

Twisted Intramolecular Charge Transfer of p-N, N-Dimethylaminobenzoic Acid in Cetyltrimethylammonium Chloride Micelle*

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Twisted intramolecular charge transfer (TICT) is one of the hot points in condensed phase photochemistry at the present time^[1]. Most of the studies on TICT up to now, however, are performed in organic medium, which leads to a correlation that the intensity ratio of the long-wavelength TICT fluorescence band (a band) to short-wavelength normal fluorescence band (b band), I_a/I_b , increases with the medium polarity^[2]. It is unknown whether such a correlation is applicable to aqueous solution or it is in the transition from organic solvent through water. Thus a systematic study of TICT in aqueous solution and its comparison with that in organic medium are significant for the development and deepening of the theory and application of TICT. In the present note, a steady-state fluorescence spectroscopic study of TICT of p-N, N-dimethylaminobenzoic acid (DMABOA) in aqueous cetyltrimethylammonium chloride (CTMAC) micellar solution is described.

1 Experimental

DMABOA was synthesized according to Ref. [3] and purified by recrystallizing twice from 95% ethanol. CTMAC (assay ~25% in water) was a Fluka product, whose precise concentration was determined by titration with AgNO_3 . Water was twice deionized.

Fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer. The excitation wavelength was 280 nm. The slits of excitation and emission monochromators were 6 nm and 4 nm, respectively, and the scanning rate was 120 nm/min. Relative fluorescence intensity was obtained by weighing the paper covered by the emission spectrum. pH was determined on an HM-20E pH meter (TOA, Japan). All the experiments were performed at room temperature ($21 \pm 1^\circ\text{C}$).

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2 Results and Discussion

Figure 1 shows the fluorescence spectra of DMABOA in aqueous CTMAC solution.

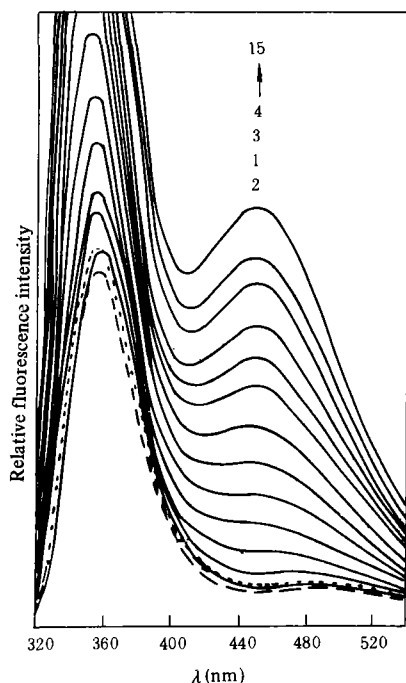


Fig. 1. Fluorescence spectra of DMABOA in aqueous CTMAC solution. DMABOA concentration is 2.5×10^{-5} mol/L. CTMAC concentration is increased from 0 of curve 1 to 1.75×10^{-3} mol/L of curve 15 with the same interval.

transfer but the polarity of this state, though higher than that of the ground state, is much lower than that of TICT state. It is easy to see that, in this concentration region, the CTMAC molecules start to aggregate and even to form micelle and, as a consequence, offer a nonpolar microenvironment. Thus the TICT fluorescence characteristics can be employed to probe the micelle formation in aqueous solution. Secondly, the fluorescence intensities of a band, I_a , and of b band, I_b , and the total fluorescence intensity, I_F , gradually

Dual fluorescence, typical of TICT, can be easily seen and shows a strong dependence on the CTMAC concentration. At CTMAC concentration lower than 2.5×10^{-4} mol/L, the fluorescence spectra and I_a/I_b did not change (Fig. 2), indicating that CTMAC does not cause substantial change in the property of the aqueous solution and exists in monomer. The fluorescence spectra, however, dramatically vary when the CTMAC concentration is higher than 2.5×10^{-4} mol/L. First, the TICT fluorescence band shifts to blue and reaches a limit of 450 nm at the CTMAC concentration of 8.75×10^{-4} mol/L, blue-shifting from 480 nm in aqueous solution by 30 nm, indicating that the DMABOA molecule is individually solubilized in a nonpolar micro-environment. It is noted that, at the same time, the normal fluorescence band also slightly shifts to blue, suggesting that the LE state involves an intramolecular charge

