

FLUORESCENCE POLARIZATION SPECTRUM OF RHODAMINE 6G

THE fluorescence emission from Rhodamine 6G consists of a broad band extending from 540 nm to 580 nm which corresponds to the electronic transition from $S_1 \rightarrow S_0$. Some dyes¹ are known to have several excitation bands corresponding to different excited states, viz., the first excited state ($S_0 \rightarrow S_1$), the second excited state ($S_0 \rightarrow S_2$), etc. But these different excited states are found to give the same fluorescence emission. In order to get the information about these excited states, the polarization spectrum of Rhodamine 6G in glycerol was investigated for two different excitation wavelengths. The polarization of fluorescence was measured using Aminco Bowman Spectrofluorometer at room temperature (30°C) for conc. 2.3×10^{-6} Moles/liter of Rhodamine 6G in glycerol. Though Rhodamine 6G is reported to have several excitation wavelengths, the present investigations were carried out for $\lambda_{ex} = 350$ nm and 534 nm. The emission peak for both was observed at 554 nm. Keeping the excitation monochromator fixed at 534 nm, the emission monochromator was varied from 540 nm to 580 nm and polarization of fluorescence calculated using Azumi's relation²:

$$P = \frac{I_{EB} - GI_{EB}}{I_{EB} + GI_{EB}} \quad (1)$$

where I is the observed intensity, the first and the second subscripts refer to the orientation of the polarizer and the analyzer and G is the grating correction factor given by $G = I_{BE}/I_{BB}$. Similarly the polarization for the other excitation wavelength (350 nm) was determined within the same fluorescence band. The effect of scattering was checked by using pure solvent in the cell. The results obtained are given in Table I and shown in Fig. 1.

TABLE I

λ_{em} (nm)	Percentage polarization	
	$\lambda_{ex} = 534$ nm	$\lambda_{ex} = 350$ nm
540	28.7	-12.3
544	28.5	-12.3
548	28.7	-12.0
552	28.7	-12.4
556	28.8	-12.2
560	28.6	-12.5
564	28.8	-12.4
568	28.7	-12.3
572	28.9	-12.2
576	28.6	-12.1
580	28.7	-12.3

The degree of polarization of fluorescence is a function of the geometrical orientation of the exciting light, absorbing dipole, emitting dipole and changes

