

## **Section I**

**Ground state EDA complex formation between [60]C<sub>60</sub> fullerene  
and a series of polynuclear aromatic hydrocarbons**

### 8.1.1. Introduction

A great deal of experimental work has been done with [60]fullerene<sup>62</sup> in the fields of material science<sup>153-162</sup>, photophysical study<sup>163-167</sup> and organic chemistry<sup>168-174</sup>. Recently it has been reported<sup>75</sup> that C<sub>60</sub> forms Diels-Alder adducts with anthracene and pentacene. Reports on the formation of ground state electron donor-acceptor (EDA) complexes involving C<sub>60</sub> are relatively few<sup>165,174</sup>. Theoretically it has been predicted<sup>76-79</sup> that the LUMO of C<sub>60</sub> can accept at least six electrons. Electrochemical studies in solution have yielded 3 to 5 -electron reduction potentials<sup>174-177</sup>. With special solvent compositions Echegoyen *et. al.*<sup>80</sup> and subsequently Diao *et. al.*<sup>178</sup> have been able to observe six- electron reduction potential corresponding to C<sub>60</sub><sup>6-</sup>. Thus C<sub>60</sub> is expected to behave as an acceptor in forming EDA complexes in solution. The object of the present section is to study the formation of EDA complexes between C<sub>60</sub> and a series of polynuclear aromatic hydrocarbons (PAH) and to obtain an estimate of the electron affinity of C<sub>60</sub>.

### 8.1.2. Experimental

Fig. 8.1 shows the electronic absorption spectrum of C<sub>60</sub> in CCl<sub>4</sub> against the solvent as reference. The absorption spectra of two mixtures, one containing pyrene and C<sub>60</sub> and the other containing naphthalene and C<sub>60</sub> in CCl<sub>4</sub>, are shown in the same figure. In the latter two cases, solution of C<sub>60</sub> at the same concentration as that in the mixture was taken as reference and it was found that the broad, longest wavelength (540 nm) absorption band of C<sub>60</sub>, attributable to its  $\pi$ - $\pi^*$  HOMO-LUMO transition<sup>174</sup>, was almost completely masked (because of the pristine [60]fullerene reference) while a new band due to the charge-transfer (CT) absorption of EDA complex appeared. Similar phenomenon was observed with each of the donors studied in the present work. In case of naphthalene and phenanthrene, closely spaced double CT peaks were observed. Anthracene, pyrene and chrysene complexes showed broad absorption bands and  $\lambda_{\text{max}}$  in these cases were determined by subjecting the spectral data to a Gaussian curve fitting. The CT transition energies of the C<sub>60</sub> complexes are given in Table 8.1 together with the Hückel energies of the highest occupied molecular orbitals (HOMO) of the PAH donors (taken from ref. 179); the AM1 ionisation potentials<sup>180</sup> (I<sub>D</sub>) of the donors are also given in the same table.

