Fluorescence Anisotropy Decays of 4-Cyano-N,N-dimethylaniline in Propylene Glycol Studied by Frequency-Domain Fluorometry

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Dedicated to Professor J. R. Lakowicz on the occasion of his 50th birthday.

The fluorescence lifetimes of 4-cyano-N,N-dimethylaniline (CDMA), measured in propylene glycol at 293 K using frequency-domain fluorometry, in the short emission (SE) and long emission (LE) bands are 20 ps and 1.65 ns, respectively. The higher emission anisotropies in the SE band compared to that in the LE band are due to weaker rotational depolarization of fluorescence. Emission anisotropy decays imply that the initial limiting emission anisotropy, r(0), is the same in the SE and LE bands and amounts to 0.28. This reflects the fact that the directions of transition moments in these bands are parallel. In the case of CDMA in propylene and ethylene glycol at temperatures from 293 to 343 K, viscosity more strongly affects the relaxation to the TICT state than does the change in polarity of the solvents used.

1. Introduction

In the preceding paper [1] we reported that the molecule of 4-cyano-dimethylaniline (CDMA) (synonym: 4-dimethylamino-benzonitrile) (Fig. 1) in strongly polar propylene glycol has two fluorescence bands, i.e. SE (short emission) and LE (long emission)* bands, and the emission anisotropy value, *r*, in the SE band is distinctly higher than that in the LE band. As assumed in paper [2], such an unusual behaviour of the emission anisotropy in the bands SE and LE observed for CDMA in propylene glycol may result from different lifetimes of this molecule in the S_1 and TICT (Twisted Intramolecular Charge Transfer [3–5]) states. The measurements of lifetimes in some other liquid solvents with different viscosities imply that the lifetimes of CDMA in state S_1 are markedly shorter than those in the TICT state [6]. Moreover, it was found for CDMA in different solvents, propylene glycol in particular, that the ratio of intensities of the two bands, $I^{\mathrm{SE}}_{\max}(350)/I^{\mathrm{LE}}_{\max}(480)$, markedly changed after several minutes of irradiation (excitation). As found in the present work, also the lifetime observed at 350 nm changes distinctly. In order to prevent this phenomenon, a cuvette whith a flow of the solution was used. The solution investigated was excited with a weakened 305 nm light intensity.

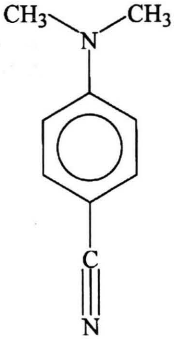

Fig. 1. Structural formula of 4-cyano-N,N-dimethylaniline (synonymous: 4-dimethylaminobenzonitrile) (CDMA).

The aim of the present work was to determine lifetimes and fluorescence emission anisotropy decays for CDMA in propylene glycol by frequency-domain measurements and to study the behaviour of the SE and LE bands in viscous solvents (propylene and ethylene glycol) at different temperatures (above 295 K), i.e. in solvents having different viscosities and polarities (see Table 1).

2. Materials and Methods

4-Cyano-N,N-dimethylaniline (CDMA) was from Aldrich Chemical Company, Inc., Steinheim, Germany, and was used without further purification. Propylene and ethylene glycol (Janssen-Chimica, anhydrous) was fraction-

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* SE and LE bands are frequently denoted by **b** and **a** bands, respectively.

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Table 1.

Liquids name	Dipole moment μ [10^{-30} Cm]*	Dynamic viscosity [7] [m Pa·s]**		Electric permittivity [8]	
		T [K]	η	T [K]	ε
Propylene glycol	7.5	298	40.4	295	32
		323	11.3		
		348	4.77		
		373	2.57		
Ethylene glycol	7.61	298	16.1	298	37.7
		323	6.55	323	33.2
		348	3.34	348	29.1
		373	1.975	373	25.6

* The conversion factor for the dipole moments from SI units to cgs (in Debye) is: $[\mu]_{cgs/D} = 0.2998 \cdot 10^{30}\,[\mu]_{SI/Cm}$.

** $1\ \text{cP} = 10^{-3}\,\frac{\text{kg}}{\text{m}\cdot\text{s}} = 10^{-3}\ \text{Pa}\cdot\text{s}$.

ally distilled under reduced pressure. The concentration of CDMA in the solvents used was about $5 \cdot 10^{-5}$ M. The fluorescence background from propylene glycol was smaller than 1% for both observation wavelengths (330 and 480 nm). The fluorescence measurements were carried out in a 1 mm × 1 cm quartz cuvette equipped with a flow system. A flow of 2 ml/min was sufficient to maintain the fluorescence signal steady throughout the measurements. Without the flow, significant changes in the fluorescence intensity were observed in both cases.

