Temperature Effect on the Absorption and Fluorescence Spectra of p-Cyano-N,N-dimethylaniline in Dichloroethane and Ethyl Acetate

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The effect of temperature (293 ÷ 413 K) upon absorption and fluorescence spectra of p-cyano-N,N-dimethylaniline (CDMA) was investigated in 1,2-dichloroethane and ethyl acetate. Two fluorescence bands, **a** and **b**, were already observed at 293 K, with the intensity of band **b** increasing strongly with temperature in both solvents. The absorption and fluorescence **b** bands of CDMA were found to be independent of the orientation interaction with the solvent. On the other hand, the longwave band of fluorescence **a** undergoes a strong hypsochromic shift resulting from the decrease in the permittivity with increasing temperature. Based on these observations, the electric dipole moment μ_e in the ^1L_b state (shortwave band of fluorescence **b**) was found to be equal to the dipole moment, μ_g, in the ground state. The electric dipole moment μ_e in the ^1L_a state (the longwave band of fluorescence **a**), which is strongly stabilized by the polar solvent, is about 2.5 times as high as μ_g, amounting to 54×10^{-30} Cm (16.2 D) for $\mu_g = 22.5 \times 10^{-30}$ Cm (=6.75 D).

1. Introduction

The origin of the double fluorescence of p-cyano-N,N-dimethylaniline (CDMA) (p-dimethylamino-benzonitrile) (Fig. 1) was the object of numerous investigations [1–13]. As found by Lippert et al. [1], CDMA emits two fluorescence bands in liquid polar solvents, i.e. longwave, **a**, and shortwave, **b**, bands. Characteristic of the band of fluorescence **a**, absent in nonpolar solvents, is a strong dependence of its position upon the solvent's polarity, i.e. on the permittivity, ε, and the refractive index, n. According to Lippert et al. [1], this phenomenon results from the inversion of close enough states ^1L_a and ^1L_b. The band **a** was attributed to the emission from a strongly polar state ^1L_a with energy slightly lower than that of a less polar ^1L_b state. The ^1L_a state is preferentially stabilized by the polar solvent.

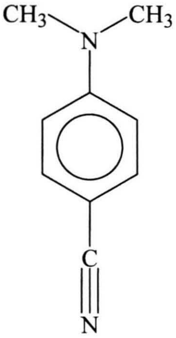

Fig. 1. Structural formula of p-cyano-N,N-dimethylaniline (CDMA) (or p-dimethylamino-benzonitrile).

Several other interpretations of the double fluorescence of CDMA and the nature of the state responsible for the emission of band **a** were formulated later [2–13].

Recently, the hypothesis of TICT (Twisted Intramolecular Charge Transfer) states has generally been accepted [2, 12, 13]. The knowledge of the exact value of the electric dipole moment of the state responsible for the emission of fluorescence **a** is essential for the elucidation of its electronic nature [14].

The position of the fluorescence band of solute molecules in liquid solvents is strongly affected by temperature which, when growing, causes the decrease in the permittivity, ε, and in the refractive index, n [15]. The effect of temperature on the position of the electronic bands of CDMA molecules was so far investigated by Lippert et al. [1] and Suppan [16, 17]. The studies of Lippert et al. [1] were carried out at low temperatures (below 300 K) while those of Suppan [16] were performed at higher temperatures (to about 330 K).

As already shown, when using a high-pressure cuvette to measure absorption and fluorescence spectra, markedly broader temperature range (from 293 to

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473 K, depending on the solvent) can be achieved, which means a considerable lowering of the permittivity [18].

The present paper reports the studies on the effect of temperature upon absorption and fluorescence spectra of CDMA in two solvents, dichloroethane and ethyl acetate. Based on the changes in ε and n, electric dipole moments in excited states were evaluated for fluorescence from states ^1L_a and ^1L_b.

