

Effects of NaCl on the J-aggregation of two thiacyanine dyes in aqueous solutions

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Abstract

The effects of NaCl on the aggregation of two typical thiacyanine dyes (3, 3'-di(3-sulfopropyl)-4, 5, 4', 5'-dibenzo-9-phenyl-thiacyanine triethyl ammonium salt (Dye 1) and 3, 3'-di(3-sulfopropyl)-4, 5, 4', 5'-dibenzo-9-methyl-thiacyanine triethyl ammonium salt (Dye 2)) in aqueous solution have been studied by using absorption spectroscopy, fluorescence spectroscopy, and ¹H- and ²³Na-NMR measurements. It is found that the J-aggregation of two dyes can be promoted by the addition of NaCl and that the effective coherence length of the J-aggregate is shorter than that obtained without NaCl. Fluorescence spectra demonstrate that the fluorescence intensities of the J-aggregates of two dyes are quenched by addition of NaCl. This is consistent with the decrease of the effective coherence length of J-aggregates of the two dyes in the presence of NaCl. ¹H-NMR spectra of two dyes show that the Na⁺ ions penetrate into the J-aggregates and replace the counterion (triethylammonium ions) in two dyes. The measurements of the chemical shifts of ²³Na nuclei provide further information about the interaction between the Na⁺ ions and dye anions in the J-aggregates of the two dyes. Due to this interaction, the electrostatic repulsion between the dye anions in the J-aggregates can be reduced and thus accelerate the aggregation of the two dyes in the presence of NaCl. The apparent association constants between Na⁺ ions and dye molecules in J-aggregates of Dye 1 and Dye 2 estimated from the measured chemical shifts of ²³Na nuclei are about 2.38 M⁻¹ and 1.35 M⁻¹, respectively.

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1. Introduction

J-aggregates have been the subject of keen interest in the scientific community for many years. This interest is based on the following:

- (1) they are used for the spectral sensitization of photographic emulsion;
- (2) they have shown great promise for use in the field of optoelectronics;
- (3) they are considered to be intermediates between single molecules and bulk phases, making them ideal models

to investigate the change of physical properties between these two extremes.

J-aggregates of some cyanine dyes exist in aqueous solution and several matrices. It has long been recognized that the self-association of ionic dyes in aqueous solution can be enhanced by either decreased temperature or increased dye concentration, or by the addition of inorganic salts or certain substrates [1–3]. Generally it can be stated that increased salt concentration causes an increase in the screening factor or effective dielectric constant and thus promotes aggregation [4,5].

After Jelly [6], who, together with Scheibe [7], first described the properties of J-aggregates, J-aggregates have been studied using different methods, including absorption spectroscopy, time-resolved fluorescence spectroscopy

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[8–14], the accumulated photon-echo technique [12–14], Raman spectroscopy [15], femtosecond pump-probe spectroscopy [16], electromodulation spectroscopy [17], near-field scanning optical microscopy [18], and atomic force microscopy [19]. However, the investigations with NMR spectroscopy were seldom reported, especially with multinuclear NMR spectroscopy, although multinuclear NMR has become a powerful tool for the investigation of concentrated electrolyte solutions and can give much information about both ion–ion and ion–solvent interactions [20–23].

In this paper, the effects of NaCl on the J-aggregates of two thiacyanine dyes (3, 3'-di(3-sulfopropyl)-4, 5, 4', 5'-dibenzo-9-phenyl-thiacyanine triethyl ammonium salt (Dye 1) and 3, 3'-di(3-sulfopropyl)-4, 5, 4', 5'-dibenzo-9-methyl-thiacyanine triethyl ammonium salt (Dye 2)) in aqueous solutions have been investigated using UV–visible spectroscopy, fluorescence spectroscopy, and ^1H -NMR as well as ^{23}Na -NMR spectroscopy.

2. Experimental

2.1. Materials

The two thiacyanine dyes used in the experiments, (Dye 1 and Dye 2) were synthesized according to the methods suggested by Hamer [24] and Ficken [25]. The structural formulas are shown in Scheme 1.

Analytical NaCl, deuterated water (D_2O), and deuterated methanol (CD_3OD) were purchased from Beijing Chemical Co. Double-distilled water was used in the absorption and fluorescence measurements.

2.2. Apparatus

The absorption spectra in aqueous solutions were taken by UVIKON-810 spectrophotometer and emission spectra were measured using a Hitachi F 3000 fluorescence spectrometer. A quartz cuvette with 1-cm path length was used in the experiments. Because the concentration of the dyes in CD_3OD and D_2O is too high to directly measure the absorption spectra with the convenient quartz cuvette, the samples were prepared as follows: Samples (40 μl) were dropped onto a 10×40 mm quartz plate, another 10×40 mm quartz plate was placed upon it, and the two plates were fixed with adhesive tape to obtain uniform samples. The ^1H -NMR and

^{23}Na -NMR spectra were obtained with a DMX 300 NMR spectrometer at 300 K.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of 2.37×10^{-6} M Dye 1 and 6.06×10^{-6} M Dye 2 in methanol solvent each show one band (at 600 and 571 nm, respectively), as illustrated in Fig. 1. However, Fig. 2 shows two bands at 545 and 678 nm in the aqueous solution of 8.3×10^{-6} M Dye 1. According to the absorption spectral data of similar cyanine dyes reported

