CHAPTER FOUR

DISCUSSION

In the present work of donor-acceptor systems, .four
systems have been investigated at different temperatures in
dichloromethane solvent. These systems constitute two substituted
1,4-naphthoquinone acceptors viz., 2,3-dichloro-1,4-naphthoquinone
and 2,3-dichloro-5-nitro-1,4-naphthoquinone, and two substituted
aromatic amine donors particularly o-Ethylaniline and
2,6-dimethylaniline. It is well-known that the naphthoquinones are
π-acceptors.[51] The electron affinities of the derivatives of
1,4-naphthoquinones are enhanced when electron withdrawing groups
such as chloro-, nitro- and cyano-groups are substituted on
the naphthoquinone π-system.[52] The electron affinity of
2,3-dichloro-1,4-naphthoquinone has the smallest value, that of
2,3-dicyano-1,4-naphthoquinone has the highest value and that
of 2,3-dichloro-5-nitro-1,4-naphthoquinone lies in between the
two. The visible absorption spectra of the two acceptors studied
in this work are shown in Fig. 2.1. The typical charge transfer
absorption spectra of some complexes are shown in Figs. 3.1, 3.2,
3.7 and 3.8. These complexes are formed by the interaction of
donors with acceptors and are characterised by the appearance of
a charge transfer absorption band in each case at much longer
wavelengths where neither the donor nor the acceptor molecules
absorb. This observation is in accordance with the expectations.[53-56]
The values of the peak frequencies ($\overline{\nu}_{max}$) of the charge transfer
band for a given acceptor decrease with increase in the electron
donating ability of the donor as expected.[14,57] Similarly, the
$\overline{\nu}_{max}$ values decrease with increase in the electron affinity

of the acceptor.[13] Tables 3.1 and 3.6 depict these observations. The electron affinity of 2,3-dichloro—5-nitro-1,4-naphthoquinone is greater than that of 2,3-dichloro-1,4-naphthoquinone. The electron donating ability of 2,6-dimethylaniline is higher than that of o-Ethylaniline. Thus the energy of the charge transfer band $h\bar{\nu}_{max}$, for a given complex agrees well with the electron donating and accepting properties of the two components.

The relationship between the energy of the charge transfer band ($h\bar{\nu}_{CT}$) and the ionization potentials (I^D) of the donor with a common acceptor species has been given by McConnell et al.[58] in the form

$$h\bar{\nu}_{CT} = I^D - E^A - W$$

where E^A is the electron affinity of the acceptor and W is the dissociation energy of the charge transfer excited state. If I^D and E^A are known one can evaluate W. Similar linear relationships have been described for complexes of many other acceptors.[25] In general:

$$h\bar{\nu}_{CT} = aI^D + b$$

The coefficients a and b have different values for different acceptors. The plot of $h\bar{\nu}_{CT}$ Vs I^D would be a straight line.

In most of the previous work, the formation constants and molar absorptivities of the charge transfer complexes were estimated by assuming the existence of only 1:1 complexes. At an early stage in the study of EDA complexes, it was suggested

that, in some solutions at least, significant quantities of termolecular complexes may exist in equilibrium with the components and the 1:1 complexes.[59-61] Over the years evidence has been accumulated to support this suggestion.[25] In some cases these termolecular complexes may be present in sufficient concentration to affect seriously the evaluation of the association constant for the 1:1 complex based on calculations in which the formation of higher complexes is ignored.[62-64] Johnson and Bowen[65] showed that the Benesi-Hildebrand equations give straight line plots, even when relatively large amounts of higher order complexes are present. When the concentrations of the components are in the limited range even Scott[42] and Scatchard[43] plots also give straight lines even though higher order complexes are present in appreciable amounts. Under such conditions the linearity of these plots does not supply an adequate test for the absence of complexes with stoichiometry other than 1:1. In case of 2,3-dichloro-1,4-naphthoquinone acceptor complexes with some substituted aniline donors, it was shown by Budni[66] that there exist both 1:1 and 2:1 complexes in equilibrium with the components. He has reported the values of the formation constants for 1:1 species (K_C^{AD}) as well as 2:1 species ($K_C^{AD_2}$) which have been calculated by computerised method.