2. Experimental

Absorption and fluorescence spectra were measured at different temperatures using a high-pressure cuvette described in detail in [18], where empirical formulae for ε (T) and n (T) were also given for a number of different solvents. Two solvents selected, ethyl acetate and 1,2-dichloroethane, had permittivitys $\varepsilon = 6.11$ and 10.46 and refractive indices $n = 1.372$ and 1.444, respectively, at $T = 293$ K. At temperature 413 K, ε decreased to 4.10 in ethyl acetate, while in 1,2-dichloroethane to 7.14 at 373 K. Above this temperature, the solution of CDMA in 1,2-dichloroethane became distinctly yellow. Therefore it was ethyl acetate that was chosen for determining electric dipole moments in the excited state of CDMA.

The method of thermochromic continuous shift of electronic bands, based on the temperature dependence of the permittivity, ε, yields much better results compared with solvatochromic method involving different solvents with different ε values. Absorption and fluorescence spectra were measured by methods described previously [19].

3. Results and Discussion

3.1. Absorption and Fluorescence Spectra of CDMA in 1,2-Dichloroethane and Ethyl Acetate at Different Temperatures

Figures 2 and 3 show absorption and fluorescence spectra of CDMA at different temperatures in 1,2-dichloroethane (293 ÷ 373 K) and in ethyl acetate (293 ÷ 393 K). In the temperature range studied, the positions of the absorption band maxima practically do not change while the bands of fluorescence **a** are strongly shifted. With increasing temperature of the solution, the fluorescence **a** band shifts distinctly towards shorter wavelengths (hypsochromic shift) with simultaneous increase in the intensity of band **b** for CDMA both in 1,2-dichloroethane and ethyl acetate. The increase in temperature causes a decrease of the permittivity ε and the refractive index, n, of these solvents. A particularly strong effect of temperature on the CDMA fluorescence bands is observed in ethyl acetate. At 393 K, the intensity of band **b** increased strongly enough to exceed that of the longwave band **a**. Hence, it seems clear that while lowering the permit-

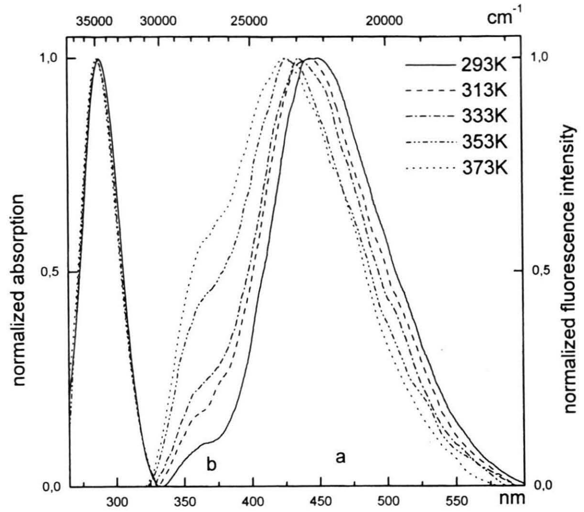

Fig. 2. Absorption and fluorescence spectra of CDMA in 1,2-dichloroethane measured at different temperatures (293 ÷ 373 K).

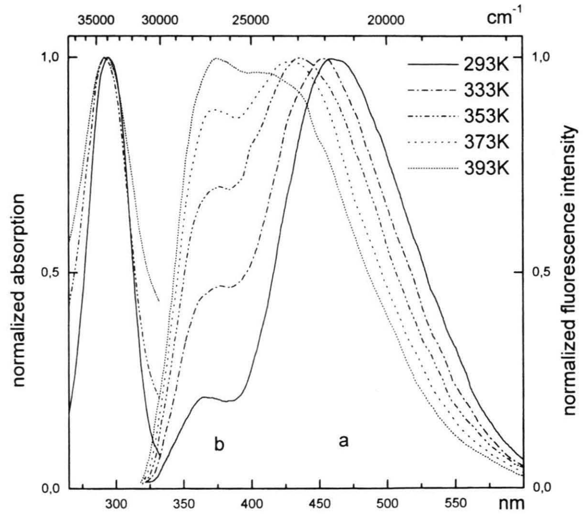

Fig. 3. Absorption and fluorescence spectra of CDMA in ethyl acetate measured at different temperatures (293 ÷ 393 K).

