The Inertial Effect in Rotational Fluorescence Depolarization

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The influence of the moment of inertia on the rotational fluorescence depolarization is discussed. Based on experimental results obtained for five luminescent compounds: 2,5-diphenyloxazole (PPO), 2,2′-p-phenylene-bis(5-phenyloxazole) (POPOP), p-bis[2-(5-α-naphthyloxazolyl)]-benzene (α-NOPON), 4-dimethylamino-ω-methylsulphonyl-trans-styrene (3 a) in n-parafines at low viscosity (from 0.22×10^{-3} Pa · s to 0.993×10^{-3} Pa · s) and diphenylenestilbene (DPS) in different solvents, a semi-empirical equation is proposed, yielding moments of inertia that are only two to five times higher than those estimated from the molecular geometry.

It was recently discovered that the initial evolution of the emission anisotropy $r(t)$ and its stationary value r depend on the moment of inertia of a luminescent molecule (LM) [1–3]. This effect is related to the change of the state of the rotating LM being conditioned not only by the acting instantaneous moment of a force but also by the LM's moment of inertia.

In the generalized diffusion equation for the rotational motions of molecules employed by Alicki et al. [2, 3] in the rotational fluorescence depolarization theory, the introduced angular velocity autocorrelation function describes the "memory" effect (convolution integral) related with the moment of inertia.

For a prolate LM the change of the emission anisotropy, r, with time is given by [2]

$$\frac{\mathrm{d}r(t)}{\mathrm{d}t} = -6 \int_0^t G(s)\, r(t-s)\, \mathrm{d}s\,, \tag{1}$$

where $G(s) = \langle \omega(0)\, \omega(s) \rangle$ is the autocorrelation function of the angular velocity with respect to the molecular axis (in the case of a prolate LM, with respect to the axes 1 and 2 perpendicular to the longitudinal axis 3).

Applying the Laplace transform to both sides of (1) at a point $1/\tau$ one obtains

$$\frac{\tau}{\frac{r_0}{r}-1} = \frac{1}{6\int_0^\infty G(t) \exp\{-t/\tau\}\, \mathrm{d}t} = \frac{1}{6\mathscr{L}[\langle \omega(0)\, \omega(t) \rangle]}. \tag{2}$$

The substitution of the autocorrelation function

$$G(t) = \frac{kT}{I} \exp\left\{-\frac{6V\eta}{I}\, t\right\}, \tag{3}$$

derived from the Langevin equation, into (2) yields [2]

$$\frac{\tau}{\frac{r_0}{r}-1} = \frac{V}{kT}\,\eta + \frac{I}{6kT\tau}\,, \tag{4}$$

where η is the viscosity, T the absolute temperature, r_0 the limiting emission anisotropy, V the effective volume of the LM, I the moment of inertia with respect to axes perpendicular to the long axis of the LM and τ its mean lifetime in the excited state.

For $I = 0$, the second term on the right-hand side of (4) disappears and the well-known Perrin equation is obtained.

The I values previously determined from (4) for a great number of prolate LMs in nonpolar and polar solvents with different viscosities are about three orders of magnitude greater than those calculated from its geometry [2, 4–7]. One of the reasons may be the specific interaction of the LM with the different solvent molecules. Investigations on the long living (about 1.25 ns) molecules 2,5-diphenyloxazole (PPO), 2,2′-p-phenylene-bis(5-phenyloxazole) (POPOP) and p-bis[2-(5-α-naphthyloxazolyl)]-benzene (α-NOPON) in n-paraffins, in the absence of strong solute-solvent interactions, at low viscosities (from 0.22×10^{-3} Pa · s to 0.993×10^{-3} Pa · s) have not given better results

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Table 1. Moments of inertia, I, and effective volumes, V, of luminescent molecules.

Compound	r_0	τ_0 [ps]	$\frac{V}{kT}$ [10^{-9} 1/pa]	V [10^{-30} m^3]	I [10^{-44} kg · m^2]	I_{geom}	$\frac{I}{I_{geom}}$
PPO	0.324	3	44	186	9	4.5	2
POPOP	0.339	8	164	690	58	19	3
α-NOPON	0.315	14	219	919	174	33.4	5.2
3a	0.375	5.4	42.4	171	22.6	5.0	4.5
DPS	0.3030	5	222	898	17	18.7	1.1

