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Thermodynamic Study of the Effects of Monovalent Cations on Dimerization of a Dianionic Azo Dye, 2-[(2-Hydroxy-1-naphthyl)azo]-5-[(4-sulfonatophenyl)azo]benzenesulfonate, in Aqueous Salt Solution

Kiyofumi Murakami,* **Yuko Kimura, and Masahiko Saito**

Department of Chemistry, Faculty of Education, Yamaguchi University, Yamaguchi 753

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Thermodynamics of the dimerization of 2-[(2-hydroxy-1-naphthyl)azo]-5-[(4-sulfonatophenyl)azo]benzenesulfonate in the presence of 0.05 mol dm^{-3} alkali metal cations and tetralkylammonium cations has been studied spectrophotometrically. From the dimerization constant and its temperature dependence, the values of standard enthalpy change and entropy change of dimerization have been calculated. The results show that both of them increase in the order of $K^+ < Li^+ < Na^+ < Rb^+ < Cs^+$ and $NH_4^+ < (CH_3)_4N^+ < (C_2H_5)_4N^+ < (C_3H_7)_4N^+$, and further, an enthalpy–entropy compensation relation with the compensation temperature of 300 K does hold. Dimer structure has also been examined using exciton theory. The angle between long molecular axes of monomers in the dimer lies in 43—44° for Na^+, K^+, Rb^+, and Cs^+, and is about 52° for Li^+, but, that for tetralkylammonium cations has a tendency to increase with an increase in the size of the alkyl chain up to tetraethylammonium ion and somewhat decreases for tetrapropylammonium ion, i.e., 38° $(NH_4^+) < 41^\circ$ $((CH_3)_4N^+) < 59^\circ$ $((C_2H_5)_4N^+) > 46^\circ$ $((C_3H_7)_4N^+)$. These results clearly show the participation of the cations in the thermodynamic and structural properties of the dimerization. By comparing the data with those in the absence of added salt, the results have been interpreted in terms of the condensation of cations around the dimer and the hydration structure of cations.

Dimerization of dyes in aqueous solution has been studied extensively as the most fundamental model of self-aggregation of biological molecules and biomacromolecule-ligand interactions,[1—4] and as the basis for the application to tunable lasers and other practical uses.[5—7]

Various factors have been found to affect the dimerization behavior, i.e., dye structure, solvent, coexisting salt, temperature, and pressure. Thermodynamic parameters such as standard enthalpy change and standard entropy change of dimerization, which are derived from the temperature dependence of the dimerization constant, have given some insight into the forces that maintain the dimer structure in solution. Among them, dispersion forces, electrostatic forces including coulombic repulsion between like charges, hydrogen bonding, and hydrophobic forces, which arise from hydration around nonpolar solutes, have been believed to be important.[1,7—9] Especially, the importance of water structure around dye molecules has frequently been emphasized. Murakami et al.[10] have shown that the standard enthalpy and entropy changes of dimerization of Acridine Orange and its 10-alkyl derivatives decrease with an increase in the concentration of coexisting NaCl, and have suggested that the order-destroying effect of Cl^- upon water structure may be responsible. However, there is no systematical investigation of the effects of coexisting salt on the thermodynamic parameters of dimerization.

In this study, the effects of alkali metal cations and tetralkylammonium cations on the thermodynamics of dimerization and the dimer structure of a dianionic azo dye, 2-[(2-hydroxy-1-naphthyl)azo]-5-[(4-sulfonatophenyl)azo]benzenesulfonate, has been studied to clarify the effects of electrostatic interactions and of hydration structures of coexisting cations. This dye has been found to dimerize in the presence of salt,[11] and to inhibit some hydrolases.[12—15] This study is also of interest in the clarification of the binding mechanism.

Experimental

Materials. Disodium 2-[(2-hydroxy-1-naphthyl)azo]-5-[(4-sulfonatophenyl)azo]benzenesulfonate purchased from Chroma was purified by three recrystallizations from an aqueous ethanol solution, and was dried at 383.15 K in a vacuum for 20 h. Figure 1 shows the chemical structure of the anionic form of the dye (**1**). Alkali metal chlorides and tetralkylammonium chlorides used were the reagent grade of Wako Pure Chemical Industries. Double-distilled water was used for all sample preparations.