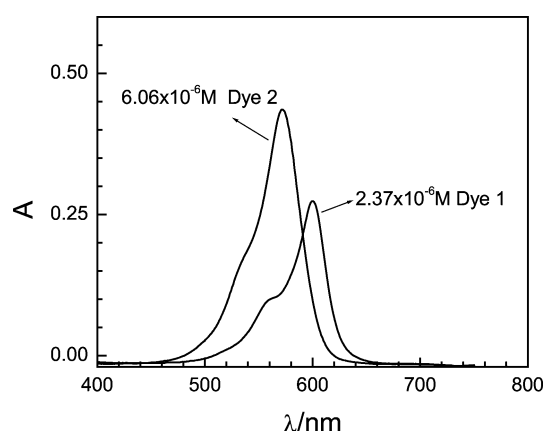


Fig. 1. The absorption spectra of Dye 1 and Dye 2 in methanol solvent.

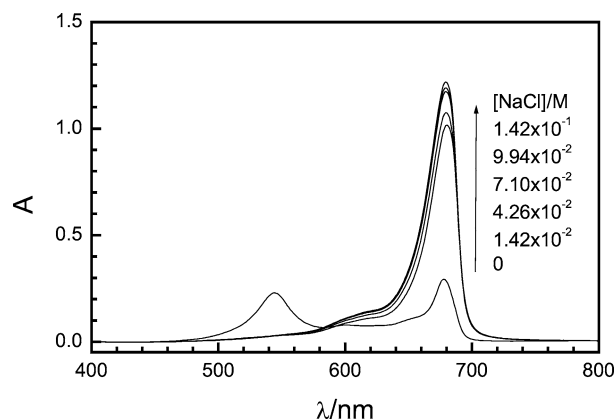
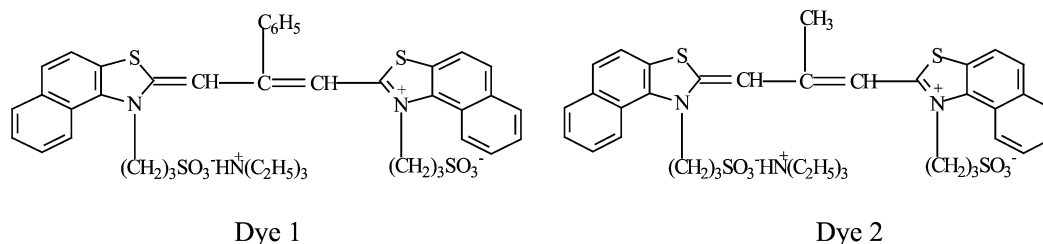


Fig. 2. The absorption spectra of 8.3×10^{-6} M Dye 1 in aqueous solution with different concentrations of NaCl.



Scheme 1.

in the literatures [3,26–28], the absorption bands of Dye 1 at $\lambda_{\max} = 545, 600,$ and 678 nm can be assigned to the H-band, M-band, and J-band of the dye, respectively. The absorption spectra of Dye 2 in aqueous solution also show similar behavior, with two bands at 513 and 647 nm, which are attributed to the absorption of H-aggregate and J-aggregate, respectively.

When NaCl is added to the aqueous solution of 8.3×10^{-6} M Dye 1, the H-band disappears and the absorption intensity of the J-band increases simultaneously with increasing NaCl concentration, as shown in Fig. 2. The aqueous solution of Dye 2 also has the same tendency when NaCl solution is added. Because inorganic salts promote J-aggregation of cyanine dye in water by increasing its effective dielectric constant [5,29], we may predict that, in our studied system, the role of NaCl is to reduce the electrostatic repulsion between dye anions, thus accelerating their aggregation.

From the bandwidths of the monomer absorption band ($\Delta\nu_{1/2}(M)$, measured in methanol) and of the J-aggregate absorption band ($\Delta\nu_{1/2}(J)$) of the two dyes, the effective coherence length of the J-aggregates ($N(J)$) is estimated using the following equation [12,30]:

$$N(J)^{1/2} = \Delta\nu_{1/2}(M)/\Delta\nu_{1/2}(J). \quad (1)$$

The values of $N(J)$ for aqueous solutions of Dye 1 in the absence and presence of NaCl are 5 and 3, respectively; those for Dye 2 are 4 and 2, respectively. It is worth noting that the effective coherence length of the J-aggregates of Dye 1 (or Dye 2) decreases with increasing NaCl concentration, while the absorption intensity of the J-band increases with increasing NaCl concentration. The reason is that the former is a measurement of the number of monomer units over which the exciton wave function is delocalized and the delocalization range is determined by the relative magnitude of the intermolecular coupling compared to the energetic disorder, instead of by the physical size of the aggregate [31–33]. In contrast, the latter is a measurement of the concentration of the J-aggregates.

The absorption spectra of Dye 1 in CD_3OD and D_2O shown in Fig. 3a were similar to those in CH_3OH and H_2O , as shown in Fig. 3b. The absorption spectra of Dye 2 in CD_3OD and D_2O were also similar to those of Dye 2 in CH_3OH and H_2O , respectively.

