

The effect of micelle–water interface electric field on the intramolecular charge transfer within ionic micelle

Dual fluorescence of sodium *p*-dialkylaminobenzoates in cetyltrimethylammonium micelles

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Abstract

Photoinduced intramolecular charge transfer (CT) of sodium *p*-(dimethylamino)- and *p*-(diethylamino) benzoates (SDMAB and SDEAB) in cetyltrimethylammonium bromide and chloride (CTAB and CTAC) micellar solutions was investigated by the CT typical dual fluorescence, in order to identify the effect of micelle–water interface electric field on the CT process occurring within ionic micelle. The CT fluorescence in CTAB and CTAC micelles was blue shifted and enhanced compared to those in pure water. The intensity ratio of the CT fluorescence to the LE fluorescence, I_a/I_b , of either SDMAB or SDEAB was found to be higher in CTAC micelle than in CTAB micelle, while these fluorophores experience the same polarity in both micelle environments. It was proposed that the higher I_a/I_b ratio in CTAC micelle was due to stronger electric field at CTAC micelle–water interface. This was supported by experiments on the dual fluorescence of SDEAB and SDMAB of different CT-state dipole moment in CTAB micelles of varying micelle–water interface electric field. It was demonstrated that the electric field at the ionic micelle–water interface indeed affected the CT process occurring within micelle that the CT process is promoted and the CT emission is enhanced at higher electric field. Ionic micelle was shown capable of acting as the electric field ‘mediator’ for chemo- and biosensing based on the dependence of the CT dual fluorescence on electric field. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Intramolecular charge transfer; Dual fluorescence; Sodium *p*-(dialkylamino) benzoate; Cetyltrimethylammonium micelle; Ionic micelle–water interface; Electric field effect

1. Introduction

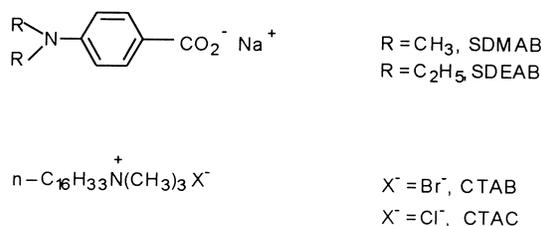
Since the first observation by Lippert et al. in the late 1950s [1] of the dual fluorescence of *p*-(dimethylamino)benzonitrile (DMABN) in polar solvents, the investigation of the origin of the ‘‘abnormal’’ long wavelength emission has been a subject of intensive interest. It has been well-accepted [2–10] that the dual fluorescence is due to two excited states in equilibrium. The emissive state responsible for the ‘‘abnormal’’ long-wavelength emission is a photo-induced intramolecular charge transfer (CT) state with much higher dipole moment than that of its precursor, the locally excited (LE) state which gives off the short wavelength emission. A molecular configuration change was proposed occurring

upon the charge transfer¹, although the nature of the configuration change is still under discussion [2–13].

The high dipole moment of the fluorescent CT state makes the fluorophores very useful in probing both the bulk and microenvironments of different media, such as supercritical

¹ Several models have been proposed to account for the configuration change upon charge transfer reaction. The TICT (twisted intramolecular charge transfer) model [2,3] proposed a twisting of the electron donor group relative to the aromatic plane, whereas the PICT (planar ICT) model [5] claimed a planar CT state. Some rehybridization of the nitrogen atom in donor group [4] or the carbon atom in acceptor group [9,10] have also been suggested. In the present report we thus simply take CT to represent the state responsible for the lower energy emission. It should be pointed out that there have been several other proposals on the origin of the here referred CT emission. Representative examples [11,12] are the solvent–solute exciplex mechanism proposed by Chandross and Varma et al. and solvent–solute hydrogen-bonding mechanism by Cazeau-Dubroca et al.

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Scheme 1. The structures of the CT fluorophores SDMAB and SDEAB and surfactants CTAB and CTAC.

fluids [14–16], cyclodextrins [17–27], and micelles [28–35], and in fluorescent sensing [36,37]. These researches were based on the dependence on the medium polarity of the formation and emission of the CT state. While the sensitive dependence of the CT emission on the external electric field has been theoretically established and practically used to determine the dipole moment of the CT state [38–41], related study in fluorescence probing and/or chemo/biosensing has been scarce [42–47]. This sensitive dependence on external electric field should, however, be of high significance in both chemical and biological sensing. The slow progress in this regard is likely due to the difficulty in bridging the physical quantity, the electric field strength, to a chemical quantity.

It is well known that ionic micelle has a charged micelle–water interface and the interface electric field can be modified through counter ion binding and/or incorporation of neutral species at the interface [48]. Therefore, we proposed to take an ionic micelle as such a bridge: a CT fluorophore solubilized in the ionic micelle can be considered as that it exists under an external electric field [42–47] and the CT emission could be varied by the introduced species via modifying the electric field at the micelle–water interface. In that manner these species are sensed and the ionic micelle actually acts as a ‘mediator’ [46]. Following this line it should be possible to develop a new fluorescence sensing mode for ions, in particular anions, and neutral molecules by employing the electric field dependence of the CT dual fluorescence. It is therefore of importance to establish whether an ionic micelle can act as a ‘mediator’ for utilizing the electric field dependence of the CT fluorescence. To this goal, the effect of the micelle–water interface electric field on the CT process occurring within the ionic micelle should be examined.

