# Photoinduced intramolecular charge transfer of sodium 4-(N,N-dimethylamino)benzenesulfonate

LIN Lirong (          ) & JIANG Yunbao (          )

Department of Chemistry and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China

Correspondence should be addressed to Jiang Yunbao (email: ybjiang@xmu.edu.cn)

**Abstract**   A new dual fluorescent N,N-dimethylaniline derivative, sodium 4-(N,N-dimethylamino)-benzenesulfonate (SDMAS), is reported. In SDMAS, the electron acceptor is linked to the phenyl ring via a sulfur atom at the para-position of the electron donor. It was found that SDMAS emits dual fluorescence only in highly polar solvent water but not in organic solvents such as formamide, methanol and acetonitrile. In organic solvents only a single-band emission at *ca.*360 nm was observed in the short wavelength region. The dual fluorescence of SDMAS in water was found at 365 and 475 nm, respectively. Introduction of organic solvent such as ethanol, acetonitrile, and 1,4-dioxane into aqueous solution of SDMAS leads to blue-shift and quenching of the long-wavelength emission. Measurements of steady-state and picosecond time-resolved fluorescence indicate that the long wavelength fluorescence is emitted from a charge transfer (CT) state that is populated from the locally excited (LE) state, with the latter giving off the short wavelength fluorescence. The fact that a highly polar solvent is required to bring out the dual fluorescence suggests that the CT process of SDMAS has a high activation energy ($E_a$). In supporting this assumption the time-resolved fluorescence measurements give an $E_a$ of 15.35 kJ·mol$^{-1}$. It was assumed that the participation of the sulfur atom d-orbital in the conjugation of sulfonate group with phenyl ring and the strong twisting and inverting of the dimethylamino plane relative to the phenyl ring could be the reasons for the high activation energy. A molecular configuration change upon charge transfer in water was suggested for SDMAS based on the thermodynamic data. SDMAS reported here represents the example of the dual fluorescent amine substituted aromatic sulfonate.

**Keywords:   intramolecular charge transfer, dual fluorescence, picosecond time-resolved fluorescence, ultra-fast kinetics, excited-state structural relaxation, sodium 4-(N, N-dimethylamino)benzenesulfonate.**

Dual fluorescence of N, N-dimethylaniline (DMA) derivative with electron acceptor at the para-position of the donor was first reported for 4-(N, N-dimethylamino)benzonitrile (DMABN) by Lippert et al.[1] in the late 1950s. Since then a huge amount of dual fluorescent DMA derivatives have been reported [2] and the two emission bands were assigned to the locally excited (LE) state and the charge transfer (CT) state, respectively [2—4]. The atoms that link the electron acceptor to the phenyl ring are mainly carbons of different hybrid (sp, sp$^2$ and sp$^3$)[2], silicon, boron [2], sulfur [5], and phosphor [6]. While the investigations with the former group of DMA derivatives have been carried out extensively, those with the latter groups yet await further efforts.

We were interested in the investigations of the dual fluorescent DMA derivatives in which the electron acceptor is linked via a heteroatom to DMA molecule at the para-position of the ami-

no group. Our first attempt was made to sodium 4-(N, N-dimethylamino)benzenesulfonate. This was because that (i) the carboxylic derivatives of DMA, 4-(N,N-dimethylamino)benzoic acid and sodium 4-(N, N-dimethylamino)benzoate are dual fluorescent[7—9], and the electron accepting ability of $—SO_3^-$ is higher than that of $—CO_2^-$, according to their Hammett constants ($s_p$ = 0.35 and 0.00, respectively[10]), (ii) introducing to DMA a sulfonic group instead of a carboxylic group would increase the water solubility of the DMA derivatives and thus make the new dual fluorophore a better probe for aqueous media, and (iii) aminonaphthalenesulfonates, such as 1-dimethylamino-5-naphthalenesulfonyl        chloride        (dansyl        chloride)        and        1-anilino-8-naphthalenesulfonate (ANS), are important fluorescent probes in biological assays[11] and chemical probing[12]. In spite of the fact that the emissive state of these amininaphthalene sulfonates is reportedly of charge transfer character, these sulfonates give off only single-band emission. Therefore, searching for dual fluorescent amine substituted aromatic sulfonates would be significant in demonstrating their charge transfer mechanism and developing direct and efficient fluorescent probes.

