Effect of solvent on polarization of fluorescence of eosin

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The polarization of fluorescence of cosin is studied in different solvents of varying dipole-moments. The results are interpreted in terms of dipole-dipole interaction as the extrinsic cause of depolarization.

1. INTRODUCTION

Perrin's formula (Perrin 1926) giving a correlation between polarization and viscosity is not able to explain completely the effect of solvent on polarization, particularly when the viscosity is low. The dipole-dipole interaction between the solvent and the solute (Machwe *et al* 1976) could be one such contributing factor to explain the phenomena. The present study was therefore, undertaken to investigate the effect of the dipole moment of the solvent on the polarization of fluorescence of cosin.

2. EXPERIMENTAL PROCEDURE

The polarization of eosin in different solvents (conc. $\sim 10^{-5}$ g/cc.) has been measured at room temperature ($\sim 20^{\circ}$ C) with an Amineo Bowman Spectrophotofluorometer. For solution in each solvent, the excitation and emission peaks were located and then polarization was calculated using the method adopted by Azumi *et al* (1962). The effect of scattered light and background for each solvent was measured by using pure solvent in the cell. The contribution of this effect to the intensity of fluorescence was found to be less than 0.5 per cent. The observed fluorescence intensity was accordingly corrected. The results obtained for polarization along with peak excitation and emission wavelengths are given in Table 1. The Table also includes the values of dipole moment and viscosity which are taken from standard tables (Kaye & Laby 1966; Hand Book of Physics and Chemistry).

3. RESULTS AND DISCUSSION

It is obvious from the observations in Table 1 that a plot between $\frac{1}{p}$ and $\frac{1}{n}$ (Perrin—plot) will not be linear and hence the observed variation of polarization can not be accounted for as viscosity effect alone. Also as the concentration is low ($\sim 10_n^{-5}$ g/cc.), the electromagnetic coupling of neighbouring molecules

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and its effect on decrease in polarization due to energy migration is small. The solvents in Table 1 are so arranged that as we go down the Table, the value of the dipole moment decreases. The corresponding column giving the values of P_{0}^{\prime} also shows a decrease in P as we move down the table, with the only exception of acetone. However, it may be noted that the viscosity of acetone is very low and hence low value of polarization is expected. But comparing the values of P for acetone and methanol, it is seen that the observed polarization is higher in acetone though its viscosity is lower than methanol. This being contrary to viscosity effect, establishes the effect of dipolemoment.

Solvent	Dipole moment	$\frac{Viscosity}{n}$	λ _{ex} (nm)	λ _{em} (nm)	%P
Formamide	3.25	3.31	550	570	7.0
Acotone	2.88	0.32	550	570	2.4
Water	2-3	1.00	536	558	5.(
Ethanol	1.70	1.20	544	564	4.6
n-Butanol	1.67	2.90	554	570	4.:
Methanol	1.65	0.59	542	564	2.(

Table 1

This effect can be explained as follows : when a molecule is excited, its dipole moment changes. But during the short interval of time in which the absorption of excitation energy takes place, the orientation of the emission-dipole remains unchanged. But just before a radiative transition takes place, the solute molecules gets itself reoriented in the surrounding solvent medium due to dipoledipole interaction to get a new equilibrium position thus resulting in depolarization of fluorescence. The Brownian rotation tends to destroy this equilibrium orientation and causes further depolarization. But the Brownian motion is opposed by the dipole-dipole interaction between solvent and solute molecules which for a given solute depends upon the dipole moment of the solvent. Thus this interaction tries to reduce the depolarization caused by the Brownian rotawhich for a given solute depends upon the dipole moment of the solvent. Thus this interaction tries to reduce the depolarization caused by the Brownian rotation. The polarization therefore, is expected to be higher in a solvent with higher dipole moment.

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In addition to a purely mechanical environmental effect of the above type, there may be a super imposed structural effect. The dipole-dipole interaction can cause a distortion in the planer symmetry of the molecule. As the polarization of fluorescence depends on the orientation of the emission dipole moment in the molecule, any change in the symmetry of the molecule will cause a corresponding change in polarization. If an increase in dipole-dipole interaction tries to align the emission dipole with the plane of the molecule, the polarization increases. This seems to be so in the present case of eosin. Of course, it is possible to have some structurally different fluorescent molecule where a reverse effect will be obtained.

The above study, therefore, clearly indicates the effect of dipole moment of the solvent on the polarization of fluorescence.

ACKNOWLEDGMENTS

The authors are thankful to Prof. S. N. Biswas, Head of the Physics Department, Delhi University, for providing facilities to carry on the experimental work. One of us (MLP) gratefully acknowledges the financial assistance of U.G.C.

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