tivity (by increasing the temperature) to $\varepsilon \approx 2$, which corresponds to nonpolar solvents, band **a** gradually decays, thus leaving only band **b**. Therefore, the shape of the total CDMA fluorescence band in ethyl acetate at 393 K corresponds to a weakly polar solvent.

3.2. Thermochromic Excited-State Dipole Moments Measurements

It was found, based on the investigation of the temperature effect on the position of absorption and two fluorescence, **a** and **b**, bands for the CDMA molecule in ethyl acetate, that the absorption band is not influenced by the orientation polarization of the solvent molecules. The emission spectra were recovered from these two component bands, **a** and **b**, by a computer simulation in which the band envelope $I_i(\nu)$ of the i-th component band was assumed to have the conventional form of a Gaussian error function at a given wavenumber ν [20]:

$$I_i(\nu) = I_{i,\max} \cdot \exp\left(-\frac{(\nu-\nu_{i,\max})^2}{2\,\delta_i}\right), \tag{1}$$

where $\nu_{i,\max}$, $I_{i,\max}$ and δ_i are the peak position, the maximum fluorescence intensity at $\nu_{i,\max}$ and the corresponding halfwidth of the i-th band, respectively. As an illustration, Fig. 4 shows the fluorescence spectra of CDMA in ethyl acetate at 353 K, resolved into two Gaussian bands.

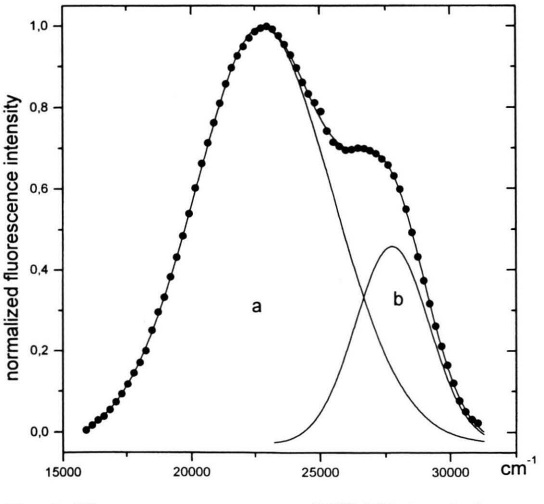

Fig. 4. Fluorescence spectrum of CDMA in ethyl acetate at 353 K resolved into two Gaussian bands.

It was found, based on this peak analysis, that the shift of the fluorescence **b** band is only slight when the temperature grows, whereas the band of fluorescence **a** is distinctly affected by orientation interactions.

According to the theory [21] of the solvent effect upon the absorption and fluorescence band position, a slope parameter occurs in the equation for the absorption band shift, $\Delta\nu_A$ [15]:

$$m_3 = \frac{m_2 - m_1}{2} \tag{2}$$

which in the case considered is equal to zero, since $\Delta\nu_A \approx$ const, i.e. the absorption spectra of CDMA are not shifted with a change in temperature (ε and n). Hence, based on (2), one obtains $m_1 = m_2$. In this case, the shift of the fluorescence band maximum $\nu_F^{\max}$ (in wavenumbers) can be expressed as [15, 22]