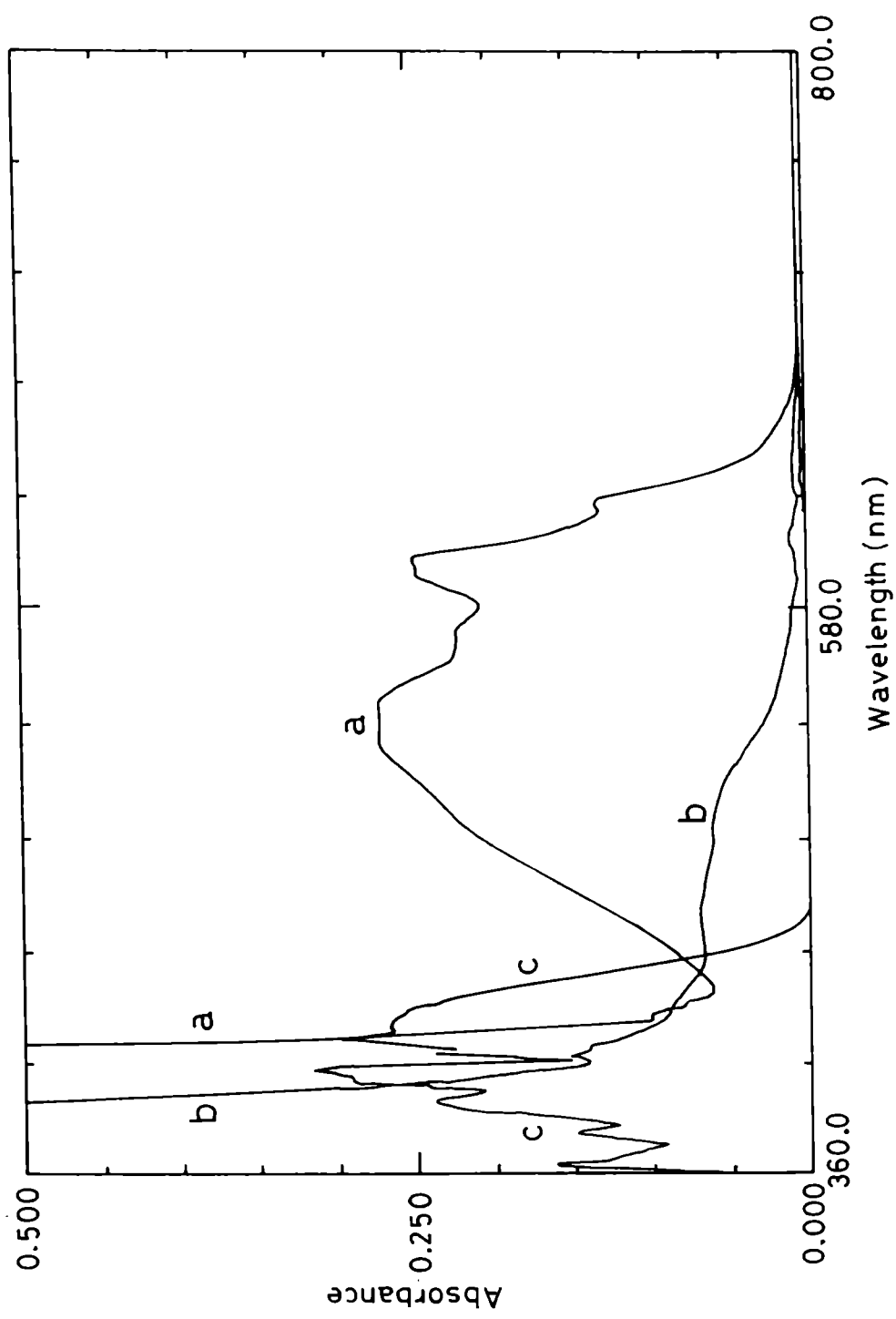


Fig. 8.1. Absorption spectra of C<sub>60</sub> and two of its EDA complexes in CCl<sub>4</sub> :

- (a) C<sub>60</sub> ( $3.585 \times 10^{-4} \text{ mol.dm}^{-3}$ ) in CCl<sub>4</sub> against solvent as reference, (b) C<sub>60</sub> ( $1.883 \times 10^{-4} \text{ mol.dm}^{-3}$ ) + pyrene ( $8.751 \times 10^{-2} \text{ mol.dm}^{-3}$ ), (c) C<sub>60</sub> ( $3.585 \times 10^{-4} \text{ mol.dm}^{-3}$ ) + naphthalene ( $6.893 \times 10^{-1} \text{ mol.dm}^{-3}$ ) against the respective C<sub>60</sub> solutions as reference.

Table 8.1. CT absorption maxima and transition energies of C<sub>60</sub> - polynuclear aromatic hydrocarbon complexes and HOMO energies (in Hückel β unit) and AM1 ionisation potentials of the donors.

Donor	λ <sub>CT</sub> (nm)*	hν <sub>CT</sub> (eV)	E <sub>HOMO</sub>	I <sub>D</sub> (eV)
naphthalene	413	3.008	0.618	8.711
phenanthrene	413	3.008	0.605	8.617
anthracene	511	2.431	0.414	8.123
chrysene	472	2.632	0.520	8.371
pyrene	454	2.737	0.445	8.131

\* The longer wavelength in case of double peaks

According to Mulliken's theory<sup>1</sup> the CT transition energies are related to the vertical ionisation potentials (I<sub>D</sub><sup>v</sup>) of the donors by the relation,

$$h\nu_{CT} = I_D^v - C_1 + C_2 / (I_D^v - C_1) \quad \dots (8.1)$$

Here,

$$C_1 = E_A^v + G_1 + G_0 \quad \dots (8.2)$$

where E<sub>A</sub><sup>v</sup> is the vertical electron affinity of the acceptor, G<sub>0</sub> is the sum of several energy terms (like dipole-dipole, van der Waals interaction, etc) in the 'no-bond' state and G<sub>1</sub> is the sum of a number of energy terms in the 'dative' state. In most cases, G<sub>0</sub> is small and can be neglected while G<sub>1</sub> is largely the electrostatic energy of attraction between D<sup>+</sup> and A<sup>-</sup>. The term C<sub>2</sub> in eqn. (8.1) is related to the resonance energy of interaction between the 'no-bond' and 'dative' forms in the ground and excited states and for a given acceptor it may be supposed constant<sup>1</sup>. A rearrangement of eqn.(8.1) yields

$$2 I_D^v - h\nu_{CT} = (1/C_1) I_D^v(I_D^v - h\nu_{CT}) + (C_1 + C_2 / C_1) \quad \dots (8.3)$$

The ground state I<sub>D</sub> values calculated for the PAH's under study by the AM1 method may be taken as their I<sub>D</sub><sup>v</sup> and with the observed transition energies we have obtained the

correlation ,

$$2 I_D^v - h\nu_{CT} = (0.1551 \pm 0.00991) I_D^v (I_D^v - h\nu_{CT}) + (6.6907 \pm 0.4717) \quad \dots (8.4)$$

with a correlation coefficient of 0.99. This confirms the CT nature of the transitions observed and yields  $C_1 = 6.45 \text{ eV}$ . Neglecting  $G_0$  and taking the typical D-A distance in  $\pi$ -type EDA complexes to be  $3.5 \text{ \AA}$ , the major part of  $G_1$  is estimated as  $e^2/4\pi\epsilon_0 r = 4.13 \text{ eV}$ . Now using eqn.(8.2) the electron affinity of  $C_{60}$  in solution is found to be  $2.32 \text{ eV}$ . This is in fair agreement with the value  $2.65 \text{ eV}$  obtained in gas phase by Smalley et.al<sup>181</sup> which was later confirmed by Boltalina et. al<sup>182</sup> and Chen et. al.<sup>183</sup> by mass spectrometric method and also by theoretical calculation (Apostol<sup>184</sup>).

