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Photophysics of 1-dimethylaminonaphthalene in aqueous-organic binary solvents

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Abstract

Fluorescence and absorption spectra of 1-dimethylaminonaphthalene (DMAN) in aqueous-organic binary solvents were recorded as a function of the content of organic components (methanol, ethanol, *n*- and *i*-propanol, and acetonitrile) for the purpose of understanding the photophysics of DMAN. Whereas the absorption spectra underwent minor change with increasing organic component, the fluorescence spectra experienced a continuous blue-shift in the band position and the fluorescence quantum yield increased reaching a maximum before continuous decrease. It was found that, in a series of aqueous-organic binary solvents, the variations of the quantum yield versus solvent polarity turned at nearly the same solvent polarity equivalent to an $E_T(30)$ value of ca. 57 kcal mol⁻¹. It is hence suggested that while the emissive state is intramolecular charge transfer in nature, the radiationless decay channel is solvent-polarity dependent. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

A systematic investigation of the photophysics of 1-dimethylaminonaphthalene (DMAN) was first reported by Phillips et al. in early 1980s [1], in which the emissive state of DMAN was ascribed as intramolecular charge transfer (ICT) in nature. However, the ICT photophysics appears to be quite ‘abnormal’ in that the quantum yield and lifetime increase with increasing solvent polarity, in opposite to those of aminonaphthalene sulfates whose emissive state was also ICT in character [2–6]. Recent researches [7–11] have shown that with DMAN and other 1-dialkylaminonaphthalenes a fast radiationless internal

conversion (IC) occurs via vibronic coupling of the proximate S_1 and S_2 states, in which S_1 is the emissive state of ICT character [7,9–11]. The IC was shown to be thermally activated with an activation energy, E_{IC} , depending on the energy gap, $\Delta E(S_1, S_2)$, between S_1 and S_2 states [7,9–11]. With increasing solvent polarity, the energy of the S_1 state decreases more appreciably, leading to higher $\Delta E(S_1, S_2)$ and hence higher E_{IC} . The thermally activated IC of DMAN is thus suppressed in polar solvent, resulting in increased fluorescence quantum yield and lengthened lifetime.

It is then envisioned that, in highly polar solvents such as in aqueous solution, the emissive S_1 state of ICT character will be strongly solvated and its energy is dramatically lowered. As a consequence, the energy gap $\Delta E(S_1, S_2)$ is enlarged so that the coupling of S_1 and S_2 states is blocked whereas the

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radiationless coupling of the S_1 state directly to the ground state opened and the intersystem crossing from S_1 to T_1 state enhanced. In that case, the emission quantum yield and lifetime will decrease with increasing solvent polarity as what happens with aminonaphthalene sulfates whose emissive state energy [3,4] is in general lower than that of DMAN [9,10]. Therefore, the purpose of the present Letter is to show whether the radiationless decay pathway of DMAN is solvent polarity dependent and, if yes, what is the polarity threshold for the turnover at which the decay pathway changes. We use aqueous-organic binary solvents to vary the solvent polarity that could extend to as high as that of water.

2. Experimental

DMAN (Fluka) was used after TLC purification. Organic solvents were purified before use such that no fluorescent impurity was detected at the used excitation wavelength. Twice de-ionized water was further distilled in the presence of KMnO_4 .

Corrected fluorescence spectra were taken on Hitachi F-4500 fluorescence spectrophotometer at excitation of ca. 305 nm by an Xenon lamp of 150 W. Fluorescence quantum yields were measured using quinine sulfate as standard ($\Phi_{\text{flu}} = 0.546$ in 1 N H_2SO_4 at 25°C [12]). Absorption spectra were measured on CRT UV-760 Spectrophotometer (The Third Analytical Instruments, Shanghai) using an 1-cm quartz cell.

3. Results and discussion

The absorption spectra of DMAN in aqueous-organic binary solvents undergoes a blue-shift with increasing organic solvent content, in agreement with the observations made in pure organic solvents of decreasing polarity [7–11]. The variations in the absorption spectra, however, are minor. For example, the absorption spectra of DMAN in methanol–water mixtures showed a spectral shifting within 10 nm and a variation in molar absorptivity within 9%. For recording fluorescence spectra, the excitation wavelength of ca. 305 nm was chosen because the ab-

sorbance at this wavelength underwent little change, thereby any change in the emission intensity indicating changes in the fluorescence quantum yield.

