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# Intramolecular charge transfer at reverse micelle–water pool interface: *p*-*N*,*N*-dimethylaminobenzoic acid in AOT/cyclohexane/water reverse micelle

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**Abstract**

Photoinduced intramolecular charge transfer (ICT) of *p*-*N*,*N*-dimethylaminobenzoic acid (DMABOA) in AOT/cyclohexane/$H_2O$ reverse micelle was investigated and compared with that in CTAB/1-heptanol/$H_2O$ reverse micelle. It is proposed that the DMABOA molecule exists at the AOT reverse micelle–water pool interface with its carboxylic group heading toward the water pool while the dimethylaminophenyl moiety buried in the micellar phase. Dual fluorescence of DMABOA that is indicative of the ICT reaction in the excited state was observed over the investigated water pool size, $W$ of 3–17, in the AOT reverse micelle. The ICT emission of DMABOA in the AOT reverse micelle–water pool interface was found to be much weaker than that in the CTAB reverse micelle–water pool interface, and was attributed to the parallel direction of the electric field at the AOT reverse micelle–water pool interface to the charge transfer. 

*Keywords:* Intramolecular charge transfer; AOT/cyclohexane/$H_2O$ reverse micelle; Dual fluorescence

## 1. Introduction

It has been established that both the strength and the relative direction of the electric field govern the charge transfer process occurring under the electric field [1]. Our investigations by dual fluorescence of the intramolecular charge transfer (ICT) of *p*-*N*,*N*-dimethylaminobenzoic acid (DMABOA), an electron-acceptor *para*-substituted *N*,*N*-dimethylaniline [2–4], in normal [5–9] and reverse [10] micelles have demonstrated the effect of the micelle–water interface electric field strength on the ICT process within the micelles. The effect of the micelle–water interface electric field direction relative to the intermolecular charge transfer has not been addressed. As the results pointed to the possibility of developing a novel fluorescence sensing mode for anions [9], it would be of importance to establish the role that the relative direction of the micelle–water inter-

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face electric field may play in the ICT process. This will help in searching for a suitable ionic micelle/ICT fluorophore combination for maximal sensing efficiency for anions. It should be pointed out that there have been several reports that indicated the impact of the relative electric field direction in some other charge transfer processes such as exciplex formation [11,12] and proton-coupled electron transfer [13]. We thus decided to extend our research on the ICT process at the micelle–water interfaces in order to establish the role that the relative direction of the micelle–water interface electric field may play in the ICT process. For this purpose we examined and compared the ICT process in micelles with similar structural characteristics but opposite surface charge.

In the present paper the intramolecular charge transfer of DMABOA in AOT/cyclohexane/$H_2O$ reverse micelle [14–16] investigated by the ICT typical dual fluorescence [2–4] and its comparison to that in CTAB/1-heptanol/$H_2O$ reverse micelle [10] are described.

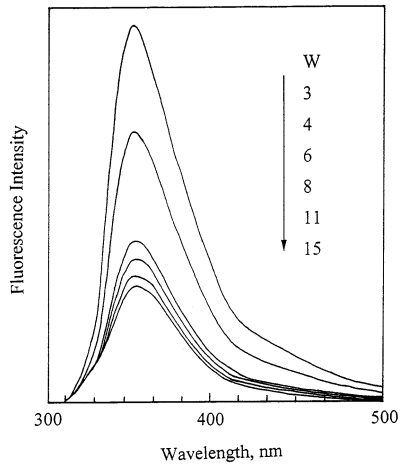



Fig. 1. Fluorescence spectra of DMABOA in AOT/cyclohexane/$H_2O$ reverse micelles [AOT] = 0.05 mol/l, [DMABOA] = $2.5 \times 10^{-5}$ mol/l.

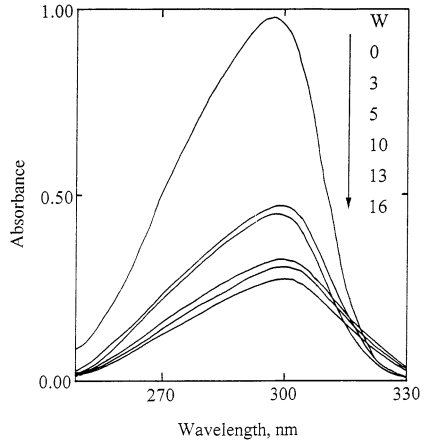



Fig. 2. Absorption spectra of DMABOA in the AOT reverse micelles of different water pool size.

## 2. Experimental

DMABOA was synthesized from *p*-aminobenzoic acid as described elsewhere [17]. Aerosol OT, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was purchased from Tokyo Kasei, Japan, and dried before use for more than 48 h under vacuum at room temperature in the presence of $P_2O_5$. Cyclohexane was dried overnight by 4 Å molecular sieve and redistilled just before use. Water was twice deionized and redistilled. Reverse micelles, in clear solution phase, were prepared by first dissolving the dry AOT in cyclohexane to which was added the requisite amount of water containing DMABOA.