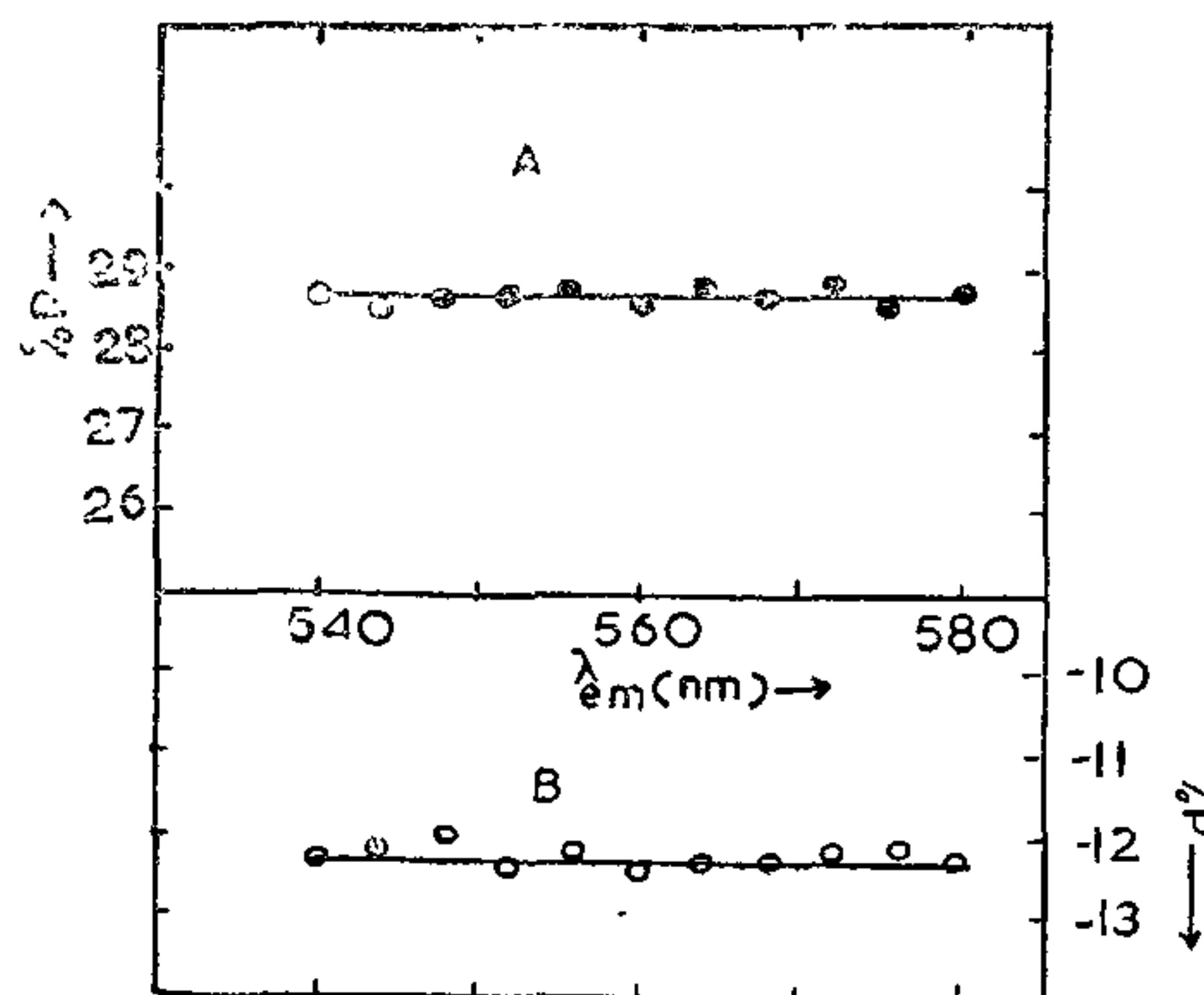


FIG. 1. Percentage polarization v/s emission wavelength for A $\lambda_{ex} = 534$ nm; B $\lambda_{ex} = 350$ nm.

of dipole orientation while in the excited state. When the exciting light is plane polarized, the polarization as a function of the angle θ , between the absorption and emission dipoles is given as³:

$$P = \frac{3 \cos^2 \theta - 1}{\cos^2 \theta + 3} \quad (2)$$

When

$$\theta = 0, P = 1/2$$

When

$$\theta = \pi/2, P = -1/3.$$

This shows that when the absorption and emission dipoles are parallel, the polarization is positive and when they are at right angles, the polarization is negative. From Table I it is seen that the polarization is positive for the longer excitation wavelength (534 nm) which indicates that the transition moment direction for these levels is almost parallel. But when the excitation wavelength 350 nm is used, fluorescence is negatively polarized. It appears that with this excitation, the dye molecule is excited to the second excited singlet state S_2 which by internal conversion gets down to the first excited singlet state ($S_2 \rightarrow S_1$) before the molecule returns to the ground state ($S_1 \rightarrow S_0$) by fluorescence emission^{4,5}. The negative polarization suggests that the transition moment of the main absorption band occurring around 540 nm is oriented parallel to the long axis of the molecule. Some of the transitions at shorter wavelengths are oriented perpendicular to the long axis^{6,7}. It is also seen from the table that the observed polarization is higher for the first excited wavelength than the second. This may possibly be due to the fact that during the time, the higher level drops to the lower one, electron reorientation takes place causing depolarization. Also during this radiationless conversion ($S_2 \rightarrow S_1$), loss of orientation may occur by transfer to non-parallel dipoles

thus leading to depolarization. The observed polarization for the second excited state should, therefore, be less. From the Table I average value of the polarization for $\lambda_{ex} = 534 \text{ nm}$ is $\approx 29\%$ but for $\lambda_{ex} = 350 \text{ nm}$ it is far less $\approx -12\%$.

