Experimental Verification of the Theory on Rotational Motions of Prolate Luminescent Molecules in Solution

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Theories I [1] and II [2] on rotational motions of prolate molecules in solvents of different viscosities were verified for a series of luminescent compounds, the transition moments of which lie along their longer axes. Better agreement between the experimental and theoretical results was found with theory I. Effective volumes and moments of inertia were determined for the molecules studied.

We have recently detected an essential effect of the moment of inertia of a prolate luminescent molecule, the transition moment of which lies along its longer axis, on the behaviour of the fluorescence anisotropy (FA) r as a function of the viscosity η of a solvent [1]. Basing on the generalized equation of rotational diffusion, theory [1] enables simultaneous determinations of the effective volume (V) and the effective moment of inertia (I) of the luminescent molecule.

The same effect has been treated theoretically by Sarshevskii et al. [2]. The aim of the present paper is to compare these theories with measurements carried out within the last three years.

From theory [1], we have obtained the following equation for the FA on continuous excitation of a solution by linearly polarized light as a function of viscosity:

$$\frac{r_0}{r} = \frac{1 + (1 + A)\,x}{1 + A x}\,, \tag{1}$$

where

$$x = \frac{\tau}{\theta}\,, \quad A = \frac{I}{6\,k\,T\,\tau^2}\,, \quad \theta = \frac{V\eta}{kT} \qquad (2), (3), (4)$$

(τ — mean lifetime, r_0 — limiting FA).

Equation (1) is a special case of an equation derived in another way [3, 4]. For $A x \ll 1$ the Perrin equation [5] is obtained.

The theory of Sarshevskii et al. [2], using the same variables, yields the more complex expression

$$\frac{r_0}{r} = (1 + x) \left\{ \sum_{k=0}^{\infty} \frac{(A x^2)^k}{[1 + A x (1 + x)]_k} \right\}^{-1}, \tag{5}$$

where with $1 + A x (1 + x) \equiv a$ the following expressions are valid:

$$[a]_{k=0} = 1\,,$$

$$[a]_{k \geqq 1} = a (a + 1)(a + 2) \cdots (a + k - 1)\,.$$

Numerical calculations were carried out on an R-32 digital computer.

We have compared our experimental results [3, 4, 6, 7] with expressions (1) and (5), and determined r_0 and V for high viscosities (from the Perrin equation) and the magnitude of A for the whole viscosity range. The results thus obtained for a series of luminescent compounds (4-amino-4′-nitrostilbene (ANS), 4-dimethylamino-4′-nitrostilbene

Table 1

Compound	τ [ns]	Equation (1)			Equation (5)		
		A	χ^2*	$I \cdot 10^{40}$ [kg m^2] Eq. (3)	A	χ^2*	$I \cdot 10^{40}$ [kg m^2] Eq. (3)
ANS	2.30	0.2567	0.0831	334.23	0.0604	0.2725	78.64
DNS	2.59	0.2878	0.0943	475.18	0.0672	0.2566	110.95
POPOP	1.36	0.1372	0.1015	62.46	0.0246	0.4464	11.20
2MPOPOP	1.67	0.1217	0.2134	83.54	0.0204	0.7035	14.00
DPS	1.17	0.1086	0.0432	36.59	0.0184	0.3004	6.20
α-NOPON	1.65	0.1010	0.2012	67.68	0.0152	0.6039	10.19
pTP	1.18	0.0086	36.12	2.95	0.0019	58.74	0.65
BBOT	1.22	0.0300	0.3942	10.99	0.0029	0.6116	1.06

* The mean squares deviation of experimental points from the best fitted curve. The effective volumes V and r_0 for the compounds are given in [3, 4, 6, 7]. For BBOT: $V = 584 \cdot 10^{-30}\,\mathrm{m}^3$, $r_0 = 0.3636$.

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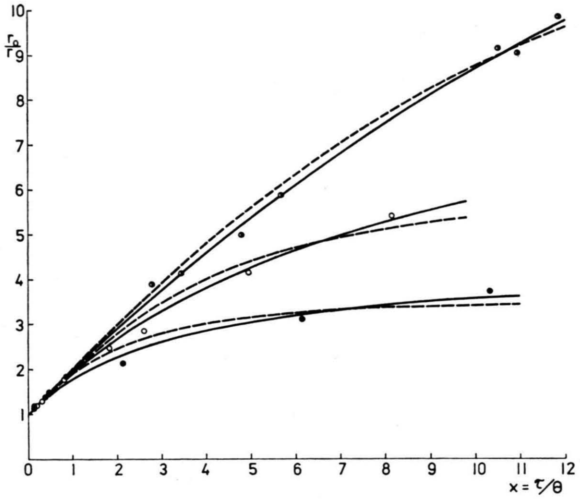

Fig. 1. Theoretical curves and experimental points of FA as a function of τ/θ. Solid curves have been obtained from (1) and dashed curves from (5). Experimental values: ● for DNS, ○ for DPS and ◑ for BBOT.

(DNS), 2,2′-p-phenylenebis(5-phenyloxazole) (POPOP), 2,2′-p-phenylenebis(4-methyl-5-phenyloxazole) (2MPOPOP), diphenylenestilbene (DPS), p-bis[2-(5-α-naphthyloxazolyl)]-benzene (α-NOPON), p-terphenyl (pTP), 2,5-bis[5-tert-butylbenzoxazolyl-(2)]-thiophen (BBOT)), are listed in Table 1. Figure 1 shows a comparison of some of the experimental data with the theoretical curves obtained from (1) and (5). Better agreement between experiment and (1) is apparent. The values of the effective moments of inertia determined from (1) and (5) differ by less than an order of magnitude. Formula (3) includes I and τ of the molecule under investigation. In order that I might be determined, τ should be constant in the whole viscosity range (i.e. in different solvents). For the majority of the luminescent compounds investigated, this condition has been fulfilled [3, 4, 6, 7].

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