Solvent Effect on Charge-transfer Emission Spectra of Dimethylaniline as Donor & Anthracene, Benzopyrene, Chrysene & Phenanthrene as Acceptors

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Charge-transfer emission spectra of dimethylaniline as donor and pyrene, anthracene, benzopyrene, chrysene and phenanthrene as acceptors have been measured in solvents of different dielectric constants. The emission peak has been found to shift to longer wavelength with increasing dielectric constant of the medium in all the cases. Utilizing the Onsagar model for liquid dielectrics, the spectral shift has been used to calculate the dipole moment of the complex, from which it has been estimated that the charge transfer is in the range of 78 to 82% in these systems.

THE concentration dependent association of perylene and dialkylanilines giving rise to a broad structureless emission on the longer wavelength side of the characteristic fluorescence of aromatic hydrocarbon has been ascribed to the charge-transfer complex formation in the electronically excited state of the hydrocarbon[1]. It has also been shown that the diffusion-controlled formation of such complexes in solvents of low dielectric constant according to Eq. (1)

$$^1A^* + D \rightarrow (DA)^* + (D^+ - A^-) \qquad \ldots (1)$$
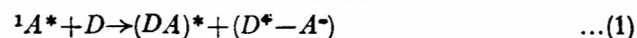
is the rule rather than exception[2], provided the charge-transfer state is below the locally excited

TABLE 1 — SOLVENT EFFECT ON CT-EMISSION

Solvent	ϵ	n	$\left[\dfrac{\epsilon-1}{\epsilon+2} - \dfrac{n^2-1}{n^2+2}\right]$	ν_{CT} (cm^{-1})	$h\nu_{CT}$ (eV)	μD
SYSTEM I: PYRENE ($4\cdot8 \times 10^{-5} M$) + DMA ($1 \times 10^{-1} M$)						
Cyclohexane	2·02	1·424	0·000	22,781	2·81	
Chloroform	4·72	1·442	0·291	20,830	2·58	
n-Butyl acetate	5·01	1·394	0·334	20,410	2·53	12·0
n-Butyl alcohol	17·10	1·397	0·586	19,610	2·43	
SYSTEM II: ANTHRACENE ($8\cdot2 \times 10^{-5}M$) + DMA ($1 \times 10^{-1}M$)						
Cyclohexane	2·02	1·424	0·000	22,222	2·75	
Chloroform	4·72	1·442	0·291	20,202	2·55	11·7
n-Butyl acetate	5·01	1·394	0·334	20,203	2·56	
n-Butyl alcohol	17·10	1·397	0·586	19,230	2·38	
SYSTEM III — BENZOPYRENE ($1\cdot5 \times 10^{-3}M$) + DMA ($1\cdot5 \times 10^{-1}M$)						
Cyclohexane	2·02	1·424	0·000	21,190	2·62	
Chloroform	4·72	1·442	0·291	19,310	2·39	
n-Butyl acetate	5·01	1·394	0·334	19,610	2·43	11·3
n-Butyl alcohol	17·10	1·397	0·586	18,870	2·34	
SYSTEM IV: CHRYSENE ($1 \times 10^{-3}M$) + DMA ($1 \times 10^{-1}M$)						
Cyclohexane	2·02	1·424	0·000	23,530	2·91	
Chloroform	4·72	1·442	0·291	21,740	2·69	11·4
n-Butyl acetate	5·01	1·394	0·334	21,740	2·69	
n-Butyl alcohol	17·10	1·397	0·586	20,620	2·65	
SYSTEM V: PHENANTHRENE ($1\cdot2 \times 10^{-1}M$) + DMA ($1\cdot6 \times 10^{-1}M$)						
Cyclohexane	2·02	1·424	0·000	22,120	2·74	
Chloroform	4·72	1·442	0·291	20,000	2·48	12·2
n-Butyl acetate	5·01	1·394	0·334	19,800	2·45	

singlet state of D. Further the complex maximum emission frequencies have been found to be directly related (Eq. 2) to the differences of polarographic oxidation and reduction potentials of the constituents[3].

$$h\nu_{(CT)} = E_{(D/D^+)} - E_{(A^-/A)} - \Delta \qquad \ldots(2)$$

Although a relation of this type indicates the participation of charge-transfer state in the interaction, it is of doubtful validity for the excited state interaction since half-wave potentials of excited states are never obtained. One straightforward method of estimating the charge-transfer character of the states involved is to study the effect of solvents of different dielectric constants on the emission frequency.

