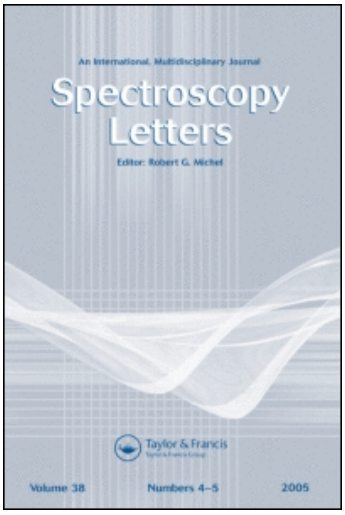

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Dual Fluorescence of Sodium p-Dimethylaminobenzoate in Aqueous Solution of Positive Ionic Surfactant. Probing Micelle Formation and Strength of Electric Field at Micelle Interface

Keywords: Dual fluorescence, Twisted intramolecular charge transfer (TICT), Sodium p-dimethylaminobenzoate, Positive ionic micelle, Micelle interface electric field.

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ABSTRACT

Fluorescence spectrum of sodium p-dimethylaminobenzoate (SDMAB) in aqueous solution was recorded as a function of the concentration of positive ionic surfactant, Zeph, CTAC, and CTAB, respectively. Dual fluorescence which is characteristic of the excited state TICT of SDMAB was observed in aqueous surfactant solution. Micelle formation can be identified by the break that appears in curve of intensity ratio of TICT emission band to LE band, Ia/Ib, versus surfactant concentration. The TICT band is shifted to blue in micelle as compared to that in

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pure water, which is an indication that SDMAB is buried in the apolar portion of the positively charged micelle, and the micellar phase polarity is probed to be the same for the three micelles. The Ia/Ib ratio in three micelles takes an order as Zeph > CTAC > CTAB. This order is shown to be due to the differnce in strength of electric field at micelle interface. A blue-shift of TICT band with surfactant concentration before micelle formation was noted, which can be taken as a new evidence for self-coiling of surfcatnt molecule in aqueous solution.

INTRODUCTION

Dual fluorescence of para-electron-donor and acceptor substituted benzene, such as p-dimethylaminobenzonitrile (DMABN) and ethyl p-dimethyl-aminobenzoate (EDMAB), has been attributed to two excited states, the locally excited (LE) state and the followed TICT state [1, 2]. In the TICT model, the TICT state is formed by twisting the electron donating group to a conformation in which the donating group is in a plane perpendicular to that of the aromatic ring. As a result, the TICT state has a complete charge separation and a high dipole moment [1, 2]. Thus the formation of TICT state and TICT fluorescence which appears at longer wavelength should be very sensitive to the polarity of medium around fluorophore and could be used to probe medium polarity. It is following this line that we try to examine the TICT dual fluorescence in micelle in an attempt to probe the properties of micelle. It is expected that, upon micelle formation, the TICT fluorophore could be solubilized into the apolar micellar phase and experience a remarkable change in medium polarity.

There have been several reports on the TICT dual fluorescence in micelles [3-6]. It appears that the micelle formation could be indicated by some changes in the dual fluorescence, such as the intensities of the two emission bands [3] and/or the intensity ratio [4-6]. However the application of

TICT dual fluorescence is limited only to probing micelle formation. Two points may be drawn to accont for this limitation. The one is that the TICT fluorophore is neutral [3, 4] which lead to a distribution of the fluorophore in micellar phase, and the other is that the TICT fluorescence in these cases depends on the concentration of TICT fluorophore [4,6,7]. As a consequence, the parameters of the TICT dual fluorescence such as TICT emission energy and intensity ratio still depend on surfactant concentration after micelle formation, which results in an uncertainty in analysizing experimental data. Therefore a TICT fluorophore whose position in micelle is anchored and whose dual fluorescence is independent of its concentration should be appreciated for sake of probing the characteristics of micelle in addition to micelle formation.

p-Dimethylaminobenzoic acid (DMABOA) is such a TICT fluorophore whose dual fluorescence in aqueous solution does not depend on its concentration [8]. Meanwhile, DMABOA is an organic acid that can dissociate into anionic base. Thus the base form of DMABOA, sodium p-dimethylaminobenzoic acid (SDMAB), could be anchored in positive micelle by both the hydrophobic and electrostatic interactions between SDMAB and micelle. In the present letter, we present the dual fluorescence of SDMAB in aqueous solutions of three positive surfactants and try to check these presumptions and to examine the possibility to probe, by using the dual fluorescence, the properties of micelle as well as those of surfactant itself.

