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Effect of cyclodextrin inclusion complex formation on the twisted intramolecular charge transfer (TICT) of the included compound: the *p*-dimethylaminobenzoic acid–β-cyclodextrin system

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Abstract

The effect of cyclodextrin inclusion complex formation on the twisted intramolecular charge transfer (TICT) of the included compound was examined using the TICT-typical dual fluorescence for the *p*-dimethylaminobenzoic acid (DMABOA)–β-cyclodextrin (β-CD) system in buffered (pH 4.12 and 8.00) and unbuffered (pH 5.06) solutions. The host-to-guest ratio of the DMABOA–β-CD inclusion complex is evaluated to be 1:1 in the three solutions from an analysis of the fluorescence intensity data by two methods. Enhanced LE (locally excited state) and TICT emissions and I_a/I_b ratio, a blue-shifted TICT fluorescence band and a stronger excitation wavelength dependence of the TICT fluorescence for DMABOA in the β-CD inclusion complex are observed. The correlation of the I_a/I_b ratio with the medium polarity is opposite in the inclusion complex to that observed in organic solvents. The TICT fluorescence of the DMABOA–β-CD inclusion complex with DMABOA in the basic form shows a stronger excitation wavelength dependence than that with DMABOA in the acidic form. A decreased pK_a of DMABOA in the β-CD inclusion complex is determined. This is taken as evidence that the Me_2N group of the DMABOA molecule is in the β-CD cavity. TICT is shown to be viscosity dependent in the cyclodextrin inclusion complex. The dependence of the TICT fluorescence of DMABOA in the inclusion complex on the polarity, viscosity and excitation wavelength is discussed in detail with regard to the dynamic scheme of the TICT model and the structural characteristics of the ground and excited states.

Keywords: Twisted intramolecular charge transfer; Dual fluorescence; Supramolecular inclusion complex; p-Dimethylaminobenzoic acid; β-Cyclodextrin

1. Introduction

The formation of a cyclodextrin inclusion complex means that compatibility is reached between the host and guest in terms of the polarity and stereochemistry [1,2]. On formation of the complex, the guest molecule experiences a non-polar environment and possesses a decreased freedom for bulk and intramolecular rotations in the rigid non-polar cyclodextrin cavity. The twisted intramolecular charge transfer (TICT) [3,4] is strongly dependent on the medium polarity and viscosity. Thus the formation of a cyclodextrin inclusion complex is expected to have a significant effect on the TICT process of the included compound. Such an effect has already been observed [5–12]. It should be recognized, however, that such effects remain to be investigated and understood thoroughly.

Nag et al. [6–9] have reported the TICT behaviour of *p*-dimethylaminobenzonitrile (DMABN) in aqueous α-, β- and γ-cyclodextrin solutions and three coumarins in aqueous γ-cyclodextrin solution, and concluded that TICT was strongly suppressed in the non-polar medium in aqueous cyclodextrin solution. We have performed a study of the TICT of *p*-dimethylaminobenzaldehyde (DMABA) [10] and methyl-*p*-dimethylaminobenzoate (MDMAB) [11] in aqueous β-cyclodextrin solution, and *p*-dimethylaminobenzoic acid (DMABOA) in aqueous α-cyclodextrin solution [12]. Our results have indicated that TICT in aqueous solution is different from that in pure organic solvents and that from the polarity point of view, the environment of the non-polar cyclodextrin cavity is not exactly the same as a non-polar organic solvent, but manifests itself by a microenvi-

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ronmental trait [12]. A typical characteristic of the different TICT behaviour in aqueous solution is that the correlation between the intensity ratio of the TICT dual fluorescence bands (I_a/I_b) and the medium polarity is opposite to that in organic solvents; this has been attributed to the fact that TICT in aqueous solution is controlled by the energy gaps between the TICT state and the low-lying states [10–12].

Al-Hassan et al. [13,14] have recently studied the dual fluorescence of DMABN and its ethyl derivative DEABN in aqueous α-cyclodextrin solution. The formation of three kinds of inclusion complex was assumed. The results have been discussed in terms of the dependence of TICT on the polarity and viscosity.

The viscosity dependence of TICT in a cyclodextrin inclusion complex has not been investigated in detail. There is no direct evidence in Refs. [4–14] indicating that TICT is not affected by viscosity. Nag et al. [6–8] have concluded that TICT is independent of viscosity. The basis for this conclusion is that enhanced TICT fluorescence emission of DMABN is observed in the restricted cyclodextrin cavity. Strictly speaking, however, this evidence only indicates that the viscosity may be a trivial effect in the TICT process. In fact, recent work on the TICT of DMABOA in aqueous α-cyclodextrin solutions has shown that TICT may be correlated with viscosity [12]. A similar conclusion has also recently been drawn in the DMABN(DEABN)–α-cyclodextrin system [13,14].