3.2. Fluorescence spectra

In methanol solvent, the fluorescence spectrum of Dye 1 or Dye 2 ($\sim 1.0 \times 10^{-5}$ M) has only one emission band at 630 or 612 nm with excitation at 560 nm. Using the excitation wavelength at $580, 600,$ and 650 nm, no J-aggregate emission band is observed for either dye. This indicates that Dye 1 or Dye 2 molecules exist in monomer form in methanol. This result is consistent with that of the absorption spectrum.

The fluorescence spectra of the aqueous solution of 8.3×10^{-6} M Dye 1 in the absence and presence of NaCl upon

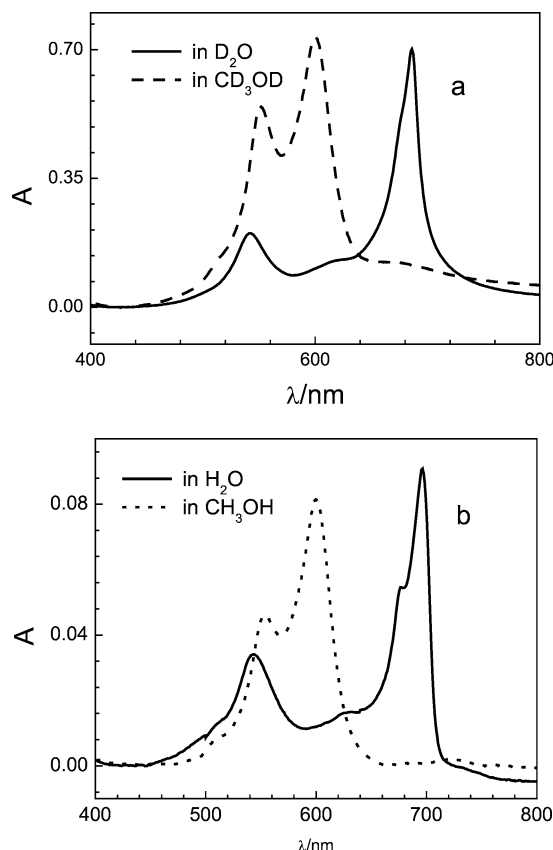


Fig. 3. (a) The absorption spectra of 1.0×10^{-2} M Dye 1 in CD_3OD and 4.0×10^{-3} M Dye 1 in D_2O ; (b) the absorption spectra of 1.47×10^{-2} M Dye 1 in CH_3OH and 4.0×10^{-3} M Dye 1 in H_2O .

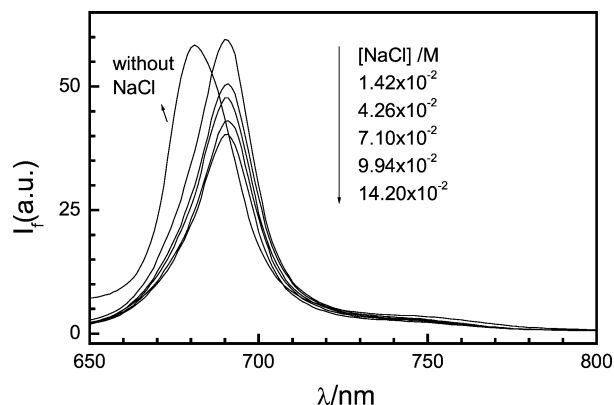


Fig. 4. The fluorescence spectra of 8.3×10^{-6} M Dye 1 in aqueous solution with different concentrations of NaCl.

excitation at 640 nm are shown in Fig. 4. It can be seen that only one fluorescence emission band at 680 nm is observed in the absence of NaCl, which is the fluorescence band of the J-aggregate [29,34,35]. The relative fluorescence quantum yield of J-aggregate can be calculated by the equation

$$\frac{\phi_f}{\phi_f^0} = \frac{I_f(OD)^0}{I_f^0(OD)}, \quad (2)$$

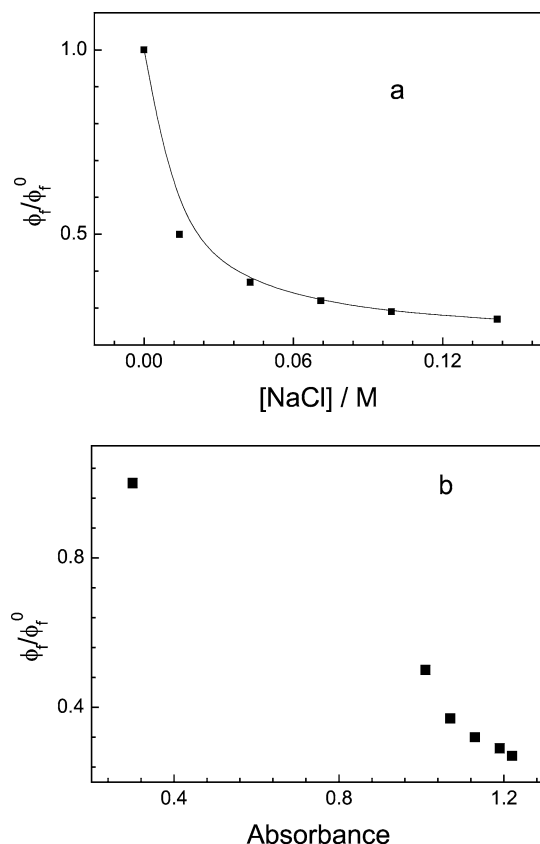


Fig. 5. (a) The change of relative fluorescence quantum yield of 8.3×10^{-6} M Dye 1 in aqueous solution with different concentrations of NaCl; (b) the dependence of the relative fluorescence quantum yield of 8.3×10^{-6} M Dye 1 on the absorbance of J-aggregate.