The intensity decays of CDMA in propylene glycol were measured using the frequency-domain method [9–11]. The intensity decay was assumed to be multi-exponential,

$$I(t) = \sum_{i=1}^{n} \alpha_i e^{-t/\tau_i}\,, \tag{1}$$

where τ_i are the decay times and n is the number of exponential components.

In frequency-domain fluorometry, the sample is excited with an intensity-modulated light source. In the present case, the frequency-doubled output of a pyridine 2 dye laser was pumped by an argon ion model-locked laser. The phase angle (φ_ω) and the modulation (m_ω) of the emission are related to the intensity decay parameters, α_i and τ_i, and modulation frequency ω by

$$\varphi_\omega = \arctan(N_\omega / D_\omega) \tag{2}$$

and

$$m_\omega = (N_\omega^2 + D_\omega^2)^{1/2}, \tag{3}$$

where

$$N_\omega = \frac{1}{J}\sum_{i=1}^{n} \frac{\omega \alpha_i \tau_i^2}{1+\omega^2\tau_i^2}\,,$$

$$D_\omega = \frac{1}{J}\sum_{i=1}^{n} \frac{\alpha_i \tau_i}{1+\omega^2\tau_i^2}\,, \quad J = \sum_{i=1}^{n} \alpha_i \tau_i\,. \tag{4}$$

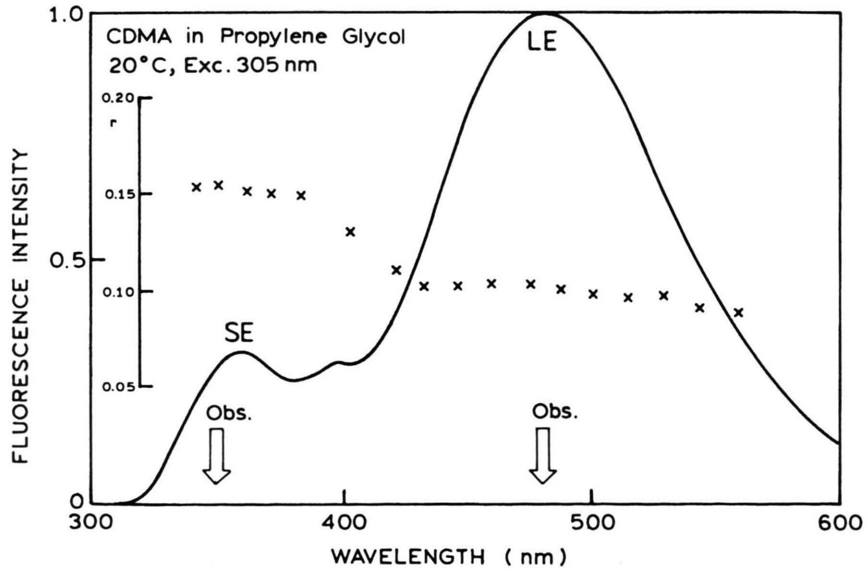

Fig. 2. Fluorescence and emission anisotropy spectra (×) of CDMA in propylene glycol at 293 K. The arrows indicate observation wavelengths in time-resolved measurements.

The values α_i and τ_i are determined by minimization of the goodness-of-fit parameter

$$\chi_R^2 = \frac{1}{\nu}\sum_{\omega}\left(\frac{\varphi_{\omega} - \varphi_{\omega c}}{\delta\varphi}\right)^2 + \frac{1}{\nu}\sum_{\omega}\left(\frac{m_{\omega} - m_{\omega c}}{\delta m}\right)^2, \qquad (5)$$

where the subscript c indicates values calculated for known α_i and τ_i, $\delta\varphi$ and δ_m are the experimental uncertainties in the measured phase and modulation values, and ν is the number of degrees of freedom.

3. Results and Discussion

3.1 Fluorescence and Emission Anisotropy Spectra of CDMA in Propylene Glycol at 293 K

Figure 2 shows fluorescence and emission anisotropy spectra of CDMA measured in propylene glycol at 293 K. It should be pointed out that the emission anisotropy values in the SE band (~0.16) markedly exceed those in the LE band (~0.11), similarly as observed previously [1]. However, the ratio of intensities of the two bands, $I_{\max}^{\mathrm{SE}}(350)/I_{\max}^{\mathrm{LE}}(480)$, is not the same due to the evident effect of the excitation light (irradiation) during the measurement reported in the previous paper [1]. In the present work, the effect of irradiation was minimized, using the already mentioned cuvette with a flow system.