In addition, DMABOA in the α-cyclodextrin cavity is oriented with the dimethylamino group in the cavity [12]. For DMABN, Cox et al. [5] have proposed that the dimethylamino group protrudes out of the cavity. However, Al-Hassan et al. [13,14] recently proposed the formation of a DMABN(DEABN)–α-cyclodextrin inclusion complex with the dialkylamino group in both possible directions in the cyclodextrin cavity. Therefore the orientation of the TICT fluorophore in the cyclodextrin cavity and its effect on the TICT behaviour deserve further study.

In this paper, the effect of the formation of a DMABOA–β-cyclodextrin (β-CD) inclusion complex, in buffered and unbuffered aqueous solutions, on the TICT-typical dual fluorescence and the excitation wavelength dependence of the TICT fluorescence of DMABOA is reported. The orientation of the DMABOA molecule in the β-CD cavity is established, and the polarity and viscosity correlations of the TICT of DMABOA in the β-CD inclusion complex are discussed.

2. Experimental details

DMABOA was synthesized and purified as described previously [12]. β-CD was used as received from Fluka. Tris(hydroxymethyl)-aminomethane (Tris) was a biological reagent from Shanghai Reagent Station. Cetyltrimethylammonium bromide (CTAB) was a CP grade product of the First Shanghai Reagent Factory. HAc, NaAc, HCl and NaOH were all of GR grade. Water was twice deionized.

The fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer. The excitation wavelength was 280 nm; the slits for excitation and emission monochromators were 6 nm and 4 nm respectively. The relative fluorescence intensity was calculated from the weight of the paper covered by the emission spectrum; the intensity in the absence of β-CD was assigned to be unity. The G-factor correction was adopted in the determination of the fluorescence polarization. The absorption spectra were obtained on a Shimadzu UV–Vis 210 spectrophotometer using a 1 cm cell. The blanks used for recording the absorption spectra were the corresponding β-CD solutions without DMABOA. The acid–base titration of the DMABOA–β-CD solution was performed as described elsewhere [12] for DMABOA–α-CD solution.

3. Results and discussion

3.1. Dual fluorescence of DMABOA in the presence of β-CD

Fig. 1 shows the fluorescence spectra of DMABOA as a function of the β-CD concentration in 0.10 mol l^{-1} HAc + 0.05 mol l^{-1} NaAc (pH 4.12) and 0.10 mol l^{-1} Tris–HCl (pH 8.00) buffer solutions and in pure water (pH 5.06 ± 0.13). The dual fluorescence typical of TICT can be seen easily. The characteristics of the variation of the spectra with the β-CD concentration at different pH values are similar. Typically, both the LE (locally excited state) band (band b, short wavelength) and the TICT band (band a, long wavelength) are enhanced, and the TICT band is shifted to the blue while the LE band is not shifted. Due to the high polarity of the TICT state [3,4], this result should mean that the DMABOA molecule has penetrated into the non-polar β-CD cavity and a DMABOA–β-CD inclusion complex has been formed [1,2]. It is interesting to note that the pH value (5.06 ± 0.13, $n = 24$) of the DMABOA–β-CD solution is independent of the β-CD concentration, which is different from that observed in the DMABOA–α-CD system [12], where a decrease in the pH value occurred with increasing α-CD concentration.

In Fig. 2, the fluorescence intensity ratio of the TICT band to the LE band (I_a/I_b) and the total fluorescence intensity I of the DMABOA–β-CD system in buffered and unbuffered solutions as a function of the β-CD concentration are plotted. It can be seen in Fig. 2 that, during the course of enhancement of the total fluor-