where ϕ_f^0 , I_f^0 , $(OD)^0$, and ϕ_f , I_f , (OD) are the fluorescence quantum yield, fluorescence intensity, and optical densities of the J-aggregate in the absence and presence NaCl, respectively. The behaviors of the relative fluorescence quantum yield after adding of NaCl are shown in Fig. 5. It is interesting that the fluorescence intensity of the J-band decreases with increasing NaCl concentration. This seems in contradiction to the results obtained in absorption spectra that the absorbance of the J-band increases with increasing NaCl concentration. As pointed out in absorption spectra section, adding NaCl leads to a decrease in the effective coherence length of the J-aggregates. It implies that the J-aggregates contain some disorders (both nondiagonal and diagonal ones), which may affect the delocalization behavior and the observed optical properties. Therefore the decrease in the fluorescence can probably be attributed to the increase in the nonradiative decay rate (K_{nr}) [10,36–38]. On the other hand, one should consider the effect of reabsorption of the J-aggregates on fluorescence intensity. To determine whether the decrease of fluorescence intensity (I_f) with increasing NaCl concentration is caused by the decrease of effective coherence length of J-aggregate or by the reabsorption of J-aggregate, or by both, the absorption and fluorescence spectra of aqueous solutions of Dye 1 (or Dye 2) with various concentrations have been measured. The results

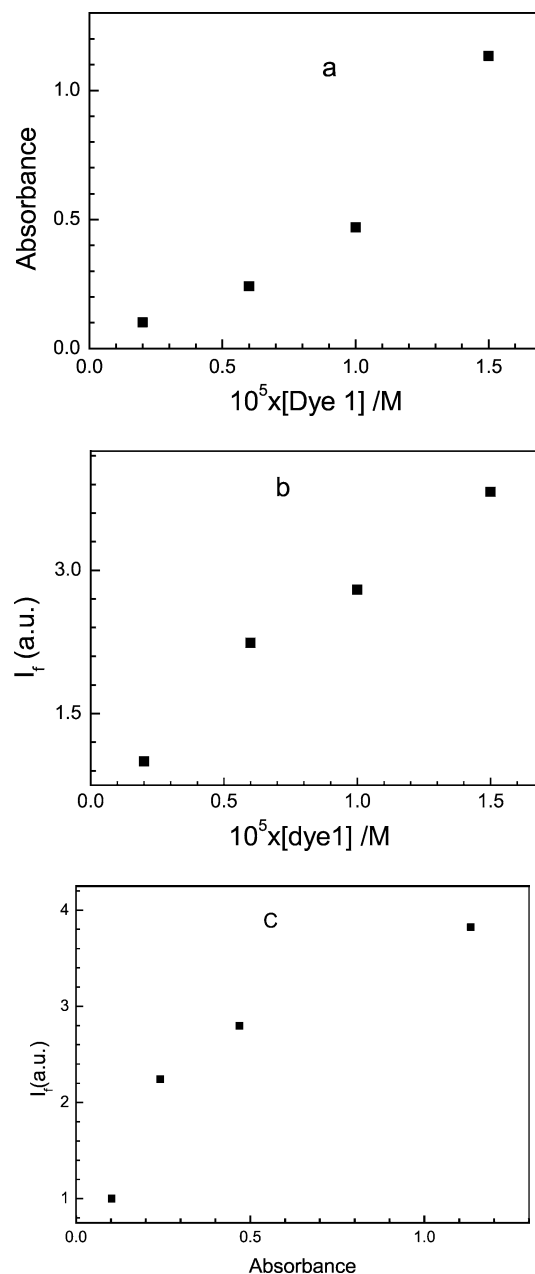


Fig. 6. (a) The dependence of the absorbance of J-aggregate on $[Dye 1]$; (b) the dependence of the fluorescence intensity of J-aggregate on $[Dye 1]$; (c) the dependence of the fluorescence intensity on the absorbance of J-aggregate.

show that both the absorbance and fluorescence intensity of J-aggregates increase with increasing concentration of Dye 1 in the concentration range from 2×10^{-6} M to 1.5×10^{-5} M, as shown in Figs. 6a and 6b, respectively. However, the plot of I_f vs absorbance, as shown in Fig. 6c, indicates that, at high absorbance, the plot deviates from a straight line, but I_f still increases with increasing absorbance of J-aggregates. Furthermore, comparing Fig. 6c with Fig. 5b clearly demonstrates that both the decrease of effective coherence length and the reabsorption of J-aggregates affect the I_f , but the effect of the former seems larger than that of the latter.