A plot of  $h\nu_{CT}$  against  $E_{HOMO}$  of the PAH donors (the Hückel energy of HOMO with  $\alpha$  as the zero and  $\beta$  as the unit of energy) is also found to be linear (Fig.8.2); the slope of this line must be equal to  $\beta$ , the resonance integral between two  $sp^2$ -C atoms, in accordance with the empirical McConnell-Ham-Platt equation<sup>185</sup>,

$$\begin{aligned} h\nu_{CT} &= I_D - E_A + \Delta \\ &= -E_{HOMO} \beta + \text{constant} \quad \dots (8.5) \end{aligned}$$

where  $E_A$  is the electron affinity of the acceptor ( $C_{60}$ ) and  $\Delta$  is an energy term coming from solvation etc. which may be regarded as approximately constant for a given solvent and a series of structurally similar donors. In fact eqn. (8.5) is an approximate form of Mulliken's eqn.(8.1). The value of  $\beta$  obtained from the linear plot shown in Fig. 8.2 is  $-2.98 \text{ eV}$ , which is in very good agreement with the value of  $-3.1 \text{ eV}$ , obtained from the first four singlet-singlet transitions in benzene. All these observations definitely establish that  $C_{60}$  acts as an electron acceptor in forming EDA complexes with the polynuclear aromatic hydrocarbons studied. Stoichiometry and formation constants of the complexes were determined by using Benesi-Hildebrand<sup>186</sup> (B-H) and Rose-Drago<sup>141</sup> equations equation (8.6) and (8.7) respectively for cells with 1 cm optical length :

$$[A]_0 [B]_0 / d = [B]_0 / \epsilon' + 1/K\epsilon' \quad \dots (8.6)$$

$$[A]_0 [B]_0 / d = ([A]_0 + [B]_0) / \epsilon' - d / \epsilon'^2 + 1/K\epsilon' \quad \dots (8.7)$$

where  $[A]_0$  and  $[B]_0$  are the initial concentrations of the acceptor and donor respectively,  $d$

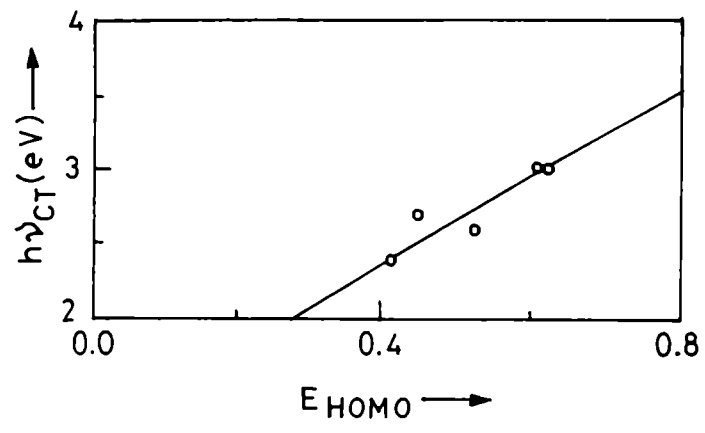


Fig.8.2. Plot of  $h\nu_{\text{CT}}$  against  $E_{\text{HOMO}}$  in  $\beta$  unit.

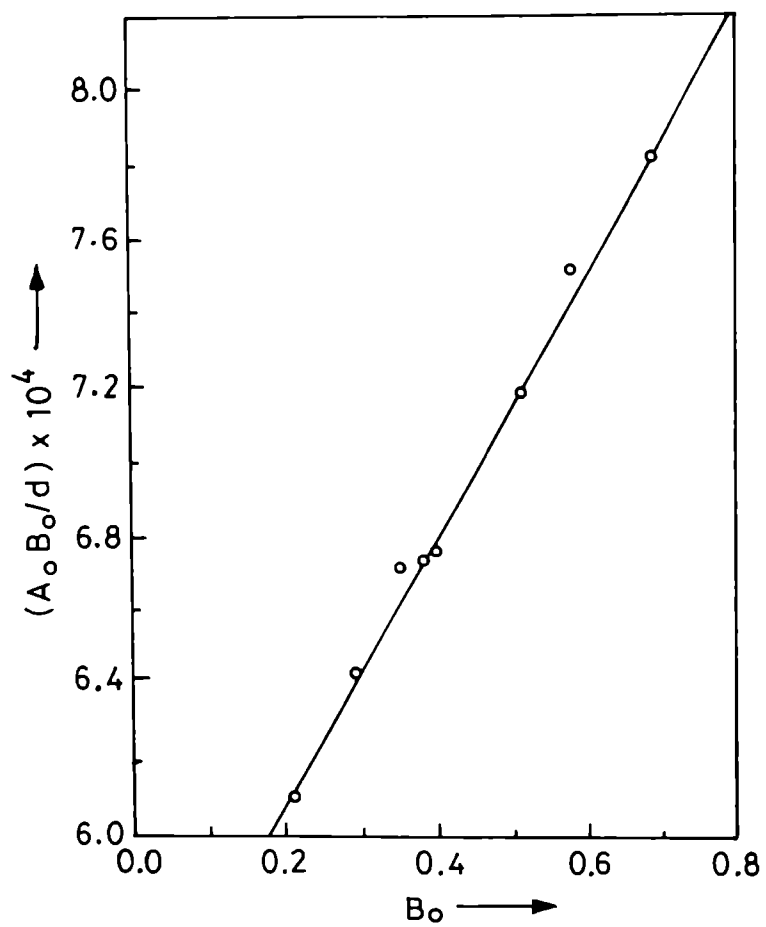


Fig.8.3. Benesi-Hildebrand plot for C<sub>60</sub> - naphthalene complex.