It is for this purpose that the photoinduced CT behavior of SDMAB and SDEAB in CTAB and CTAC micelles (see Scheme 1 for the structures of SDMAB, SDEAB, CTAB, and CTAC) was investigated by their dual fluorescence which is typical of the presence of excited-state CT reaction coordinate [2–10]. As CTAB and CTAC micelle–water interfaces have different electric field strength and SDMAB and SDEAB are expected to have different CT-state dipole moment, they are combined in this research to offer a variation of the micelle–water interface electric field and CT-state dipole moment, respectively. These two factors were considered useful in establishing the role the micelle–water electric field plays in the CT process occurring within the

ionic micelle. The counter ion binding in CTAB micellar solution was also employed to vary the electric field at the micelle–water interface. Systematic and comparative investigations of the CT dual fluorescence lead to the conclusion that the micelle–water interface electric field indeed exerts effect on the CT process within the ionic micelle and the ionic micelle could act as an electric field ‘mediator’.

2. Experimental

SDMAB was prepared from *p*-dimethylaminobenzoic acid, which was synthesized as described elsewhere [49], by neutralization with NaOH. SDEAB was synthesized by refluxing *p*-aminobenzoic acid in ethyl iodide in the presence of anhydrous Na₂CO₃ followed by alkaline hydrolysis. Cetyltrimethylammonium bromide (CTAB) was an AR reagent of Shanghai the First Chemical, China, and was used after recrystallization from absolute ethanol. Cetyltrimethylammonium chloride (CTAC) was used as received from Tokyo Kasei, Japan. Both sodium dodecylsulfate (SDS) and sodium deoxycholate (SDOC) were products of Serva. All the inorganic salts were of GR grade. Organic solvents used for solvatochromic measurements were of spectroscopic grade and subject to column chromatographic purification before use. Re-distilled double deionized water was used for all experiments.

Fluorescence spectra were recorded on Shimadzu RF-5000 or Hitachi F-4500 fluorescence spectrophotometer (Japan). Slits for excitation and emission monochromators were both 5 nm and a medium scan rate was chosen in spectral recording. Excitation wavelength of 290 nm was used for recording all emission spectra. Electric conductivities were measured on an Model DDS-11A electroconductometer (Shanghai, China) using a platinum-black electrode.

3. Results and discussion

3.1. Dual fluorescence of SDMAB and SDEAB in CTAB and CTAC solutions

Fig. 1 presents fluorescence spectra of SDEAB in CTAB and CTAC solutions. Dual fluorescence that is characteristic of the presence of the excited state intramolecular charge transfer (CT) process of *p*-dialkylaminobenzoic acid [42–47,49] can be identified. The long wavelength emission band is due to the CT state of higher dipole moment and is also called a band, while the short wavelength emission, called b band emission, is given off by the locally excited (LE) state. Dual fluorescence in these two surfactants’ solutions was found responding sensitively to surfactant concentration. Apparently, the fluorescence spectral changes are similar in CTAB and CTAC solutions. These changes occur in both the intensities and the positions of the two emission bands, in particular in those of the CT emission. With

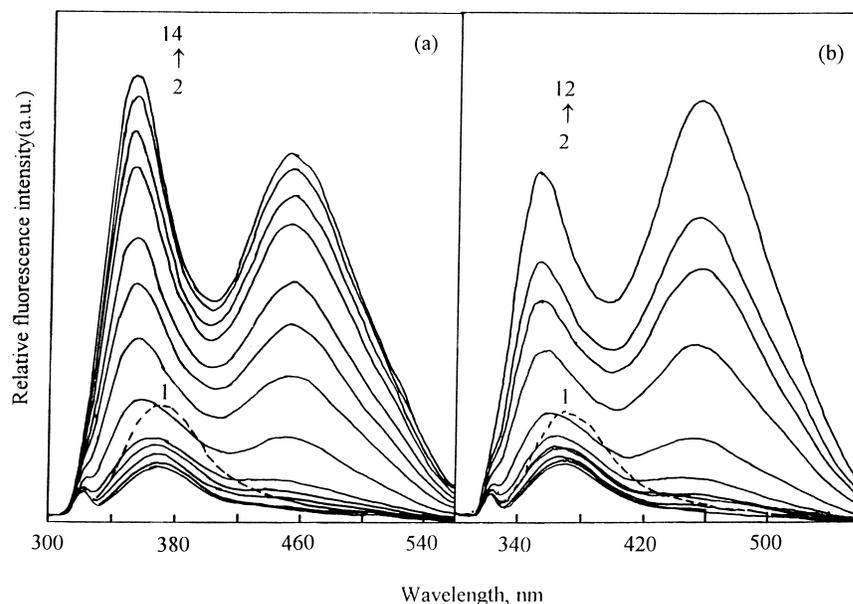


Fig. 1. Fluorescence spectra of SDEAB in (a) CTAB and (b) CTAC solutions. $[SDEAB] = 2.5 \times 10^{-5}$ mol/l. (a) $[CTAB]/10^{-3} = 0(1), 0.2(2), 0.4(3), 0.6(4), 0.7(5), 0.8(6), 0.9(7), 1.0(8), 1.1(9), 1.2(10), 1.4(11), 1.6(12), 1.8(13),$ and $2.0(14)$ mol/l, respectively. (b) $[CTAC]/10^{-3} = 0(1), 0.2(2), 0.4(3), 0.6(4), 0.8(5), 0.9(6), 1.0(7), 1.1(8), 1.2(9), 1.3(10), 1.4(11), 1.6(12)$ mol/l, respectively.