Methods. Spectrophotometric measurements were done with a Hitachi U-2000 spectrophotometer. In the presence of 0.05

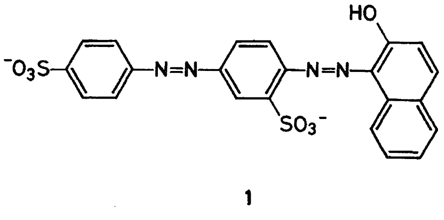

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Fig. 1. Chemical structure of 2-[(2-hydroxy-1-naphthyl)-azo]-5-[(4-sulfonatophenyl)azo]benzenesulfonate.

mol dm^{-3} salt, a data set of absorption spectra for twelve dye concentrations from 3×10^{-7} to 2×10^{-5} mol dm^{-3} was recorded using quartz cells of path length from 10 to 100 mm. Thermodynamic parameters have been calculated from the data measured over the temperature range 293.15—313.15 K with 5 K intervals. All the measurements were repeated two or three times.

For examination of dimer structure using exciton theory,[16,17] monomer and dimer spectra have been resolved into constituent bands with log-normal distribution functions,[18,19] by a program of least-squares fitting.

Results

1. Dimerization Constant and Thermodynamic Parameters. Figure 2(A) shows typical absorption spectra of **1** in the presence of 0.05 mol dm^{-3} LiCl. Similar spectral changes were observed in the presence of other salts. Isosbestic points were found at 360 and 556 nm. This suggests an equilibrium between two spectral species, i.e., a monomer–dimer equilibrium. The data were then analyzed on the basis of the equation:

$$2\mathrm{M} \overset{K_\mathrm{D}}{\rightleftarrows} \mathrm{D}, \qquad (1)$$

where K_D is the dimerization constant defined by

$$K_\mathrm{D} = \frac{[\mathrm{D}]}{[\mathrm{M}]^2}. \qquad (2)$$

Using the momomer fraction of dye (α_M), the apparent molar extinction coefficient at a given wavelength can be expressed by

$$\varepsilon = (\varepsilon_\mathrm{M} - \varepsilon_\mathrm{D})\alpha_\mathrm{M} + \varepsilon_\mathrm{D}, \qquad (3)$$

where ε_M and ε_D are molar extinction coefficients per monomer unit in the monomer and dimer forms, respectively. α_M can be expressed by the dimerization constant K_D and total concentration of dye C_0 as

$$\alpha_\mathrm{M} = \frac{(1+8K_\mathrm{D}C_0)^{1/2} - 1}{4K_\mathrm{D}C_0}. \qquad (4)$$

If an assumed K_D value is true, the ε vs. α_M plot in Eq. 3 must give a straight line with the minimum least-squares error from the best fitted line. The value of K_D was chosen so as to give the minimum value of the product of least-squares errors calculated for 11 wavelengths from 520 to 540 nm. K_D and standard free energy change of dimerization are listed in Table 1. Momomer and dimer spectra were obtained from the intercepts of the straight lines at $\alpha_\mathrm{M}=1$ and $\alpha_\mathrm{M}=0$, respectively (Figure 2(B)).

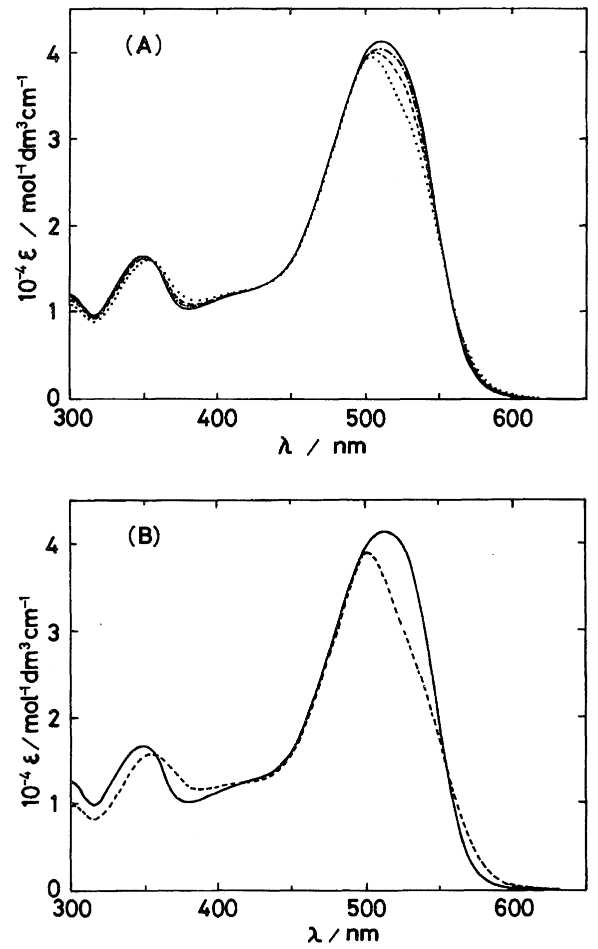

Fig. 2. Absorption spectra and monomer and dimer spectra of **1** in the presence of 0.05 mol dm^{-3} LiCl at 298.15 K. (A) Absorption spectra, (——): 3×10^{-7} mol dm^{-3}, (–•–): 1×10^{-6} mol dm^{-3}, (- - -): 5×10^{-6} mol dm^{-3}, (••••): 2×10^{-5} mol dm^{-3}, (B) Monomer spectrum (solid curve) and dimer spectrum (broken curve).

