

Alcohol recognition based on twisted intramolecular charge transfer

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Twisted intramolecular charge transfer (TICT) is one of the hot points in condensed state

photochemistry at the present time^[1], which has attracted much attention due to its peculiar photophysical and photochemical behavior. Most of the studies on TICT up to now, however, are focused on the microenvironmental effects, such as the effect of introducing micelle^[2], inorganic salt^[3] or aliphatic alcohols^[4] and their synthetic effect in TICT^[5, 6]. Sample analysis using TICT was seldom reported. In the present note, we describe the alcohol molecular recognition of p-N, N-dimethylaminobenzoic acid (DMABOA) in aqueous methylated β -cyclodextrin (β -MCD).

1 Experimental

DMABOA was synthesized by ourselves and purified by recrystallizing twice from 95% ethanol, whose constitution was confirmed by the melting point and IR spectrum. β -MCD was kindly donated by the Cyclolab of Hungary. Alcohols were redistilled and twice-redistilled water was used for all measurements. Other reagents used were of analytical grade.

Fluorescence spectra of DMABOA were recorded on a Hitachi 650-10S spectrofluorometer with a 1-cm cell. The excitation wavelength was 280 nm, both the slits of excitation and emission monochromators were 5 nm, and the scanning rate was 120 nm/min. All the experiments were performed at room temperature.

2 Results and discussion

Figure 1 shows the fluorescence spectra of DMABOA in aqueous β -MCD solution. The typical dual fluorescence of DMABOA can be observed in pure water and aqueous β -MCD solution, of which the band at short wavelength (band b) is a normal fluorescence band, and that at long wavelength (band a) the TICT band. The presence of β -MCD enhances the fluorescence of band a and band b, and variations of their peak wavelengths also take place. Band a shifts remarkably to blue and band b slightly to blue, meaning that the excited state of DMABOA is protected by the addition of β -MCD. We postulate that DMABOA was included in the hydrophobic cavity of β -MCD due to the formation of hydrogen bonding between the polar carboxyl of DMABOA and the hydroxyl existing on the rim of β -MCD cavity, which promoted the formation of TICT state and resulted in the blue-shifting of two bands and sharp enhancement of the fluorescence intensity.

Figure 2 shows the plot of I_a/I_b of DMABOA vs. β -MCD concentration. It can be found that, with the increase of β -MCD concentration, the ratio of I_a/I_b initially increases fast; then slowly increases and finally levels off. We think that the addition of β -MCD causes the competition of two factors, the yield of TICT state (it is the main nonradiation pathway in the normal state), and the nonradiative rate of the TICT state. Obviously, when β -MCD concentration is below $2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, the former factor is predominate; as a result, the ratio of I_a/I_b fastly increases. When β -MCD concentration is in the range of $2 \times 10^{-4} - 4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, the effect of the latter factor progressively increases; thus the ratio of I_a/I_b enhances slowly. Until the β -MCD concentration is above $4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, the effects of two factors balance, thus the ratio of I_a/I_b is nearing a constant. Therefore, $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ β -MCD was used in the following work.

In fig. 3, the responses of DMABOA- β -MCD system are plotted as a function of the concentration of linear alcohols. It can be seen that the ratio of I_a/I_b linearly decreases with increasing the chain length of the alcohol having the same concentration. It can be understood

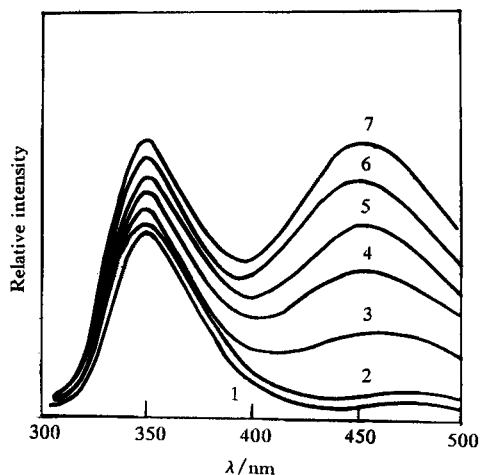


Fig. 1. Fluorescence spectra of DMABOA in aqueous β -MCD solution. DMABOA concentration: 2.5×10^{-5} mol/L; β -MCD concentration (mol/L): 1, 0; 2, 1.0×10^{-4} ; 3, 5.0×10^{-4} ; 4, 1.2×10^{-3} ; 5, 2.0×10^{-3} ; 6, 3.0×10^{-3} ; 7, 4.0×10^{-3} .