increasing surfactant concentration the intensities of both the LE and the CT bands are enhanced and, whereas the LE band does not shift too much to the blue, the CT band shifts dramatically to the blue. For example, the CT emission of SDEAB is located at ca. 480 nm in pure water and at ca. 452 nm in aqueous solution of high surfactant concentration. As the CT state has a dipole moment much higher than that of the ground state [2–10], this blue shift in the CT emission should suggest a less polar microenvironment around the CT fluorophore at high surfactant concentration. According to the solution behavior of surfactant with increasing concentration [48], this would mean the onset of micelle at high surfactant concentration and the solubilization of the CT fluorophores into the nonpolar micellar phase [48,50]. This is shown more clearly by plotting the intensity ratio of the CT band to the LE band, I_a/I_b , against surfactant concentration. The curves for SDEAB in CTAB and CTAC solutions are given in Fig. 2. The ‘S’-shaped curves indicate evidently the onset of the micelles, if a ‘two-state’ model [48,50] for micelle formation is assumed. The critical micelle concentrations (CMCs) of the two surfactants were obtained by taking the concentrations at the inflection points of those ‘S’-shaped curves. The CMC values thus obtained, 8.5×10^{-4} mol/l for CTAB and 1.1×10^{-3} mol/l for CTAC, are in agreement with reported data (see Table 1). Similar observations were made in SDTAB/CTAB and SDTAB/CTAC systems and reasonable CMC data for CTAB and CTAC were obtained (Table 1). The CMC values for each surfactant obtained by using SDTAB and SDEAB probes agree well. These findings establish that the current CT fluorophores can be employed as new fluorescent probes for cationic micelle onset in aqueous solution.

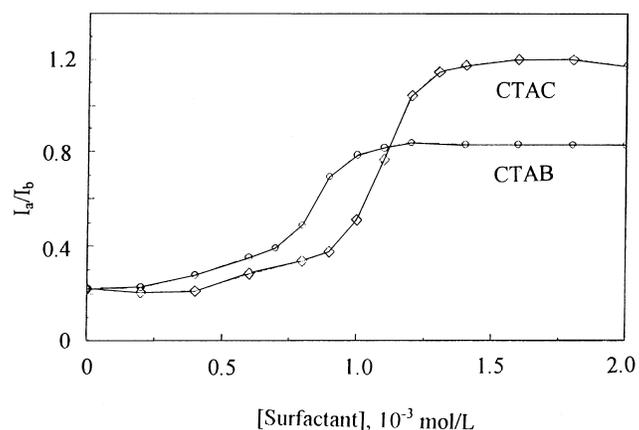


Fig. 2. Fluorescence intensity ratio of the CT band to the LE band, I_a/I_b , of SDEAB versus CTAB and CTAC concentration in aqueous solution.

Table 1
 I_a/I_b ratios of the CT fluorophores in CTAB and CTAC micelles and the measured CMCs of CTAB and CTAC

Fluorophore	I_a/I_b		CMC ^a	
	CTAB	CTAC	CTAB	CTAC
SDTAB	0.43	0.50	0.83	1.12
SDEAB	0.84	1.21	0.85	1.10

^a The CMC value is in 10^{-3} mol/l. Reported CMCs for CTAB and CTAC is 0.92×10^{-3} and 1.50×10^{-3} mol/l, respectively [51].

Two important features can be noted from the I_a/I_b versus surfactant concentration curves, see Fig. 2. First, the I_a/I_b ratios in CTAB and CTAC solutions were found leveling off after micelle formation, in spite of the continuous increase in the micelle concentration with increasing

surfactant concentration. The further increase in the fluorescence intensity after micelle formation, as seen in Fig. 1 for example, should mean that increasing amount of CT fluorophore is solubilized into micellar phase. It is therefore made clear that the I_a/I_b ratios of SDMAB and SDEAB in CTAB or CTAC micelles do not depend on micelle concentration and/or the amount of the CT fluorophore that has been solubilized in the micellar phase. The latter was further experimentally supported by the fact that the I_a/I_b ratio of SDMAB in CTAB micelle remains constant over the investigated SDMAB concentration range of 1.3×10^{-5} to 3.9×10^{-5} mol/l, although the total fluorescence intensity linearly increases with SDMAB concentration which suggests that all SDMAB molecules have been solubilized in the micellar phases. It is hence reasonable to take the I_a/I_b ratios of SDMAB and SDEAB after CTAB or CTAC micelle formation as those in the micellar phase. Those I_a/I_b ratios of SDMAB and SDEAB in CTAB and CTAC micelles are compiled in Table 1. The second feature that follows from Fig. 2 and Table 1 is that the I_a/I_b ratio of either SDMAB or SDEAB is higher in CTAC micelle than in CTAB micelle. It is obvious that the CT process of SDMAB and SDEAB is more favored in CTAC micelle than in CTAB micelle.

3.2. Solubilization position of SDMAB and SDEAB in CTAB and CTAC micelles

Structural differences between CTAB and CTAC micelles should be considered as the reasons for the difference in the I_a/I_b ratios observed in these two micelles. Meanwhile, the effects of these structural differences in micelles are subject to the position of the fluorophores in the micelles. Therefore, solubilization position of the CT fluorophores in CTAB and CTAC micelles should be discussed first.