EXPERIMENTAL

SDMAB is prepared by neutralizing DMABOA by NaOH. The acid, DMABOA, is synthesized as reported previously [8]. Cetyltrimethylammonium bromide (CTAB) and tetradecyl-benzyldimethylammonium chloride (Zeph), are of AR grade from Shanghai the first reagent factory. Cetyltrimethyl-ammonium chloride (CTAC) is purchased from Tokyo Kasei.

Potassium fluoride (KF), chloride (KCl), and bromide (KBr) are GR reagents from Shanhai the first reagent factory. Water is twice deionized.

Fluorescence spectra were recorded on a Shimadzu RF-5000 fluorescence spectrophotometer. The excitation wavelength is 290 nm. Both the excitation and emission slits are 5 nm and the spectral scan rate is selected in fast mode.

RESULTS AND DISCUSSION

Figure 1 presents the fluorescence spectra of SDMAB in the presence of different concentration of CTAC. The TICT typical dual fluorescence can be identified in the spectra. It is observed that the change in SDMAB spectra is not very appreciable when CTAC concentration is lower than 1.0×10^{-3} mol/L. However strong enhancements of the intensities of the two bands and a blue-shifting in TICT band are seen with CTAC concentration is higher than 1.0×10^{-3} mol/L. This observation should serve as an indication for CTAC micelle formation and the change in the environment of SDMAB molecule, that is SDMAB is transfered to apolar micellar phase from polar bulk aqueous phase. Similar observations were also noted for the other two surfactants, CTAB and Zeph. The fluorescence parameters are presented more clearly in Figure 2, in which the wavelength of TICT band and the intensity ratio of TICT band to LE band, Ia/Ib, are plotted versus surfactant concentration. Two points can be indentified from this figure. The one is that a break is present in the curve of Ia/Ib versus [surfactant]. This break must correspond to micelle foramtion. Thus the critical micelle concentration (cmc) of the surfactant can be easily evaluated by the surfactant concentration corresponding to the break. The other is that both the Ia/Ib ratio and the TICT band position level off after micelle formation, suggesting that the TICT dual fluorescence of SDMAB is independent of its concentration in micelle. This means that SDMAB has met the requirements as a TICT fluorophore for probing micelle

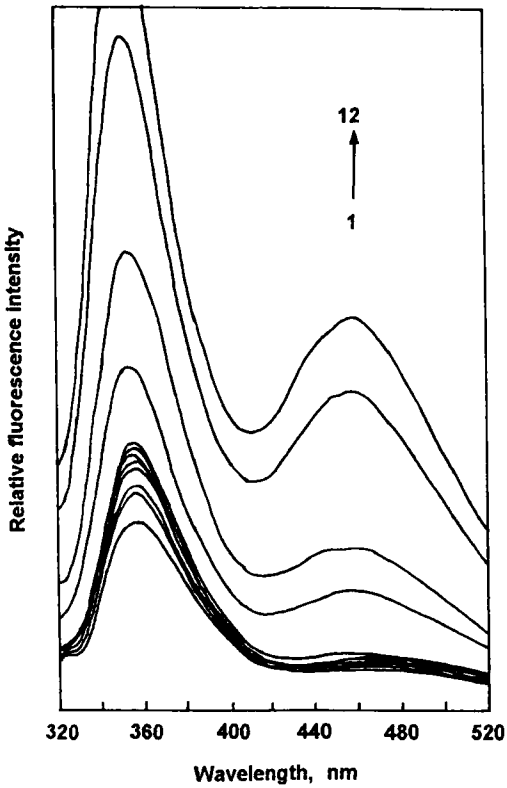

Figure 1 **Fluorescence spectra of SDMAB in aqueous CTAC solution**

SDMAB concentration is 1.25×10^{-5} mol/L. CTAC concentration is 0, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.4, 1.6×10^{-3} mol/L, respectively, from curve 1 to 12.

systems. It is reasonable, from this observation, to assume that the constant values for Ia/Ib and TICT wavelength after micelle formation can be taken as those in micellar phase and empolyed to reflect the nature of micellar phase. The data that are abstracted from Figure 2 are compiled in Table 1.