The present paper reports the fluorescence spectra of the newly synthesized sodium 4-(N, N-dimethylamino)benzenesulfonate (SDMAS) (scheme 1) in water and organic solvents. Dual fluorescence can be observed in highly polar solvent water. Picosecond time-resolved fluorescence decay data show that the long wavelength fluorescence of SDMAS is emitted from the charge transfer (CT) state. It is shown that the CT process requires high activation energy ($E_a$). To our knowledge, SDMAS is the first amine substituted aromatic sulfonate that shows dual fluorescence.
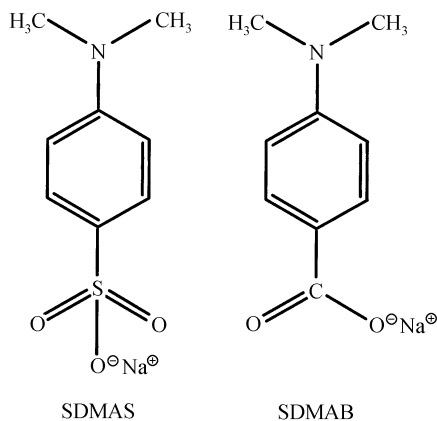


Scheme 1.    Molecular structures of SDMAS and SDMAB.

## 1    Experimental

SDMAS was synthesized from the reaction of 4-aminobenzenesulfonic acid with dimethyl-sulfate in alkaline solution[13]. Sodium 4-(N, N-dimethylaminobenzoate) (SDMAB) was prepared as described elsewhere[9]. Organic solvents were purified by standard procedures and checked to

have no fluorescent impurity at the excitation wavelength used for samples. Water was twice de-ionized and distilled.

Corrected fluorescence spectra were taken on Hitachi F-4500 fluorescence spectrophotometer using excitation wavelength of 280 nm. Picosecond time-resolved fluorescence decay was measured by means of time-correlated single photon counting (TCSPC)[4]. Mode-locked $Ar^+$ laser pumped Rhodamine-6G dye laser outputs pulse of 592 nm which is frequence-doubled by $LiIO_3$ to produce ultraviolet light pulse at 296 nm used for sample excitation. The sample was either bubbled by $N_2$ for 15 min or degassed by freeze-pump-thaw cycles. To avoid the scattering light interference a polarizer was set in the emission optical path at 54.7°(magic angle) relative to that in the excitation optical path. The fluorescence was detected by a micro-channel plate photomultiplier tube. The time response function of the whole detection system has a width of *ca*. 30 ps at the excitation wavelength of 296 nm. The fluorescence decay curves were analyzed in exponential functions with deconvolution method. Absorption spectra were recorded on UV-760 CRC spectrophotometer (Shanghai). pH values of aqueous solutions were measured on HM-20 pH-meter (TOA Model, Japan). Electrical conductivities were measured on DDS-11a Electrical Conductometer (Shanghai).

## 2   Results and discussion

Fig. 1 shows representative fluorescence spectra of SDMAS in solvents of different polarity. It is found that SDMAS is dual fluorescent in strongly polar solvent, water, with two bands peaked at 365 and 475 nm, respectively. In polar organic solvents such as formamide, methanol (MeOH), ethanol (EtOH) and acetonitrile (ACN), however, SDMAS only gives off a single-band emission at around 360 nm. That band slightly red-shifts with increasing polarity, indicating that the emissive state has a dipole moment higher than the ground state. The fluorescence emission behavior of SDMAS in organic solvents is apparently similar to that of 1-aminonaphthalene-8- sulfonate (ANS)[11, 12].



Fig. 1. Fluorescence spectra of SDMAS in different solvents. The spectra were taken from SDMAS solution of $1.25 \times 10^{-5}$ mol •L$^{-1}$ under 280 nm photon excitation. Solvents are water (1), formamide (2), methanol (3), ethanol (4) and acetonitrile (5), respectively.