Based on the molecular structures of SDMAB and SDEAB (Scheme 1) and the structure of the CTAB and CTAC micelles [48,50], it is somewhat straightforward that both electrostatic and hydrophobic interactions occur between the CT fluorophores and the micelles. Therefore, it is energetically favorable that the CT fluorophores locate at the ionic micelle–water interface with its hydrophobic moiety, dialkylaminophenyl group, buried in the non-polar phase while the carboxylic group heading to the aqueous phase and interacting with the polar head of the surfactant in micelle. In this manner both the hydrophobic and electrostatic interactions between CT fluorophore and micelle are facilitated.

The magnitude of the CT fluorophore–micelle binding constant, K , should provide more direct support for the occurrence of these two interactions. As the hydrophobicity of SDEAB is higher than that of SDMAB while the effective electric charge at the CTAC micelle surface is higher than that at the CTAB micelle surface [52,53], the combination of SDEAB with CTAC micelle should have the highest affinity if these two interactions are assumed. The binding

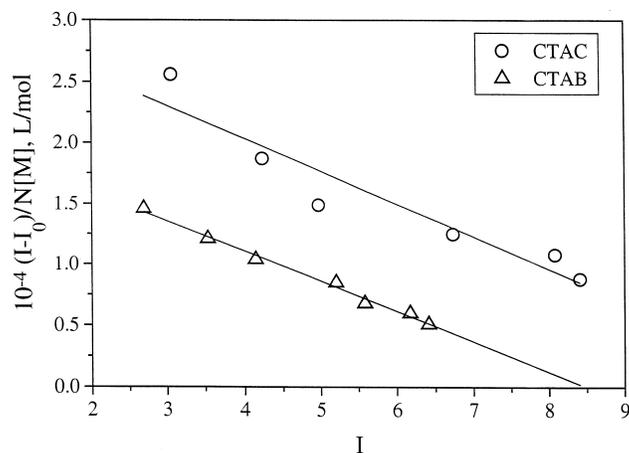


Fig. 3. Plots for evaluation of the binding constants of SDEAB to CTAB and CTAC micelles.

constants, K 's, of the CT fluorophores to CTAB and CTAC micelles were measured by a method applied successfully in cyclodextrin system (Eqs. (1) and (2)) [25,54,55]. For these measurements micelle was taken as a host similar to cyclodextrin and K 's were determined according to Eq. (3), where I_0 , I , and I_c are fluorescence intensity of the fluorophore (F) in the absence of micelle, in the presence of a given amount of micelle, and when the fluorophore is completely bound to the micelle (M), and $[M]$ is the concentration of micelle which is related to surfactant concentration, C , and average aggregation number, N , by Eq. (4).



$$K = [F - M]/[F][M] \quad (2)$$

$$(I - I_0)/[M] = K I_c - K I \quad (3)$$

$$[M] = (C - CMC)/N \quad (4)$$

Typical curves according to Eq. (3) are shown in Fig. 3. The K values of SDEAB/CTAB-micelle, SDMAB/CTAC-micelle, and SDEAB/CTAC-micelle were obtained as 2.3×10^5 , 1.7×10^5 , and 2.8×10^5 l/mol, respectively. The SDEAB/CTAC-micelle binding constant is higher than that of SDEAB/CTAB-micelle, while the SDEAB/CTAC-micelle binding constant is higher than that of SDMAB/CTAC-micelle. These data clearly point to the presence of both electrostatic and hydrophobic interactions between the CT fluorophores and CTAB or CTAC micelle, supporting the assumption that SDMAB or SDEAB is solubilized at the CTAB or CTAC micelle–water interface. At this position the CT fluorophore certainly experiences the ionic micelle–water interface electric field as that it exists in an external electric field, as discussed early in the introduction section.

The hydrophobic interaction between fluorophore and the micellar nonpolar phase was also indirectly indicated by the effect of anionic micelles, SDS and SDOC micelles, on the dual fluorescence of SDEAB and SDMAB. It was observed that, whereas the dual fluorescence of SDMAB was not affected by the presence of SDS and SDOC micelles (not

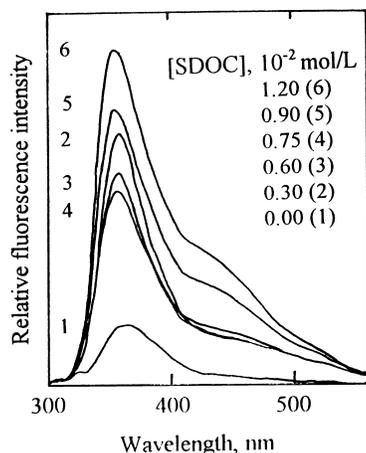


Fig. 4. Dual fluorescence of SDEAB in sodium deoxycholate solution. $[SDEAB] = 2.5 \times 10^{-5}$ mol/l.

shown), the CT emission of SDEAB in these two anionic micelles was indeed obviously enhanced and blue-shifted. The fluorescence spectra of SDEAB in SDOC solutions, as example, are presented in Fig. 4. This observation indicates that at higher SDS or SDOC concentration SDEAB is solubilized in the non-polar micellar phase. As the electrostatic repulsions between CT fluorophores (SDMAB and SDEAB) and anionic micelle (SDS or SDOC) are the same, the fact that the enhancement of and the blue shift in the CT emission in anionic micelle is only observed with SDEAB but not with SDMAB should point to a stronger hydrophobic interaction of SDEAB than of SDMAB with the anionic micelle. This can be expected from the higher hydrophobicity of SDEAB than that of SDMAB (see structures shown in Scheme 1). This stronger hydrophobic interaction of SDEAB with anionic micelle would overcome to some extent the electrostatic repulsion between SDEAB and anionic micelle, thereby bringing SDEAB into the nonpolar micellar phase. The presence of the hydrophobic interaction of SDMAB and SDEAB with the nonpolar micellar phase could therefore be ascertained.

