

CHAPTER TWO

EXPERIMENTAL



The present investigation covers studies involving systems comprising two acceptors derived from 1,4-naphthoquinone and two aromatic amine donors in dichloromethane solvent. These are presented in Table 2.1.

Table 2.1

Concentration ranges of donor and acceptor molecules employed in the equilibrium studies.

Acceptor	Donor	Range of donor concentration (Moles/litre)
i) 2,3-dichloro-1,4-naphthoquinone (DC1NQ) $\sim 10^{-3}M$	a) o-Ethylaniline	1.12 - 1.92
	b) 2,6-dimethylaniline	0.48 - 0.96
ii) 2,3-dichloro-5-nitro-1,4-naphthoquinone (DC1NO <sub>2</sub> NQ) $\sim 10^{-3}M$	a) o-Ethylaniline	0.4 - 0.8
	b) 2,6-dimethylaniline	0.32 - 0.72

The optical absorbance measurements were made with the help of a Carl-Zeiss Jena make "Spekol" UV-Visible single beam spectrometer. It was calibrated by making use of standard solutions of potassium dichromate and potassium permanganate. The optical density could be read with an accuracy of  $\pm 0.5\%$ . The wavelength was read with an accuracy of  $\pm 1$  nm. The desired temperature was maintained within  $\pm 0.5^{\circ}C$ . The solutions were allowed to attain thermal equilibrium before measurements were

made.

Fresh stock solutions were prepared before each measurement by weighing the required quantity of respective substance directly into the volumetric flask and then making it up with the solvent, dichloromethane. The solutions were protected from light as far as possible. Corning 'A' grade glassware were used in all investigations.

In case of 2,3-dichloro-1,4-naphthoquinone acceptor, the charge transfer bands appeared on the shorter wavelength side of the visible region with the two donors studied. The band maxima in these cases did not overlap the acceptor band maximum. The acceptor does not absorb significantly in the region of absorption of the complex. The pure solvent was used in the reference cell. In case of 2,3-dichloro-5-nitro-1,4-naphthoquinone acceptor and amine donor complexes, broad charge transfer bands appeared at the region where neither the acceptor nor the donor absorb. In this case also the pure solvent was used in the reference cell. The spectrum was scanned twice with the same solution to check the reproducibility. The optical densities were within the experimental error.

#### MATERIALS :

##### Acceptors

- i) 2,3-dichloro-1,4-naphthoquinone 'Aldrich' product was

used for the investigation. This compound was recrystallized twice-thrice from chloroform. Yellow fine crystals were obtained. Melting point agreed with the literature value of 195°C.

ii) 2,3-dichloro-5-nitro-1,4-naphthoquinone was prepared by nitrating 2,3-dichloro-1,4-naphthoquinone. The detailed procedure is given below.

#### Donors

o-Ethylaniline and 2,6-dimethylaniline were 'Fluka' samples and were freshly distilled under reduced pressure just before use. Refractive indices and boiling points were compared with the literature values.

#### Solvent

Dichloromethane from E. Merk (India) was distilled twice and only the middle fraction was collected and was used for the work.

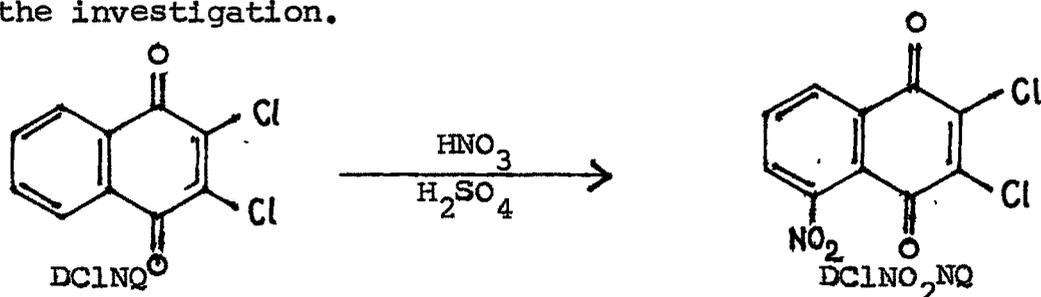
#### Preparation of 2,3-dichloro-5-nitro-1,4-naphthoquinone

2,3-dichloro-1,4-naphthoquinone was prepared by the method reported by Wilbur and Day.<sup>50</sup>

25 gm of 2,3-dichloro-1,4-naphthoquinone 'Aldrich' product was mixed with 33 ml of concentrated sulphuric acid. The slurry was stirred well. Then while stirring 65 ml of red fuming nitric

acid was added dropwise. A vigorous exothermic reaction occurred after the addition of about 15 ml of nitric acid. It was cooled and the temperature of the reaction mixture was kept below 100°C. If the temperature of the reaction mixture were above 120°C there is a possibility of decomposition of the product. Thus, the reaction mixture was heated on water bath. The remaining nitric acid was added slowly by maintaining the temperature between 80-90°C. The mixture was heated at this temperature for about 7 hours and then the hot solution was poured on to cracked ice. Yellow solid product was separated out. The solid was filtered and was washed with cold water thoroughly till it was free from acid. The solid was then stirred with 1N sodium carbonate solution for about 8 hours. The product was filtered and was washed with cold water till the filtrate was colourless. It was purified by recrystallization from chloroform using decolourising carbon. It was further recrystallized twice from chloroform. Yellow fine needle-like sample with melting point 175°C was obtained.

