

# Concentration dependent dual fluorescence of 4-(*N,N*-dimethylamino)benzoic acid in chloroform

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## Abstract

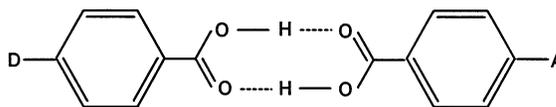
The intramolecular charge transfer (ICT) dual fluorescence of 4-(*N,N*-dimethylamino)benzoic acid (DMABOA) in chloroform was found concentration dependent and the fluorescence quantum yield ratio of the ICT to the locally excited (LE) state band,  $\Phi'/\Phi$ , increases with DMABOA concentration. Whereas the shape of absorption spectrum remains unchanged, the IR data establish the formation of ground state intermolecular hydrogen bonding between DMABOA molecules. The excitation spectra of DMABOA corresponding to the ICT and the LE emission were found identical at each DMABOA concentration but changing with increasing DMABOA concentration. These observations point to the possibility that the H-bonding mediated excited-state proton transfer facilitates the intramolecular charge transfer process. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Intramolecular charge transfer; Proton transfer; Hydrogen bonding; Dual fluorescence; 4-(*N,N*-Dimethylamino)benzoic acid

## 1. Introduction

Proton transfer (PT) coupled electron transfer (ET) has turned out to be a new dimension in the investigation of electron transfer [1–3]. Among the proposed ways, hydrogen bonding (H-bonding) appears to be an important interface. In that manner the ET process is facilitated via H-bond mediated proton transfer, see Scheme 1 [2–4]. Examples have been reported where the ET process from electron donor (D) to acceptor (A) was substantially enhanced [1–9]. It would then be of interest to examine the case where the intermolecular ET is not possible ( $D = A$ ) while the in-

tramolecular ET or charge transfer (ICT) is possible. In the present paper we report our first attempt in this regard. 4-(*N,N*-dimethylamino)benzoic acid (DMABOA) was chosen for the investigation because the ICT of DMABOA and the accompanied dual fluorescence have been well established [10–14]. Therefore, the effect of



Scheme 1. Hydrogen bond interfaced electron transfer from donor to acceptor.

the intermolecular H-bonding on the ICT process of DMABOA was investigated by its dual fluorescence.

## 2. Experimental

DMABOA was synthesized from 4-aminobenzoic acid as described elsewhere [12]. Chloroform ( $\text{CHCl}_3$ ) was dried by 4 Å molecular sieve overnight and distilled just before use. The other organic solvents, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), tetrachlorocarbon ( $\text{CCl}_4$ ) and 1,4-dioxane ( $c\text{-C}_4\text{H}_8\text{O}_2$ ) were dried and purified in a similar manner.

Fluorescence spectra were recorded on Hitachi 650-10S fluorescence spectrophotometer. The samples were excited by 280 nm light from an 150 W xenon lamp. Absorption spectra were scanned on Beckmann DU-7HS spectrophotometer by using 1-cm quartz cell. IR spectra were measured on Shimadzu IR-408 spectrophotometer. The liquid samples were sandwiched between two KBr IR plates spaced by 2 mm by silicon rubber.

## 3. Results and discussion

Intramolecular charge transfer (ICT) occurring in the electron-donor substituted aromatic acid, DMABOA, has been established by its dual fluorescence in solvents over a large polarity range [10–14]. The short wavelength fluorescence is emitted from the locally excited (LE) state while the long wavelength band comes from the ICT state of much higher dipole moment [15–17]. Meanwhile the formation of cyclic hydrogen bond of aromatic acids in chloroform is also known [18]. The up-to-date exciting progress in the investigation of proton transfer coupled ET (PTET) promoted us to examine how the ICT would be affected by the intermolecular H-bonding by taking DMABOA as an example. The concentration dependence of the ICT dual fluorescence of DMABOA in  $\text{CHCl}_3$  was thus investigated.