The CT emission band position was also analyzed in order to provide further evidence for the solubilization position of the CT fluorophore in CTAB and CTAC micelles. As the CT state has a higher dipole moment than the ground state [2–10], the CT emission band position is indeed able to probe the polarity of the environment around the CT fluorophore in the micellar phase. The fact that the CT emission position remains constant after micelle formation (see Fig. 1) is actually similar to what was found with the leveling off of the I_a/I_b ratio (see Fig. 2). Therefore, the CT emission position after micelle formation would represent that in the micellar phase. For SDMAB and SDEAB in CTAB and CTAC micellar solutions, we measured the CT emission band at 452 ± 2 nm (22.12×10^3 cm⁻¹). This reflects an environment polarity in between those of methanol (CT band at 21.57×10^3 cm⁻¹) and ethanol (CT band at 22.81×10^3 cm⁻¹), according to the solvatochromic measurements (see Fig. 7 below). It is inter-

esting to note that these polarities of CTAB and CTAC micelles probed by SDMAB and SDEAB are in agreement with those probed by other fluorescence probes such as pyrene and pyrenealdehyde-1 [56]. This agreement might suggest that the chromophores of the current CT fluorophores locate in the CTAB and CTAC micelles in a similar region as those of pyrene and pyrenealdehyde-1, i.e. the Stern-layer [56], supporting the assignment that the whole CT fluorophore inserts at the ionic micelle–water interface with its dialkylaminophenyl moiety (the chromophore) buried towards the micellar phase. It is therefore concluded that the SDMAB and SDEAB molecules are solubilized at the micelle–water interface with chromophores buried in the micellar phase and experience the electric field at the interface.

3.3. Micelle–water interface electric field effect on the intramolecular charge transfer occurring within ionic micelle

We have shown that one of the important features of the CT dual fluorescence of SDMAB and SDEAB in CTAB and CTAC micelles is that the intensity ratio I_a/I_b of the same CT fluorophore, either SDMAB or SDEAB, is higher in CTAC micelle than in CTAB micelle. Obviously this difference in I_a/I_b ratio should be due to the structural differences between CTAB and CTAC micelles that afford the CT fluorophore with different surrounding environments. The well-accepted conclusions on the photoinduced CT process show that a dipole moment development and a molecular configuration change occur during the CT process [2–10]. Accordingly, the surroundings of the CT fluorophores in the CTAB and CTAC micelles could in general differ in viscosity, polarity, and micelle–water interface electric field, that may influence the charge transfer process and thus the I_a/I_b ratio within the micelle.

The polarities of the CTAB and CTAC micellar phases were previously reported to be similar [53]. The current CT fluorophores SDMAB and SDEAB also reported similar polarities of their environments in these two micelles. For instance, the position of the CT emission band of SDEAB in CTAB micelle is the same as that in CTAC micelle, both at 454 nm. The viscosity of CTAB micellar phase was reported to be slightly higher than that of CTAC micellar phase [57–60]. It is thus possible that the CT fluorophore might experience different viscosities in these two micelles. However, recent investigations of the pressure effect on the CT dual fluorescence have ruled out the viscosity effect in the CT process [61,62]. Therefore, the slightly higher viscosity of the CTAB micelle is not the reason for the lower I_a/I_b ratio observed in this micelle compared to that observed in CTAC micelle.

The reason for the higher I_a/I_b ratio observed in CTAC micelle is thus likely the difference in the electric field at the micelle–water interface. It has been reported that the electric field at the CTAC micelle–water interface is higher than

that at the CTAB micelle–water interface [52,53]. SDEAB or SDMAB molecules that are solubilized at the micelle–water interface will hence experience a higher electric field in CTAC micelle than in CTAB micelle. Theoretically, it was shown [38–41] that the fluorescence intensity, I , is related to the external electric field strength, E , by Eq. (5),