In this investigation it is shown that the complexes formed between the four systems studied have 2:1 stoichiometry. In all these cases the Benesi-Hildebrand plots are linear indicating

the presence of 1:1 species. Typical plots are shown in Figs. 4.1 and 4.2 and the data for these plots are given in Table 4.1. The Rose-Drago 1:1 plots are non-linear indicating the absence of 1:1 species. Figs. 3.3 and 3.9 depict this non-linearity. However the Benesi-Hildebrand plot for 2,3-dichloro-1,4-naphthoquinone complex with o-Ethylaniline gave a straight line passing through the origin. Fig. 4.1 shows this plot. This may imply that the equilibrium constant K_C^{AD}, for the complex formation is very nearly zero.[67] This agrees with our plot of Rose-Drago, i.e., Fig. 3.3. However, it should be noted that some times little reliance can be placed upon small K_C^{AD} values determined from optical measurements. But the Benesi-Hildebrand plots in case of 2,3-dichloro-5-nitro-1,4-naphthoquinone and 2,6-dimethyl-aniline complex the straight line does not pass through the origin (Fig. 4.2) indicating the existence of small amounts of 1:1 complex. This observation is in accordance with the observations of Johnson and Bowen.[65] Budni[66] has proved this by calculating K_C^{AD} and $K_C^{AD_2}$.

Temperature dependent studies of formation constants in the case of the above systems were used for determining the thermodynamic quantities such as enthalpies, entropies and free energies of formation of complexes. The familiar van't Hoff plots of $\log K_C^{AD}$ Vs $1/T$ can be used for determining ΔH^O which is supposed to be constant over the temperature range used. Generally, the quantitative simultaneous determination of

Fig. 4.1: Benesi-Hildebrand plot $(C_A^O/d$ Vs $1/C_D^O)$

for the complex between 2,3-dichloro-1,4-
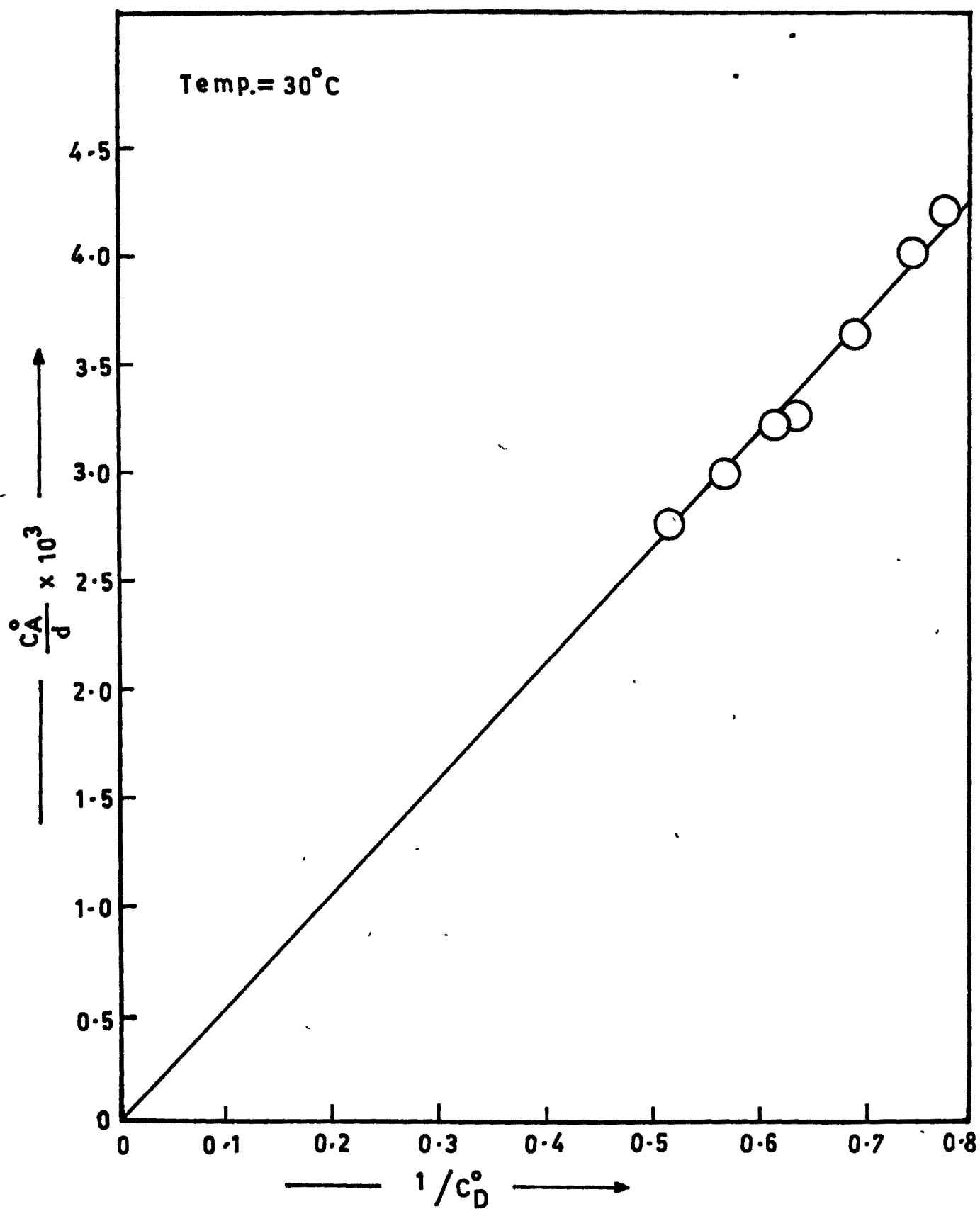
naphthoquinone and o-Ethylaniline in