$$\nu_F^{\max} = -m_2\,(f(\varepsilon, n) + g(n)) + \text{const}, \tag{3}$$

where

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{\beta\, a^3}, \tag{4}$$

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) \tag{5}$$

and

$$g(n) = \frac{3}{2}\,\frac{n^4-1}{(n^2+2)^2}. \tag{6}$$

The slope parameters, m_1 and m_2, occur in general equations for the difference $\nu_A - \nu_F$ and the sum $\nu_A + \nu_F$ of the wavenumbers, respectively, as a function of the orientation polarization of the solvent, $f(\varepsilon, n)$, (5) and to the sum of $f(\varepsilon, n)$ and $2g(n)$, respectively. In (4), μ_g and μ_e denote electric dipole moments in the ground and excited state, respectively, a is the radius of the Onsager cavity, $\beta = 2\pi\,\varepsilon_0\, h c = 1.105110440 \times 10^{-30}\,\mathrm{C}^2$ is an universal constant, h is Planck's constant, c the velocity of light in vacuum and ε_0 the electric permittivity of vacuum.

Since the band of fluorescence **b** is not affected by the orientation interaction with the solvent (Fig. 5), $m_2 \approx 0$ in (3). From (4) one obtains

$$\mu_e \approx \mu_g,$$

which means that the S_1 state of CDMA, being the ^1L_b state [1, 23], is only very slightly sensitive to orientation interactions with the solvent. This is in accor-

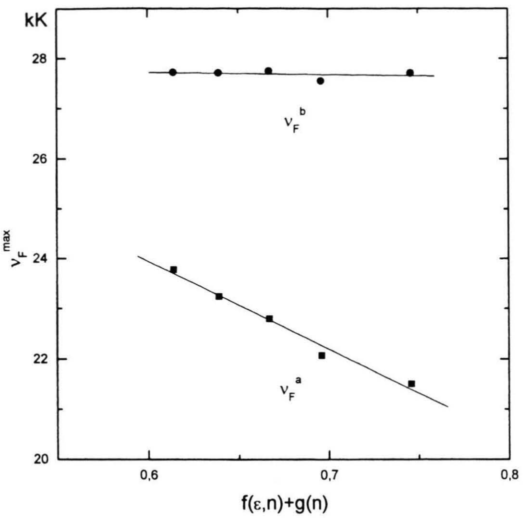

Fig. 5. Thermochromic shift of the fluorescence bands ν_F^b and ν_F^a for CDMA in ethyl acetate, according to (3).

dance with conclusions of Baumann et al. [14] (cf. Chapt. 4.1.1, p. 54).

The band of fluorescence **a**, in turn, shifts markedly with increasing temperature (Figure 5).

According to (3), the slope of the straight line ν_F^a as a function of $f(\varepsilon, n) + g(n)$ is $m_2 = 17\,500\ \mathrm{cm}^{-1} = 17.5$ kK. Assuming the Onsager radius to be 5×10^{-10} m [1] and $\mu_g = 18.35 \times 10^{-30}$ Cm ($= 5.5$ D) [16], for $m_2 = 17\,500\ \mathrm{cm}^{-1}$ and based on formula (4), $\mu_e = 52.5 \times 10^{-30}$ Cm ($= 15.7$ D) is obtained. For $\mu_g = 22.5 \times 10^{-30}$ Cm ($= 6.75$ D) [14] and for the same values of m_2 and a one obtains $\mu_e = 54 \times 10^{-30}$ Cm ($= 16.2$ D). Thus, as a result of excitation, the state S_2, being also the ^1L_a state, has a markedly higher dipole moment them the ground state. The dipole moment, which is 2.5 times higher in the ^1L_a state, causes strong orientation interaction with the solvent and lowers the energy of state ^1L_a below the energy of state ^1L_b according to the assumed level scheme of Lippert et al. [1, 24] (see Fig. 4 in [24]). With growing temperature (decreasing ε) of the CDMA solution in ethyl acetate, a hyposochromic shift of band **a** occurs due to the weakening stabilization of state ^1L_a by the surrounding solvent. Finally, for a low enough value of ε (equal or close to that of the nonpolar solvent) the band **b** only appeared, and the energy level system returned to the initial configuration, according to Lippert's scheme [1].

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