Figure 3 shows T^{-1} dependence of ln (K_D). The solid lines are the best straight-line fits for the data, showing that the slope highly depends on the coexisting cation species. The standard enthalpy change and entropy change of dimerization were calculated using the well known relationships:

Table 1. Dimerization Constant and Thermodynamic Parameters for the Dimerization of **1** in the Presence of 0.05 mol dm^{-3} Salt at 298.15 K

Salt	$10^{-4}K_\mathrm{D}$	ΔG°	ΔH°	ΔS°
	mol^{-1} dm^3	kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
LiCl	12.9	−28.9	−36.5	−25.5
	(2.6)[a]	(0.5)	(5.5)	(18.5)
NaCl	4.19	−26.38	−6.5	66.8
	(0.03)	(0.02)	(5.0)	(16.8)
KCl	3.5	−26.0	−43.9	−60.3
	(0.6)	(0.5)	(2.2)	(7.7)
RbCl	6.1	−26.9	−2.8	80.8
	(3.9)	(1.5)	(9.4)	(32.1)
CsCl	4.3	−26.3	6.3	109.6
	(1.4)	(0.8)	(8.0)	(26.9)
NH_4Cl	2.7	−25.3	−12.3	43.7
	(0.1)	(0.1)	(6.3)	(21.1)
$(CH_3)_4NCl$	7.9	−28.0	−4.8	73.9
	(0.7)	(0.2)	(6.8)	(22.9)
$(C_2H_5)_4NCl$	10.1	−28.8	48.0	256.6
	(0.8)	(0.2)	(3.8)	(12.6)
$(C_3H_7)_4NCl$	2.9	−25.4	157.2	612.4
	(0.5)	(0.4)	(9.3)	(31.2)

a) The numbers in the parentheses show standard deviations determined from two or three times measurements.

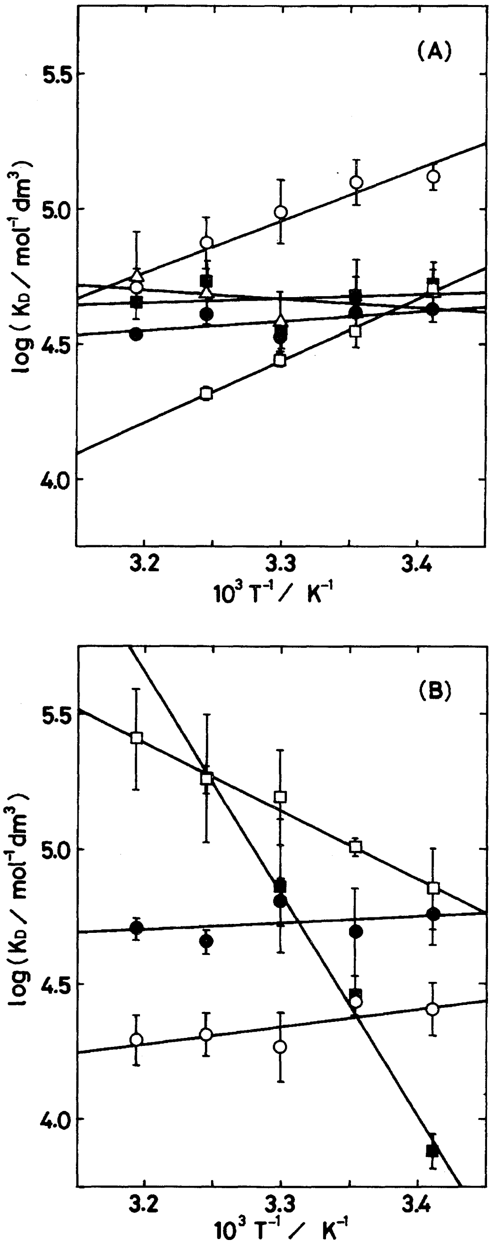

Fig. 3. Plots of log (K_D) vs. T^{-1} for the dimerization of **1** in the presence of 0.05 mol dm^{-3} alkali metal cations (A) and tetralkylammonium cations (B). (A): Li^+ (open circle), Na^+ (filled circle), K^+ (open square), Rb^+ (filled square), Cs^+ (triangle), and (B): NH_4^+ (open circle), $(CH_3)_4N^+$ (filled circle), $(C_2H_5)_4N^+$ (open square), $(C_3H_7)_4N^+$ (filled square).