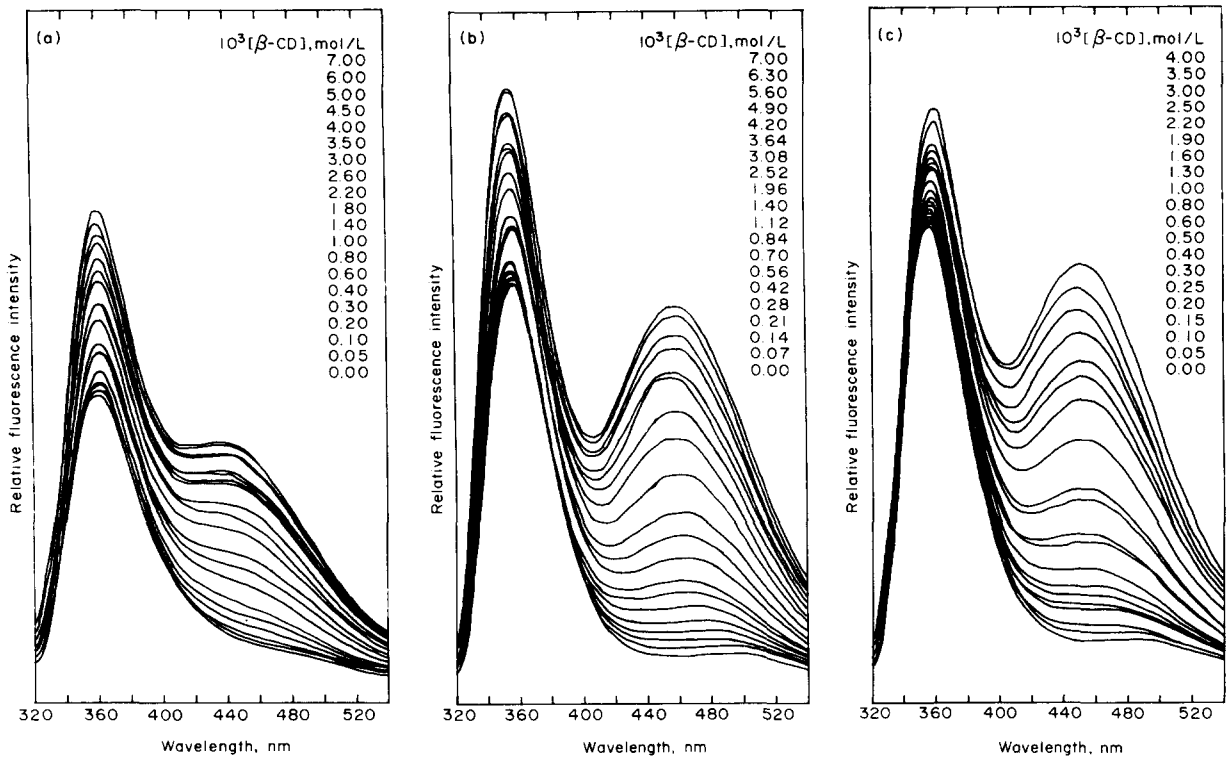

Fig. 1. Fluorescence spectra of DMABOA as a function of the β-CD concentration in buffered (a,b) and unbuffered (c) solutions: (a) pH 4.12 (0.10 mol l^{-1} HAc+0.05 mol l^{-1} NaAc); (b) pH 8.00 (0.10 mol l^{-1} Tris); (c) pH 5.06. The DMABOA concentration is 2.5×10^{-5} mol l^{-1}. The β-CD concentrations are given in the figure.

escence intensity, the I_a/I_b ratio increases initially and levels off later on, indicating that the enhancement rate of β-CD on the TICT band is higher than that on the LE band. This provides further evidence for the formation of a DMABOA–β-CD inclusion complex. The constant value of I_a/I_b at high β-CD concentration can be taken as the I_a/I_b value of the DMABOA–β-CD inclusion complex. Thus the I_a/I_b values of the DMABOA–β-CD inclusion complex in pH 4.12 (buffered), 5.06 (unbuffered) and 8.00 (buffered) solutions are 0.54, 0.72 and 0.65 respectively, all larger than those in the absence of β-CD.

The results shown in Figs. 1 and 2 indicate that the TICT behaviour of DMABOA is dramatically affected by the formation of the DMABOA–β-CD inclusion complex. This influence could be the result of the altered dissociation of DMABOA (an organic acid) and the polarity and viscosity experienced by DMABOA in the inclusion complex. Fig. 2 shows that the correlations of the two fluorescence parameters (I_a/I_b and I) with the β-CD concentration are similar in solutions with a pH value lower than, compatible with and higher than the pK_a ($pK_a=5.0$ [15]) of DMABOA implying that the change in the dissociation of DMABOA is not the main cause of the variation in the TICT behaviour in the presence of β-CD. Thus the polarity and viscosity variations may play a more important role in the change in the TICT behaviour of DMABOA.

3.2. The orientation of the DMABOA molecule in the β-CD cavity

In the investigation of TICT in cyclodextrin systems, the orientation of the TICT fluorophore in the cyclodextrin cavity has not been studied in detail [5–8,12–14] and the effect of the orientation has not been examined. Cox et al. [5] have reported, on the basis of molecular models, that the DMABN molecule is included in the cyclodextrin cavity with the dimethylamino group protruding into the bulk phase. Such an orientation has been applied to explain the TICT behaviour of DMABN in α-, β- and γ-CD systems [6–8].

Alternatively, both possible directions of DMABN and DEABN in the α-CD cavity have been assumed by Al-Hassan et al. [13,14]. This may be the case since DMABN and DEABN are neutral and therefore can be included in either of the two directions in the neutral cyclodextrin cavity. However, on comparing the fluorescence spectra of DMABN and DEABN in the presence of a very high concentration of α-CD (0.02 mol l^{-1}) [14], it seems that the dialkylamino group protrudes into the bulk phase (as in complex **II** in Refs. [13] and [14]). In 0.02 mol l^{-1} α-CD solution, the TICT band of DEABN is located at much longer wavelength (520 nm) than that of DMABN (460 nm). In addition, the TICT band of DEABN is only slightly shifted to the