The short wavelength emission of SDMAS in organic solvents and water can be readily assigned to the locally excited (LE) state as done with DMABN family molecules[2—4]. This assignation is supported by the observation that the fluorescence excitation spectra are similar to the absorption spectrum (see fig. 2). It should be noted that the absence of dual fluorescence of SDMAS in organic solvents is different from the case with the carboxylic derivative, SDMAB (scheme 1), which is dual fluorescent in organic
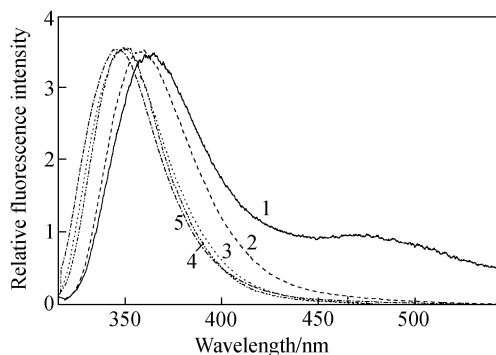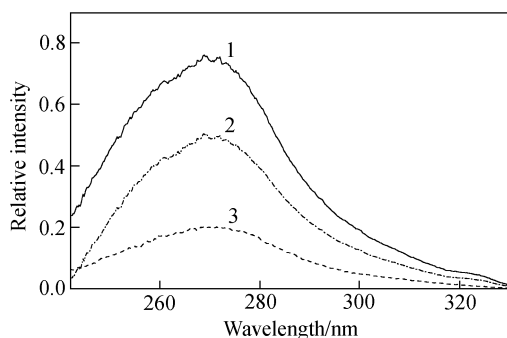
Fig. 2. Fluorescence excitation spectra and absorption spectrum of SDMAS in water. Curves represent: 1, excitation spectrum with $I_{em}=364$ nm; 2, absorption spectrum with $\lg\varepsilon_{270nm}=4.34$; 3, excitation spectrum at $I_{em}=470$ nm, respectively.

solvents of polarity higher than that of toluene. The fact that only in water dual emission is observed with SDMAS suggests that a much higher solvent polarity be required to bring out the dual emission from SDMAS.

In principle, dual fluorescence could be due to excimer formation, excited-state intramolecular proton transfer (ESIPT) or acid-base dissociation equilibrium, and intramolecular charge transfer (CT). In order to identify the origin of the dual fluorescence from SDMAS in water, the concentration dependence of the dual emission, the effect of aqueous 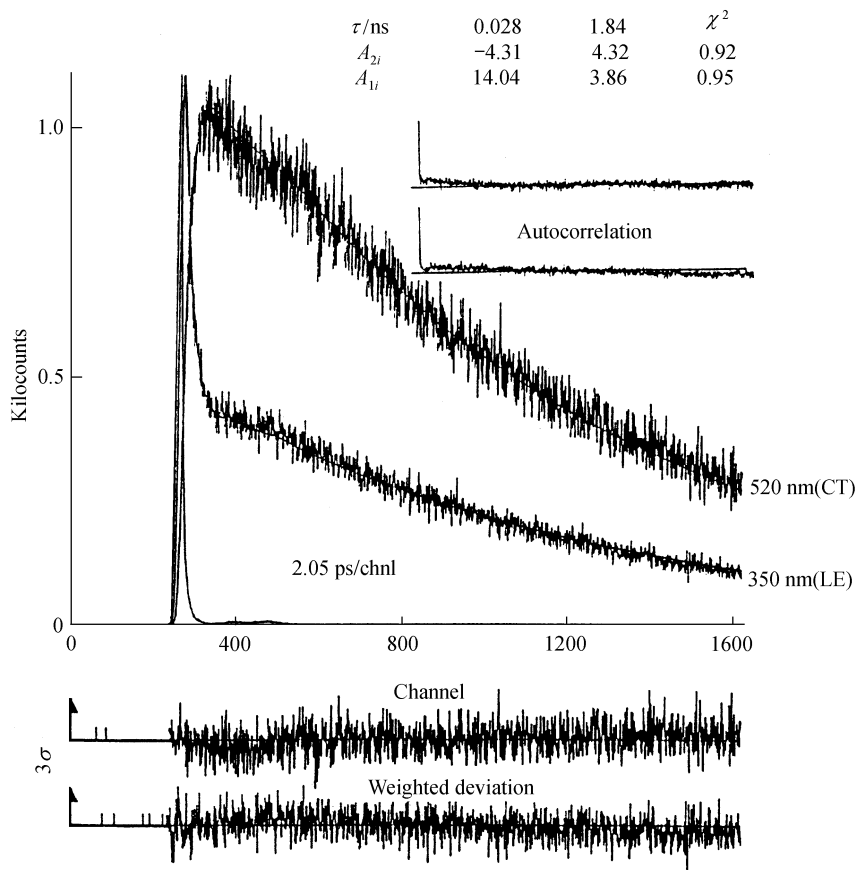solution pH, and solvent polarity dependence of the fluorescence spectra in water-EtOH, water-ACN and water-1,4-dioxane (DiOX) binary mixtures as well as the picosecond time-resolved fluorescence decay in water were investigated.

