

Short Communication

Solvent effect on charge transfer emission from pyrene-DMA and pyrene-DEA complexes

DEBASISH GUPTA and SADHAN BASU

Department of Pure Chemistry, University College of Science, Calcutta-9 (India)

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The long wavelength emission observed from pyrene-dimethylaniline (DMA) and pyrene-diethylaniline (DEA) system in n-hexane has been attributed to the charge transfer complex formation in which an electron is transferred from *N*-alkyl aniline to the excited pyrene molecule [1]. The excited state wave function may be written as $\Psi \approx a\psi(F.A)^* + b\psi(F^- - A^+)$. This means that the excited state will be polar and will be stabilized by solvent-solute interaction, the stabilizing energy decreasing with increase in dielectric constant of the medium. Consequently, the charge transfer emission should show a forward shift with increasing dielectric constant of the solvent. To test this contention charge transfer emission spectra have been recorded for pyrene-DMA and pyrene-DEA system in different solvents. The peak position for 10^{-4} M pyrene and 10^{-1} M DMA (DEA) in different solvents were: cyclohexane, 22,727 cm^{-1} (23,255 cm^{-1}); chloroform, 20,833 (21,276 cm^{-1}); butyl acetate, 20,619 (21,279 cm^{-1}); *t*-butyl alcohol, 20,408 (20,408 cm^{-1}); *n*-butyl alcohol, 19,802 (20,202 cm^{-1}). Following the procedure outlined in a previous communication [2] the shift in the emission spectra ($\Delta\nu$) may be correlated with the excited state dipole moment μ_e by the relation:

$$\Delta\nu = \frac{\mu_e^2}{a^3} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$

where a is Onsager's cavity radius and n and ϵ are solvent refractive index and dielectric constant respectively. The plot of $\Delta\nu$ vs. $[(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]$ was fairly linear (Fig. 1), from the slope of which μ_e was estimated to be 12.4 D (a was taken as the sum of molecular radius of the constituent molecules). Since completely charge separated state has a $\mu = 15$ D, it may be estimated that the charge transfer state makes about 81% contribution to the complex formation. This may be compared with only 16% charge-transfer contribution in the case of eximer formation in pyrene.

Similar results have been obtained with anthracene-DMA and anthracene-DEA systems. The excited state dipole moment was 11.8 D and the charge transfer contribution was 77%.

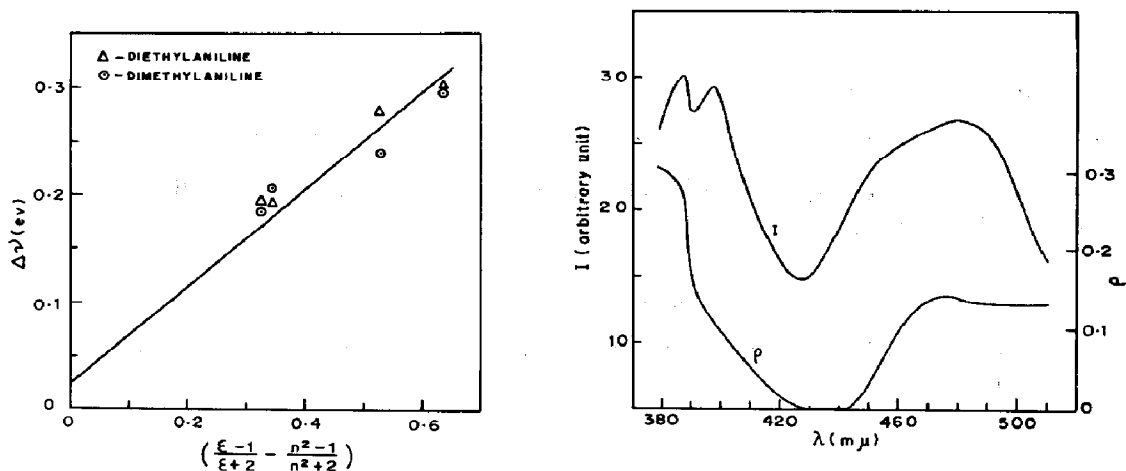


Fig. 1. Solvent shift on long wave emission from pyrene-DMA and pyrene-DEA system.

Fig. 2. Depolarization factor for pyrene-DMA system in polystyrene.

Since charge-transfer emission from pyrene and anthracene has been observed only with aromatic *N*-alkyl amines, it has been surmised that the π -orbitals of the aromatic amines are involved in the complex formation [1]. If we assume for charge-transfer complex a structure similar to pyrene eximer, then the emission oscillators from pyrene monomer and pyrene-DMA complex should be perpendicular to each other. The depolarization factor ρ in rigid glass medium should pass from a positive value for the monomer emission to a negative value for charge-transfer emission [3]. The results of ρ measurements in 22% polystyrene in cyclohexane containing 10^{-4} M pyrene and 10^{-2} M DMA are shown graphically in Fig. 2. It may be observed that on passing from monomer to charge transfer band ρ goes to zero from a positive value and then rises again to a positive value. This according to Perrin-Jablonski [3] means that the two oscillators are not mutually perpendicular as is the case with eximers. The angle between these two oscillators estimated by Perrin-Jablonski relation using ρ values for charge-transfer state was found to be 36° [3], which means that the donor π -orbital centre is not lying on the six fold axis of symmetry of the pyrene molecule. That is, the complex must have an off-centered structure.

1 N. Mataga, K. Ezumi and T. Okada, *Mol. Phys.*, 10 (1965/66) 201.

2 A. S. Ghosh and S. Basu, *J. Photochem.*, 3 (1974) 247.

3 A. S. Ghosh, D. Gupta and S. Basu, *J. Photochem.*, in press.