It may also be noted that the polarization for emission wavelengths from 540 nm to 580 nm is almost constant for both the excitation wavelengths. This is in conformity with Kwaski's observations⁸. In a classical sense this corresponds to one type of emission oscillator which could mean that for this concentration, the dye molecules in solution exist only in one molecular form.

The present investigation, therefore, suggests that:

1. There are two excited states for Rhodamine 6G in glycerol solution (con. $\sim 2.3 \times 10^{-6}$ Moles liter⁻¹—one corresponding to 534 nm and the other corresponding to 350 nm.
2. The absorption and emission oscillators are parallel in the first excited state while perpendicular in the second excited state.
3. Polarization for the first excited state is higher and positive while for the second state, it is negative.
4. The low value is due to depolarization caused by the reorientation of the dipole during the non-radiative transition $S_2 \rightarrow S_1$.

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SPECTRAL STUDIES ON RARE EARTH COMPLEXES OF SCHIFF BASES

SCHIFF base, N-4-acetoacetonaphthylidene-anthranilic acid (HAANAA) and N-4-acylacetonaphthylidene-o-aminophenol (HAANAP) have been used to prepare the complexes of rare earth ions, Pr(III), Nd(III) and Sm(III). These compounds have been characterised on the basis of their analytical, conductometric, magnetic, visible and i.r. spectral data¹⁻³.

Results and Discussion

Analytical results (Table I) show 1:2 (metal : ligand) stoichiometry. All the complexes behave as univalent electrolytes as revealed by their molar conductance data (98–130 ohm⁻¹ mole⁻¹ cm²) in nitrobenzene^{4,5}. The presence of hydrogen, chloride and nitrate ions outside the co-ordination sphere of the complexes is indicated by neutralising with 1 gm-equivalent of caustic soda, adding alcoholic silver nitrate and by copper turnings test respectively.

Visible spectra.—Electronic spectral data of Pr(III), Nd(III) and Sm(III) complexes are given in Table II. For comparison, data for aqueous salt solutions are also given.

The visible spectra of the complexes have been analysed to get information about the application of the nephelauxetic effect to the lanthanide series⁶. The nephelauxetic parameter (β) was determined by the method of Jorgensen and coworkers⁷ using the relation

$$(1 - \beta) = \frac{\bar{\nu}_{\text{aquo}} - \bar{\nu}_{\text{complex}}}{\bar{\nu}_{\text{aquo}}}$$

where $\bar{\nu}$ stands for the wave number of the band. It is evident from Table II that the shift in band positions in the spectra of Pr(III), Nd(III) and Sm(III) complexes is towards lower wave numbers relative to the aquo complex. Assuming that each J level of $4f^n$ configuration linearly depends on the radial integrals, the $\Delta\bar{\nu}/\bar{\nu}_{\text{aquo}}$ of all bands of the same rare earth complex should be identical. However earlier observations⁷ as well as the present data show that the $\Delta\bar{\nu}/\bar{\nu}_{\text{aquo}}$ values for different J levels vary considerably.

We have observed hypersensitivity in DMSO solutions of neodymium complexes. Small differences in band positions occur except for the hypersensitive⁸ transition $4I_{9/2} \rightarrow 4G_{5/2}$. Since the interaction between DMSO molecules and the rather sterically hindered metal ion is likely to be small, hypersensitivity cannot be explained on the basis of phenomenon involving solvent participation⁹. The influence of the asymmetric terms of the ligand field on the electric dipole transition is likely to be the dominant factor.

The values of $(1 - \beta)$ for the present complexes show that the covalent contribution increases in the order: (HAANAP) complexes < (HAANAA) complexes,