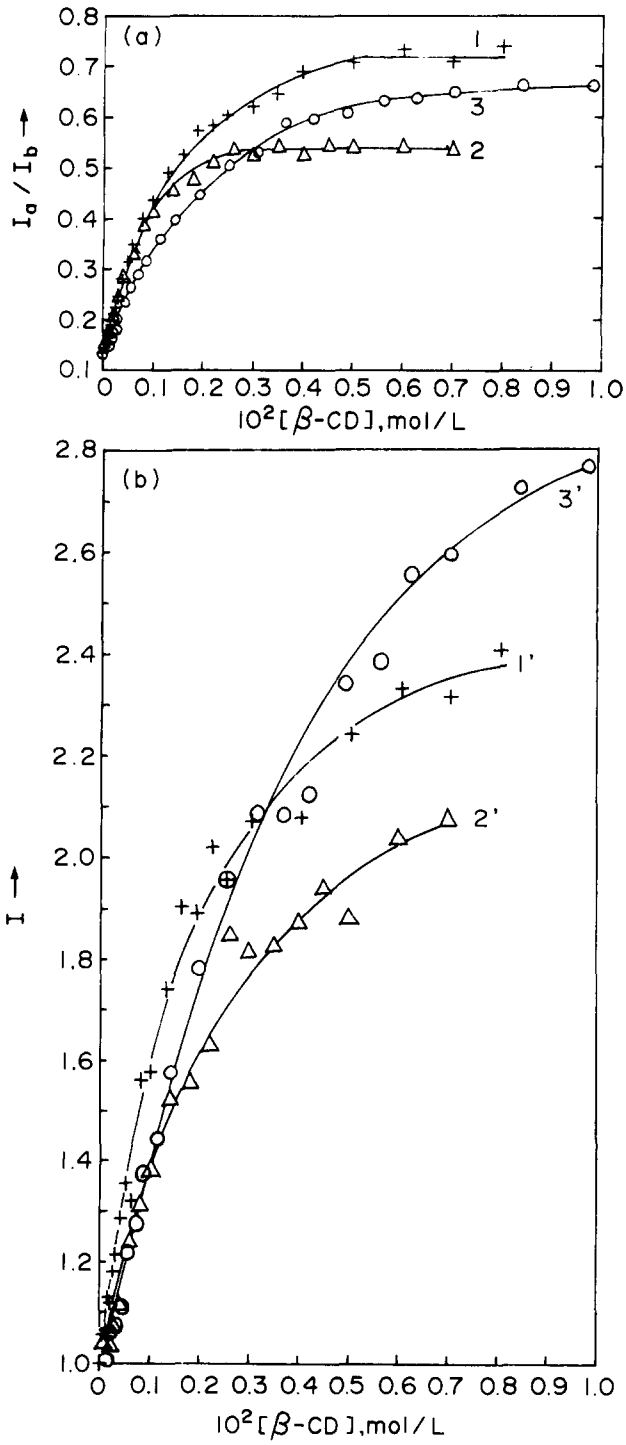

Fig. 2. Plots of the I_a/I_b ratio (a) and the total fluorescence intensity I (b) vs. β-CD concentration: (1,1′) pH 5.06 (unbuffered solution); (2,2′) pH 4.12 (buffered solution); (3,3′) pH 8.00 (buffered solution).

blue with increasing α-CD concentration, whereas that of DMABN shifts dramatically [13,14]. These results clearly show that, on average, DEABN locates in a much more polar environment in aqueous α-CD solution than does DMABN. This provides strong evidence for the protrusion of the dialkylamino group into the bulk aqueous phase. In accord with this orientation, the TICT emission of DEABN is much more strongly quenched by the polar water molecule and has a lower I_a/I_b ratio than that of DMABN [14], although it has been reported that the I_a/I_b ratio of DEABN is much higher than that of DMABN in organic solvents [16]. The argument that DEABN in the DEABN–α-CD complex with its diethylamino group located within the cavity (as in complex **I**) cannot form the TICT state, due to the inability of the diethylamino group inside the cavity to rotate [14], is difficult to support, because TICT emission has been observed in solid polymer matrices and/or under pressure (see for example, Ref. [17]).

For the DMABOA molecule in the α-CD cavity, we have shown [12] that it is included with the dimethylamino group within the α-CD cavity. This is reasonable since one end of the DMABOA molecule, i.e. COOH, is more polar and can form hydrogen bonds with either the hydroxyl groups on the cyclodextrin cavity rim or bulk water molecules, or both. It should be preferable for the COOH group to protrude into the polar aqueous phase. Because of the similarity of the β-CD and α-CD cavities, it can be assumed that the orientation of DMABOA in the β-CD cavity is the same as that in the α-CD cavity. Determination of the pK_a value of DMABOA indicates that it decreases in the presence of β-CD. For example, the pK_a values are 5.07, 4.80, 4.79 and 4.52 at β-CD concentrations of 0, 1.0×10^{-3} mol l^{-1}, 2.0×10^{-3} mol l^{-1} and 4.0×10^{-3} mol l^{-1} respectively. This result must mean that the carboxylic group of the DMABOA molecule protrudes into the bulk phase and the dimethylamino group is included in the cavity of β-CD, otherwise the pK_a value should be significantly increased or, at least, not altered [1].