$$\Delta H^\circ = -R\frac{\mathrm{d}\ln(K_D)}{\mathrm{d}(1/T)} \tag{5}$$

and

$$\Delta S^\circ = -(\Delta G^\circ - \Delta H^\circ)/T. \tag{6}$$

The results are also summarized in Table 1. We can see from this table that the standard enthalpy change of dimerization increases, from negative values (exothermic reaction) to positive ones (endothermic reaction), in the order: $K^+ < Li^+ < Na^+ < Rb^+ < Cs^+$ and $NH_4^+ < (CH_3)_4N^+ < (C_2H_5)_4N^+ < (C_3H_7)_4N^+$. The standard entropy change increases also in the same order. Figure 4 shows the plot of ΔH° vs. ΔS°, indicating that an enthalpy-entropy compensation relation does hold with the compensation temperature $T_C = 300.0$ K. To compare the results with those for the systems in which no salt was added, the thermodynamic parameters for some alkali metal salts of the dye have also been measured (Table 2), and plotted in Fig. 4.

2. Dimer Structure. As can be seen in Fig. 5, the monomer and dimer spectra are well resolved by the four bands of log–normal function. Among these, the bands to which we must pay attention are the principal band of the monomer at around 19800 cm^{-1}, which is due to a transition moment along the long molecular axis, and the two splitting bands of the dimer at around 19100 and 20500 cm^{-1}, which arise from the interaction between the monomer transition moments in the dimer. The additional band of the monomer at 18600 cm^{-1} may be attributed to the quinone hydrazon tautomer,[20] and seems to be lost in the dimer. According

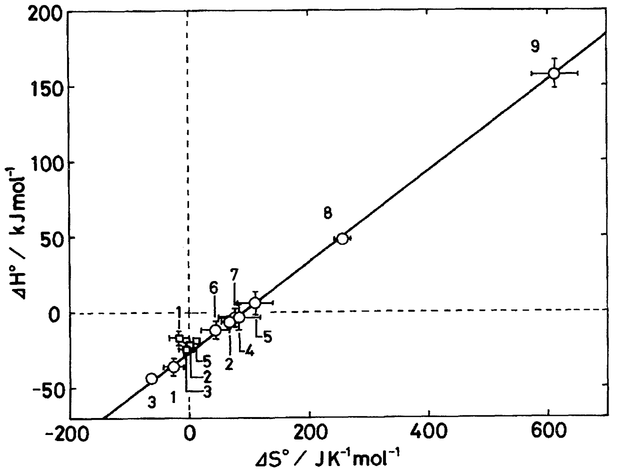

Fig. 4. Plot of ΔH° vs. ΔS° for the dimerization of **1** in the presence of 0.05 mol dm^{-3} salt (circle) and in the absence of added salt (square). The numbers refer to the cation species of the salt or counter ion; 1: Li^+, 2: Na^+, 3: K^+, 4: Rb^+, 5: Cs^+, 6: NH_4^+, 7: $(CH_3)_4N^+$, 8: $(C_2H_5)_4N^+$, and 9: $(C_3H_7)_4N^+$. The solid line represents the compensation line with the compensation temperature of 300.0 K (see text).

Table 2. Dimerization Constant and Thermodynamic Parameters for the Dimerization of **1** at 298.15 K, in the Absence of Added Salt

Counter ion	$10^{-3}K_D$ mol^{-1} dm^3	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
Li^+	8.4	−22.1	−17.1	−16.9
	(0.2)[a]	(0.7)	(5.2)	(17.7)
Na^+	8.4	−22.5	−21.8	2.4
	(0.9)	(0.2)	(1.8)	(5.9)
K^+	8.8	−22.5	−23.8	−4.3
	(0.2)	(0.1)	(4.2)	(13.9)
Cs^+	8.2	−22.3	−18.6	12.4
	(1.0)	(0.3)	(2.1)	(7.0)

[a] The numbers in the parentheses show standard deviations determined from two or three times measurements.