Concentration dependence of the SDMAS fluorescence spectra in water shows that, while both emission bands are enhanced at higher concentration, the quantum yield ratio of the two bands (long wavelength to short wavelength), $F'/F$, remains constant over the studied concentration range of $2.5\times10^{-6}$—$7.5\times10^{-5}$ mol·L$^{-1}$. It hence follows that the long wavelength emission is not due to the excimer formation. Ground-state intermolecular association and/or aggregation are ruled out by the fact that a nice linearity is found between the solution electrical conductivity and SDMAS concentration.

The excitation spectra of SDMAS in water obtained by monitoring the short and long wavelength fluorescence are found identical (fig. 2, curves 1 and 3) and similar to the absorption spectrum (fig. 2, curve 2). This observation shows that the two emissive states of SDMAS in water have the same origin of excitation. The presence of two excited states and the relationship between them were further investigated by picosecond time-resolved fluorescence decay measurements. Fig. 3 shows the fluorescence decay curves of SDMAS in water at 20°C, measured at both short (350 nm) and long (520 nm) wavelengths, and the global fitting to both of the curves according to eqs. (1) and (2).

$$I_{LE}(t) = A_{12}\, e^{-t/t_2} + A_{11}\, e^{-t/t_1}, \tag{1}$$

$$I_{CT}(t) = A_{22}\, e^{-t/t_2} + A_{21}\, e^{-t/t_1}, \tag{2}$$

where $I_{LE}(t)$ and $I_{CT}(t)$ represent LE and CT fluorescence intensities at time $t$ after pulse excitation, $t_i$ the decay times, and $A_{ij}$ the pre-exponential amplitudes. Double exponential kinetics is found from the decay of short wavelength LE fluorescence, indicating that a two-state process indeed

Fig. 3. Decays of SDMAS fluorescence in water at 20℃ measured at (LE) 350 nm and (CT) 520 nm, and the global fitting to the curves. $t_i$, $A_{2i}$ (CT) and $A_{1i}$ (LE) are decay times and pre-exponential amplitudes, respectively. $\chi^2$ represents the goodness of the fitting.

occurs in the LE state[4]. Meanwhile, the same values but opposite sign of the pre-exponential amplitudes are fitted out of the decay curve of long wavelength fluorescence, i.e. $A_{22} = -A_{21}$ (fig. 3). It is then clear from eq. (2) that at excitation, i.e. at $t = 0$, $I_{CT}(0)$ is zero, indicating that the emissive state for the long wavelength fluorescence be populated from the LE state[4].