In contrast to the absorption spectra, the fluorescence spectra of DMAN in organic solvent–water change dramatically as the solvent composition is varied. Fig. 1 presents the typical fluorescence spectrum variation with solvent composition in methanol–water binary mixtures. It is noted that, while the emission maximum continuously shifts to the blue with increasing methanol content, the emission intensity shows a ‘bell’-shaped variation, with an intensity increase at the beginning and a decrease at higher methanol content (see directly from the inset in Fig. 1). The blue-shift in the emission maximum, from 449 nm in pure water to 419 nm in methanol, is obviously stronger than that in the absorption maximum. Several other organic solvent/water binary solvent systems (such as ethanol, *n*-propanol, *i*-propanol and acetonitrile/water) were also used and similar phenomenon was observed. Similar blue-shift in the fluorescence spectrum of DMAN has also been reported in organic solvents of decreasing polarity [1,7–11]. The observation made in the organic/aqueous solution is again indicative of a higher dipole moment of the emissive state than that of the ground state. Also, the continuous blue-shift in the emission spectrum suggests that the same emissive state is operative during the solvent composition variations, whereas the appearance of a turn in the intensity variation against solvent polarity would indicate that the radiationless decay pathway changes with solvent polarity. We use the emission energy in wavenumber (cm^{-1}) as solvent polarity index and plot the total fluorescence intensity (proximately proportional to the fluorescence quantum yield as the absorbance hardly changes with solvent composition) against solvent polarity (see Fig. 2). What we noted was that in the examined five binary solvent series, the curves turned at the same solvent polarity that corresponds to an emission maximum of $23.0 \times 10^3 \text{ cm}^{-1}$. A similar turn has also been reported for DMAN in 1,4-dioxane-water binary solvent [3]. This polarity is likely the threshold for the turnover of the radiationless decay pathway of DMAN. The value of this polarity was estimated in $E_{\text{T}}(30)$ value [12] as ca. 57 kcal mol⁻¹ by combining our data with those in [3] on the emission

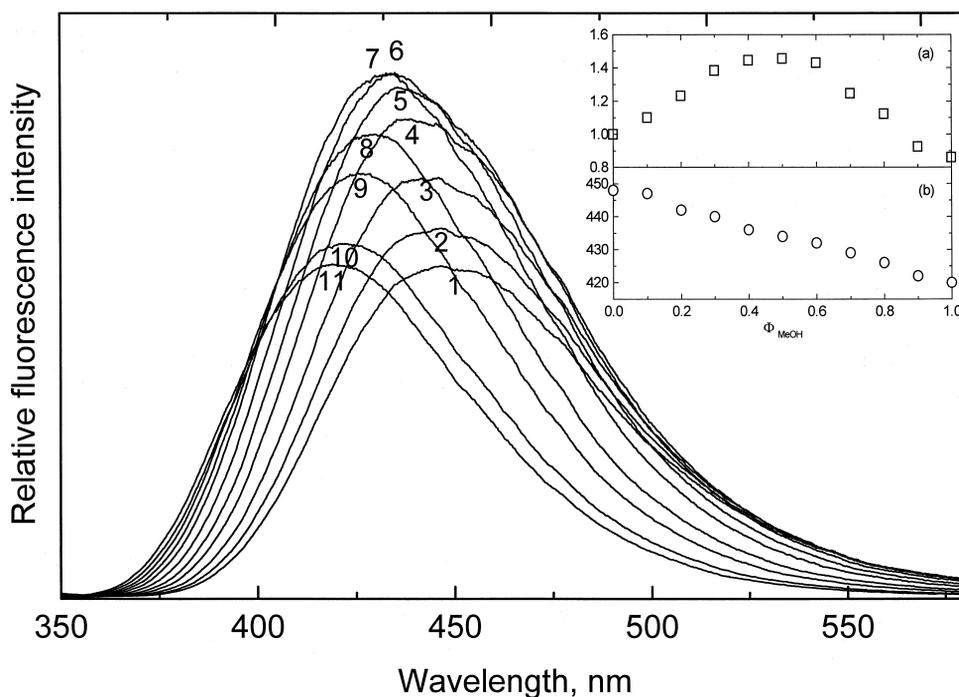


Fig. 1. Fluorescence spectra of DMAN in methanol–water binary solvents. Curves 1–11 show the spectra with methanol volume fraction in the binary mixture varying from 0 to 1 by the same interval of 0.1, respectively. Inset plots (a) the relative fluorescence intensity and (b) fluorescence maximum in nanometer against methanol volume fraction.

maximum as a function of solvent composition in dioxane–water binary solvents and the $E_T(30)$ val-

