Solvent Effect on Emission Anisotropy of Fluorescence of Polar Molecules *

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The emission anisotropy (EA) of 4-Dimethyl-amino-4′-nitrostilbene (DNS), 4-Amino-4′-nitrostilbene (ANS) and 2,5-Di(4-biphenylyl)oxazole (BBO) was observed to be decreasing with increasing dielectric constant ε of the solvent. The effect is interpreted as an influence of the Onsager reaction field on the volume of the solvent shell, which in the excited state is smaller in solvents with larger ε. This favors the depolarisation by the irrregular Brownian rotation.

The emission anisotropy (EA) of the fluorescence of solute molecules

$$r = \frac{J_{\parallel} - J_{\perp}}{J_{\parallel} + 2 J_{\perp}} = \frac{2P}{3 - P}$$

($J_{\parallel}$, $J_{\perp}$ fluorescence intensity,
P the degree of polarisation)

is influenced by the following depolarising factors:

a) thermal motion of the fluorescent molecules (temperature, viscosity) [1],

b) migration of the excitation energy between excited and unexcited molecules (concentration effect; relevant expecially in rigid or very viscous solutions) [1],

c) irregular torsinal vibrations of the fluorescent molecules in rigid solutions [2].

The aim of the present communication was to investigate the effect of the effective electric field (the Onsager reaction field) on the EA of polar fluorescent molecules. We have investigated the following polar compounds: 4-Dimethyl-amino-4′-nitrostilbene (DNS), 4-Amino-4′-nitrostilbene (ANS) and 2,5-Di(4-biphenylyl)oxazole (BBO). In the case of DNS and ANS the electric dipole moments in the ground state (μ_g) and in the lowest excited single state (μ_e) are parallel to the transition dipole moment [3]. The electric dipole moments of these molecules are: $\mu_g = 7.2$ D, $\mu_e = 23.1$ D for DNS [3], $\mu_g = 6.5$ D, $\mu_e = 20.7$ D for ANS [3] and $\mu_g = 3.6$ D, $\mu_e = 8.0$ D for BBO [4].

Solvents of different ε, but of the same viscosity, were used spectroscopically pure. The EA was measured on a Bauer-Rozwadowski compensation polarimeter [5, 6]. For excitation we used a Xenon lamp XBO 450 W combined with a SPM 2 monochromator. The excitation wavelength corresponded to the 0–0 transition of the investigated molecules. The EA is independent of the wavelength in the fluorescene band [7].

Table 1.

No.	Solvent	Viscosity η at 20 °C [cP]	Dielectric constant ε at 20 °C	Fluorescence emission anisotropy (EA) ** r		
				DNS	ANS	BBO
1	cyclohexene	0.65	2.22	—	0.084	0.044
2	benzene	0.652	2.3	0.088	0.082	0.044
3	p-xylene	0.648	2.3	0.086	0.080	0.042
4	toluene	0.583	2.4	0.085	0.080	0.041
5	chloroform	0.563	4.8	0.082	0.079	0.036
6	ethyl acetate	0.455	6.11	0.077	0.075	—
7	ethylene dichloride	0.887 *	10.16	—	0.073	0.035
8	acetic anhydride	0.901	20.7	0.074	0.068	0.034
9	methyl alcohol	0.611	32.3	—	—	0.033
10	dimethyl formamide	0.757	36.7	—	—	0.034

* at 15 °C. ** The EA were measured with an accurateness of 1%.

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The results obtained for the EA of DNS, ANS and BBO in solvents with different ε are given in Table 1. The EA decreases with growing ε. That can be explained in the following way:

In liquid solutions the Brownian rotational motions depends not only on the viscosity and temperature but also on the shape and size of the fluorescent molecule [8]. The partial polarization of the fluorescence light depends on the ratio of the lifetime τ_F in the excited state to the rotational relaxation time Θ [9]:

$$\frac{\tau_F}{\Theta} = \frac{kT\,\tau_F}{\eta}\,\frac{1}{V} = \text{const}\,\frac{1}{V}, \tag{1}$$

where k = Boltzmann constant, T = absolute temperature, η = viscosity of the solvent and V = effective volume of the solute molecule together with the solvent shell.

In our case, the relation $kT\,\tau_F/\eta = \text{const}$ is valid for a given solute and solvent, because the lifetime τ_F of the molecules investigated is constant and independent of the viscosity and dielectric constant of the solvent, as was shown in our last paper [7].

Immediately after excitation to an excited Franck-Condon state the molecules in the solvent shell are reoriented ($\sim 2 \cdot 10^{-11} - 2 \cdot 10^{-12}$ s [10]), because $\mu_e > \mu_g$. The emission takes place from an equilibrium state. The excess of the vibrational and partially the electronic energy of the solute is transferred to the environment of the solute. The only reason of the depolarization of fluorescence light of the solute at larger dielectric constants of the solvent may be due to the influence of the interaction field upon the volume of the solvent shell. With an increase in the dipole moment of the solute ($\mu_e > \mu_g$) the reaction field becomes stronger in the excited state than it is in the ground state and it increases with growing ε of the solvent [11, 12].

Therefore, the larger ε, the more the polar solvent molecules are attracted towards the solute molecule and the smaller becomes the effective volume of the solvent shell. Thus, according to Eq. (1), the rotational relaxation time Θ decreases with growing ε and the irregular Brownian rotations cause further depolarization of the fluorescence light.

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