By assuming this orientation for the DMABOA molecule in the β-CD cavity, it is still not easy to understand the decrease in the pK_a value of DMABOA in the presence of β-CD, since the cyclodextrin cavity favours the neutral form of the benzoic acid derivative [1]. We interpret this apparently abnormal phenomenon in terms of the increased basicity of water near the cavity rim of β-CD due to the extensive network of hydroxyl groups [18]. The diameter of the β-CD cavity is larger than that of the α-CD cavity [1,2]; the DMABOA molecule is therefore expected to penetrate further into the β-CD cavity. Thus, with the above-mentioned orientation, the carboxylic group of the DMABOA molecule will be near the cavity rim of β-CD in the DMABOA–β-CD inclusion complex and the dissociation of DMABOA is accelerated by the basic water molecules near the cavity rim. Therefore, the orientation of the DMABOA molecule in the β-CD cavity is the same as that in the α-CD cavity, with the dimethylamino group in the cavity.

3.3. Viscosity correlation of the TICT emission of DMABOA in the β-CD inclusion complex

It can be expected that, if the medium viscosity plays a part in the TICT process, the TICT process will be hindered in viscous media. The fact that the I_a/I_b ratio of DMABOA increases when the fluorophore is included in the β-CD cavity suggests that the viscosity is not the main factor affecting the TICT emission in the present system, but TICT may not be independent of the viscosity as reported in Refs. [6–8]. Comparison of the TICT of DMABOA in the β-CD cavity with that in the α-CD cavity and in CTAB micelles supports this conclusion.

There is a range of cyclodextrin concentrations over which the I_a/I_b ratio of DMABOA in the β-CD inclusion complex is higher than that in the α-CD inclusion complex [12]; this is shown in Fig. 3 in which the I_a/I_b ratio of DMABOA is plotted vs. the concentration of the DMABOA–cyclodextrin inclusion complex. The concentration of the inclusion complex is calculated from the association constant of the complex. The determination of the association constant of the β-CD inclusion complex is described in detail in Section 3.4. Since β-CD is larger than α-CD, and thus there is greater freedom in the β-CD cavity for the rotation of the electron donor group of DMABOA which is responsible for TICT, the results shown in Fig. 3 should imply the intramolecular rotation dependence of the TICT process. In other words, the microviscosity (here not the bulk phase viscosity) plays a role in the TICT process in the inclusion complex.

The I_a/I_b ratio of the basic form of DMABOA in the β-CD inclusion complex (0.65) is higher than that in CTAB micelles (0.44) [19]; the fluorophore experiences nearly the same polarity (TICT band at about 450 nm in both cases), although there is an interfacial electric field in the CTAB micelle which will preferentially enhance the TICT emission [20,21] and should increase the I_a/I_b ratio in the micellar system. Fluorescence polarization measurements indicate that the polarization of DMABOA in 8.0×10^{-3} mol l^{-1} β-CD solution is lower than that in 2.0×10^{-3} mol l^{-1} CTAB solution (the critical micelle concentration of CTAB is 9.2×10^{-4} mol l^{-1} [22]), suggesting that DMABOA in the β-CD cavity experiences a lower viscosity than that in the CTAB micellar core. This result also means that the microviscosity plays a role in the TICT process in cyclodextrin inclusion complexes and other organized media, such as micelles; the higher the viscosity, the lower the I_a/I_b ratio and the more difficult it is for the TICT process to take place.

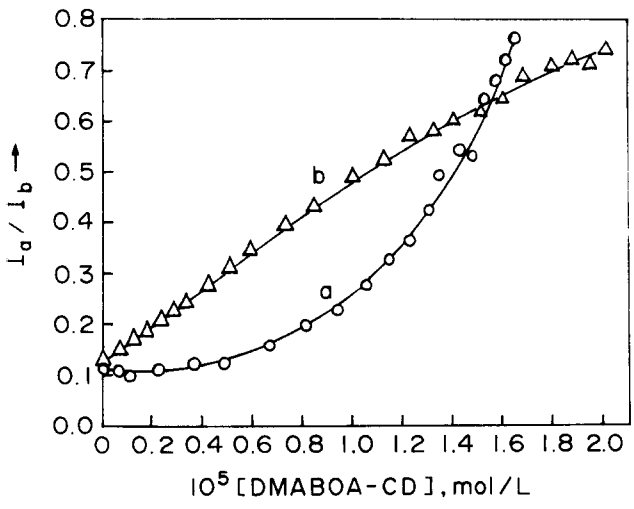

Fig. 3. Variations in the I_a/I_b ratio with the concentration of the DMABOA–cyclodextrin inclusion complex: (a) DMABOA–α-CD inclusion complex; (b) DMABOA–β-CD inclusion complex.