In Fig. 1 the fluorescence spectra of DMABOA in  $\text{CHCl}_3$  are presented. It is seen that the LE as well as the ICT fluorescence increases with

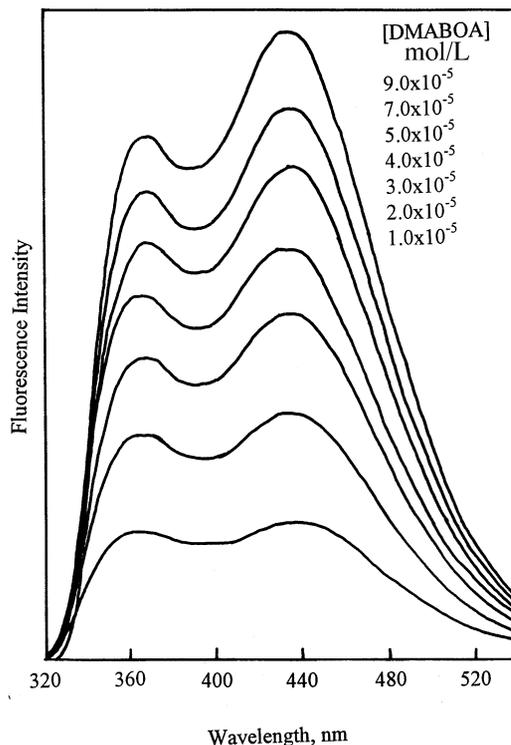


Fig. 1. Dual fluorescence of DMABOA in  $\text{CHCl}_3$ .

DMABOA concentration. By calculating the fluorescence quantum yield ratio of the ICT to the LE band,  $\Phi'/\Phi$ , we found an increase of this ratio with DMABOA concentration (Fig. 2). This means that the increase in the ICT fluorescence is faster than that in the LE fluorescence.

The absorption spectra were also recorded (Fig. 3). The shape of the spectra were found not changed before the spectrophotometer saturated at higher DMABOA concentration and an origin-through linearity was found between the absorbency and DMABOA concentration in that case (see Fig. 2). No ground state interaction between DMABOA molecules can then be detected by absorption spectra.

However, in agreement with the known knowledge, the formation of cyclic H-bond between carboxylic groups of two DMABOA molecules was established, according to the reported method [4,19], by IR measurements of stretching band of the free O-H bond. The association constant of

130 l/mol was measured and the molar absorption coefficient of the O–H stretching band of 109 l/mol·cm obtained. These data agree well with those of related systems in similar solvents [4,19]. The percentage of the DMABOA molecules in cyclic H-bonding state hence increases at higher DMABOA concentration when the  $\Phi'/\Phi$  ratio was found higher (Fig. 2). These may point to the possibility that the intermolecular H-bonding also facilitates the ICT process.

It should be pointed out that the other possibility of H-bonding between DMABOA molecules such as that of the carboxylic group to amine nitrogen seems not likely, otherwise the ICT emission would have been quenched due to the decrease of the electron density at the amino group and this is not the case. The less favored steric and energetic (one H-bond) factors in this (H···N) H-bonding compared to those in the cyclic H-bonding (two H-bonds) may also be the reasons. The complete proton transfer from the carboxylic group to dimethylamino group, leading to a zwitterionic species can be ruled out as in that case the ICT process is blocked which is opposite to the experimental observations. The reason that this proton transfer does not happen can be found from the  $pK_a$ s of the carboxylic group and the dimethylammonium group in DMABOA molecule. In aqueous solution the  $pK_a$  of the carboxylic group of DMABOA is ca. 5.0 and the

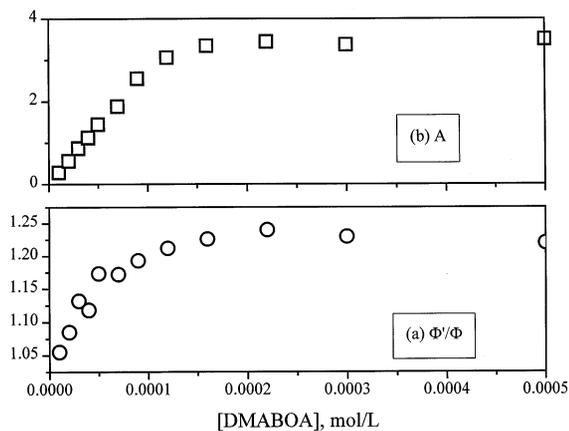


Fig. 2. Fluorescence quantum yield ratio (○) and absorbance (△) of DMABOA in  $\text{CHCl}_3$  as a function of DMABOA concentration.