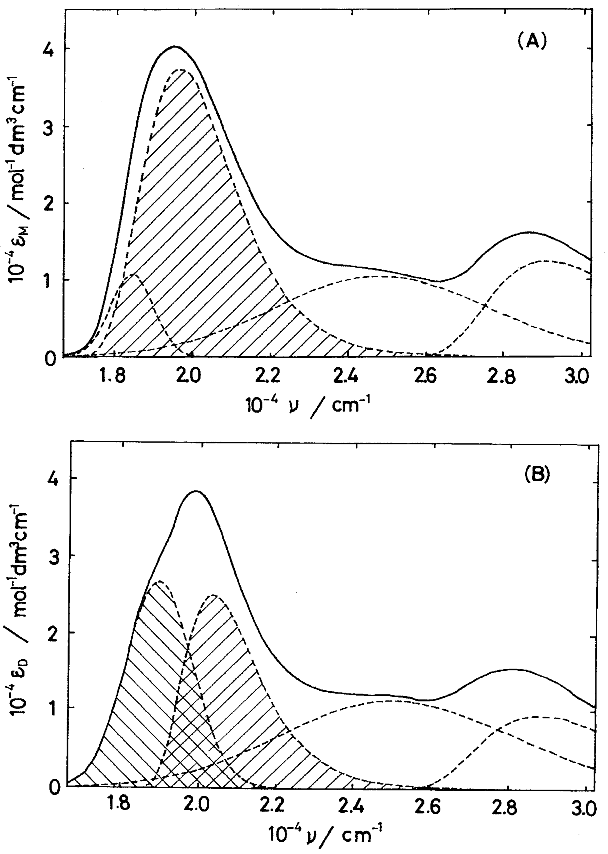

Fig. 5. Resolution of the monomer (A) and dimer (B) spectra of **1** in the presence of 0.05 mol dm^{-3} LiCl by log–normal functions. The shaded bands represent the principal band of monomer (A) and its splitting (B) due to the interaction between the monomer transition moments in the dimer.

to exciton theory, the angle between transition moments of monomers in the dimer may be calculated by[21)]

$$\alpha = 2\tan^{-1}(\nu_H f_J/\nu_J f_H)^{1/2}, \tag{7}$$

where ν and f are the peak position and oscillator strength, and the subscripts J and H refer to the low energy band and the high energy band of the dimer, respectively. The splitting $\Delta\nu$ is given by[22)]

$$\Delta\nu = \frac{2D}{hcR^3}G. \tag{8}$$

where D is the monomer dipole strength, h is Plank's constant, c is the speed of light, R is the center to center distance between monomers, and G is the geometry factor which depends on dimer structure. Three models were examined (Fig. 6). Model 1 refers to the parallel plane dimer. This is the most frequently used model for the consideration of dimer structure. Model 2 refers to the in-plane oblique transition dipoles dimer. Model 3 refers to the nonplaner inclined transition dipole dimer. This model involves model 1 in the limit of θ=90°. The geometical factors of these model becomes[16)]

$$G = \cos\alpha \qquad \text{(Model 1)}, \tag{9}$$

$$G = \cos\alpha + 3\sin^2(\alpha/2) \qquad \text{(Model 2)}, \tag{10}$$

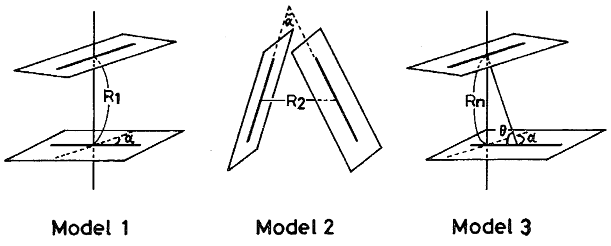

Fig. 6. Three models of dimer structure.

$$G = \cos\alpha - 3\cos^2\theta \qquad \text{(Model 3)}. \tag{11}$$

In the cases of Models 1 and 2, R can be measured from the observed splitting $\Delta\nu$ by using the value of α calculated from Eq. 7. In the case of Model 3, however, we cannot uniquely decide the set of the values of the parameters (R, θ) from the data. Therefore, we have estimated possible combinations of R and θ for the following three cases. The first is the contact case in which monomer planes in the dimer are in contact with each other, and the normal distance between the plane R_n is equal to 3.4 Å. The second is the one-water separation case in which R_n is equal to 6.2 Å. The third is the two-water separation case in which R_n=9 Å. It was found from the analysis that three values of θ are possible for the former two cases but only one value is possible for the last case. The values of exitonic parameters and of structural parameters of dimer are summarized in Table 3.

Discussion

It can be seen from Table 2 that the dimerization constants and the thermodynamic parameters for the systems in which no salt was added take similar values around K_D=8400 mol^{-1} dm^3, $\Delta H°$=−20 kJ mol^{-1} and $\Delta S°$=0 J K^{-1} mol^{-1}, irrespective of coexisting counter cations. In the presence of 0.05 mol dm^{-3} salt, on the other hand, the dimerization constants are larger than this by more than several times (Table 1), and the values of $\Delta H°$ and $\Delta S°$ are distributed over a wide range along the compensation line (Fig. 4). These facts clearly show the participation of cations in the dimerization.