From the kinetic scheme of the TICT model [3,4], it can be inferred that the viscosity correlation will be present in the TICT process when the excited state equilibrium between the LE and TICT states occurs on a time scale slower than the TICT emission. This has been verified by the results of the temperature-dependent quantum yield ratio of the TICT state to the LE state of DMABN derivatives with different volumes of electron donating groups [23]. The viscosity correlation of the TICT process in the cyclodextrin inclusion complex may thus be due to the slower time scale of the excited state equilibrium, which may result from the slower time scale of twisting and the solvation time [24]. Judging from the observation that twisting occurs on a slower time scale than the solvation time for the TICT fluorophore bianthryl in strongly polar acetonitrile [24], and taking into account the high solvation ability of the strongly polar water (the solvent in the present system), we can argue that the slower twisting of the electron donor of DMABOA in the restricted β-CD cavity is the main cause of the viscosity dependence of TICT in the inclusion complex. This result suggests that the orientation of the TICT fluorophore in the cyclodextrin cavity may exert an influence on the TICT behaviour.

It should be noted that, for the DMABN–cyclodextrin system [6,7], in which the Me_2N group of the DMABN molecule protrudes into the bulk phase (opposite to the orientation of DMABOA in the cyclodextrin cavity), the ratio I_a/I_b of DMABN at the same DMABN–cyclodextrin inclusion complex concentration is higher in α-CD than in β-CD (opposite to the case for the DMABOA–cyclodextrin systems shown in Fig. 3). This result provides further evidence for the conclusion on the effect of the orientation of the fluorophore in the cyclodextrin cavity on the TICT behaviour.

3.4. Polarity effect on the TICT process in the DMABOA–β-CD inclusion complex

The viscosity and polarity are considered as the two main factors of the environment which affect the TICT process [4]. Although the viscosity correlation has been recognized for the TICT process in the present cyclodextrin inclusion complex, it is only a minor factor, since the I_a/I_b ratio is increased by the presence of β-CD. Thus the polarity should play a more important role. When we combine Figs. 1 and 2, surprisingly, we note that an enhanced I_a/I_b is accompanied by a blue shift of the TICT band. This means that the higher ratio is observed in the less polar medium. Such a correlation is opposite to that in organic solvents [4,25,26]. In the fluorescence spectrum of DMABN in dilute aqueous β-CD solutions, a similar correlation holds. Nag et al. [7] have given an explanation on the basis of the presence of different types of DMABN–β-CD inclusion complex, i.e. the enhanced TICT emission is due to the DMABN molecules partially included in the β-CD cavity which therefore experience the high polarity of the bulk aqueous phase, while the enhanced LE emission is due to the DMABN molecules totally included in the cavity. This interpretation is still based on the polarity dependence of TICT in organic solvents [4,25,26] and cannot account for the contradiction that the enhanced I_a/I_b ratio is accompanied by a blue shift in the TICT band of DMABN in aqueous β-CD solution. Thus a more reasonable explanation for the polarity correlation of the TICT emission in aqueous solution is required.

Strong evidence for the conclusion of Nag et al. [7] is the absence of an isosbestic point in the absorption spectrum of DMABN as a function of β-CD concentration. In fact, this observation does not necessarily suggest the absence of a well-defined 1:1 association compound [12,27]. The absorption spectrum of DMABOA as a function of β-CD concentration in unbuffered solution is shown in Fig. 4. An isosbestic point at about 296 nm is observed in the absorption spectrum, suggesting that a 1:1 DMABOA–β-CD inclusion complex is formed. Fluorescence intensity data analysis also indicates the formation of a 1:1 DMABOA–β-CD inclusion complex in the unbuffered and buffered solutions. The fluorescence intensity data (I) were processed against the β-CD concentration in two different ways, i.e. plots of the ratio $(I-I_0)/[\beta\text{-CD}]$ vs. I [28] and plots of the reciprocal of $(I-I_0)$ vs. the reciprocal of the β-CD concentration (double reciprocal plot) [29]. Fig. 5 shows the plots. Both methods yield straight lines, indicating that a 1:1 DMABOA–β-CD inclusion complex is formed in all the buffered and unbuffered solutions. The association constants of the complex in the three kinds of media are 510 ± 25 l mol^{-1} (in pH 5.06 unbuffered solution), 330 ± 25 l mol^{-1} (in pH 4.12 buffered solution) and 150 ± 50 l mol^{-1} (in pH 8.00 buffered solution). Thus the opposite polarity correlation of the TICT emission in the present system is not due to the presence of different forms of the inclusion complex.

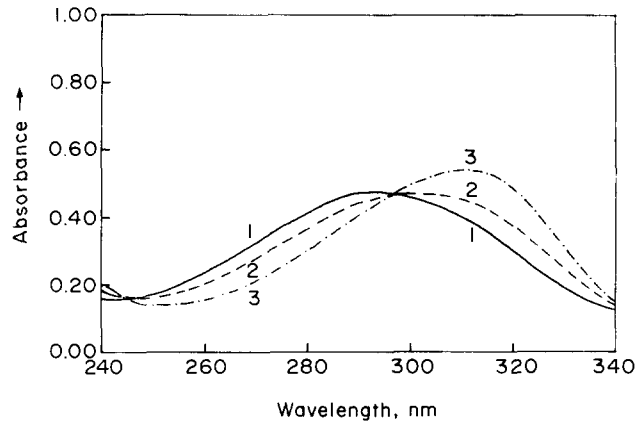

Fig. 4. Absorption spectra of DMABOA in unbuffered β-CD solutions. DMABOA concentration is 2.5×10^{-5} mol l^{-1}. β-CD concentrations are 0 (1), 2.0×10^{-3} mol l^{-1} (2) and 8.0×10^{-3} mol l^{-1} (3).