The run of the emission anisotropy in the SE and LE bands is substantially affected by the viscosity of the solution. For example, when the temperature of the CDMA solution in glycerol is raised to 353 K (see [2]), which more or less corresponds to the viscosity of propylene glycol at 293 K, in both cases identical emission anisotropy runs are observed in the SE and LE bands. Higher values of emission anisotropy in the SE band compared to those in the LE band can be attributed to either lower or higher rotational depolarization of fluorescence.

3.2 Frequency-Domain Intensity and Emission Anisotropy Decays of CDMA in Propylene Glycol at 293 K

Figure 3 shows the runs of the phase angle and modulation for CDMA in propylene glycol at 293 K, at excitation wavelength 305 nm and observation in the SE (350 nm) and LE (480 nm) bands. Solid lines represent the best double exponential fits to the data. The lifetime τ_1 for the observation in the SE band at 350 nm is very short and amounts to 20 ps, while in the LE band at 480 nm the observation wavelength τ_2 equals 1.65 ns (Table 2). Thus, the lifetimes τ_2 measured at 480 nm observation is about 80 times longer than τ_1 at 350 nm observation.

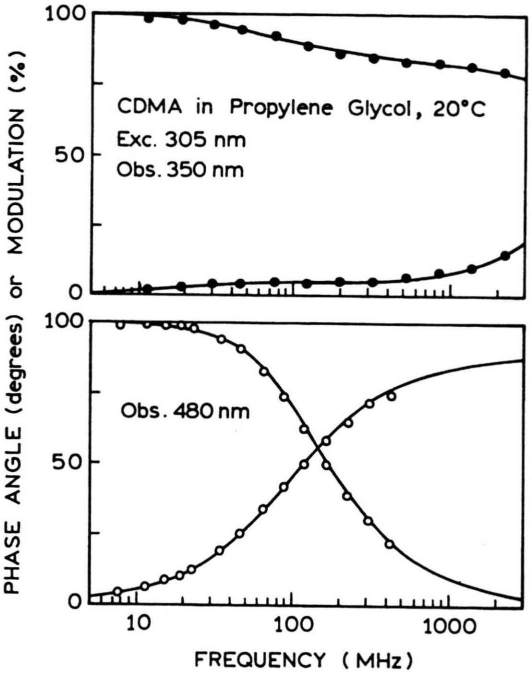

Fig. 3. Frequency-domain intensity decays of CDMA in propylene glycol at 293 K, at short (●, λ_{obs} = 350 nm) and long (○, λ_{obs} = 480 nm) observation wavelengths.

Table 2. Intensity decay parameters of CDMA in propylene glycol at 293 K.

Observation wavelength [nm]	τ_1 [ns]	α_1[a]	τ_2 [ns]	α_2[a]	χ_R^2[b]
350	0.020 (0.001)[c]	0.998 (0.001)	2.11 (0.14)	0.002 (0.001)	3.5
480	0.060 (0.022)	0.212 (0.031)	1.65 (0.02)	0.788 0.027)	1.3

[a] $\alpha_{1,2}$ are the preexponential factors (normalized relative fluorescence intensities, $\alpha_1 + \alpha_2 = 1$) representing the fractional contributions to the time-resolved decay of the components with lifetime $\tau_{1,2}$.

[b] From least-squares analysis of time resolved decays.

[c] The numbers in parentheses are standard deviations.

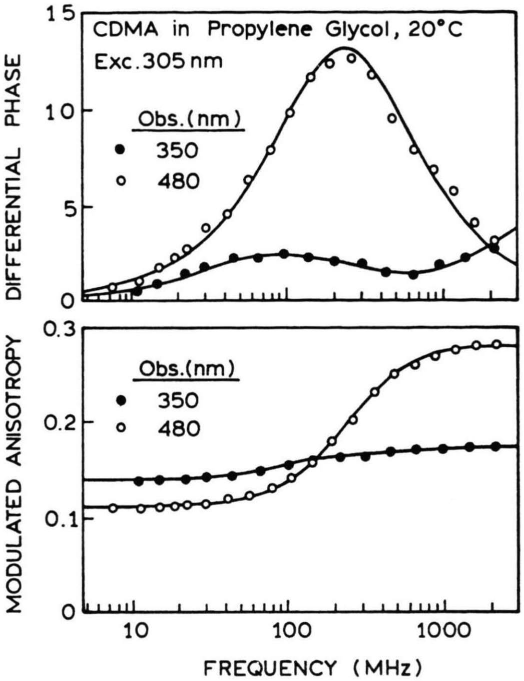

Fig. 4. Frequency-domain fluorescence anisotropy decays of CDMA in propylene glycol at 293 K for 350 nm (●) and 480 nm (○) observation, respectively.