is the absorbance at the  $\lambda_{\text{max}}$  of the CT absorption band measured against the acceptor solutions, at the same molar concentration as that in the donor-acceptor mixture taken as reference.  $\epsilon' = \epsilon_c - \epsilon_A$ , where  $\epsilon_c$  is the molar absorptivity of the complex and  $\epsilon_A$  is that of the acceptor, at the wavelength of measurement.  $K$  is the formation constant of the complex. Eqn.(8.6) is valid under the condition<sup>186</sup>  $[B]_0 \gg [A]_0$  while eqn. (8.7) does not require such a condition; however, both are valid for 1:1 (donor-acceptor) complexes. Absorbances at the maxima of the CT absorption bands at various concentrations of the components are shown in Table 8.2. Fig. 8.3 shows a typical B-H plot.  $K$  and  $\epsilon'$  values for each system except the chrysene-fullerene complex were obtained by using the eqn.(8.6). In the latter case eqn.(8.7) was solved iteratively to get the values of  $K$  and  $\epsilon'$ . Owing to low solubility of chrysene in  $\text{CCl}_4$ , B-H condition could not be maintained in this case. Results are given in Table 8.2.



Table 8.2. Data for determination of stoichiometry, formation constants and molar absorptivities of the C<sub>60</sub>-polynuclear aromatic hydrocarbon complexes.

Donor	[A] <sub>0</sub> (mol dm <sup>-3</sup> )	[B] <sub>0</sub> (mol dm <sup>-3</sup> )	Absorbance at λ <sub>CT</sub>	K (dm <sup>3</sup> mol <sup>-1</sup> )	ε
naphthalene	3.5853×10 <sup>-4</sup>	0.20781	0.111	0.67 ± 0.01	2778
		0.29219	0.150		
		0.35104	0.172		
		0.38359	0.187		
		0.40373	0.198		
		0.51354	0.235		
		0.58307	0.258		
		0.68932	0.294		
phenanthrene	1.6129×10 <sup>-4</sup>	0.06134	0.052	1.67± 0.19	3333
		0.07593	0.059		
		0.13578	0.095		
		0.17468	0.124		
		0.19002	0.127		
		0.22368	0.148		
anthracene	1.6414×10 <sup>-4</sup>	1.2764×10 <sup>-2</sup>	0.012	10.24 ± 4.66	465
		1.6692×10 <sup>-2</sup>	0.010		
		2.8334×10 <sup>-2</sup>	0.014		
		3.8714×10 <sup>-2</sup>	0.024		
		5.9333×10 <sup>-2</sup>	0.030		
chrysene	1.7450×10 <sup>-4</sup>	2.4822×10 <sup>-3</sup>	0.003	65.5 ± 15.19	139
		5.5485×10 <sup>-3</sup>	0.006		
		9.7829×10 <sup>-3</sup>	0.007		
		10.6005×10 <sup>-3</sup>	0.012		
		11.9730×10 <sup>-3</sup>	0.013		
		13.3289×10 <sup>-3</sup>	0.010		
pyrene	1.8827×10 <sup>-4</sup>	3.7575×10 <sup>-2</sup>	0.039	6.8 ± 1.03	980
		4.7299×10 <sup>-2</sup>	0.056		
		4.7368×10 <sup>-2</sup>	0.041		
		5.3397×10 <sup>-2</sup>	0.049		
		6.9053×10 <sup>-2</sup>	0.059		
		8.0919×10 <sup>-2</sup>	0.076		
		8.7511×10 <sup>-2</sup>	0.068		

$C_{60}$  is thus shown to form ground state EDA complexes of 1:1 stoichiometry with each of the PAHs studied. Except for chrysene, the  $K$  – values are of the order of the formation constants of typical  $\pi$  - type EDA complexes; for example<sup>187</sup>,  $K$  of the naphthalene–tetrachloro-phthalicanhydride complex in  $CCl_4$  medium at 301K is  $2.8 \text{ dm}^3 \cdot \text{mol}^{-1}$ . The relatively high  $K$ -value for the chrysene –  $[60]C_{60}$  fullerene complex may be attributed to the fact that the arrangement of hexagonal rings in chrysene molecules is similar to that in the belt region of the  $C_{60}$  surface, thereby leading to a good  $\pi$  - overlap. A reasonable value of Hückel parameter  $\beta$  and also the electron affinity of  $[60]C_{60}$  fullerene have been obtained from the present study.