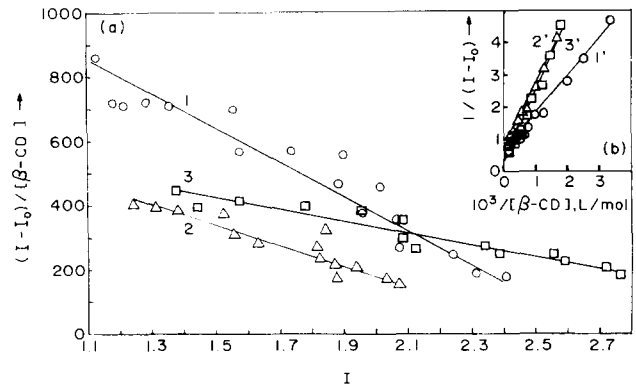

Fig. 5. Plots of $(I-I_0)/[\beta\text{-CD}]$ vs. I (a) and $1/(I-I_0)$ vs. $1/[\beta\text{-CD}]$ (b): (1,1') pH 5.06; (2,2') pH 4.12; (3,3') pH 8.00.

The medium polarity affects the dual fluorescence of the TICT fluorophore in two opposite ways [26]. An increase in polarity results in a decrease in the energy barrier for the conversion of the LE state to the TICT state. This will raise the yield of TICT emission at the expense of the yield of LE emission. At the same time, the energy gaps between the highly polar TICT state and the low-lying states are narrowed, which will lead to an enhancement of the radiationless and intersystem crossing rates, decreasing the yield of the TICT emission. Therefore the net polarity effect should be governed by the more important factor. In organic solvents, the fact that the I_a/I_b ratio increases with polarity suggests that the energy barrier is the controlling factor [26]. In the present aqueous DMABOA–β-CD system, the fact that I_a/I_b decreases with polarity should mean that the energy gaps between the TICT state and the low-lying states govern the TICT process [10–12]. This conclusion is reasonable if we take the particularly

high polarity of water into account. In aqueous solution, the highly polar TICT state is so strongly solvated and stabilized that the energy barrier for the formation of the TICT state becomes negligible, while the energy gaps become more important in affecting the TICT process. According to this assumption, we expect that, with decreasing polarity of the aqueous solution, although the LE emission yield could increase due to the shift of the equilibrium between LE and TICT states to the LE state, the yield of the TICT emission increases much more markedly. As a result, the I_a/I_b ratio and the total fluorescence intensity are enhanced. This is indeed observed for the present aqueous system as shown in Figs. 1 and 2.

It is interesting to note that, although the DMABOA molecule in the β-CD cavity experiences a non-polar environment as in common organic solvents (see the blue-shifted TICT band of DMABOA in Fig. 1), the polarity correlation of the TICT emission is opposite to that in organic solvents. This suggests that the cyclodextrin cavity has a microenvironmental effect.

3.5. Excitation wavelength dependence of the TICT fluorescence of DMABOA in the β-CD inclusion complex

The excitation wavelength dependence of the TICT emission of DMABOA in aqueous solution has been observed [15]. Using the curvature of the plot of the I_a/I_b ratio vs. the excitation wavelength as a measurement of the dependence, it was found that the basic form of DMABOA has a stronger dependence [15]. The excitation wavelength dependence of the TICT fluorescence of DMABOA in aqueous β-CD solution is also observed. Fig. 6 shows the plots of the I_a/I_b ratio of DMABOA vs. the excitation wavelength in buffered and unbuffered aqueous β-CD solutions. It is seen that the dependence is strengthened by the presence of the cyclodextrin, or that the dependence is stronger in the cyclodextrin inclusion complex. Because the dependence is observed at different pH values when the DMABOA molecule exists exclusively in the acidic (pH 4.12) or basic (pH 8.00) form or in both basic and acidic forms (pH 5.06), the enhanced dependence should not be due to a change in the acid–base dissociation of DMABOA induced by the presence of β-CD.

Another observation from Fig. 6 is that the dependence becomes more sensitive to the β-CD concentration when the pH value is increased, although in the latter case the association constant between DMABOA and β-CD is smaller (Section 3.4). This observation means that the TICT fluorescence of the DMABOA–β-CD inclusion complex with DMABOA in the basic form has a higher excitation wavelength dependence. This is similar to the case in the absence of β-CD [15].