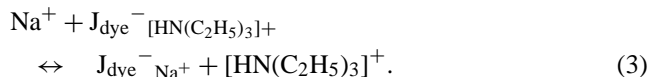
The absorption and fluorescence spectra of Dye 2 in aqueous solution also have similar behavior. The fluorescence emission band of J-aggregate is located at 659 nm.

3.3. ^1H -NMR measurements

To elucidate the effect of NaCl on the aggregation of Dye 1 (or Dye 2) in aqueous solution, the ^1H -NMR spectra of Dye 1 (or Dye 2) in D_2O with and without NaCl and Dye 1 (or Dye 2) in CD_3OD have been measured. Figure 7 shows the high-resolution ^1H -NMR spectrum of 20 mM Dye 1 in CD_3OD . This spectrum is similar to the ^1H -NMR spectra of other thiacyanocarbonyl dyes with similar structures, which can be attributed to the contribution of the monomer [39,40]. However, in D_2O solution, the ^1H -NMR spectrum of Dye 1, as shown in Fig. 8, is characterized by three broad lines, which can be assigned to CH_3 and CH_2 of triethylammonium ion ($\text{HN}(\text{C}_2\text{H}_5)_3^+$) and DOH , respectively. The ^1H -NMR spectrum of Dye 2 in D_2O solution is similar to that of Dye 1. It is evident that, in D_2O solution, Dye 1 (or Dye 2) exists mainly in the form of aggregate. Therefore the lines resulting from individual dye protons are no longer resolved mainly due to the magnetic dipolar interactions generated among the nuclei of the individual dye molecule in the J-aggregate, because the tumbling motion of each dye molecule in the J-

aggregate is strongly limited compared to the unaggregated (or free) dye molecule [41,42]. Similar phenomena have been observed for dyes with similar structure [43]. The results are consistent with those obtained from absorption spectra at the same concentration of Dye 1 or Dye 2 in CD_3OD and D_2O .

When NaCl is added to the D_2O solution of Dye 1 (or Dye 2), the ^1H -NMR signals of CH_3 and CH_2 of triethylammonium ion show highly resolved triplet and quartet patterns, respectively. One example is shown in Fig. 9. This implies that Na^+ ions may penetrate into the dye aggregates and replace the triethylammonium ions; thus the triethylammonium ions leave the dye aggregates and rotate freely. This process can be expressed as



If this is true, one may expect that the integral intensities ratio of the signals of CH_3 to CH_2 would remain constant (3/2) with increasing NaCl concentration. The measured results confirm this interpretation. It is worth noting that the ^1H -NMR spectrum of 7.6×10^{-6} M Dye 1 (or Dye 2) in D_2O reveals two very weak, broad signals of CH_3 and CH_2 of triethylammonium ion, as shown in Fig. 10a. When 0.11 M NaCl is added to the D_2O solution of Dye 1, the ^1H -NMR signals of CH_3 and CH_2 show well-resolved triplet

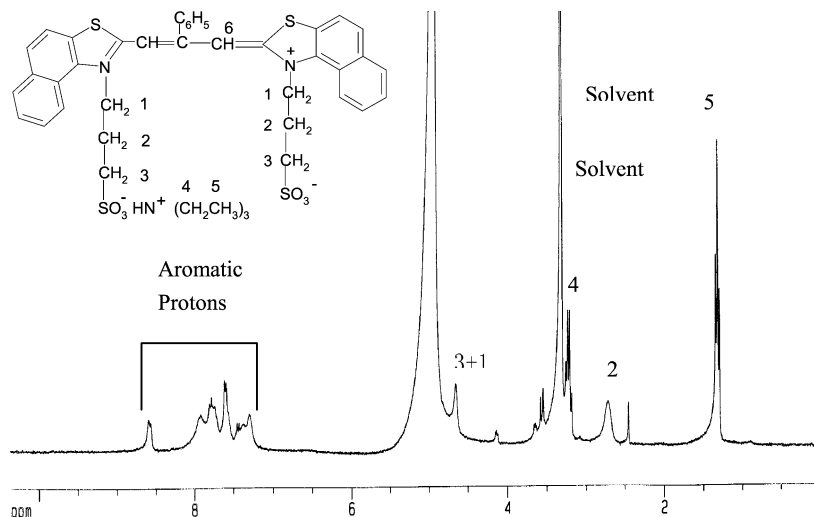


Fig. 7. The ^1H -NMR spectrum of 1.0×10^{-2} M Dye 1 in CD_3OD solution.

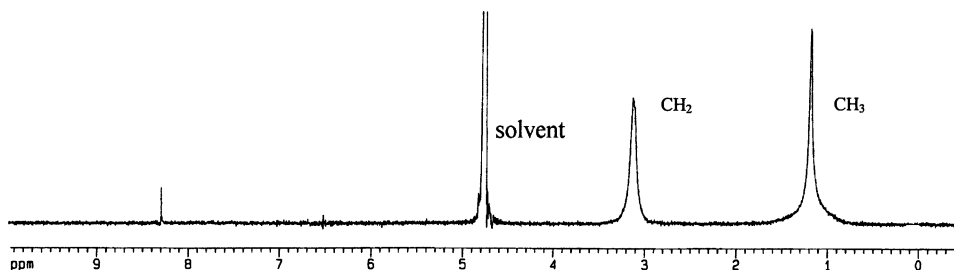


Fig. 8. The ^1H -NMR spectrum of 4.1×10^{-3} M Dye 1 in D_2O solution.