As SDMAS is the conjugate base of an organic acid, an excited-state acid-base dissociation process can happen and lead to dual fluorescence emission. The pH dependence of the dual emission of SDMAS in water was hence investigated. The results are presented in fig. 4 in which the total fluorescence intensity, $I_f$, and $F'/F$ are plotted against solution pH. Clear breaks at the same pH are noted from the two curves, from which a p$K_a$* of 3.4 can be obtained which is close to the ground state p$K_a$ (3.42[14]). This should mean that at pH higher than p$K_a$ the emission is from the anionic form of SDMAS while at pH lower than p$K_a$ the emission is due to the neutral acid form of SDMAS. It is therefore concluded that the excited-state proton transfer between SDMAS ani-
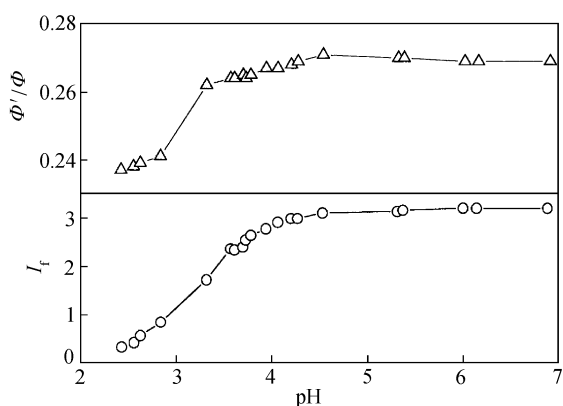
Fig. 4. pH dependence of $F'$ /$F$ ratio and total fluorescence intensity ($I_f$) of SDMAS in aqueous solution. pH was tuned by NaOH or HCl.

onic/neutral form and water is slower than the fluorescence of each species, which is similar to what was found with SDMAB in water[9]. Evidently from fig. 4 the anionic form of SDMAS has a relative CT fluorescence quantum yield ($F'$ /$F$ = 0.27) slightly higher than the neutral form ($F'$ /$F$ = 0.24). As this difference is small, the shifting of the acid-base equilibrium of SDMAS in water should not be the reason for the appearance of the dual fluorescence.

Solvent polarity effect was examined in an attempt to demonstrate the CT character of the emissive state of SDMAS long-wavelength fluorescence in water. Water-soluble organic solvents, EtOH, ACN, and DiOX, were used for tuning the polarity of the aqueous solution. Fig. 5 presents the fluorescence spectra of SDMAS in water-EtOH mixtures, in which the LE band intensity is normalized. It can be found from fig. 5 that, with the water content increasing, the long wavelength band is red-shifted and enhanced. The enhancement in the long wavelength band is directly reported in fig. 6 in which $F'$ /$F$ is plotted against water content by volume in the binary mixtures. Similar observations were made in water-ACN and water-DiOX binary mixtures (see also fig. 6). The red shift in the long-wavelength band of SDMAS with increasing solvent polarity clearly points to the charge transfer (CT) character of the emissive state, as also found with other
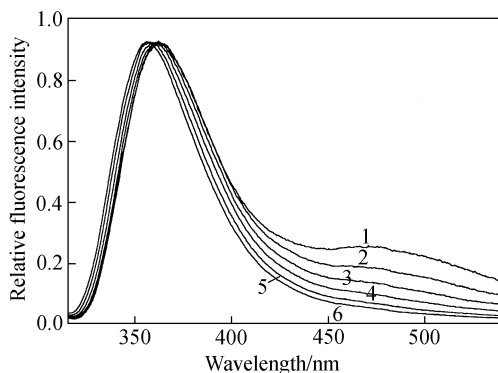


Fig. 5. Fluorescence spectra of SDMAS in water-EtOH mixtures of different water content. EtOH represents ethanol. Water contents (v/v) are 1, 100%; 2, 90%; 3, 80%; 4, 70%; 5, 60%; 6, 50%, respectively.
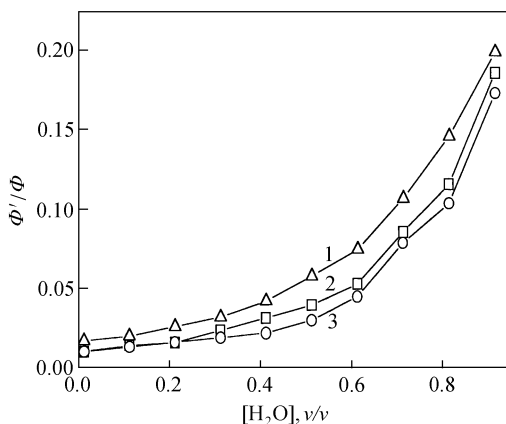