### 8.2.1. Introduction

Emission properties of compounds of intramolecular charge transfer type are being intensively used for many significant purposes<sup>188-198</sup>. Such studies with intermolecular charge transfer (i.e., EDA) complexes should be important for similar reason .

The fluorescence properties of C<sub>60</sub> and some of its pyrrolidine derivatives have been studied<sup>199</sup> and their fluorescence life-times have been measured by the frequency domain method . Quenching of their fluorescence due to concentration and also due to added N, N-dimethyl aniline has been reported in the same study. On the other hand C<sub>60</sub> itself acts as a quencher of pyrene fluorescence which has been shown<sup>200</sup> by measurement on Langmuir-Blodgett layers containing mixtures of pyrene and varying concentrations of C<sub>60</sub>. The fluorescence of a donor (D) must be quenched on addition of an electron acceptor (A). This is expected because formation of EDA complex in the ground state of both D and A should reduce the concentration of free D. Since C<sub>60</sub> has been shown to form EDA complex with polynuclear aromatic hydrocarbons in section I of this chapter, the object of the present section is to see whether C<sub>60</sub> quenches the fluorescence of a representative system, viz., anthracene.

### 8.2.2. Experimental

Solution of anthracene in n-hexane, when excited at 355nm (one absorption maximum of anthracene in n-hexane) emits at 377nm, 397nm, 420nm and 446nm . The fluorescence spectra at a number of concentrations of anthracene are shown in Fig. 8.4 . The concentration below which no concentration-quenching occurs was determined first . For this purpose, fluorescence intensities at each of the emission maxima were plotted against anthracene concentration . A typical plot is shown in Fig. 8.5 . It was found that at concentrations lower than  $7.0 \times 10^{-5} \text{ mol.dm}^{-3}$  , concentration quenching could be avoided. These concentrations were used to study the effect of added C<sub>60</sub> . Emission spectra of anthracene solutions containing varying concentrations of C<sub>60</sub> are shown in Fig. 8.6. It is observed that added C<sub>60</sub> decreases the fluorescence intensities of anthracene at each of the aforesaid wavelengths .

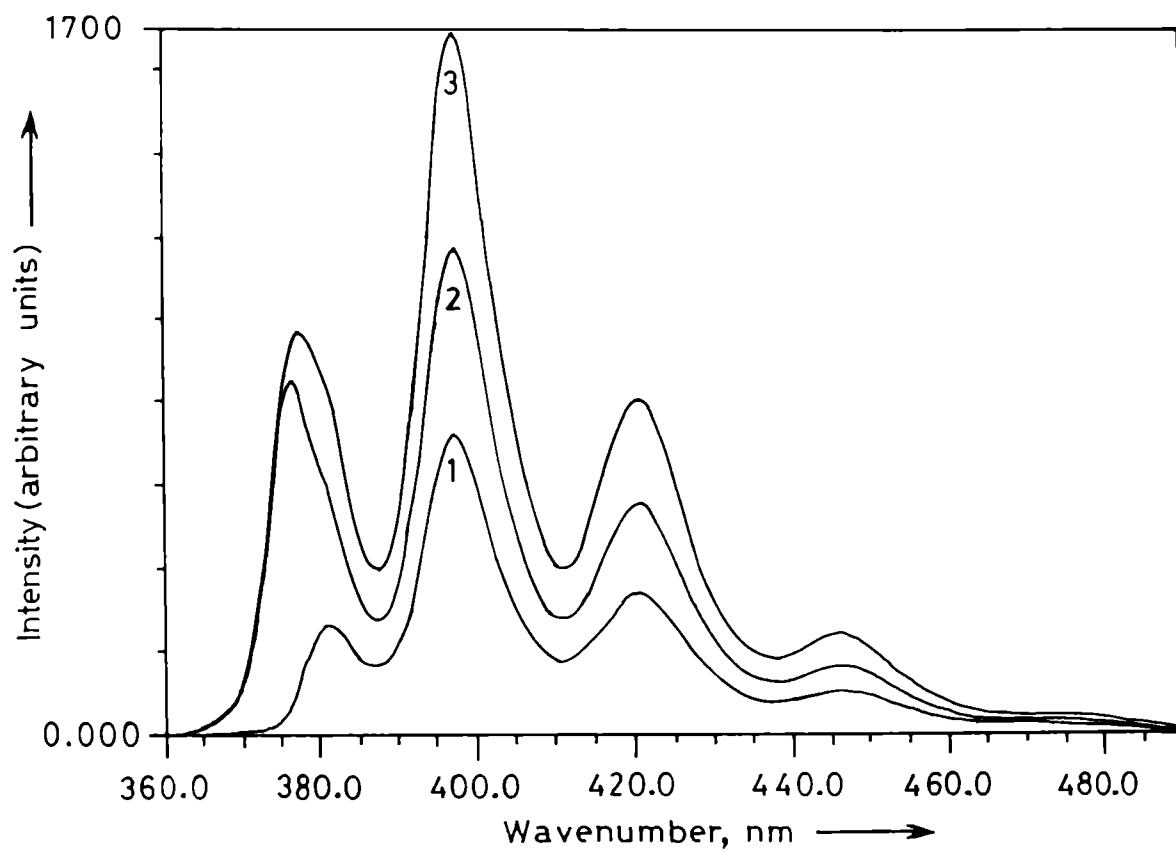


Fig. 8.4. Fluorescence spectra of anthracene in n-hexane exhibiting concentration quenching : (1)  $4.6609 \times 10^{-4} \text{ mol.dm}^{-3}$ , (2)  $4.2372 \times 10^{-5} \text{ mol.dm}^{-3}$ , (3)  $9.3219 \times 10^{-5} \text{ mol.dm}^{-3}$ .