Fluorescence spectra were recorded on a Shimadzu RF-5000 fluorescence spectrophotometer by exciting at 290 nm. Both excitation and emission monochromators' slits were set at 5 nm and the spectral scan rate at medium. *G*-factor correction was included in the fluorescence polarization measurements. Absorption spectra were recorded on a Shimadzu UV-240 absorption spectrophotometer by using an 1-cm quartz cell and the solutions without chromophore as blanks.

## 3. Results and discussion

Figs. 1 and 2 show the fluorescence and absorption spectra of DMABOA in AOT/cyclohexane/$H_2O$ reverse micelles as a function of water pool size, $W$. Here $W$ is the molar ratio of water to surfactant, i.e. $W = [H_2O]/[AOT]$. A sensitive re-

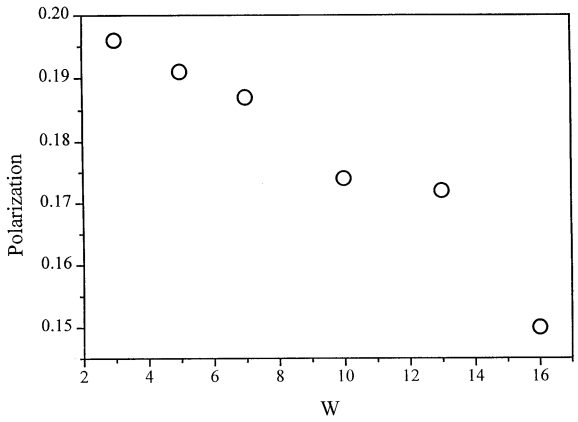
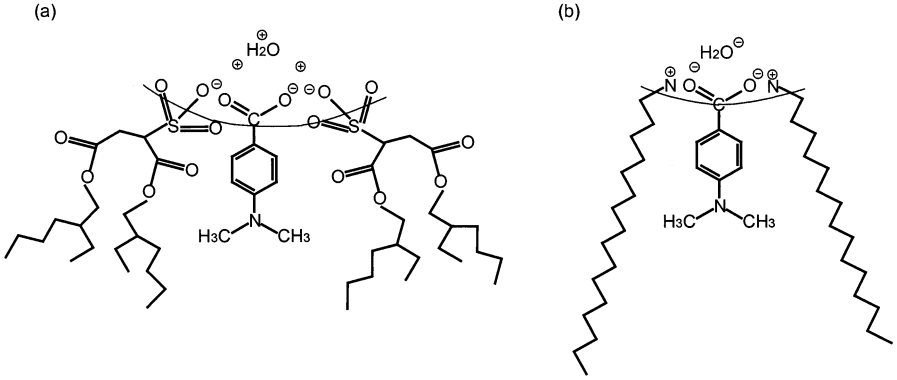



Fig. 3. Fluorescence polarization of DMABOA in the AOT/cyclohexane/$H_2O$ reverse micelle.

sponse of the spectrum to the variation of $W$ can be seen. This finding suggests that the DMABOA molecule in the AOT reverse micelle is water accessible, which means that DMABOA molecule is either in the water pool of the reverse micelle or at the micelle–water pool interface or in both regions, or that the DMABOA molecule is in the micellar phase whose properties are subject to the water pool size. As DMABOA molecule is an organic acid and exists in the present reverse micelle in an mixture of neutral and anionic forms as will be discussed later based on absorption spectra, it would be not likely for it to be located in the nonpolar micellar phase. Therefore, this possibility is ruled out. In order to determine the location of DMABOA in the AOT reverse micelle, the fluorescence polarizations of DMABOA were measured as a function of W. In either bulk water or cyclohexane no appreciable fluorescence polarization has been detected for DMABOA. However, a high polarization value was measured in the AOT reverse micelle. The data are shown in Fig. 3. As seen in Fig. 3 the polarization value at higher $W$, when the viscosity in the water pool was reported to be close to that of the bulk water [18,19], is still high. For instance, the polarization value is 0.15 at $W$ of 16. This indicates that the fluorophore is located in a highly viscous environment in the AOT reverse micelle. It is thus concluded that, in analogy to what has been assigned for $p$-nitrophenol in an AOT reverse micelle [20], the DMABOA molecules are inserted at the reverse micelle–water pool interface, with its carboxylic group towards the water pool while the dimethylaminophenyl moiety remains buried in the micellar phase (Scheme 1a). The decrease in the fluorescence polarization with increasing $W$, as seen in Fig. 3, coincides well with this assignment, since the expansion of the water pool at higher $W$ will lead to a less compact reverse micelle–water pool interface as indicated by a decrease in surfactant unit per $cm^2$ of the AOT/cyclohexane/$H_2O$ reverse micelle interface with increasing $W$ [14,21]. It is important to point out that this solubilization region of DMABOA in the AOT reverse micelle is also similar to what has been assigned for DMABOA in the CTAB/1-heptanol/$H_2O$ reverse micelle (Scheme 1b) reported previously from this laboratory [10].