The TLC of the sample was carried out (using slurry made with chloroform and benzene, 1:1 by volume). The TLC showed only one spot indicating no impurities. The compound was used for the investigation.



The absorption spectra of the two acceptors viz., 2,3-dichloro-1,4-naphthoquinone and 2,3-dichloro-5-nitro-1,4-naphthoquinone have been recorded at room temperature in the visible region using the solvent dichloromethane. The absorption spectra of these compounds are shown in Fig. 2.1.

Fig. 2.1: Absorption spectra in the visible region  
of the acceptors in dichloromethane at  
room temperature -

a) 2,3-dichloro-1,4-naphthoquinone

b) 2,3-dichloro-5-nitro-1,4-naphthoquinone

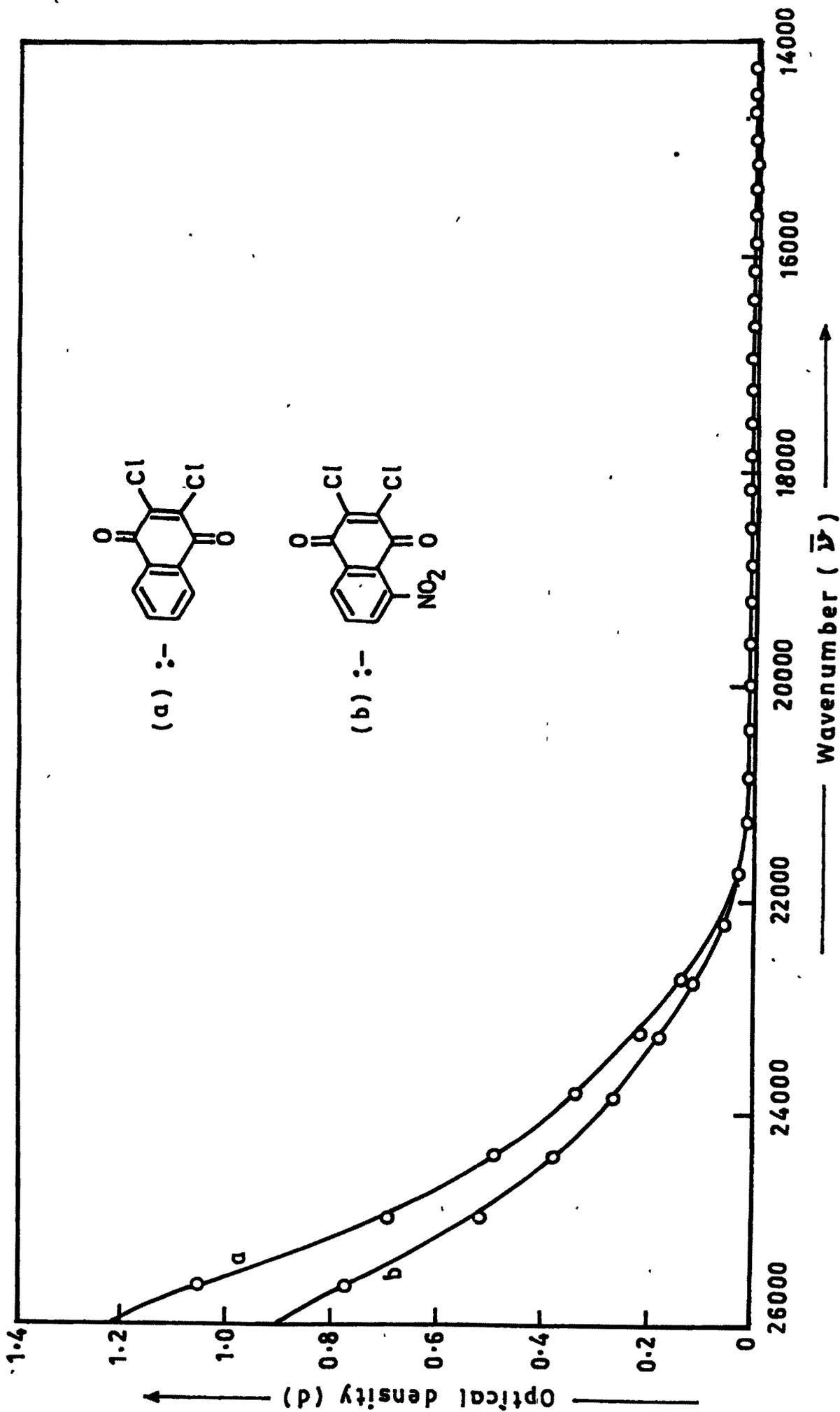


Fig. 2.1