According to Onsager theory of liquid dielectrics the energy change associated with the transfer of a dipole from vacuum to a medium of dielectric constant and refractive index n is given[5] by Eq. (3)

$$\Delta E = \frac{2\mu^2}{a^3} \left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2} \right] \qquad \ldots(3)$$

where a is the radius of a circular cavity surrounding the molecule. This is normally taken to be equal to molecular radius calculated from molar volume. So if we know the emission frequency in vacuum and that in the solvent of dielectric constant ϵ,

then the difference $\Delta\nu$ will be related to ΔE by the relation (4)

$$h\Delta\nu = \Delta E \qquad \ldots(4)$$

A plot of $h\Delta\nu$ vs $\left[\dfrac{\epsilon-1}{\epsilon+2} - \dfrac{n^2-1}{n^2+2} \right]$ should be linear from the slope of which μ the dipole moment of the CT state may be calculated. Since the completely charge separated dative structure should have a dipole moment $15 \cdot 3D$, it is thus possible to estimate the extent of excited state charge-transfer from the shift in the emission spectra in medium of different dielectric constants.

In this paper are reported the results of measurements of CT emission from N,N-dimethylaniline-polynuclear aromatic hydrocarbon systems in solvents of different dielectric constants and subsequent correlation of the shift with the extent of charge transfer.
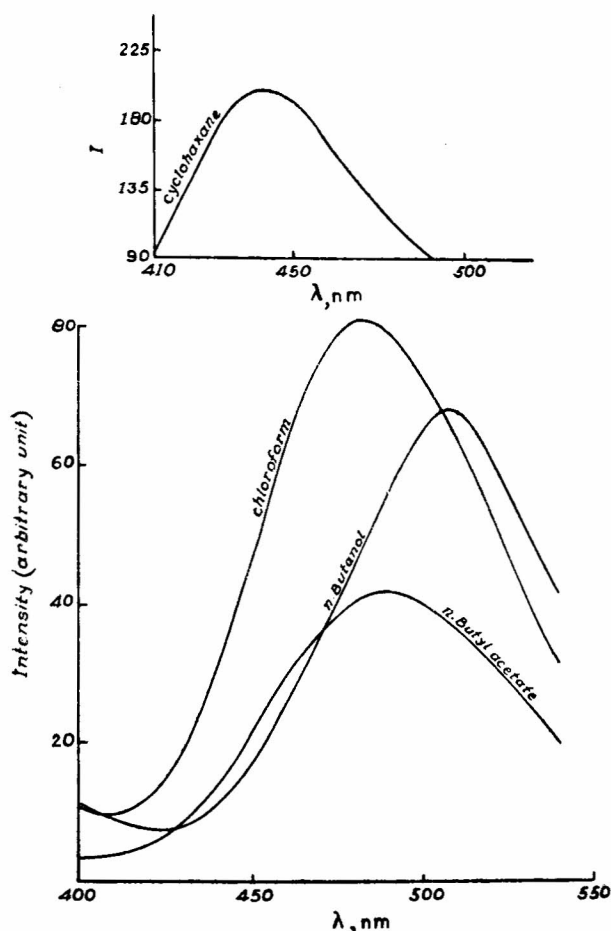