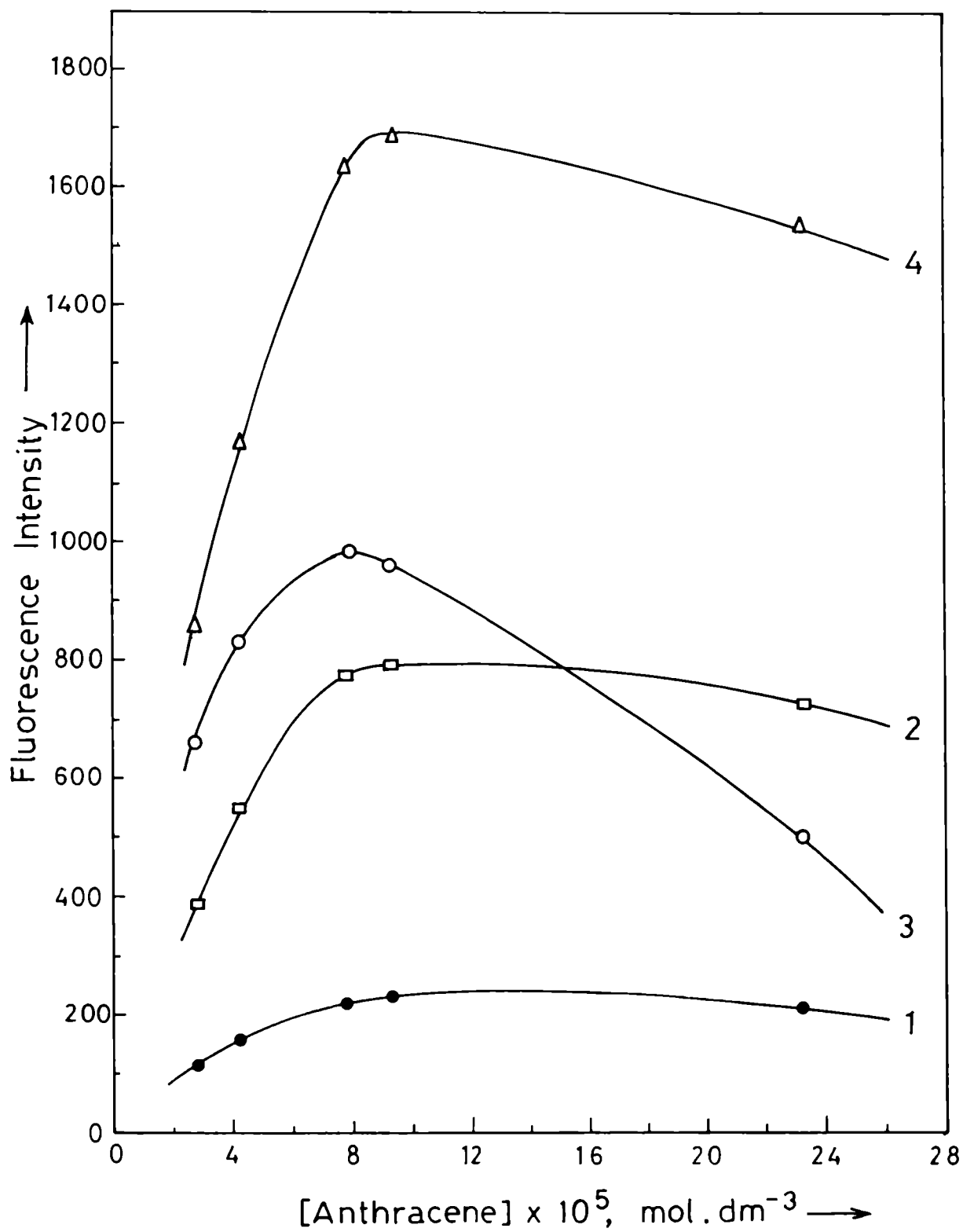


Fig. 8.5. Variation of fluorescence intensity with conc. of anthracene at four different band positions in n-hexane medium : (1) 446 nm, (2) 420 nm, (3) 377 nm, (4) 397 nm.