It is useful to compare data in Table 1 with the structure of micelle. The difference of these three surfactant relies on the length of the hydrophobic alkyl chain and coumterion. These differences could lead to different polarity and viscosity in micellar phase, and strength of electric field at micellar interface. Variations in these three structural parameters of micelle can all be reflected by the TICT dual fluorescence [1, 2, 9]. It is clear in Table 1 that the TICT wavelength of SDMAB in three micelles is centered at 453 ± 3 nm, pointing out that the polarities of micellar phases are nearly the same. This result implyies that the micellar phase polarity is not a factor that leads to different Ia/Ib ratios in three micelles, as seen in Table 1.

As also noted in aqueous cyclodextrin systems [10, 11], the Ia/Ib ratio of SDMAB increases in micellar phase although SDMAB molecule experiences a decreased polarity and an increased viscosity compared with those in bulk aqueous phase. From TICT model [2] it is expected that incrasing medium viscosity will unfavour TICT process and decrease Ia/Ib ratio. Thus the fact that an increased Ia/Ib ratio is observed in more viscous micellar phase indicates that, at leaset, the viscosity factor is not important in the present case to affect the TICT process. This conclusion rules out the possibility that viscosity attributes anything to the different Ia/Ib ratios in three micelles. Therefore this difference in Ia/Ib in three micelles can only be attributed to the difference in the strength of electric field at micelle interface.

This is reasonable because a TICT fluorophore that is solubilized in ionic micelle looks like that it is put in an elctric field, and the TICT process is inherently affected by electric field, due to the change in the dipole moment in TICT state formation [1, 2, 9]. As the dipole moment of TICT state is

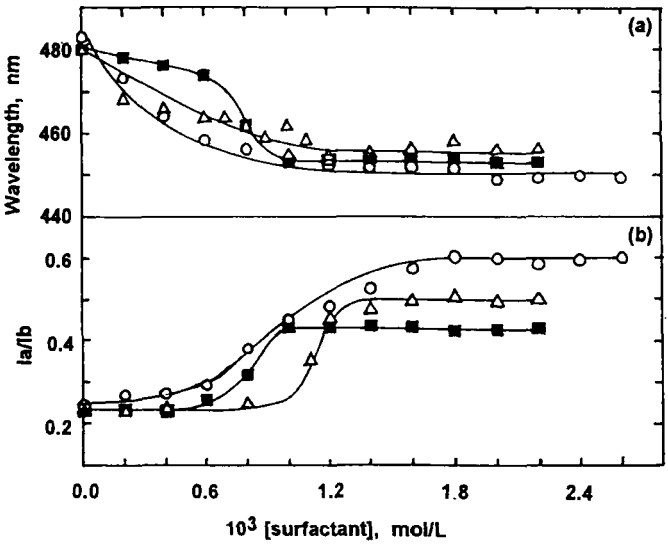

Figure 2 Wavelength of TICT band (a) and Ia/Ib ratio (b) of SDMAB as a function of surfactant concentration Surfactants are Zeph (○), CTAC (△), and CTAB(■).