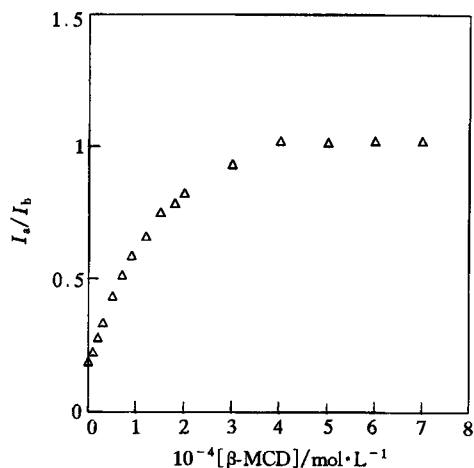


Fig. 2. Relation between the I_a/I_b ratio of DMABOA and β -MCD concentration (v/v).

that the longer the alkyl chain is, the more hydrophobic the linear alcohol must be; thus the alcohol molecule can be more easily included in the cavity of β -MCD, which increases the non-radiative deactivation rate of TICT and leads to the decrease of I_a and the slight increase of I_b . As a result, the ratio of I_a/I_b is further decreased.

Figure 4 shows the response curves of DMABOA- β -MCD system vs. the concentration of different isomeric propanols. Because isopropanol has a larger steric hindrance than propanol,

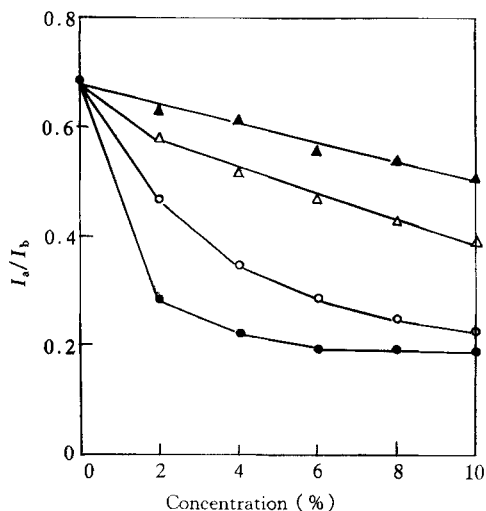


Fig. 3. Response of DMABOA- β -MCD system to the concentration (v/v) of linear alcohols. \blacktriangle , methanol; \triangle , ethanol, \circ , propanol; \bullet , butanol.

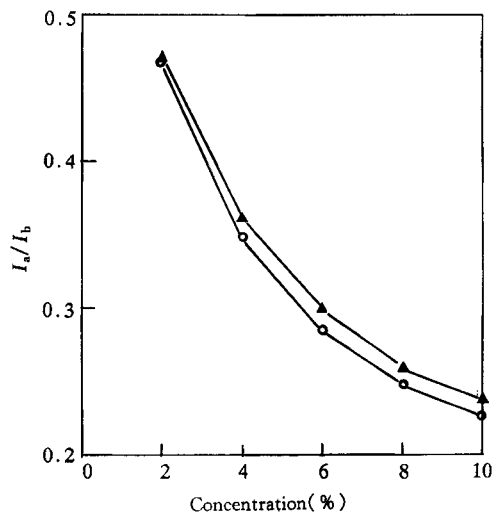


Fig. 4. Response of DMABOA- β -MCD system to different isomeric propanols concentration (v/v). \blacktriangle , isopropanol; \circ , propanol.

it cannot be included in the β -MCD cavity as easily as propanol, resulting in a smaller decrement of I_a/I_b compared with propanol with the same concentration.

Shown in fig. 5 are the response curves of DMABOA- β -MCD system against propanol, propanediol and glycerol. It can be explained that the possibility of forming the hydrogen bonding between alcohol molecule and water molecule increases with the increase of the hydroxyl number contained in different propanols. Therefore, glycerol is more difficult to be included in the β -MCD cavity than propanediol and propanol, having the smallest effect on the ratio of I_a/I_b among these three alcohols.

From the above results, it can be noted that the present TICT system can not only be used as molecular recognition of the chain length and structure, but also the hydroxyl number of alcohols.

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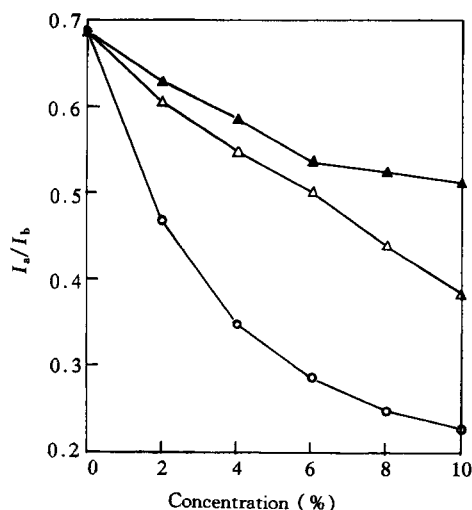


Fig. 5. Response of DMABOA- β -MCD system to the hydroxy number of alcohols. \blacktriangle , glycerol; \triangle , propanediol; \circ , propanol.