The Debye length of the ionic atmosphere for the non-salt systems may be estimated as larger than 150 Å from the observed concentration range of the dye solutions, by regarding the solutions as 1 : 1 electrolyte. This value reduces to 13.6 Å in the presence of 0.05 mol dm^{-3} salt. That is, the cations which compensate for the negative charges on dye molecules are distributed in a large space for the non-salt systems, but greatly condense in the narrow space comparable to the molecular size for the systems of 0.05 mol dm^{-3} salt. Because the monomer and dimer have respectively two and four negative charges, the condensation of cations must be increased. Further, it would also be expected that the dimer takes in more cations than the monomer. For a brief experimental evaluation of the difference in the amounts of cations that are confined in the vicinity of the monomer and dimer, consider the equilibrium:

Table 3. Exitonic and Structural Parameters for the Dimerization of **1** in the Presence of 0.05 mol dm^{-3} Cations at 298.15 K

Cation	ν_M	ν_{DJ}	ν_{DH}	$\Delta\nu$	f_M	f_{DJ}	f_{DH}	α	R_1	R_2	$\theta(R_n=3.4$ Å$)$	$\theta(R_n=6.2$ Å$)$	$\theta(R_n=9$ Å$)$
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}				deg	Å	Å	deg	deg	deg
Li^+	19784	19119	20501	1382	1.40	0.424	0.942	51.5	8.80	10.93	(15,62,64)	(31,54,70)	—
	(4)[a)]	(6)	(9)	(8)	(0.03)	(0.018)	(0.009)	(2.1)	(0.10)	(0.11)			
Na^+	19807	19084	20434	1351	1.32	0.414	1.088	44.4	9.12	10.66	(15,59,62)	(34,50,68)	90
	(15)	(4)	(3)	(1)	(0.06)	(0.002)	(0.009)	(0.5)	(0.16)	(0.14)			
K^+	19851	19089	20450	1360	1.26	0.411	1.101	43.6	8.97	10.44	(15,59,62)	(35,49,68)	88
	(1)	(22)	(20)	(2)	(0.02)	(0.011)	(0.023)	(1.9)	(0.13)	(0.01)			
Rb^+	19845	19076	20422	1345	1.26	0.432	1.171	43.1	9.02	10.45	(15,59,62)	(34,50,68)	90
	(1)	(6)	(2)	(7)	(0.002)	(0.012)	(0.002)	(1.1)	(0.04)	(0.04)			
Cs^+	19847	19140	20501	1360	1.27	0.381	1.027	43.4	9.01	10.47	(15,58,62)	(35,49,67)	85
	(1)	(52)	(33)	(19)	(0.01)	(0.006)	(0.039)	(2.2)	(0.13)	(0.02)			
NH_4^+	19811	19042	20404	1363	1.33	0.416	1.306	37.7	9.41	10.52	(15,58,60)	(34,48,66)	81
	(3)	(1)	(4)	(5)	(0.004)	(0.012)	(0.047)	(0.3)	(0.03)	(0.02)			
$(CH_3)_4N^+$	19845	19082	20456	1375	1.29	0.401	1.146	41.2	9.14	10.44	(16,59,61)	(34,49,68)	87
	(1)	(11)	(6)	(6)	(0.002)	(0.008)	(0.089)	(2.2)	(0.11)	(0.03)			
$(C_2H_5)_4N^+$	19853	19141	20513	1372	1.46	0.420	0.797	58.9	8.40	11.26	(14,64,66)	(29,58,72)	—
	(2)	(10)	(13)	(3)	(0.017)	(0.007)	(0.004)	(0.5)	(0.08)	(0.04)			
$(C_3H_7)_4N^+$	19818	18997	20373	1376	1.05	0.428	1.095	46.2	8.27	9.84	(17,61,64)	(39,48,72)	—
	(2)	(54)	(61)	(22)	(0.003)	(0.037)	(0.225)	(6.8)	(0.37)	(0.07)			

a) The numbers in the parentheses show standard deviations determined from two or three times measurements.

$$2\ M + n\mathrm{Cat} \overset{K_0}{\rightleftarrows} \mathrm{D(Cat)}_n, \tag{11}$$

where Cat means cation. The equilibrium constant may be expressed by

$$K_0 = \frac{[\mathrm{D(Cat)}_n]}{[\mathrm{M}]^2[\mathrm{Cat}]^n} = K_\mathrm{D}[\mathrm{Cat}]^{-n}. \tag{12}$$

The logarithm of both sides of this equation gives

$$\log K_\mathrm{D} = \log K_0 + n \log\,[\mathrm{Cat}]. \tag{13}$$

Figure 7 shows the plot of $\log K_\mathrm{D}$ vs. log [Na] for the system in which NaCl was added as a salt. From the slope we have estimated n=0.33. The condensation of cations in the vicinity of the dimer in the presence of 0.05 mol dm^{-3} salt results necessarily in shortrange interactions between the cations and the sulfonato groups of the dye, in which negative charges are localized. In the presence of such shortrange interactions, the hydration properties of cations would affect the thermodynamic parameters of dimerization as well as the dimer structure.