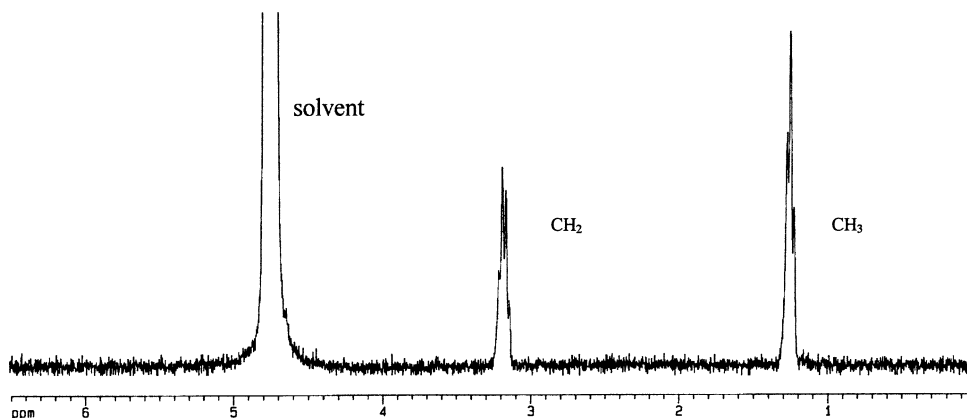


Fig. 9. The ^1H -NMR spectrum of 4.1×10^{-3} M Dye 1 in D_2O solution with $[\text{NaCl}] = 1.46$ M.

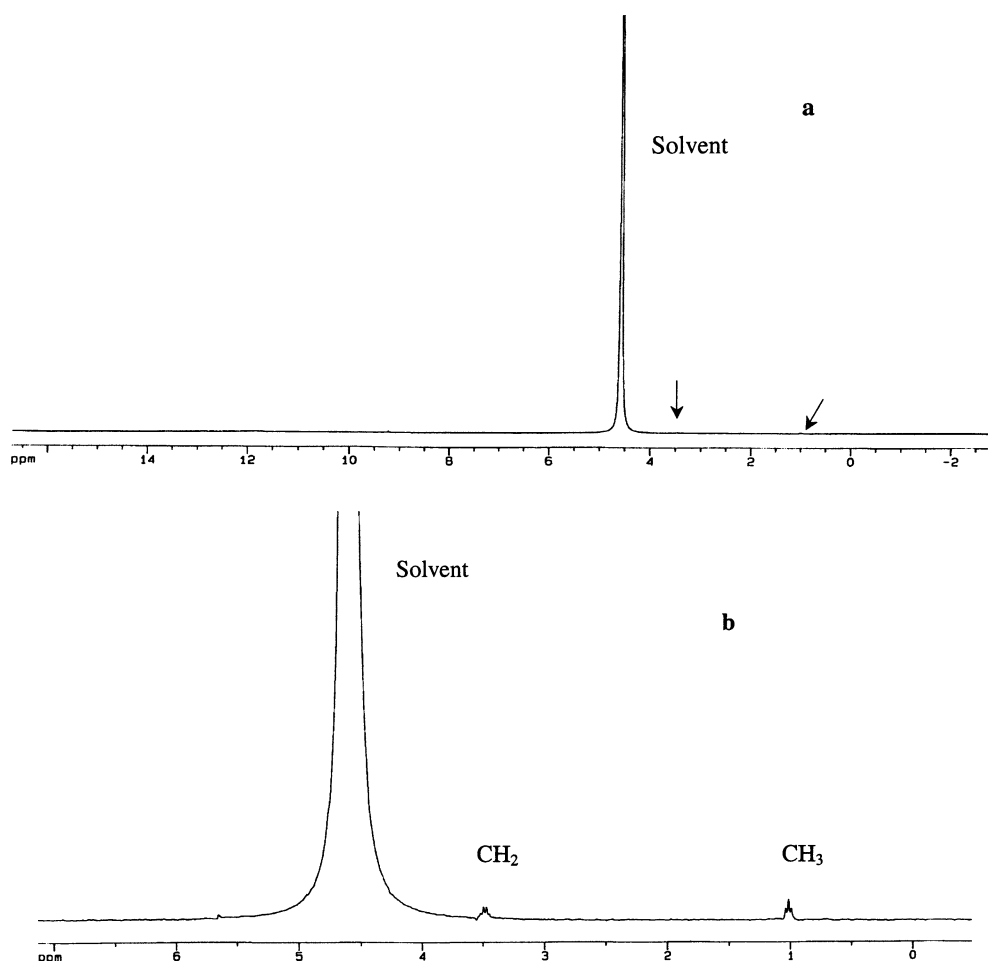


Fig. 10. The ^1H -NMR spectra of 7.6×10^{-6} M Dye 1 in D_2O solution (a) without NaCl and (b) with $[\text{NaCl}] = 0.11$ M.

and quantlet structures, respectively, as shown in Fig. 10b. Therefore, by combining the absorption spectra shown in Fig. 2, one may conclude that, in the dilute D_2O solution of Dye 1 with NaCl, during the process of NaCl promoting the J-aggregation, Na^+ ions replace the triethylammonium ions, as in the concentrated D_2O solution of Dye 1 (or Dye 2) with NaCl previously mentioned.