$$I = I_0(1 + LE^2) \quad (5)$$

in which I_0 is the intensity in the absence of electric field and L is a constant depending on the difference between the dipole moment of the emissive state and that of the ground state, and the orientation of the emission transition moment relative to the electric field. It is thus expected from Eq. (5) that the fluorescence will be enhanced more if the dipole moment of the emissive state is higher, provided a given orientation is assumed for the transition moment relative to the electric field. It has been well known [2–10] that, with the dual fluorescent donor–acceptor substituted benzenes such as SDMAB and SDEAB reported here, the dipole moment of the LE state, although higher than that of the ground state, is much lower than that of the CT state. It was shown that similar conclusion holds for SDMAB and SDEAB in CTAB and CTAC micelles. As shown in Fig. 1, the LE fluorescence only slightly shifts to the blue in micelles compared to that in aqueous phase, which indicates that the dipole moment of the LE state of SDEAB or SDMAB is only slightly higher than that of the ground state. On the other hand, the dipole moment of the CT state of SDMAB or SDEAB is much higher than that of the ground state, as indicated by the substantial blue shift of the CT emission band in CTAB or CTAC micelle with respect to that in aqueous phase. As a consequence, the enhancement of the LE fluorescence in the presence of an external electric field will be much less than that of the CT fluorescence. An increase in the I_a/I_b ratio should be observed when an external electric field is applied and this ratio becomes larger under higher electric field. This is indeed the case we observed with SDMAB and SDEAB in CTAB and CTAC micelles, higher I_a/I_b ratio being found in CTAC micelle which has a higher micelle–water electric field [52,53]. It is therefore reasonable to conclude that it is the stronger electric field at the micelle–water interface that leads to higher I_a/I_b ratio for SDMAB or SDEAB in CTAC micelle than in CTAB micelle.

In order to bring about additional supports for this conclusion, further experiments were conducted. It was expected that, according to Eq. (5), systematic varying the electric field strength at the micelle–water interface would lead to the variation of the I_a/I_b ratio, if it is indeed the variation in the micelle–water interface electric field that induces the variation of the I_a/I_b ratio. Meanwhile, by varying the dipole moment of the CT state one should observe a different sensitivity in the response of the I_a/I_b ratio to the electric field variation and a higher sensitivity could be expected with the CT state of higher dipole moment. The former experiments were carried out by introducing external inorganic salts into micellar solutions, since it has been reported [48] that the

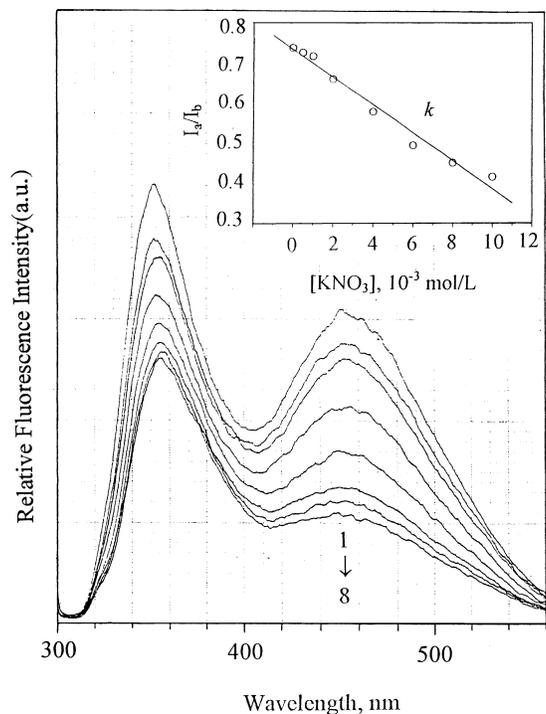


Fig. 5. Variation of the fluorescence spectra of SDEAB in CTAB micellar solutions with the concentration of externally introduced KNO_3 . Inset shows the linear response of intensity ratio I_a/I_b to $[\text{KNO}_3]$. $[\text{SDEAB}] = 2.5 \times 10^{-5} \text{ mol/l}$. $[\text{CTAB}] = 2.0 \times 10^{-3} \text{ mol/l}$.

micelle–water interface electric field could be modified via counter ion binding. For the latter experiments, salt effects on the CT dual fluorescence of SDMAB and SDEAB in CTAB micelles of varying micelle–water interface electric fields were compared. It was shown that with the dual fluorescent *p*-dialkylaminobenzonitriles [63] the dipole moment of the CT state increased with increasing alkyl chain. Thus, the dipole moment of the CT state of SDEAB was expected to be higher than that of SDMAB. This would allow for a variation in the difference of the dipole moments between the CT state and the ground state by reasonably assuming the same ground state dipole moment for SDMAB and SDEAB.

3.4. Effects of inorganic salts on the CT dual fluorescence of SDMAB and SDEAB in CTAB micelle

The effect of externally introduced inorganic salts on the CT dual fluorescence of SDEAB and SDMAB in CTAB micelles was examined. Fig. 5 shows a typical set of results for the effect of KNO_3 on the dual fluorescence of SDEAB in CTAB micelle. It is noted from Fig. 5 that, with increasing KNO_3 concentration, although both the LE and CT emissions decrease in intensity, the I_a/I_b ratio was found decreasing too, see inset in the figure. A linear decrease in I_a/I_b ratio with KNO_3 concentration was actually found. This means that the I_a/I_b ratio of SDEAB in CTAB micelle decreases in the presence of KNO_3 . It is important to point out that no such effect was observed when the same salt over the same

Table 2
Salt effect on the CT emission of SDEAB and SDMAB in CTAB micelle^a

Salt ^b	KF	KCl	KBr	K ₂ SO ₄	KNO ₃	SDS	SDOC
k_1/k_2	1.005	1.056	1.080	1.083	1.086	1.444	
$ k _{\text{SDEAB}}^c$		10.4	26.5		34.8	505	3206
$ k _{\text{SDMAB}}^d$	1.07	2.13	6.60	7.73	10.2	129	

^a [CTAB] = 2.5×10^{-3} mol/l.

^b Inorganic salt concentration varies over the range of $0\text{--}1.0 \times 10^{-2}$ mol/l, while those of surfactants, SDS and SDOC, in the range of $0 \times 10^{-4}\text{--}6.0 \times 10^{-4}$ mol/l and $0 \times 10^{-5}\text{--}3.0 \times 10^{-5}$ mol/l, respectively.