Table 3. Fluorescence anisotropy parameters of CDMA in propylene glycol at 293 K.

Observation wavelength [nm]	$r(0)$	τ_c [ns]	χ_R^2
350	0.28 (0.012)	0.028 (0.003)	1.0
480	0.28 (0.001)	1.063 (0.02)	1.9

For the determination of the initial emission anisotropy, $r(0)$ for $t = 0$, and the rotational correlation time, τ_c, the simple correlation time anisotropy decay of Perrin's model for spherical molecules [12, 13] was employed:

$$r(t) = r(0)\, e^{-t/\tau_c} \tag{6}$$

and

$$\tau_c = \frac{V\eta}{kT}, \tag{7}$$

where V is the volume of the luminescent molecule embracing the solvent shell, and η is the dynamic viscosity of the solvent.

Figure 4 shows frequency-domain fluorescence anisotropy decays of CDMA in propylene glycol at 293 K for observations in the bands SE (350 nm) and LE (480 nm). The values of $r(0)$ and τ_c given in Table 3 were recovered from least-squares analysis of the differential polarized phase angles and modulated anisotropies using an expression similar to (5) [14]. Figure 5 gives the time-domain representation of the CDMA fluorescence anisotropy decays, $r(t)$, at 350 nm and 480 nm observations, recovered based on data from Table 3.

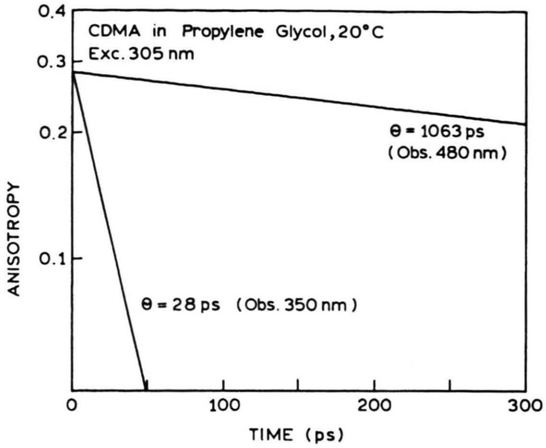

Fig. 5. Time-domain representation of CDMA fluorescence anisotropy decays at 350 nm and 480 nm observations. Reconstructed from data in Table 3 ($\theta \equiv \tau_c$).

It is worth mentioning that the observed initial (limiting) emission anisotropy, $r(t = 0)$, is equal for the SE and LE bands, amounting to 0.28 (Table 3). By averaging (6) and assuming that the decay of the total fluorescence light intensity is monoexponential, one obtains Perrin's equation [12, 13] corresponding to continuous excitation

$$r = \frac{r(0)}{1 + \tau / \tau_c}. \tag{8}$$

For the values of $r(0)$ and τ_c given in Table 3 and the fluorescence lifetimes $\tau_1 = 0.02$ ns and $\tau_2 = 1.65$ ns (Table 2), using (8) one can readily recover the run of the emission anisotropy, r, in the SE and LE bands shown in Figure 2.

It is surprising that the rotational correlation time, τ_c^{SE}, at 350 nm observation is under the same conditions (viscosity η and temperature T the same as at 480 nm observation) much shorter than τ_c^{LE}. According to (7), the rotational correlation time, τ_c, is in this case proportional to the volume of the molecule, V. One can therefore assume that around the CDMA molecule in the TICT state, a solvent shell is formed, which markedly enlarges the volume of the molecule compared to that in states S_0 or

S_1. The CDMA molecule in the TICT state has an electric dipole moment 2.5 times that in the ground state [15, 16]. This results in a strong orientational interaction in the TICT state, thus contributing to the formation of a shell around CDMA with an enlarged volume.