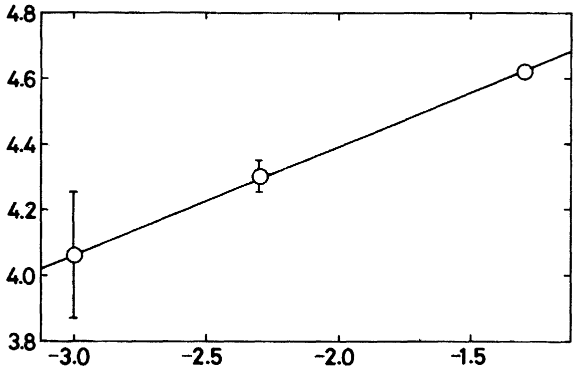

Fig. 7. Plot of log (K_D) vs. log ([Na^+]).

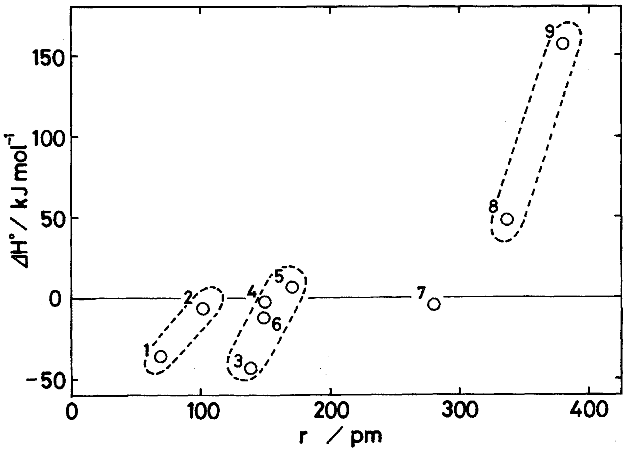

Fig. 8. Plot of $\Delta H°$ vs. r. The numbers in the figure represent coexisting cation species in the same manner as Fig. 4.

Figure 8 shows the plot of $\Delta H°$ vs. r, radius of cations.[23) The same distribution pattern was also observed for $\Delta S°$, since the enthalpy–entropy compensation relation does hold (Fig. 4). From this figure, the cations may be classified into four groups; the first group contains the cations with small r and low $\Delta H°$ (Li^+,Na^+), the second group contains those with intermediate r and low $\Delta H°$ (K^+,Rb^+,Cs^+,NH_4^+), the third group large r and high $\Delta H°$ (($(C_2H_5)_4N^+$,$(C_3H_7)_4N^+$), and the fourth one relatively large r and low $\Delta H°$ ($(CH_3)_4N^+$). There is the tendency that the value of $\Delta H°$ in each of these groups increases with an increase in r. This classification of cations agrees with that of Nightingale,[24) which is based on viscosity B coefficient and activation energy of viscous flow. The hydration state of these cations have been thought as follows. For the first group, water molecules in the vicinity of the cations are highly oriented by a strong electrostatic field due to small r, and in a state of low enthalpy and entropy ("structure-making" effect). For the second group, water molecules around the cations are in a disordered state due to breaking of the native water structure by a moderate electrostatic field, and have relatively high enthalpy and entropy ("structure-breaking" effect). For the third group, water molecules around the cations are in a so called "hydrophobic hydration" state in which nonpolar groups are surrounded by structured water molecules, and in a low enthalpy and entropy state. The hydration state of the fourth group cations is thought to be intermediate between the second and third groups.

Because the observed thermodynamic parameters are the results of an integration of many kinds of interactions such as van der Waals interactions and electrostatic ones between several constituents in this system, it is difficult to interpret the behavior of Figs. 4 and 8 quantitatively. However, it seems possible to interpret at least qualitatively this tendency that the value of ΔH° (as well as ΔS°) in each of the groups increases with an increase in r, by considering the effect of the condensed cations on the hydration of the sulfonato groups. According to Tamaki et al.,25) the sulfonato group is structure-breaker. Therefore, the water molecules around it has a disordered structure with high enthalpy and entropy. As the cations approach the sulfonato groups, a strong electric field will be formed between them. This will cause reorientations of water molecules along the field, and further, some dehydration will occur if the hydration layers of these ions overlap. Both of these effects may reduce the enthalpy and entropy, and the degree of this reduction will be greater for smaller cations (the behavior of ΔH° in each of the groups in Fig. 8). The difference in the values of ΔH° between the first and second group can be interpreted from the difference in hydration type, i.e., water molecules around the cations of the second group are in a disordered state and more liable to be reorganized by the external field than those of the first group, which are strongly bound to the cations. The reduction of ΔH° and ΔS° in the presence of salt has also been pointed out by Murakami et al.10) for the systems of Acridine Orange and its 10-alkyl derivatives-NaCl. This may also been interpreted in a similar manner as above. The large values of ΔH° for the third group are attributable to the effect of destruction of the highly ordered hydration structure around the tetralkylammonium ions being superior to the reorientation effect.