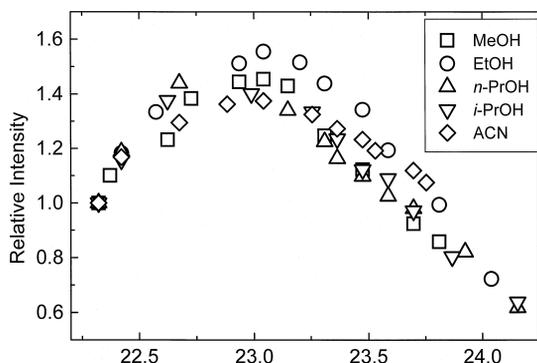


Fig. 2. Fluorescence intensity of DMAN as a function of the polarity of organic-water binary solvents. The polarity is indexed by the wavenumber of the fluorescence maximum, higher wavenumber indicating lower polarity. Organic solvents are methanol (MeOH), ethanol (EtOH), *n*-propanol (*n*-PrOH), *i*-propanol (*i*-PrOH), and acetonitrile (CAN), respectively.

ues of dioxane–water binary solvents compiled in Refs. [4,13].

We also measured the fluorescence quantum yields of DMAN in methanol–water and acetonitrile–water binary solvents as a function of solvent polarity and obtained the same variation profile as that of the fluorescence intensity (see Figs. 2 and 3). In Fig. 3 we combined our quantum yield data in aqueorganic solutions with those reported in organic solvents, and found that, with DMAN in a low solvent polarity region of the aqueous-organic binary solvents, the variation of fluorescence quantum yield followed the same profile as in pure organic solutions. It thus follows that in aqueous-organic solvent of low polarity composition region thermally activated IC plays an important role as a radiationless decay for DMAN as in organic solvent. Therefore, the turnover shown in Fig. 2 and also in Fig. 3 indicates that, in high polarity region of aqueous-organic binary solvents of $E_T(30)$ higher than ca. 57 kcal mol⁻¹, the controlling radiationless decay is not the thermally activated IC.

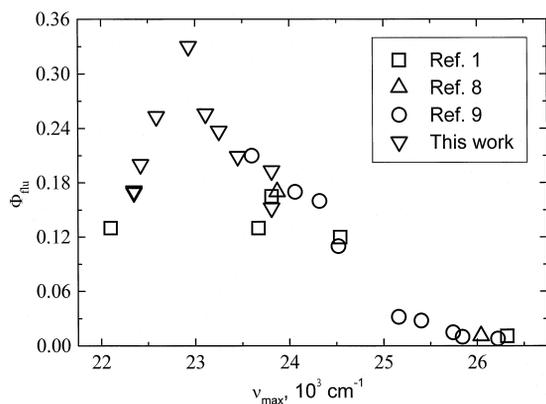


Fig. 3. Variation of the fluorescence quantum yield of DMAN with solvent polarity. The solvent polarity is indicated by the fluorescence maximum in wavenumber.

It should be admitted that at this stage the nature of the radiationless decay channel of DMAN in highly polar media is not clear. However, it is assumed that in aqueous solutions hydrogen bonding as a possible factor facilitating radiationless decay should be taken into account. In the present system hydrogen bonding does occur as being indicated by the difference in the variations of the full width at half maximum (FWHM) of the fluorescence spectra of DMAN in acetonitrile (aprotic)–water and alcohol (protic)–water binary systems. In acetonitrile–water solutions the FWHM experiences an increase from 3700 cm^{-1} in pure acetonitrile through 3900 cm^{-1} in 1:1(v/v) acetonitrile–water to 4100 cm^{-1} in pure water, whereas in alcohol (methanol, ethanol, *n*-propanol, *i*-propanol)–water solutions the FWHM remains constant at around 4000 cm^{-1} irrespective of the solvent composition. However, as shown in Fig. 3, the fluorescence intensity and hence quantum yield follows the same variation profile in both protic–water and aprotic–water binary solvents, indicating that hydrogen bonding is not a factor that influences the radiationless decay pathway. Meech et al. [1] have reached that same conclusion that the hydrogen bonding is not an accepting mode for the radiationless decay. Further experiments are needed to identify the radiationless decay channel for DMAN in highly polar media of polarity higher than $E_T(30)$ of ca. 57 kcal mol^{-1} .

4. Conclusions

In conclusion, we showed that, in spite of the same emissive state, the fluorescence quantum yield of DMAN in organic–aqueous binary solvent indicates a ‘bell’-shaped variation with decreasing solvent polarity. This is understood in terms of the solvent-dependent radiationless decay pathway. In aqueous–organic binary solvents of lower polarity, the thermally activated IC is a governing radiationless decay pathway that leads to an increase in the fluorescence quantum yield with increasing solvent polarity, whereas in the binary solvents of higher polarity, the thermally activated IC is blocked and other radiationless decay pathways should be considered, the switch occurring at solvent polarity equivalent to an $E_T(30)$ value of ca. 57 kcal mol^{-1} . Hydrogen bonding was shown to occur between DMAN and a protic solvent but is not a factor influencing the radiationless decay.

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