3.3 Fluorescence Spectra of CDMA in Polypropylene Glycol and Ethylene Glycol at Different High Temperatures

The second independent proof that the TICT state is affected by viscosity of the environment is provided by measurements of the fluorescence spectra of CDMA in viscous solvents at different temperatures. Table 1 gives viscosities of propylene and ethylene glycol at different high temperatures. Raising the temperature results in a marked decrease in dynamic viscosity. Figures 6 and 7 show fluorescence spectra of CDMA in both glycols at temperatures from 293 to 343 K. The increase in the solution temperature, which corresponds to the decrease in viscosity, is accompanied by a distinct growth of the LE band intensity, with concomitant decrease in the intensity of the SE band. In both cases, well-defined iso-emission points can be observed, which manifests the existence of two forms of CDMA in the excited state. The increase in temperature causes the decrease in permittivity, ε. In this temperature range, however, the permittivity scarcely drops to about 25–30 for both glycols (Table 1) and causes a slight shift of the LE band maximum towards the shortwave side (Figs. 6 and 7). The absorption and fluorescence band shift depends on the function of orientation polarization of the solvent, $f(\varepsilon, n)$, and the difference of dipole moments in the excited and ground state, $\Delta\mu = \mu_e - \mu_g$. The function $f(\varepsilon, n)$, depending primarily on the permittivity, ε, and the refractive index, n, changes most strongly for ε values from 2 to 10 [17, 18]. Thus, in the case of the solvents used (Table 1), the viscosity has a much stronger effect on the relaxation to the TICT state than it has on their polarity.

4. Conclusions

a) The viscosity of the solution has an essential effect on the emission anisotropy of CDMA in propylene glycol in the SE and LE bands. Higher values of the emission anisotropy in the SE band are due to a markedly shorter lifetime (20 ps) compared to that observed in the LE band (1.65 ns).

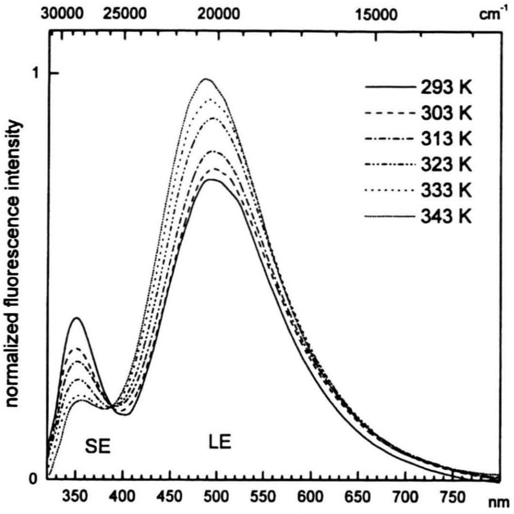

Fig. 6. Fluorescence spectra of CDMA in propylene glycol at different temperatures (293– 343 K).

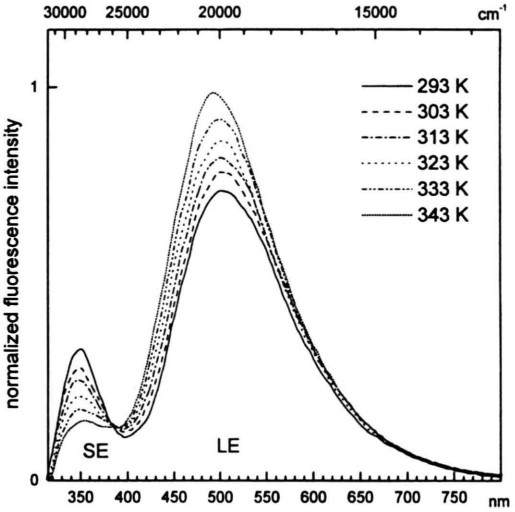

Fig. 7. Fluorescence spectra of CDMA in ethylene glycol at different temperatures (293–343 K).

b) The initial (so-called limiting) emission anisotropy, $r(t = 0)$, observed for the SE and LE bands is the same and amounts to 0.28. The positive value of the emission anisotropy proves that the transition moment directions in the SE and LE bands are parallel. Point c) in conclusions of paper [1] on page 952 is not correct. The relatively low or negative emission anisotropy observed in the SE band in papers [1, 2] for CDMA in viscous and polymer solutions can be accounted for by the vibronic coupling mechanism between two closely-lying excited states ^1L_b and ^1L_a [3, 19].

c) In the case of CDMA in propylene and ethylene glycol at temperatures from 293 to 343 K, the viscosity has a much stronger effect on the relaxation to the TICT state than has the change in polarity.

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