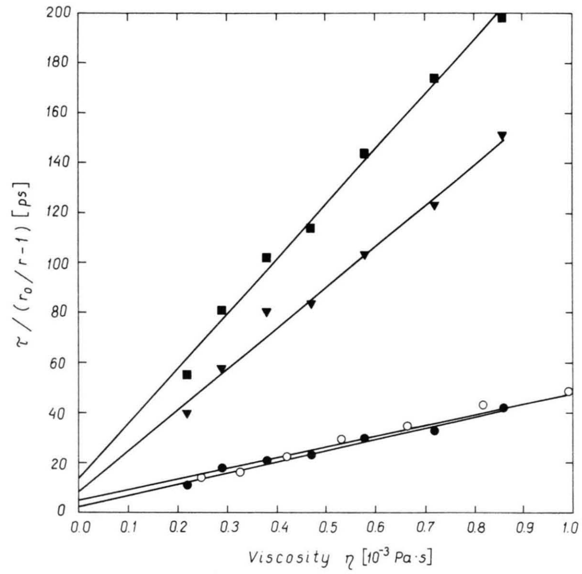

Fig. 1. Dependence of $\tau \Big/ \left(\frac{r}{r_0} - 1\right)$ on η for PPO (●), POPOP (▼) and α-NOPON (■) at 304.5 K and for 3a (○) at 293 K in different n-paraffines (pentane, hexane, heptane, octane, nonane, decane and undecane). The viscosities of the solvents are given in [8, 9]. The correlation coefficients for PPO, POPOP, α-NOPON and 3a are 0.990, 0.993, 0.996 and 0.996, respectively.

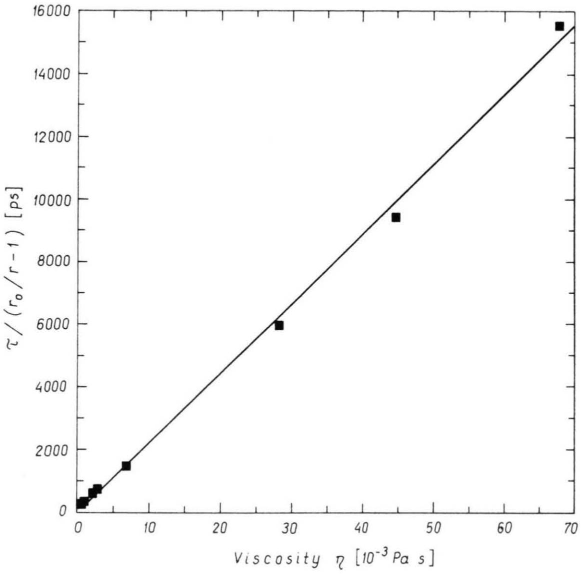

Fig. 2. Dependence of $\tau \Big/ \left(\frac{r}{r_0} - 1\right)$ on η for DPS (■) at 293 K in different solvents (benzene, cyclohexane, n-propanol, n-butanol, n-heptanol, triethyl-ester-glycerol, 1,2-propanediol, cyclohexanol). The visosities of the solvents are given in [15]. The correlation coefficient is 0.999.

[8]. For short living LMs (about 30 ps), such as trans-stilbene and 4-dimethylamino-ω-methylsulphonyl-trans-styrene (3a), the I values determined from (4) differ from those calculated for the free LM by only two orders of magnitude [6, 9].

In the present paper we report an investigation of the linear dependence of $\tau \Big/ \left(\frac{r_0}{r} - 1\right)$ on η given by (4) for extremely low viscosities, and we are searching for the zero viscosity intercept τ_0. The experimental results obtained for PPO, POPOP, α-NOPON and 3a in n-paraffins are shown in Figure 1. The data fit fairly well the straight line corresponding to (4). It can also be seen that the intercept τ_0 is not zero. Thus, both viscous and inertial effects contribute to the orientational relaxation of the LM in these solvents. Table 1 summarizes the values of V/kT and τ_0 for the investigated LMs (see Figure 1).

A similar linear dependence of the reorientation times, determined from depolarized light scattering, on viscosities was found by Bauer et al. [10, 11]. The intercept τ_0 was found to be similar to the reorientation time τ_{FR} of a classical free rotor [12–14],

$$\tau_0 \equiv \tau_{FR} = \frac{2\pi}{9}\left(\frac{I}{kT}\right)^{1/2}. \tag{5}$$

The moments of inertia, I, for PPO, POPOP, α-NOPON and 3a, determined from (5) for the intercept τ_0 values obtained (see Table 1), differ only from two to five times from those calculated for free molecules. Equation (4) can be replaced with the semiempirical equation

$$\frac{\tau}{\frac{r_0}{r}-1} = \frac{V}{kT}\eta + \frac{2\pi}{9}\left(\frac{I}{kT}\right)^{1/2}. \qquad (6)$$

Equation (6) was verified also for the previously studied nonpolar molecule of diphenylstilbene (DPS) in solvents of different polarity and viscosity [15]. The linear dependence of $\tau \Big/ \left(\frac{r_0}{r}-1\right)$ on η was obtained in a large viscosity range (from 0.65×10^{-3} Pa · s to 68×10^{-3} Pa · s) (Fig. 2) and the value of I obtained was 1.1 times as large as that calculated, I_{geom} (see Table 1).

The autocorrelation functions employed by Alicki et al. [2, 3], Morita [16] and Lynden-Bell and Steele [17] are only approximations of the true autocorrelation function. Lynden-Bell and Steele [17] have assumed that a molecule can temporarily be located in a certain limited cavity in the liquid, performing harmonic librations (restricted rotations) with different frequencies. They obtained a function similar, but not identical, to that of Morita, which for the case when the degree of fluctuations of cavities in the liquid approaches zero, is equal to the autocorrelation function used by Grzywacz and Trumpakaj [18, 19].

The search for a resonable shape of the angular velocity correlation function is fully justified and should contribute to further explanation of the nature of rotational motions of LMs in liquids.

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