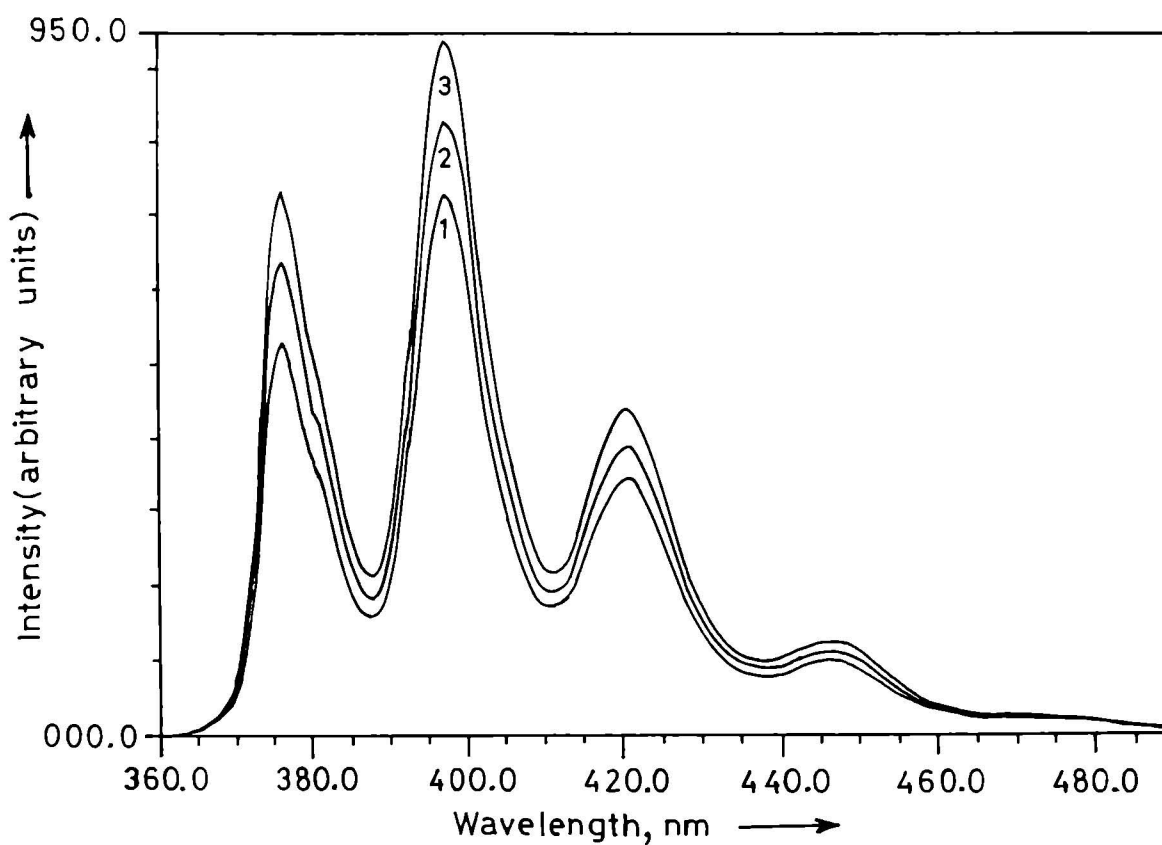


Fig. 8.6. Spectra for demonstration of quenching of anthracene emission by  $C_{60}$  in n-hexane: [anthracene] =  $3.0337 \times 10^{-5} \text{ mol.dm}^{-3}$ , [fullerene] : (1)  $2.8950 \times 10^{-5} \text{ mol.dm}^{-3}$ , (2)  $9.6498 \times 10^{-6} \text{ mol.dm}^{-3}$  (3)  $0.0000 \times 10^{-5} \text{ mol.dm}^{-3}$