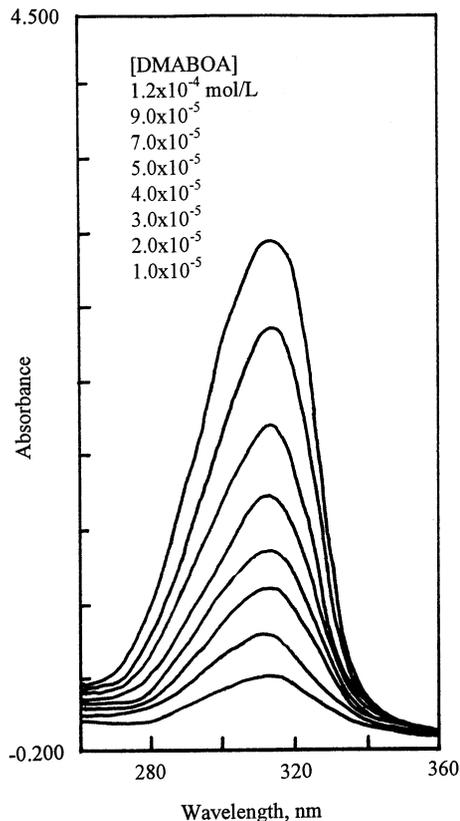


Fig. 3. Absorption spectra of DMABOA in  $\text{CHCl}_3$  at different concentration.

dimethylamino- group is not protonated even at pH 3.5 [12]. The latter means that a  $pK_a$  of lower than 3.5 could be expected for the dimethylammonium group. Therefore, it is not possible with DMABOA that a complete proton transfer from the carboxylic group to the dimethylamino group can happen in aqueous solution. In less polar organic solvents this would also be not possible.

In order to identify the possibility of excited state reaction, the excitation spectra of DMABOA were recorded by monitoring the fluorescence emission at the LE and the ICT bands, respectively. The spectra are shown in Fig. 4. It is found from Fig. 4 that the excitation spectra thus recorded are identical at each DMABOA concentration, in agreement with the known fact that the LE and the ICT states are of the same origin of excitation [15–17]. The excita-

tion spectra, however, were found splitting to two bands at higher DMABOA concentration and becoming different from the absorption spectra (Figs. 3 and 4). Therefore, an excited state reaction must have occurred and this reaction is DMABOA concentration dependent. As the two bands appearing in the excitation spectrum of DMABOA at higher concentration correspond well to the absorption bands of anionic (284 nm) and neutral (314) form of DMABOA in water [11], we would assign this excited state reaction of DMABOA in  $\text{CHCl}_3$  to the H-bond mediated proton transfer, which may in turn facilitate the ICT process as what was found in the PTET [3–9]. No direct evidence could be offered at this