dichloromethane.

Fig. 4·1

Fig. 4.2:   Benesi-Hildebrand plot (c_A^O/d Vs. $1/c_D^O$)

for the complex between 2,3-dichloro-5-

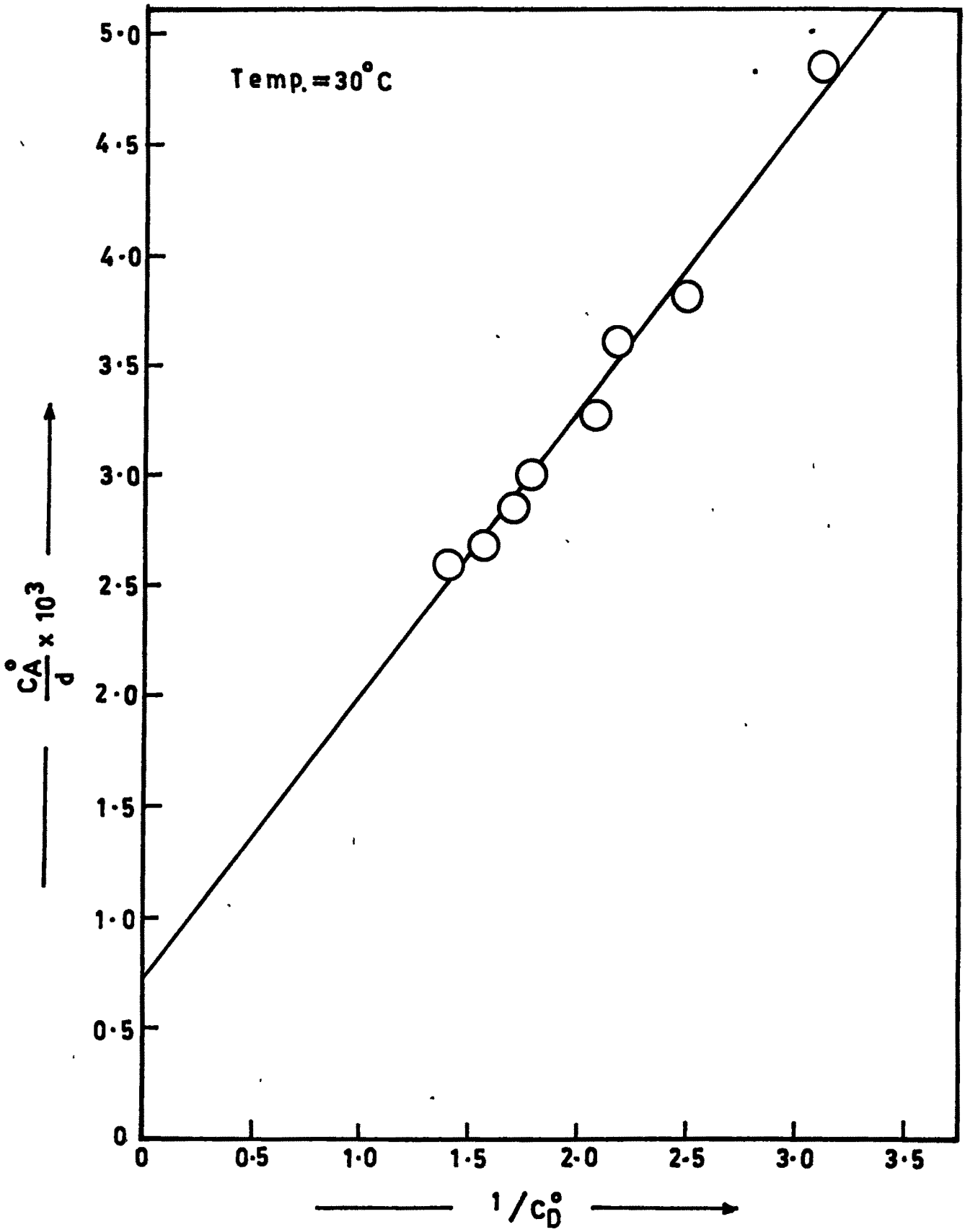nitro-1,4-naphthoquinone and

2,6-dimethylaniline in dichloromethane.