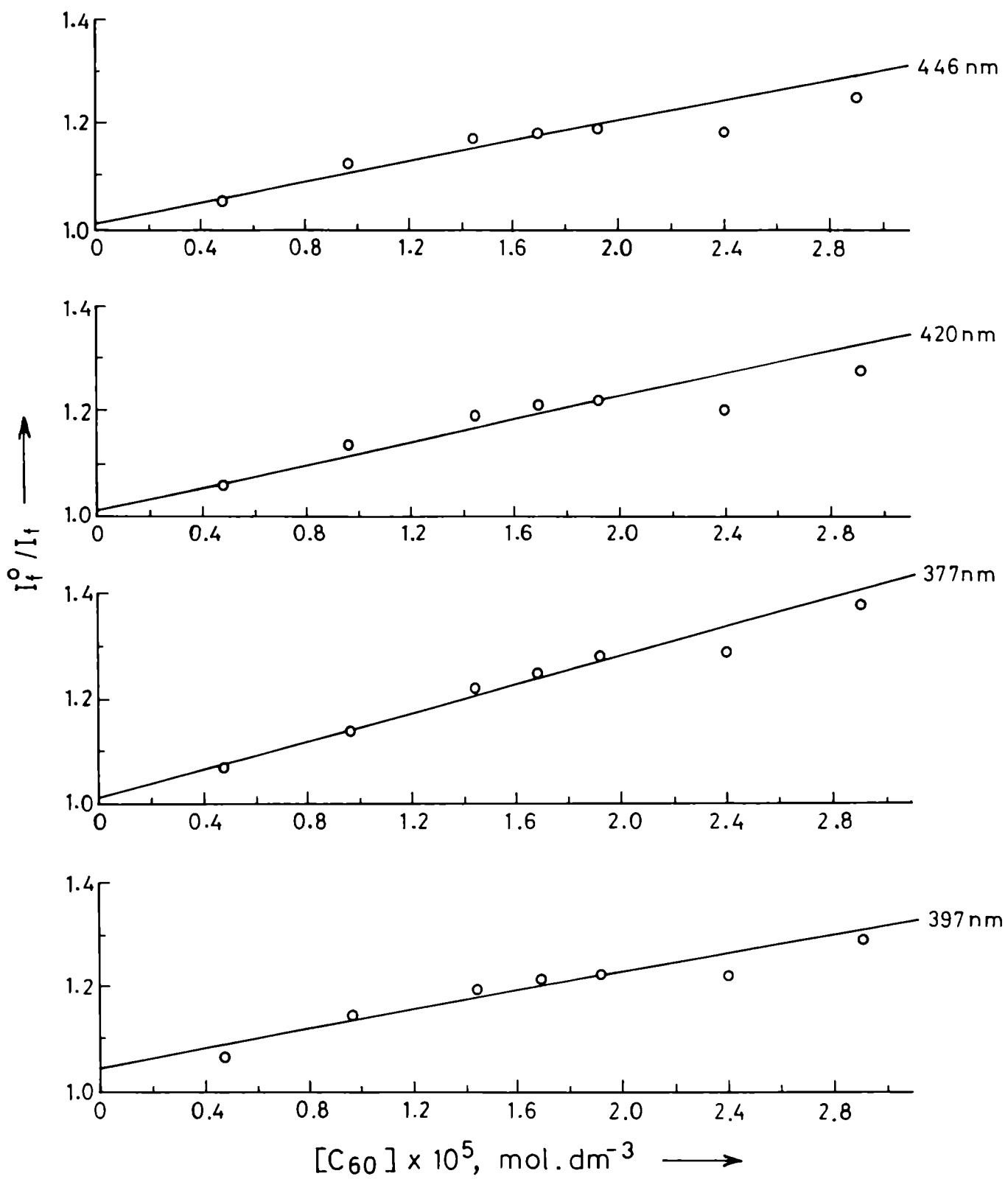


Fig.8.7. Stern-Volmer plots for quenching by  $C_{60}$  in n-hexane.

### 8.2.3. Results and discussion

The observed quenching may be due to any of the following reasons :

- (1) Ground state EDA complex formation between [60]fullerene and anthracene, occurring simultaneously with collisional quenching , (2) collisional quenching only and (3) exciplex formation .

In case (1) the modified Stern-Volmer equation<sup>201</sup> is

$$(I_f^0 / I_f - 1) / [Q] = (K_{SV} + K_C) + K_{SV} K_C [Q] \quad \dots (8.9)$$

where  $I_f^0$  is the intensity of fluorescence in absence of quencher,  $I_f$  , that in presence of quencher , and  $[Q]$  is the quencher concentration. The constants  $K_{SV}$  and  $K_C$  are respectively the Stern-Volmer constant and formation constant of the EDA complex .

Case (2) is a special case of (1), with  $K_C = 0$  . Under this condition equation (8.9) reduces to the ordinary Stern-Volmer form,

$$I_f^0 / I_f = 1 + K_{SV} [Q] \quad \dots (8.10)$$

Experimental data for the two solvents are shown in Table 8.3.

Table 8.3 . Emission spectral data

Solvent	$10^5 \times$ Conc. of anthracene (mol.dm <sup>-3</sup> )	$10^5 \times$ Conc. of C <sub>60</sub> (mol.dm <sup>-3</sup> )	Intensity of he bands* (arbitraryunits)			
			I	II	III	IV
n-hexane	3.0337	0.0000	732.9	937.8	440.3	128.0
		0.4825	682.6	881.3	415.2	121.9
		0.9650	637.4	826.0	387.9	114.1
		1.4475	599.4	790.0	369.6	109.7
		1.6887	588.7	777.1	365.1	108.4
		1.9300	570.9	766.4	360.8	107.6
		2.4125	568.8	769.6	367.1	108.8
		2.8950	531.7	729.0	343.6	102.2

\* For n-hexane the band maxima are (I) 377 nm , (II) 397 nm , (III) 420 nm and (IV) 446 nm.

By the method of least squares it was found that plot according to equation (8.9) gives a very bad correlation coefficient (0.53). This means that quenching due to EDA complex



formation is not taking place under the experimental conditions. Reason for this is that the formation constant  $K_C$  itself is low (shown in section I of this chapter) and the concentrations of both anthracene and [60]-fullerene are too low (each  $\sim 10^{-5}$  mol.dm<sup>-3</sup>) for ground state EDA complex formation . The alternative equation (8.10) was found to be valid as evident from Fig. 8.7 . No deviation from linearity in the Stern-Volmer plot is also an indication<sup>202</sup> that there is no ground state EDA complex formation. The intercepts obtained from these plots are very close to 1.0 as expected and values of  $K_{SV}$  obtained from the slopes are shown in Table 8.4.

Table 8.4. Stern-Volmer constants for collisional quenching of anthracene fluorescence by C<sub>60</sub> at 303K

Solvent	Viscosity (c.p)	$10^{-3} \times K_{SV}, \text{ dm}^3 \text{ mol}^{-1}$			
		band I	band II	band III	band IV
n-hexane	0.299	13.33	8.89	10.56	10.00

The possibility of exciplex formation is discarded because (i) no new long-wavelength emission band is observed in presence of C<sub>60</sub> and (ii) there no red shift in the emission bands of anthracene upon addition of C<sub>60</sub> (Fig.8.6); detection of anthracene-chloromethane exciplex formation by observation of such red shift has been reported in ref. 203.