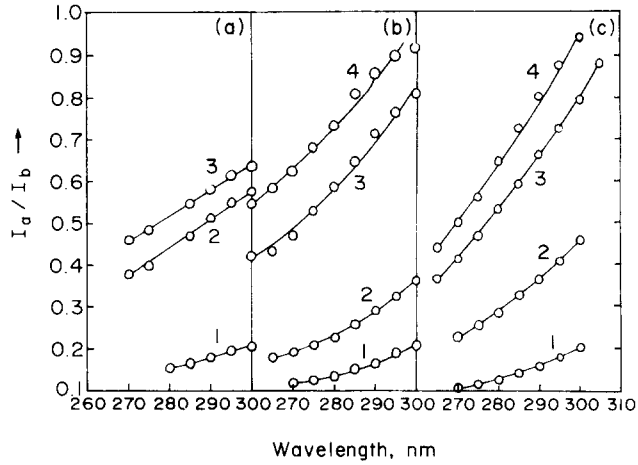

Fig. 6. Variation in the I_a/I_b ratio of DMABOA in aqueous β-CD solutions with excitation wavelength: (a) pH 4.12; β-CD concentrations are 0 (1), 1.4×10^{-3} mol l^{-1} (2) and 3.5×10^{-3} mol l^{-1} (3); (b) pH 5.6; β-CD concentrations are 0 (1), 2.5×10^{-4} mol l^{-1} (2), 3.0×10^{-3} mol l^{-1} (3) and 6.0×10^{-3} mol l^{-1} (4); (c) pH 8.00; β-CD concentrations are 0 (1), 7.0×10^{-4} mol l^{-1} (2), 3.1×10^{-3} mol l^{-1} (3) and 7.0×10^{-3} mol l^{-1} (4).

Recording of the excitation spectra of DMABOA in the presence of β-CD at different pH values indicates that, with DMABOA in the basic form, the excitation spectrum corresponding to the TICT band is located at longer wavelength than that corresponding to the LE band and the two spectra are not shifted by the presence of β-CD. For DMABOA in the acidic form, both the excitation spectra are located at the same position and are not shifted by the presence of β-CD. The excitation spectrum for DMABOA in the basic form is similar to that of DMABN and DMABA in rigid media [30,31], where the presence of a range of ground state conformers has been considered as the reason for the dependence of the TICT emission on the excitation wavelength. The excitation spectrum of DMABOA in the acidic form is similar to that for MDMAB in aqueous β-CD solution [11], where heterogeneity in excited state solvation has been assumed. Obviously the reasons for the excitation wavelength dependence are different for DMABOA–β-CD inclusion complexes with DMABOA in acidic and basic forms. Experimentally, it is also observed that the TICT band shifts slightly to the red with increasing excitation wavelength for the DMABOA inclusion complex in both acidic and basic forms. This phenomenon is typical of heterogeneity in excited state solvation [32]. Therefore, we tentatively assume that the excitation wavelength dependence of the TICT fluorescence of the DMABOA–β-CD inclusion complex with DMABOA in the basic form is due to inhomogeneity in ground state conformation [30,31] and excited state solvation [11,15,32], and that of the DMABOA–β-CD inclusion complex with DMABOA in the acidic form is due to heterogeneity in excited state solvation [11,15,32].

4. Conclusions

The LE and TICT emissions of DMABOA are enhanced by β-CD at different rates in acidic (pH 4.12) and basic (pH 8.00) buffered solutions and unbuffered solution (pH 5.06); the effect on TICT emission is higher. Meanwhile, the TICT band is shifted to the blue, but the LE band is not shifted. The correlation of the I_a/I_b ratio with the polarity experienced by the TICT fluorophore in aqueous β-CD solution is opposite to that observed in organic solvents.

The DMABOA–β-CD inclusion complex was evaluated by two methods to have 1:1 stoichiometry in the three solutions of different pH. The opposite polarity correlation of the TICT emission observed here is rationalized in terms of the fact that the TICT emission in the highly polar aqueous medium is governed by the energy gaps between the TICT state and the low-lying states. The cyclodextrin cavity is demonstrated to exert a microenvironmental effect on the TICT behaviour of the included fluorophore.

The viscosity dependence of the TICT emission of DMABOA in the cyclodextrin inclusion complex is recognized and is attributed to the slower time scale of the twisting of the electron donor in the restricted cyclodextrin cavity. The orientation of the DMABOA molecule in the β-CD cavity, namely with the dimethylamino group in the cavity, has been established. It seems that DMABN and DEABN also exhibit this orientation in the cyclodextrin cavity. The orientation of the TICT fluorophore in the cyclodextrin cavity has an effect on the TICT behaviour.

An enhanced excitation wavelength dependence of the TICT fluorescence of DMABOA is observed in the presence of β-CD with DMABOA in the basic form showing a stronger dependence than that in the acidic form. The excitation wavelength dependence of the inclusion complex with DMABOA in the acidic form is due to the heterogeneity in excited state solvation, while that of the inclusion complex with DMABOA in the basic form is due to the heterogeneity in both excited state solvation and ground state conformation.

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