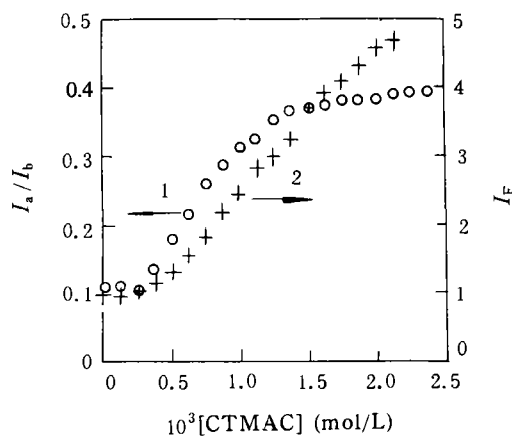


Fig. 2. Plots of I_a/I_b of DMABOA (O) and the total fluorescence intensity I_F (+) versus CTMAC concentration.

increase, also indicating the protection of the excited state of DMABOA by CTMAC aggregate and micelle. It is interesting to note that the ratio I_a/I_b varies with CTMAC concentration (Fig. 2), implying that the effects of CTMAC aggregate on TICT state are different from those on LE state, i.e. there should be other factors besides the protection. It can be seen from Fig. 2 that I_a/I_b is nearly constant when the CTMAC concentration is in the region of $0 - 2.5 \times 10^{-4}$ mol/L, and increases abruptly with the increase of the CTMAC concentration from 2.5×10^{-4} to 1.38×10^{-3} mol/L and, finally, increases linearly with the CTMAC concentration at a small rate. The total curve of I_a/I_b versus CTMAC concentration demonstrates itself by a "S" shape. The critical micelle concentration (cmc) of CTMAC is thus obtained to be 7.1×10^{-4} mol/L from the inflection point of the "S"-type curve according to the "phase separation" model of icelle formation^[4], which is in good agreement with that obtained by the classical conductometry (8.8×10^{-4} mol/L), indicating that the use of the variations of I_a/I_b of TICT fluorophore with the surfactant concentration to determine the cmc can act as a new photo-physicochemical method. By combining Fig. 1 with Fig. 2, we note that I_a/I_b increases upon the gradual blue-shift of TICT fluorescence band of DMABOA, or upon DMABOA molecules gradually solubilized into the nonpolar micellar core. Such a correlation is just opposite to that in organic medium. Water-penetration in micellar core has been widely recognized^[5]; thus the micellar core can be considered a kind of "aqueous solution". Therefore, the above-mentioned results must mean that the correlation of I_a/I_b with polarity in aqueous solution is opposite to that in organic solvent, i.e. the lower the polarity of the aqueous solution, the higher the I_a/I_b , or the correlation discontinues in the variation of the solvent from an organic solvent to water. From the excited state photophysics of TICT fluorophore, it can be understood that, due to the much higher polarity of TICT state than that of LE state, the equilibrium between LE and TICT shifts to TICT with the increase of the medium polarity, which results in the decrease of I_b and the increase of I_a and thus of I_a/I_b . Meanwhile, the energy gaps between TICT state and its triplet state and ground state decrease, which leads to the enhancement of the intersystem crossing and radiationless decay and in turn to the decrease of I_a/I_b . Obviously, the two parts are opposite to each other and the net results should be determined by the main one. In organic solvent, I_a/I_b increases with the increase of medium polarity, showing that the equilibrium between LE and TICT is the controlling factor, which has also been pointed out by the thermodynamic study^[6]. In aqueous solution the energy gaps are of course the determining factor, because the especially high polarity of water, compared with that of the common organic solvent, causes a sharp lowering of the energy of TICT state. When the polarity of aqueous solution decreases, the above-mentioned energy gaps increase and the rate of intersystem crossing and of radiationless decay of TICT state decreases; thus the fluorescence quantum yield of TICT is enhanced, resulting in increases of I_a/I_b and total quantum yield, which agrees well with that shown in Fig. 2. If the two factors stated above are comparable, the variation of I_a/I_b with medium

polarity will have a maximum or minimum point. The TICT of pN, N-dimethylaminobenzonitrile, which requires a higher activation energy for the transformation from LE state to TICT state, in aqueous β -cyclodextrin aqueous solution^[2] may belong to such a case.