Moreover, as seen from Eq. (3), there are at least two kinds of Na^+ ions in aqueous solution of dye: one binds to the dye molecule in J-aggregates; the other unbinds to the dye molecule in J-aggregates. Thus one may predict that the chemical shifts of $^{23}\text{Na}^+$ in aqueous solution of NaCl with and without Dye 1 (Dye 2) would be different from each other, and this will be discussed later.

3.4. ^{23}Na -NMR measurements

For the purpose of examining the interaction between dye molecules and Na^+ ions in aqueous solution of NaCl, the chemical shifts (δ_{Na^+}) of ^{23}Na nuclei in aqueous solution of NaCl with and without dye have been measured as a function of the concentration of NaCl. The results are shown in Fig. 11. It is found that there is a linear relationship between the chemical shifts and the concentration of NaCl for both cases, which can be expressed as follows:

$$\delta_{\text{Na}^+} = A + B [\text{NaCl}] \quad ([\text{dye}] = 0), \quad (4)$$

$$\delta'_{\text{Na}^+} = A' + B' [\text{NaCl}] \quad ([\text{dye}] \neq 0). \quad (5)$$

The results are listed in Table 1.

On the other hand, it is known that δ_{Na^+} in aqueous solution of NaCl can be formulated as [20,21]

$$\delta_{\text{obs}} = -16\alpha^2 \left\langle \frac{1}{r^3} \right\rangle_{\text{np}} \times \frac{1}{\Delta E} [\Lambda_{\text{M-M}} + \Lambda_{\text{M-X}} + \Lambda_{\text{M-W}} - \Lambda_{\text{M-W}}^0], \quad (6)$$

where α is the fine-structure constant; $\langle 1/r^3 \rangle_{\text{np}} \equiv \langle \varphi_0 | 1/r^3 | \varphi_0 \rangle$ is the expectation value of $1/r^3$ for the outer p orbitals of Na^+ ; ΔE is the mean excitation energy; $\Lambda_{\text{M-M}}$, $\Lambda_{\text{M-X}}$, and $\Lambda_{\text{M-W}}$ are the overlap integrals of the orbitals of Na^+ and other positive ions (M), negative ions (X), and

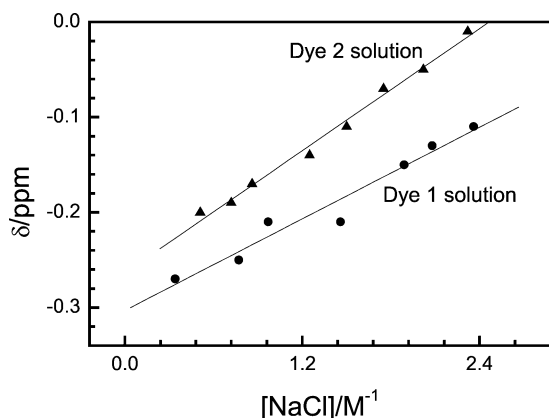


Fig. 11. The dependence of the chemical shift of ^{23}Na on the concentration of NaCl in the presence of [Dye 1] = 4.1×10^{-3} M and [Dye 2] = 4.4×10^{-3} M, respectively. (The chemical shift of ^{23}Na is measured relative to that of 1.71 M NaCl solution.)

Table 1

The fitted results of chemical shift of ^{23}Na on the variation of NaCl in different systems^a

System	Chemical shift/ppm ^b (r)
NaCl	$\delta = -0.443 + 0.263\chi$ (1.00)
Dye 1/NaCl	$\delta = -0.303 + 0.080\chi$ (0.98)
Dye 2/NaCl	$\delta = -0.264 + 0.107\chi$ (1.00)

^a The chemical shift of ^{23}Na is measured relative to that of 1.71 M NaCl solution.

^b χ is the concentration of NaCl.

water molecules, taken over all the possible orientations and separations, respectively; and $\Lambda_{\text{M-W}}^0$ is the overlap integral of the orbitals of Na^+ and surrounding water molecules at an infinite dilution of NaCl. As a good approximation, ΔE and $\langle 1/r^3 \rangle_{\text{np}}$ are independent of the concentration of NaCl and the changes in δ_{Na^+} may be attributed mainly to the overlap integrals. In the presence of dyes, it is rational to assume that δ_{Na^+} in aqueous solution of NaCl can also be formulated as [20–22]

$$\delta'_{\text{obs}} = -16\alpha^2 \left\langle \frac{1}{r^3} \right\rangle_{\text{np}} \times \frac{1}{\Delta E} [\Lambda_{\text{M-M}} + \Lambda_{\text{M-X}} + \Lambda_{\text{M-W}} + \Lambda_{\text{M-dye}}^d - \Lambda_{\text{M-W}}^0], \quad (7)$$