Fig. 6. Variations of $F'$ /$F$ of SDMAS with water content by volume in water-organic solvent mixtures. Organic solvents are ethanol (EtOH, 1), acetonitrile (ACN, 2), and 1, 4-dioxane (DiOX, 3), respectively.

well-established CT dual fluorescent molecules[2]. The long wavelength emission of SDMAS in water can then be safely assigned to a CT state. Therefore, together with the time-resolved fluorescence decay data shown in fig. 3, it is concluded that the dual fluorescence observed with SDMAS in water is due to the LE and the CT states in equilibrium and the CT state is populated directly from the LE state. The fact that the CT emission of SDMAS is only observed in highly polar water implies that the CT process occurs at high activation energy.

Direct support for this high activation energy ($E_a$) came from the measurements of the time-resolved LE fluorescence decays at different temperatures. Double exponential decay kinetics is found in the temperature range of 1—40°C. From the fittings to the decay curves two decay times ($t_1$ and $t_2$, eq.(1)), ranging from 43 to 16 ps for the short $t_2$ and from 1.79 to 1.71 ns for the long $t_1$, were obtained together with pre-exponential amplitude ratio $A_{12}/A_{11}$ (eq. (1)) ranging from 5.0 to 2.9. Using the well-known Birks' protocol[15, 16], the forward and backward CT process rate constants, $k_a$ and $k_d$, were calculated over the temperature range. The activation energy of these two processes, $E_a$ and $E_d$, were obtained fr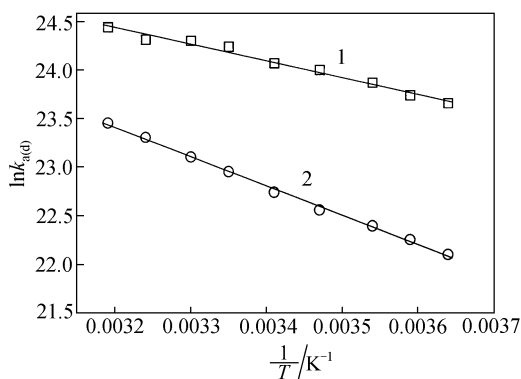om the Arrhenius plots (fig. 7). A high $E_a$ value of 15.35 kJ·mol$^{-1}$ was calculated from the slope of the straight line of ln$k_a$ against $1/T$. The CT process en-



Fig. 7. Arrehnius plots of the forward (1, $k_a$) and backward (2, $k_d$) charge transfer reaction rate constants of SDMAS in water. Temperature is varied over the range of 1—40℃. The following parameters were calculated: $E_a$ = 15.35 kJ • mol$^{-1}$, $E_d$ = 24.77 kJ • mol$^{-1}$, $\Delta H$ = -9.43 kJ • mol$^{-1}$, and $\Delta S$ = -21.15 J • mol$^{-1}$ • K$^{-1}$.

thalpy change, $\Delta H$, and entropy change, $\Delta S$, of -9.43 kJ·mol$^{-1}$ and -21.15 J·mol$^{-1}$·K$^{-1}$, respectively, were obtained from the same set of data (fig. 7). Temperature (25—80℃) dependence of steady-state fluorescence spectrum was also examined for measuring $\Delta H$ alternatively. From this measurement $\Delta H$ of -7.08 kJ·mol$^{-1}$ was obtained from Stevens-Ban's plot (ln$F'$/$F$ against the reciprocal of the absolute temperature, $1/T$[16], fig. 8). This value is compatible to that obtained from the time-resolved experiments.
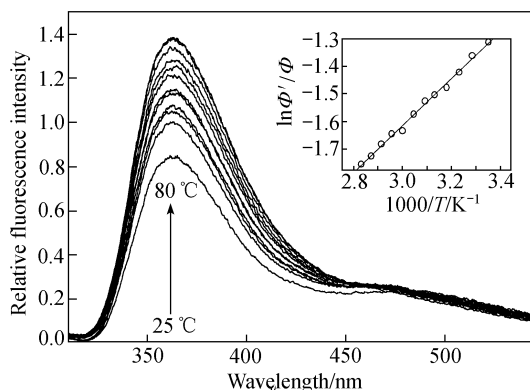


