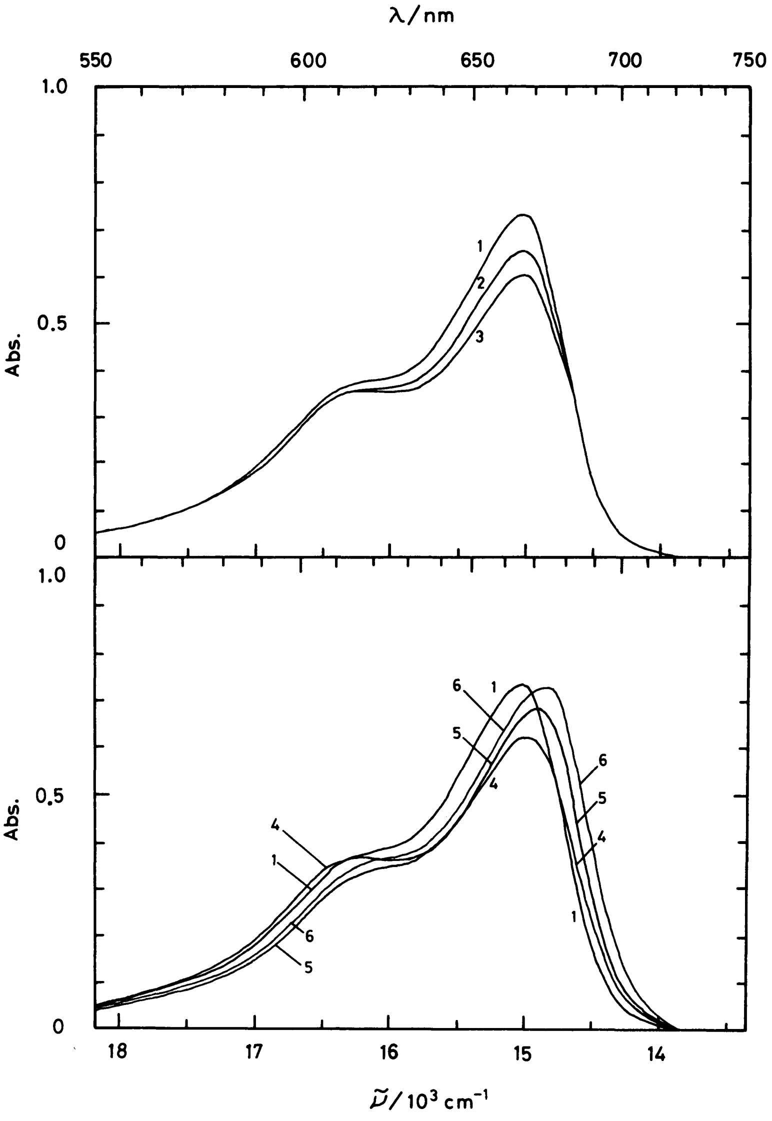

Fig. 7. Absorption spectra of MB (10^{-5} M) in aqueous solution in the presence of NTS. Concentration of NTS: 1, 0 M; 2, 5×10^{-5} M; 3, 2×10^{-4} M; 4, 10^{-3} M; 5, 10^{-2} M; 6, 5×10^{-2} M.

displayed in Fig. 7. Almost the same spectral change as in Fig. 7 was observed upon adding NDS. In contrast to the case of the monoanion (2NS, *etc.*), the absorption spectra of MB show a complicated change, exhibiting no isosbestic point. In the low-concentration range of NTS (below 10^{-3} M), the dimer peak appears at ≈610 nm and at the same time the monomer band decreases in intensity without the red shift of the monomer peak at 665 nm. However, as the concentration of NTS is increased above 10^{-2} M, the dimer peak starts to disappear accompanied by the recovery of the intensity and the red shift of the monomer band. In the low-concentration range of NTS, an MB molecule pairing with a sulfonate group substituted in an NTS molecule can easily associate with a neighboring MB molecule pairing with another sulfonate group substituted in the same NTS molecule because of the very close distance between the two MB molecules. The reason why the absorption spectra in the low-concentration range shown in Fig. 7 does not show a simple monomer-dimer equilibrium with an isosbestic point may be explained by the existence of a small amount of the 1:1 complex of MB with NTS and/or the complex of the MB dimer with NTS. Above an NTS concentration of 10^{-2} M, there is little chance that one NTS molecule is surrounded by more than one MB molecule. Under such situations, not the dimer of MB but the 1:1 complex between MB and NTS is formed. The elucidation for the absorption change shown in Fig. 7 is supported by the additional experimental result that, for a dilute (2×10^{-6} M) MB solution with NTS, the change in the absorption spectra over the whole concentration range of NTS is similar to that of MB solution with 1NS. Nonetheless, the equilibrium constant could not be estimated both for NTS and NDS because of the absence of an isosbestic point in the absorption spectra.

The fluorescence maximum of MB was observed to be shifted to the red with an increase in the concentration of NTS (or NDS), indicating the 1:1 complex formation between MB and NTS (or NDS).

Complex Formation of Other Dyes. Other types of dyes, Rhodamine 6G, Pyronine G, Safranin T, and Crystal Violet were also studied regarding the complex formation with the organic monoanions. The spectral changes in the absorption and fluorescence for all these dyes in the presence of the monoanion are quite similar to those for MB. We ascribe the spectral changes to the 1:1 complexes between the above dyes and the monoanions. No complex formation between Crystal Violet and benzenesulfonate has been reported.[22] With respect to the complex formation with benzenesulfonate as well as with 2NS, *etc.*, the behavior of Crystal Violet resembles that of MB. Irrespective of the difference in the skeletal structure from MB, the equilibrium constants of the dyes other than Rhodamine 6G are comparable with those of MB. The values of ΔH and ΔS for the complex formation of these dyes with the anions of the naphthalene derivatives are in the range from -19 to $-29\,\mathrm{kJ\,mol^{-1}}$ and from -25 to $-57\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. On the other hand, ΔH and ΔS for Rhodamine 6G are in the range from -36 to $-44\,\mathrm{kJ\,mol^{-1}}$ and from -94 to $-120\,\mathrm{J\,K^{-1}\,mol^{-1}}$ respectively. The absolute values of ΔH and ΔS for Rhodamine 6G are significantly larger than those for other dyes, including MB. There still remains a question of why ΔH and ΔS for Rhodamine 6G are strikingly different from those for other dyes.

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