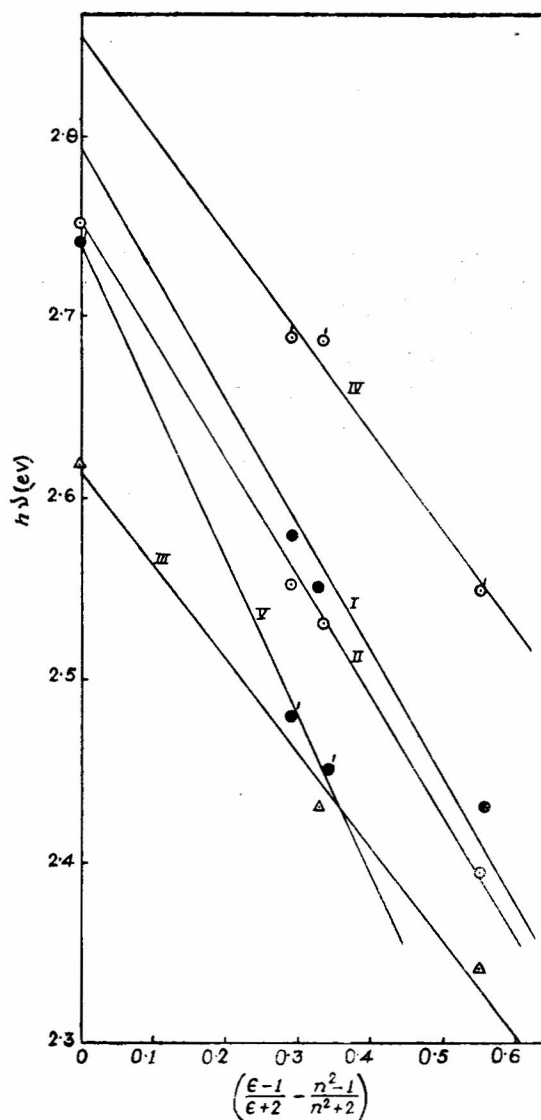Fig. 1 — Emission spectra of pyrene-DMA system in different solvents

Fig. 2 — Plots of νCT versus $\left(\dfrac{\epsilon-1}{\epsilon+2} - \dfrac{n^2-1}{n^2+2} \right)$ for all the systems studied (Systems I-V are given in Table 1)

Materials and Methods

The hydrocarbons used were supplied by E. Kodak and L. Light & Co. They were purified by chromatographic adsorption on silica gel from cyclohexane solution. Dimethylaniline was of GR (E. Merck) quality. It was always dried and freshly distilled before use. All the solvents were of GR quality. They were thoroughly dried and distilled twice. Solutions were prepared by direct weighing and all solutions were degassed before subjecting them to irradiation.

The light from a high pressure mercury arc lamp was filtered through a Chance filter isolating 3630 Å line, rendered parallel by means of combination of acromatic lenses and then passed through the testing solution in an optically clear glass cell. The fluorescent emission at 90° to the incident beam was rendered parallel by a combination of lenses and allowed to fall on the entrance mirror of a Beckman monochromator. At the exit slit of the monochromator was placed a IP28 photomultiplier tube. The output from the photomultiplier tube was amplified by means of a two-stage d.c. amplifier and displayed on a microammeter. The entrance slight was kept at 0·72 mm to get reproducibility within 2%.

Results and Discussion

In the Fig. 1 are given the emission spectra of pyrene-DMA system in different solvents. It may be observed that the emission peak shifts to longer wavelength as the dielectric constant of the medium is increased. Similar results have been obtained with other systems studied and the results are summarized in Table 1.

In Fig. 2 are given the plots of ν_{CT} versus

$$\left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right]$$

for all these systems. It may be observed that fairly good linear plots are obtained. The slope of these curves gives us $2\,\mu^2/a^3$. The cavity radius a was calculated from the molecular geometry, taking the longest end-to-end molecular length to be equal $2a$. This value varied from 10·5 to 12·3 Å. An average value of 12 Å was taken for all the systems. The dipole moment μ thus calculated are given in the Table 1. Since the completely charge-separated state has a dipole moment of 15·2D and the no-bond structure has no moment the charge transfer in these system were estimated to be 78 to 82%. The overall wave function of the state should, therefore, be written as shown in Eq. 5

$$\Psi = \Psi(D-A)^* + \lambda\Psi(D^+ - A^-) \qquad \ldots(5)$$

where the first term gives the charge resonance contribution and the second the charge transfer one. It appears therefore that the charge resonance contribution is about 20% in these systems. It may be mentioned that in the case of excimer emission from pyrene it has been shown that the charge transfer contribution is only 16%, while the remaining 84% comes from charge resonance[4]. This should be so, because in the case of excimer emission the absorption spectrum of pyrene exactly overlaps with itself, while for the systems studied in the present paper the overlapping of the donor and acceptor absorption is rather poor.

References

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