^c The absolute slope measured by using SDEAB as the CT fluorophore.

^d The absolute slope measured by using SDMAB as the CT fluorophore.

concentration range was added to SDEAB aqueous solution in the absence of the micelle. Therefore this salt effect on the CT dual fluorescence is mediated by the ionic micelle. Several potassium and sodium salts, such as KF, KCl, KBr, K₂SO₄, KNO₃, SDS, and SDOC, were examined for their effects on the CT dual fluorescence of SDMAB and SDEAB in CTAB micelles and similar phenomena were observed. Clearly the slope of the linear dependence of I_a/I_b ratio on salt concentration, k , as shown in the inset in Fig. 5, reflects the magnitude of the salt effect on the CT dual fluorescence in micelle. We employed the absolute value of this slope, $|k|$, as a measure for the effect of individual salt on the CT emission. A larger $|k|$ represents a faster decrease in the I_a/I_b ratio with increasing salt concentration and indicates a stronger salt effect on the CT dual fluorescence. The $|k|$ values of the investigated salts are presented in Table 2. From Table 2, it is found that $|k|$ value varies with salt, which implies that specific interaction of each salt with micelle, e.g. counter ion binding, take place. In order to elucidate the interaction of salt with micelle, solution electric conductance of the salts in the absence and the presence of given amount of CTAB micelle were monitored and compared. In Fig. 6 a set of data were shown, as an example, for aqueous KNO₃ solutions in the absence and the presence of CTAB micelle. It was observed that the electric conductivity of salt solution linearly depended on its concentration for both series. The slope of the linear dependence in the presence of CTAB micelle, k_2 , was found lower the slope in the absence of the micelle, k_1 . This is an indication that the counter ion binding of salt to the ionic micelle indeed occurs otherwise the slopes for the two lines should be the same. It is obvious that a stronger binding of the salt to the micelle will lead to a more appreciable decrease in the slope k_2 . The ratio k_1/k_2 could then serve as an index for the binding degree of each salt to CTAB micelle. A higher k_1/k_2 ratio should reflect a stronger binding of the salt to the micelle and thus a lower electric field at the CTAB micelle–water interface among other consequences on the micelle structure. The k_1/k_2 values of the investigated salts are given in Table 2. Relating $|k|$ to k_1/k_2 ratio, we found from Table 2 that the values of $|k|$ of SDMAB and SDEAB positively depend on k_1/k_2 : the $|k|$ value being higher in case of larger k_1/k_2 . This means that a stronger binding of the salt to the CTAB micelle (higher k_1/k_2 ratio) induces a faster decrease in the I_a/I_b ratio (higher $|k|$).

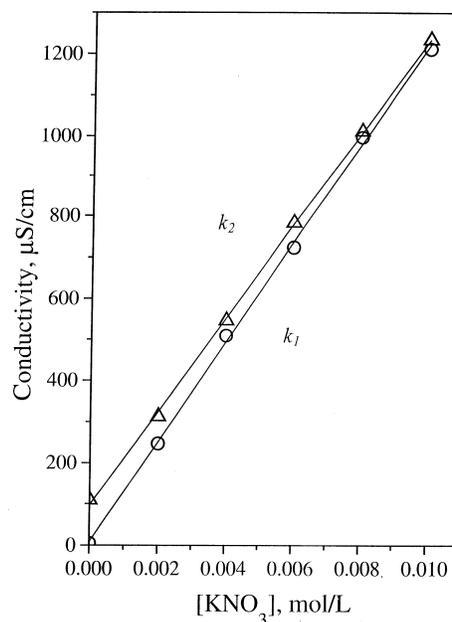


Fig. 6. Electric conductivity of KNO₃ aqueous solution as a function of its concentration (○) in the absence and (Δ) the presence of 2.0×10^{-3} mol/l CTAB.

In general, introduction of salt into ionic micellar solution will lead to changes in micelle structural parameters such as polarity, viscosity, micelle–water interface electric field, CMC, and aggregation number, N , [48] and the distribution equilibrium of the fluorophore between aqueous and micellar phases due to ‘salt-in’ or ‘salt-out’ effect as observed in cyclodextrin systems [64]. No shift in the CT band position of SDMAB or SDEAB in CTAB micelle solutions was noted when salt was introduced. This rules out the possibility of polarity change. The viscosity change is possible. However, as pointed out early in Section 3.3, viscosity is not an important factor that governs the CT process [61,62] and its role can be neglected. The changes in CMC and N will result in the change in micelle concentration, while the shift of the distribution equilibrium of the CT fluorophore between micellar and aqueous phases will lead to changes in the concentration of fluorophore in the micellar phase. These two kinds of changes, however, have been concluded early in Section 3.1 not to affect the I_a/I_b ratio in CTAB or CTAC micelle, as could also see in Fig. 2. It is hence concluded that it is the counter ion binding at

the micelle–water interface, which reduces the strength of the electric field at the interface, that leads to the decrease in the I_a/I_b ratio in the micelle. The data shown in Table 2 indeed coincide with this conclusion: more appreciable decrease in I_a/I_b ratio (higher $|k|$ value) is observed when the electric field at the micelle–water interface is reduced more (indicated by a higher k_1/k_2 value). This correlation agrees with what is expected from the theory outlined in Eq. (5), supporting the presence of the effect of micelle–water interface electric field on the CT process occurring within the ionic micelle. It is also made clear that an ionic micelle could indeed serve as an electric field ‘mediator’ to bridge the physical quantity, electric field strength, to a chemical quantity, species concentration, for chemo- and biosensing.