where $\Lambda_{\text{M-dye}}^d$ is the overlap integral of the orbitals of Na^+ ions and surrounding dye molecules. Since the concentration of NaCl is much higher than that of Dye 1 (or Dye 2) and the concentration of Dye 1 (or Dye 2) is kept constant throughout NMR experiments, the values of $\Lambda_{\text{M-M}}$, $\Lambda_{\text{M-X}}$, and $\Lambda_{\text{M-W}}$ in Eqs. (6) and (7) would be approximately the same. According to Eqs. (6) and (7), we have

$$\Delta\delta = \delta_{\text{obs}} - \delta'_{\text{obs}} = -16\alpha^2 \left\langle \frac{1}{r^3} \right\rangle_{\text{np}} \times \frac{1}{\Delta E} \times \Lambda_{\text{M-dye}}^d, \quad (8)$$

which means that in the dye/NaCl/ H_2O system, the variation of δ_{Na^+} arising from the interactions between the dye molecules and Na^+ ions is proportional to $\Lambda_{\text{M-dye}}^d$.

Unfortunately, it is difficult to directly calculate the value of the overlap integral $\Lambda_{\text{M-dye}}^d$. However, based on the results obtained in the absorption spectra, fluorescence spectra, and ^1H -NMR spectra, the interaction between Na^+ ions and dye molecules in the J-aggregate can be formally treated by the association reaction



where K is the apparent constant of association. If α is the degree of association between dye molecules and Na^+ ions, the observed chemical shift (δ_{obs}) of Na^+ ions can be expressed by the weighted mean of the chemical shifts of free (δ_{F}) and associated (δ_{B}) sodium ions by the equation [44,45]

$$\delta_{\text{obs}} = (1 - \alpha)\delta_{\text{F}} + \alpha\delta_{\text{B}}. \quad (10)$$

Because

$$K = \frac{[\text{dye} - \text{Na}^+]}{[\text{Na}^+][\text{dye}]},$$

or

$$\begin{aligned} K &= \frac{\alpha C_{\text{NaCl}}}{(1 - \alpha)C_{\text{NaCl}}(C_{\text{dye}} - \alpha C_{\text{NaCl}})} \\ &= \frac{\alpha}{(1 - \alpha)(C_{\text{dye}} - \alpha C_{\text{NaCl}})} \\ &= \frac{\alpha}{C_{\text{dye}} - \alpha C_{\text{dye}} - \alpha C_{\text{NaCl}} + \alpha^2 C_{\text{NaCl}}}, \end{aligned} \quad (11)$$

then

$$K C_{\text{dye}} = \alpha(1 + K C_{\text{dye}} + K C_{\text{NaCl}} - \alpha K C_{\text{NaCl}}),$$

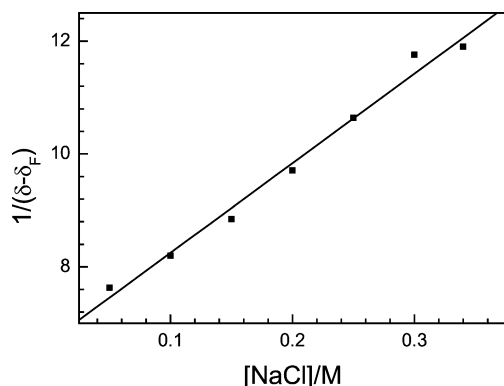


Fig. 12. The dependence of $1/(\delta - \delta_F)$ on the concentration of NaCl in Dye 1/NaCl systems.

and therefore, we have

$$\alpha = \frac{K C_{\text{dye}}}{1 + K C_{\text{dye}} + K C_{\text{NaCl}} - K \alpha C_{\text{NaCl}}} \quad (12)$$

From Eqs. (12) and (9), we obtain

$$\delta - \delta_F = (\delta_B - \delta_F) \frac{K C_{\text{dye}}}{1 + K C_{\text{dye}} + K C_{\text{NaCl}} - K \alpha C_{\text{NaCl}}},$$

$$\frac{1}{\delta - \delta_F} = \frac{1}{(\delta_B - \delta_F) K C_{\text{dye}}} + \frac{K C_{\text{dye}} + K C_{\text{NaCl}} - K \alpha C_{\text{NaCl}}}{(\delta_B - \delta_F) K C_{\text{dye}}} \quad (13)$$

Because $[\text{NaCl}] \gg [\text{dye}]$, Eq. (13) can be simplified as

$$\frac{1}{\delta_{\text{obs}} - \delta_F} = \frac{1}{(\delta_B - \delta_F) K C_{\text{dye}}} + \frac{C_{\text{NaCl}}}{(\delta_B - \delta_F) C_{\text{dye}}} \quad (14)$$

If the change of the chemical shifts of Na^+ ions were due to the association of Na^+ ions with J-aggregate, one would expect a linear dependence of $1/(\delta_{\text{obs}} - \delta_F)$ on the concentration of NaCl. Indeed, the linearity of the experimental plots confirms this behavior, and Fig. 12 shows the plot of Dye 1. The calculated values of K for Dye 1 and Dye 2/NaCl systems are 2.38 M^{-1} and 1.35 M^{-1} , respectively.

Acknowledgments

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