Scheme 1. The schematic picture for solubilization region of DMABOA in (a) AOT and (b) CTAB reverse micelles

Having established the solubilization position of DMABOA at the AOT reverse micelle–water pool interface, we now turn to its ICT properties at the interface. For DMABOA in organic and aqueous solutions the occurrence of the photo-induced intramolecular charge transfer (ICT) and the accompanied dual fluorescence have been reported [5–10,22,23]. The dual fluorescence is ascribed to two emissive states. The lower energy emission is due to the ICT state of higher dipole moment while the emission at ca.350nm comes from the locally excited (LE) state which populates the ICT state [2–4]. In Fig. 1 dual fluorescence is shown with DMABOA in the AOT/cyclohexane/$H_2O$ reverse micelle over the investigated range of W of 3–17. However, it must be recognized that the ICT emission appears only as a weak shoulder next to the LE emission. Also, the ICT emission is weaker than and is strongly blue-shifted from that in bulk water in which observable ICT emission was found from the fluorecence spectrum [23]. This observation supports the assignment of the location of DMABOA at the AOT reverse micelle–water interface of lower polarity as described in the previous paragraph (see also Scheme 1a).

It is then important to note that the ICT emission of DMABOA at the AOT reverse micelle–water pool interface is much weaker than that in the CTAB reverse micelle–water pool interface reported previously [10]. In the latter case the ICT emission at ca. 420 nm is dominant in the fluorescence spectrum [10]. Obviously, the ICT process of DMABOA at the AOT reverse micelle–water pool interface is strongly suppressed. As the ICT state has a higher dipole moment than the ground state and a molecular configuration change occurs upon the charge transfer [2–4], the reasons for the suppressed ICT process in the AOT reverse micelle must be found from the differences in the polarity, viscosity and the electric field at the AOT and CTAB reverse micelle–water interfaces. As DMABOA is an acid and its ICT dual fluorescence is sensitive to the medium pH [17,23], pH factor should also be considered.

Comparing the ICT emission of DMABOA at the AOT and CTAB reverse micelle–water pool interfaces we found that the ICT emission in both reverse micelles occur at similar position at ca. 420 nm in the fluorescence spectra. This would suggest similar polarity that DMABOA experiences at these two interfaces. The viscosity that DMABOA experiences at these two interfaces might be different. However, this difference will not contribute to the difference in the ICT emission, since recent results based on pressure effect has shown that medium viscosity plays a minor role in the ICT process [4].

The pH factor deserves detailed discussion since in current system the pH in the water pool was not controlled. The ICT dual fluorescence of DMABOA is fairly sensitive to medium pH [17,23]. At lower pH the ICT emission is weak. Although the results of Kumamaru et al. [24] might imply a lower pH in the water pool of higher W, the pH at the interface may not show appreciable change with increasing $W$. At least the latter might be the case in the present system. This can be seen from the absorption spectra of DMABOA as a function of $W$ shown in Fig. 2. In the AOT reverse micelle of $W = 0$, the absorption spectrum shows a maximum at 295 nm and at $W = 16$ it is at 300 nm. Brown et al. [22,23] reported that the anionic form of DMABOA has an absorption maximum at 284 nm while the neutral form has its absorption maximum at 314 nm. It is thus clear that in the present system DMABOA exists at the AOT reverse micelle–water pool interface in a mixture of anionic and neutral forms and it does not experience strong pH change with increasing $W$. Therefore, it is reasonable to conclude that the suppressed ICT observed with DMABOA at the AOT reverse micelle–water pool interface is not due to the pH effect.

We now must rationalize this suppression of the ICT fluorescence in the AOT reverse micelle in terms of the effects of the reverse micelle–water pool interface electric field. Although the strength of the electric field at the AOT and CTAB reverse micelle–water pool interfaces at each $W$ could be different, we observed much weaker ICT emission at the AOT reverse micelle–water interface than that at the CTAB reverse micelle–water pool interface irrespective of $W$. This suggests that it is not the difference in the strength of the electric

field at the two interfaces that leads to such a large difference in the ICT emission. Rather, we suggest that it is due to the difference in the relative direction of the electric field at the interface to the charge transfer direction. As shown in Scheme 1, the charge transfer direction is parallel to the interface electric field in the AOT reverse micelle while opposite to that at the CTAB reverse micelle–water pool interface. In the former case the charge transfer process will be retarded while in the latter case the process enhanced [1], as also shown in other charge transfer process [10–13], leading to weak ICT emission in the AOT reverse micelle while strong ICT emission in the CTAB reverse micelle. This is indeed what we observed.

In conclusion we showed by comparing the ICT emission of DMABOA at the AOT and CTAB reverse micelle–water pool interfaces that the interface electric field direction relative to that of the charge transfer does play an important role in governing the intramolecular charge transfer. This would be significant in searching for the combination of ionic micelle/ICT fluorophore for a good sensing systems for anions. The latter is of current interest in chemical sensing since anion is not as easy to be sensed as a cation [25]. In the present case, however, the ICT emission is too weak to allow a credible monitoring of the change of the ICT emission with W. We are trying to find a better ICT fluorophore that can show appreciable ICT fluorescence in both positively and negatively charged micelle–water interfaces, in that case more convincing evidence would be provided to support the conclusion we reached here.

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