Fig. 8. Fluorescence spectra of SDMAS in water as a function of temperature. Inset shows the Stevens-Ban plot. Temperature varies from 25 to 80℃.

The activation energy of the CT reaction of SDMAS in water ($E_a$ = 15.35 kJ· mol$^{-1}$) was found to be much higher than that of DMABN (7.8 kJ· mol$^{-1}$) in a nonpolar solvent toluene [16]. With sulfone substituted DMA, 4,4'-dimethylaminobenzenesulfone (DMAPS), Rettig and Chandross[5] reported an $E_a$ in EtOH of 9.3 kJ· mol$^{-1}$. This value, in spite of higher than that of DMABN in toluene[16], is much lower than that of SDMAS in water reported here. The absence of the CT dual fluorescence of SDMAS in EtOH in which DMAPS shows clear dual fluorescence[5] already reflects the difference in the CT activation energy for SDMAS and DMAPS. It was suggested[5] that the high activation energy of DMAPS is due to the participation of the sulfur atom d-orbital in the conjugation of the sulfone group with the phenyl ring. This may also be applied to current SDMAS system, since that participation is possible in SDMAS, based on the optimized structure of SDMAS anion recently reported by Oda and Sato[17]. The reported SDMAS structure indicates that one of the three S—O bonds is always in the plane of the phenyl ring, making the sulfur atom p-orbital and d-orbital possible to conjugate with the delocalized p-orbitals of the phenyl ring. Also, the optimized structure of the SDMAS anion is quite different from that of its methyl ester. The dimethylamino group in the anion is inverted and twisted by 40.9° and 48.4°, respectively, whereas in the ester the angles are 17.0° and 0.02° in the optimized structure and 4.37° and 0.77° in the crystal. This difference in the structures of SDMAS and its methyl ester was rationalized[17] in terms of preventing the nitrogen lone pair electrons in SDMAS anion from conjugating with the p-orbitals in phenyl ring. Note that the crystal structure of DMABN[18] shows that the dimethylamino group inverted only by 11.9° and no appreciable twisting is indicated. Therefore it is supposed that the strongly twisted and inverted configuration of the dimethylamino group with respect to the phenyl ring in DMABS may also account for the high activation energy of the CT reaction and a configuration relaxation could happen upon charge transfer. However, it is not yet made clear at this step the precise reasons for the high activation energy of the charge transfer reaction with SDMAS in water.

Thermodynamic analysis shows that a molecular configuration change indeed occurs upon CT process. Scheme 2 shows the potential curves of the states involved in the CT process, in which $d_{rep}$(LE) and $d_{rep}$(CT) are the repulsion energy of Frank-Condon (F-C) ground states reached immediately after the LE and CT emission and in which the structures of the LE and CT states remain. The values of $d_{rep}$(LE) and $d_{rep}$(CT) should hence reflect the differences of the excited state configurations from the equilibrated ground state and thus indicate the configuration changes in the corresponding excited states. Based on the thermodynamic cycle, $d_{rep}$(LE) and $d_{rep}$(CT) can be calculated by eqs.(3) and (4).