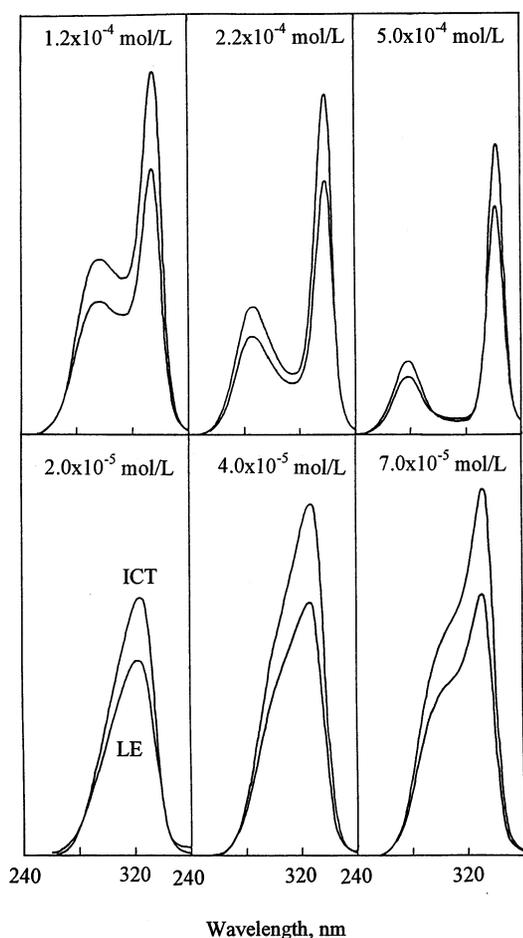


Fig. 4. Excitation spectra recorded by monitoring the LE and the ICT fluorescence.

stage. However, the observations that in *c*- $\text{C}_4\text{H}_8\text{O}_2$  (1,4-dioxane) which destroys the intermolecular H-bond between DMABOA molecules the concentration dependence of  $\Phi'/\Phi$  becomes much less appreciable (not shown) and in water no such dependence is present [12] would support this assumption.

As for the ICT process and the ICT dual fluorescence depends strongly on solvent polarity [15–17], it would be of interest to compare the effect of the intermolecular H-bonding and the effect of solvent polarity on the ICT process of DMABOA. The solvent polarity was varied by adding to  $\text{CHCl}_3$  the solvents of different polarity and H-bonding ability, such as *c*- $\text{C}_4\text{H}_8\text{O}_2$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CCl}_4$ , and it is monitored by the ICT fluorescence band position. It has been reported [16] that in case that solvent polarity mainly plays role the fluorescence quantum yield ratio,  $\Phi'/\Phi$ , linearly relates to the solvent polarity. We found

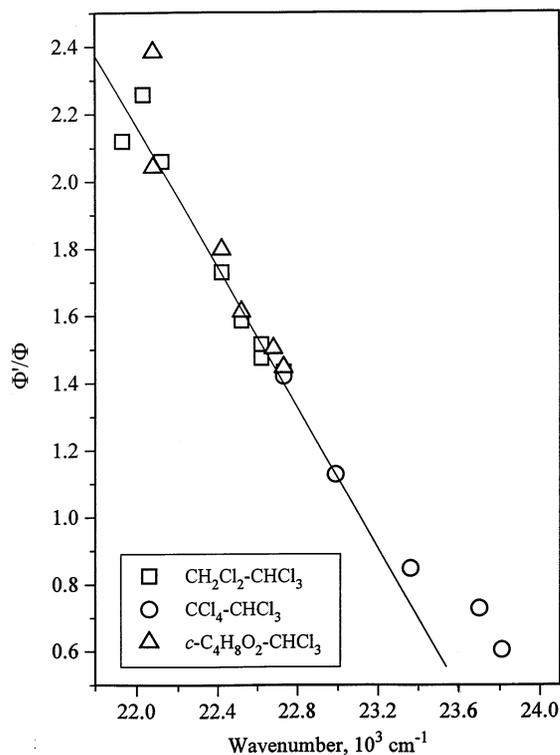


Fig. 5. Linear correlation of the fluorescence quantum yield ratio of DMABOA with solvent polarity in binary solvent mixtures.

that with DMABOA the  $\Phi'/\Phi$  ratio nicely correlated in a linearity to the polarity of solvents of different H-bonding ability (Fig. 5). This should mean that the effect of the H-bonding, if any, is weaker compared to the solvent polarity effect.

In conclusion, we showed that in case of DMABOA in  $\text{CHCl}_3$  the ICT process and the relative ICT fluorescence are facilitated by the intermolecular H-bond mediated excited state proton transfer and this effect is weaker than that of solvent polarity. Direct evidences are, however, still needed for proving and understanding this H-bonding effect.

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