It is worth noting that the I_a/I_b of DMABOA still linearly increases with CTMAC concentration after the formation of CTMAC micelle, indicating that the formation of TICT state depends on the concentration of TICT fluorophore. Thus the relationship between the I_a/I_b of DMABOA and its concentration in CTMAC micellar solution with a fixed concentration is examined as shown in Fig. 3. From Fig. 3, it can be seen that I_a/I_b of DMABOA in pure water is independent of DMABOA concentration, whereas a linear dependence is observed in CTMAC micellar solution, indicating that the TICT process relates to its concentration and involves intermolecular interaction then, and the nonpolar microenvironment of micelle is necessary for such a concentration dependence. It has been previously reported^[8] that DMABOA incorporates into CTMAB (cetyltrimethylammonium bromide) micelle in its anionic form and I_a/I_b is independent of CTMAB concentration after the formation of CTMAB micelle. Therefore, the concentration dependence of I_a/I_b of DMABOA in CTMAC micelle should relate to the neutral DMABOA molecule, or DMABOA molecule is, at least, partially solubilized in CTMAC micelle in neutral molecules, which has been verified by the data in Fig. 4. Fig. 4 shows that the curves of pH versus CTMAC concentration in the presence and absence of DMABOA are nearly parallel to each other i.e. the acid-base equilibrium of DMABOA is not affected by the free CTMAC

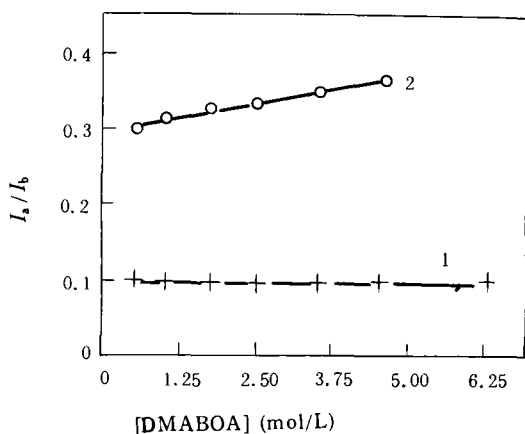


Fig. 3. Variations of I_a/I_b of DMABOA with its concentration in the absence (+) and presence (O) of CTMAC. In the latter case CTMAC concentration is 1.25×10^{-3} mol/L.

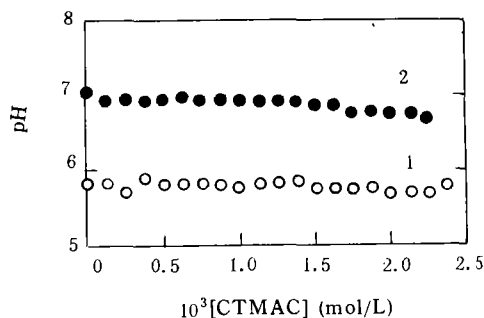


Fig. 4. pH of aqueous CTMAC solution as a function of its concentration in the absence (●) and presence (O) of DMABOA. In the latter case DMABOA concentration is 2.5×10^{-5} mol/L.

molecules and its micelles. Thus there must be neutral DMABOA molecules solubilizing in CTMAC micelles. Based on the fact that the intramolecular hydrogenbonding of carboxylic acid in nonpolar solvent such as CCl_4 , CHCl_3 , has been widely noted^[9], and the TICT of charged DMABOA anion in CTMAB micelle is self-concentration independent^[8], we postulate that the neutral DMABOA molecule is responsible for the concentration dependence of TICT of DMABOA in CTMAC micelle through the groundstate association^[10]. In addition, the variations of TICT of DMABOA in CTMAC and CTMAB micelles are considerably different, though the differences between the structure of the two micelles are mainly in the interfacial electric bilayer, suggesting that the interfacial electric bilayer of micelle may have an effect on the TICT of solubilized molecule. Such an effect is acknowledgeable considering that the TICT process involves charge transfer which is essentially affected by an external electric field. Further work on this topic is being carried on.

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