3.5. The contribution of the dipole moment of the CT state to the salt effect on the CT fluorescence in CTAB micelle

In order to provide further support for the conclusion on the presence and the role of the micelle–water interface electric field on the CT process in micelle, the salt effects on the CT dual fluorescence of SDMAb and SDEAB in CTAB micelle were compared. The results given in Table 2 indicate that for each salt, the $|k|$ value is higher for SDEAB than for SDMAb.

It was reported that the dipole moment of the CT state of *p*-dialkylaminobenzonitrile increases when the alkyl substituents at amino group become larger [63]. It is thus supposed that this trend in the CT state dipole moment variation may apply to SDMAb and SDEAB too, and if it is true the aforementioned comparison will be helpful in supporting that conclusion made for the role of the micelle–water interface electric field. A solvatochromic measurement was thus conducted for SDMAb and SDEAB in solvents of different polarities to prove the prediction on the dipole moments of the CT states of SDEAB and SDMAb. The CT emission energies in wavenumber of SDEAB were plotted against those of SDMAb, which makes the comparison of the CT state dipole moments possible [8]. As seen in Fig. 7 a straight line was found and the slope of this line, 0.98, is the ratio of $\mu_{CT}(\mu_{CT}-\mu_G)/r^3$ of SDEAB to that of SDMAb [8]. Here μ_{CT} and μ_G are the dipole moments of the CT state and the ground state, respectively, and r is the equivalent spherical radius of the solute (Onsager radius). Therefore, the ratio of $\mu_{CT}(\mu_{CT}-\mu_G)$ of SDEAB to that of SDMAb is calculated to be 1.15. As it should be reasonable to assume that the dipole moments of the ground states of SDMAb and SDEAB are close to each other, as is the case with *p*-dialkylaminobenzonitriles [63], the dipole moment of the CT state of SDEAB is proved to be higher than that of SDMAb. Therefore, the fact that a higher sensitivity to the introduction of inorganic salts of the CT dual fluorescence is observed for SDEAB than for SDMAb in CTAB micelle again support the presence of the effect of the micelle–water interface electric field that governs the CT process occurring within the micelle.

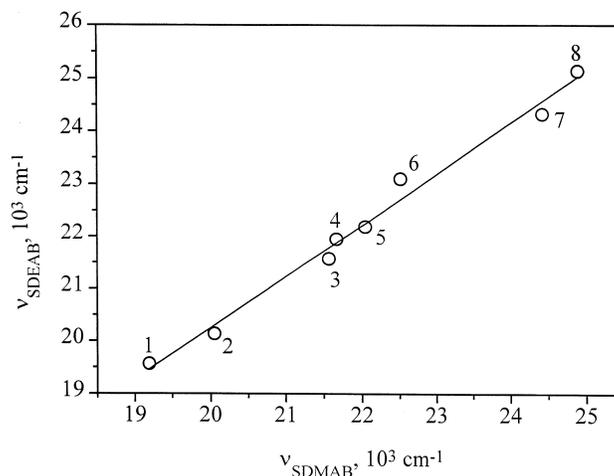


Fig. 7. Plots of the CT band positions in wavenumber of SDEAB against those of SDMAb in organic solvents of different polarity. Solvents: (1) acetonitrile, (2) propionitrile, (3) methanol, (4) ethyl acetate, (5) tetrahydrofuran, (6) ethanol, (7) diethylether, and (8) dibutylether.

4. Conclusions

Systematic investigations of the CT dual fluorescence of SDMAb and SDEAB in CTAB and CTAC micelles and in CTAB micelle in the presence of inorganic salts have shown that the micelle–water interface electric field exerts effect on the charge transfer process occurring within the ionic micelle. The CT process is promoted and the CT emission is enhanced under stronger electric field at the micelle–water interface. The magnitude of the electric field effect is also subject to the dipole moment of the CT state and higher CT dipole moment results in more appreciable effect. The CT dual fluorescence can be modified by inorganic salt through the mediation of ionic micelle, which demonstrates that ionic micelle could indeed act as an electric field ‘mediator’ for chemo- and/or biosensor based on the dependence of the highly dipolar CT emission on the external electric field strength.

The results reported here would be of significance in terms of developing novel sensing systems for anions. For example, the very high $|k|$ value observed for anionic surfactant, SDS or SDOC, in SDEAB-CTAB systems (see Table 2) is suggestive of the possibility of establishing a non-specific sensing system for anionic surfactant analogous to that for cationic surfactant [65]. Actually the present sensing system is also applicable for neutral molecules such as β -cyclodextrin [36,37] and in principle, similar system for cation sensing can also be constructed. The mechanism for ion sensing is the counter ion binding to the micelle–water interface which decreases the electric field at the interface, while that for neutral species sensing is the incorporation of neutral species at the interface which expands the interface, leading to decreased electric field at the interface. In general, it can be put that an ionic micelle with high electric field at micelle–water interface coupled with a CT

fluorophore with high CT dipole moment at a suitable relative orientation to the electric field [46,47,66–68] would afford a sensing system of high sensitivity.

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