Gilkerson and Mixon26) have shown an enthalpy–entropy compensation relation for the dimerization of aromatic substances in water, by referring to the data for benzene and its derivatives27—29) and some anionic and cationic dyes.21,30,31) From the former data, it can clearly be seen that both of the standard enthalpy and entropy changes of dimerization becomes large with an increase in the hydrophobicity of the substituent groups. This behavior has also been found for the dimerization of a homologous series of carboxylic acids.32) This result in the presence of tetralkylammonium chlorides shows a similar tendency. By using Grunwald's two-state model33) of water structure, Gilkerson and Mixon have evaluated "solvent-perturbation" terms of the thermodynamic parameters, and by assuming further that these terms are independent of dye structure, they concluded that the origin of the enthalpy–entropy compensation is due to the difference in direct interactions between dye molecules independently of the solvent network. However, the assumption seems not to be applicable. Conversely, our result clearly shows that the hydration structures of dye molecules and cations and the perturbation of them upon dimerization play a central role for the compensation behavior. The fact that coexisting cations change the thermodynamic behavior of dimerization is also of practical interest. That is, we can easily control the temperature dependence of dimerization at least for the similar dyes by changing the species of coexisting salt and their concentrations, but it is not necessary to introduce alkyl chains or other functional groups into the dyes.

Figure 9(A) shows the plot of α vs. coexisting cation species at 298.15 K. α of alkali metal cations take similar values in the range from 43° to 44° excepting the relatively large value of 52° for Li^+. In the case of tetralkylammonium ions, on the other hand, α increases with an increase in alkyl chain length up to tetraethylammonium ion and is somewhat reduced at tetrapropylammonium ion. This behavior was also assured at 308.15 K, suggesting that the dimer structures do not change in this temperature range.

Model 1 has most frequently been used for the examination of dimer structure. In this model the tendency of the change in R_1 with cation species is the reverse of α except tetrapropylammonium ion, i.e., the larger α becomes, the smaller the distance between monomers (compare Fig. 9(A) and (B)). This may be the result of a delicate balance between van der Waals interactions between aromatic parts, electrostatic repulsions between sulfonato groups, and hydration structure of the dye molecules. Another noticeable result is that the values of R_1 are about 9 Å. This is larger than any other

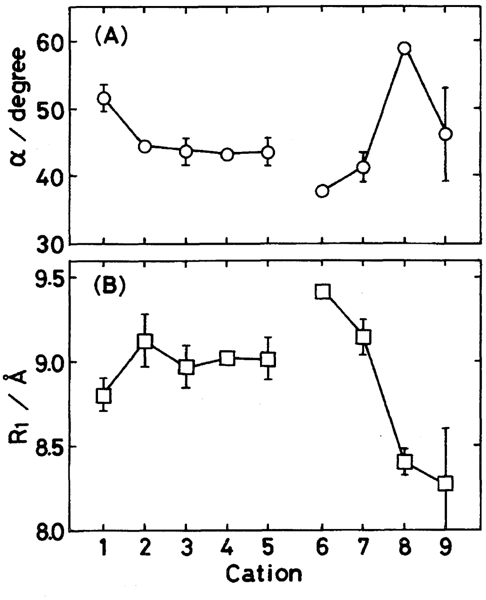

Fig. 9. Dependence of α (A) and R_1 (B) on the coexising cation species. The number in the abscissa shows cation in the same manner as Fig. 4.

result[10,17,21,22,34—37] of dye dimerization and corresponds to the separation distance in which two water-molecule layers could be inserted. Contrary to Model 1, the center-to-center distance R_2 in Model 2 becomes larger with an increase in α. In Model 3 which is the generalization of Model 1, θ has three possible values in the range of R_n smaller than about 7 Å. These values slightly change with the cation species, but the degree of the change is much smaller than that in α. Considering the possibility of other R_n values than those listed in Table 3, we can see that the number of possible sets of R_n and θ is very large. Only from these data it seems difficult to decide on the most plausible dimer structure. By the future research such as crystallographic studies and molecular dynamic simulations, more detailed insight into the dimer structure in solution will be obtained.

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