Table 1 Surfactant cmc and Ia/Ib and TICT wavelength of SDMAB in micelle

Surfactant	cmc, mol/L	Ia/Ib	TICT wavelength, nm
CTAB	0.83×10^{-3}	0.428	453
Zeph	1.03×10^{-3}	0.591	450
CTAC	1.12×10^{-3}	0.497	456

higher than that of LE state and much higher than that of ground state [1, 2], decrease in electric field will lead to a decrease in Ia/Ib ratio. The results that shown in Figure 3 would be considered as a direct support for our conclusion. It is seen that the Ia/Ib ratio of SDMAB in CTAC micelle decrases with increasing component of KX in the mixture of KX and KF (X=Cl, Br) and the decreasing rate is higher for KBr and KF mixture. Here the total concentration of KX and KF is kept constant, ruling out the possible contribution of salt-in effect. Meanwhile, no change in the positions of two emission bands has been observed when the inorganic salts are introduced to the micellar solution. Thus the decrease in the Ia/Ib ratio should be due to the counter ion binding at the micelle interface, which coherently reduces the intensity of electric field at the interface. It has been reported that bromide binds more strongly to the cetyltrimethylammonium micelle interface than chloride does and fluoride does not bind to the interface at all [12]. Thus the electric field at micelle interface will be reduced at higher rate with increasing conponent of KBr than that with KCl in KX-KF (X=Cl, Br) mixture, resulting in a higher rate in the decrease of Ia/Ib ratio in micelle. This is indeed the case as shown in Figure 3. Therefore, thevalue of Ia/Ib ratio of SDMAB in micelle, as shown in Table 1, indicates that the strength of electric field at micelle interface is in such an order as Zeph > CTAC > CTAB. This order is also in agreement with that expected from the hard-solt acid-base principle [12]. Due to the fact that micelle can serve as a mimetic model for membrane [13], this result may open a new way for measuring membrane surface electric potential by using a TICT fluorescence probe.

It is also interesting to examine the variations of the fluorescnce spectra of SDMAB with surfactant concentration before micelle formation. From Figure 2 it can be noted that, before micelle formation, the TICT band shifts to blue with increasing surfactant concentration by rates in such an order as Zeph > CTAC > CTAB, whereas the Ia/Ib ratio is nearly constant in the cases of CTAB and CTAC and is slightly increased in case of Zeph. It should be pointed out that the

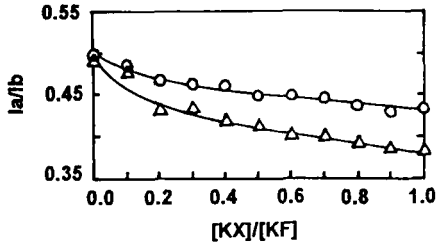

Figure 3 Variation of Ia/Ib of SDMAB in CTAC micelle with [KX]/[KF] in KX and KF mixture X=Cl(○), Br(△). [KX]+[KF]=0.01 mol/L. [CTAC] $=1.5\times10^{-3}$ mol/L. [SDMAB]=1.08×10^{-5} mol/L.

blue-shift in TICT band is observed even at surfactant concentration much lower than its cmc. That means the shift is observed in solution in which surfactant exists in monomer form. However the blue shift of the TICT band must mean that the TICT fluorophre is solubilized in a less polar microenvironment with increasing surfactant concentration.

We have previously demonstrated that surfactant molecule takes a self-coiling conformation in aqueous solution and thus provides an apolar microenvironment for hydrophobic molecule [14]. Then it is easy to understand that SDMAB is solubilized in this apolar microemvironment which may be initiated by the electrostatic binding between SDMAB and the positive surfactant polar head. From the order of the intensity of electric field at micelle interface, as indicated in former section, association of counter ion to polar head in the examined three surfactants can be decided to be in the order of Zeph < CTAC < CTAB. Thus the possibility for DMAB anion to bind to the polar head of the surfactant should take such a sequence as Zeph > CTAC > CTAB, which will lead to the same order for the possibility of TICT fluorophore being solubilized in the apolar microenvironment provided by the self-coiling of surfactant chain. One can now easily expect that the more

possible the DMAB anion binds to polar head of surfactant molecule, the higher the rate of blue-shifting of TICT band with surfactant concentration. This is the same as the observed order, as shown in Figure 2. Thus the blue-shift of TICT band observed in surfactant solution before micelle formation can be taken as a new evidence for the self-coiling of surfactant molecule in aqueous solution [14].

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