Fig. 4.2

Table 4.1

Data for Benesi-Hildebrand plot for two systems.

System I: 2,3-dichloro-1,4-naphthoquinone and o-Ethylaniline at 30^OC.

$$C_A^O = 1.0 \times 10^{-3}M.$$

Sr. No.	C_D^O (Moles/litre)	$1/C_D^O$	d (Optical density at $\overline{\nu}_{max}$)	$(C_A^O/d) \times 10^3$
1	1.12	0.8928	0.2000	5.00
2	1.28	0.7812	0.2375	4.21
3	1.34	0.7463	0.2500	4.00
4	1.44	0.6944	0.2750	3.64
5	1.57	0.6369	0.3075	3.25
6	1.60	0.6250	0.3125	3.20
7	1.76	0.5682	0.3375	2.96
8	1.92	0.5208	0.3650	2.74

System-II: 2,3-dichloro-5-nitro-1,4-naphthoquinone and 2,6-dimethylaniline at 30^OC.

1	0.32	3.1250	0.2050	4.878
2	0.40	2.5000	0.2625	3.809
3	0.46	2.1740	0.2750	3.636
4	0.48	2.0830	0.3050	3.278
5	0.56	1.7860	0.3325	3.007
6	0.59	1.6949	0.3500	2.857
7	0.64	1.5625	0.3700	2.702
8	0.72	1.3890	0.3850	2.597

K_C^{AD} and ϵ_λ^{AD} is not possible for either extremely 'strong' or extremely 'weak' complexes. Criteria for meaningful separation of K_C^{AD} and ϵ_λ^{AD} have been discussed by Person[68], by Deranleau[69] and by LaBudde and Tamres[47]. For weak complexes the separation of K_C^{AD} and ϵ_λ^{AD} is not feasible because very large error limits are associated with K_C^{AD} and ϵ_λ^{AD}, often result-ing in large and random variation of both with temperature. For weak complex, the procedure to determine ΔH^o is from a plot of log ($K_C^{AD} \cdot \epsilon_\lambda^{AD}$) Vs. $1/T$ rather than from usual van't Hoff plot. The product $K_C^{AD} \cdot \epsilon_\lambda^{AD}$ can be obtained readily from experimental results of absorbance at the band maxima. Here, it is assumed that the molar absorptivity, ϵ_λ^{AD}, is independent of temperature. Actually ϵ_λ^{AD} is temperature dependent because of band broadening but the variation is less than the experimental error in determining ϵ_λ^{AD}[27]. If both 1:1 and 2:1 complexes are present in equilibrium with the components, ϵ_λ^{AD} would change with temperature[1]. The formation constants $K_C^{AD_2}$ and the molar absorptivities, $\epsilon_\lambda^{AD_2}$, as a function of temperature are given in Tables 3.4 and 3.6. There is a slight change in these values with temperature. This indicates the presence of 1:1 complexes. But it is not possible to separate out K_C^{AD} and $K_C^{AD_2}$. Our 2:1 plots (Figs. 3.10 and 3.11) of Rose-Drago prove the presence of only single species i.e., of 2:1 complex. The values of ΔH^o and ΔS^o computed for the systems studies are all negative, indicating that the product complex becomes more stable and

undergoes more steric restraint and hence the loss of entropy. The typical values of ΔH^O, ΔS^O and ΔG^O for 2,3-dichloro-5-nitro-1,4-naphthoquinone and o-Ethylaniline and 2,6-dimethylaniline complexes are given in Table 3.9.

The oscillator strengths and transition moments have been calculated on the basis of approximate equations of Tsubumora and Lang[70] i.e., equations (1.9) and (1.10). These values depend mainly on molar absorptivities and half band widths. Typical values for 2,3-dichloro-5-nitro-1,4-naphthoquinone complexes have been given in Tables 3.11 and 3.12. Approximate constancy in oscillator strength support the presence of a single complex.[11] This observation supports the Rose-Drago 2:1 plot i.e., Figs. 3.10 and 3.11.