$$d_{rep}(CT) = E_{LE} - h\textbf{\textit{n}}_{CT} + \Delta H, \tag{3}$$

$$d_{rep}(LE) = E_{LE} - h\textbf{\textit{n}}_{LE}, \tag{4}$$

where $E_{LE}$ is the LE state energy calculated from the cross point of the normalized absorption and fluorescence spectra. $d_{rep}$(CT) and $d_{rep}$(LE) are then obtained as 106.69 kJ· mol$^{-1}$ and 39.83 kJ· mol$^{-1}$

by a difference of 66.86 kJ· mol$^{-1}$. The difference between $d_{rep}$(CT) and $d_{rep}$(LE) is *ca*. 2 times of $d_{rep}$(LE). Obviously the configuration of the F-C ground state reached from the CT state is different from that reached from the LE state and both of them away from that of the equilibrated ground state. It is hence clear that a configuration change occurs upon charge transfer with SDMAS in aqueous solution. At this stage we were not able to clarify the configurations of the LE and CT states, but a more planar configuration can be assumed for the CT state than for the LE state, as the ground state is quite far away from the planar configuration[17].
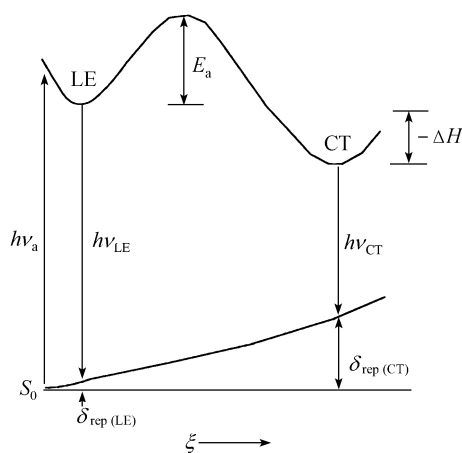


Scheme 2.    Potential curves for the states involved in the CT process.

It is of interest to point out that, based on the Hammett constants of —SO$_2$R ($s_p$ = 0.72, R = methyl; $s_p$ =0.77, R = ethyl) and —SO$_3^-$ ($s_p$ = 0.35)[10], —SO$_3^-$ is worse in electron withdrawing compared with —SO$_2$R. Experimentally, we observed no CT emission from SDMAS in organic solvents such as EtOH and ACN, whereas strong CT emission was found with DMAPS in these solvents[5]. This phenomenon is similar to the recent observation in amide derivatives of DMABN that weaker electron acceptor leads to relatively weak CT emission[19].

## 3   Conclusions

A new dual fluorescent N, N-dimethylaniline derivative, sodium 4-(N, N-dimethylamino) benzenesulfonate, in which the electron acceptor is linked via a hetero-atom, sulfur, to the phenyl ring was reported. It was found that SDMAS only shows dual fluorescence in highly polar solvent water. Steady-state and time-resolved fluorescence measurements demonstrate that, with SDMAS in water, the long wavelength band at *ca.* 475 nm is emitted by a charge transfer state while the short wavelength band at 365 nm by the LE state that populates and is in equilibrium with the CT state. Ultra-fast kinetics measurements by picosecond time-resolved fluorescence indicates that the CT process has a high activation energy of 15.35 kJ· mol$^{-1}$. This activation energy is much higher than those of other dual fluorescent DMABN derivatives in solvents of similar polarity.

The high activation energy with SDMAS was tentatively ascribed to the participation of the sulfur atom d-orbital in the conjugation of $-SO_3^-$ with the phenyl ring and the strongly twisted and inverted configuration of the dimethylamino group relative to the phenyl plane. A molecular configuration change in SDMAS upon charge transfer in water is shown by the high repulsion energy of the Frank-Condon ground state reached immediately after the CT emission. It is likely that the CT state is more planar than the LE state.

It is significant to be able to observe in water the dual fluorescence of SDMAS with appreciable CT emission. To our knowledge, SDMAS is the first amine substituted aromatic sulfonate that shows dual fluorescence. This would make it a good candidate as a protein fluorescence probe. The currently available important aminonaphthalenesulfonate protein probes only give single-band emission, thereby unable to offer message on protein structural change via CT fluorescence variation. As for SDMAS-type probe a subject deserving coming effort is to enhance the relative fluorescence quantum yield of the CT state. This could in principle be realized by increasing the size of the alkyl substitutions at the amino group from the reported data[20].

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