CHAPTER THREE

RESULTS AND TREATMENT OF DATA

a) Donor-acceptor equilibria involving 2,3-dichloro-1, 4-naphthoquinone acceptor

When solutions of o-Ethylaniline or 2,6-dimethylaniline in dichloromethane were mixed with the solutions of 2,3-dichloro-1,4-naphthoquinone in the same solvent, characteristic colours were developed indicating the formation of complex in each case. These complexes are characterised by an intermolecular charge transfer absorption band which appears in the visible region. Figs. 3.1 and 3.2 show typical charge transfer absorption spectra of these complexes. There is an absorption due to the acceptor in the wings of the band on the shorter wavelength side in case of DClNQ and o-Ethylaniline complex. The absorption maxima $\bar{\nu}_{max}$, of these complexes are given in Table 3.1.

Table 3.1

Absorption maxima, $\bar{\nu}_{max}$, of the complexes of 2,3-dichloro-1,4-naphthoquinone with o-Ethylaniline and 2,6-dimethylaniline in dichloromethane.

Sr.No.	Donor	λ_{max} (nm)	$\bar{\nu}_{max}$ (cm^{-1})
1	o-Ethylaniline	470	21,270
2	2,6-dimethylaniline	495	20,200

Experimental data show that the change in temperature and

Fig. 3.1: Absorption spectra of 2,3-dichloro-1,4-naphthoquinone complex with o-Ethylaniline in dichloromethane at various concentrations of o-Ethylaniline. The concentration of the acceptor is constant. In all runs $C_D^o \gg C_A^o$

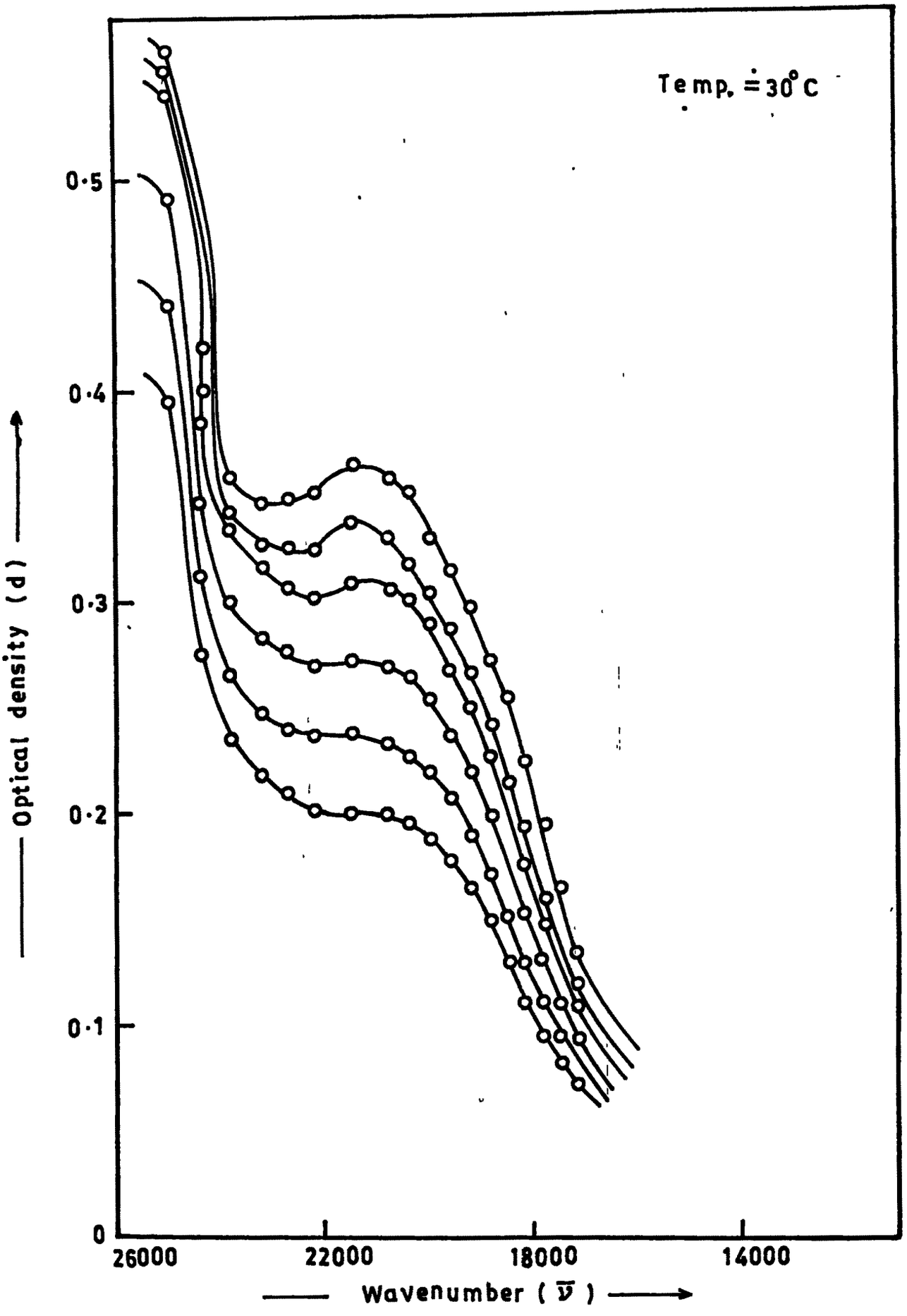
Temp. = 30°C
0·5
0·4
0·3
0·2
0·1
0
Optical density (d)
26000
22000
18000
14000
Wavenumber ($\bar{\nu}$)

Fig. 3·1

Fig. 3.2: Absorption spectra of 2,3-dichloro-1,4-naphthoquinone complex with 2,6-dimethylaniline in dichloromethane at various concentrations of the donor. The concentration of the acceptor is constant. In all the runs $C_D^o \gg C_A^o$

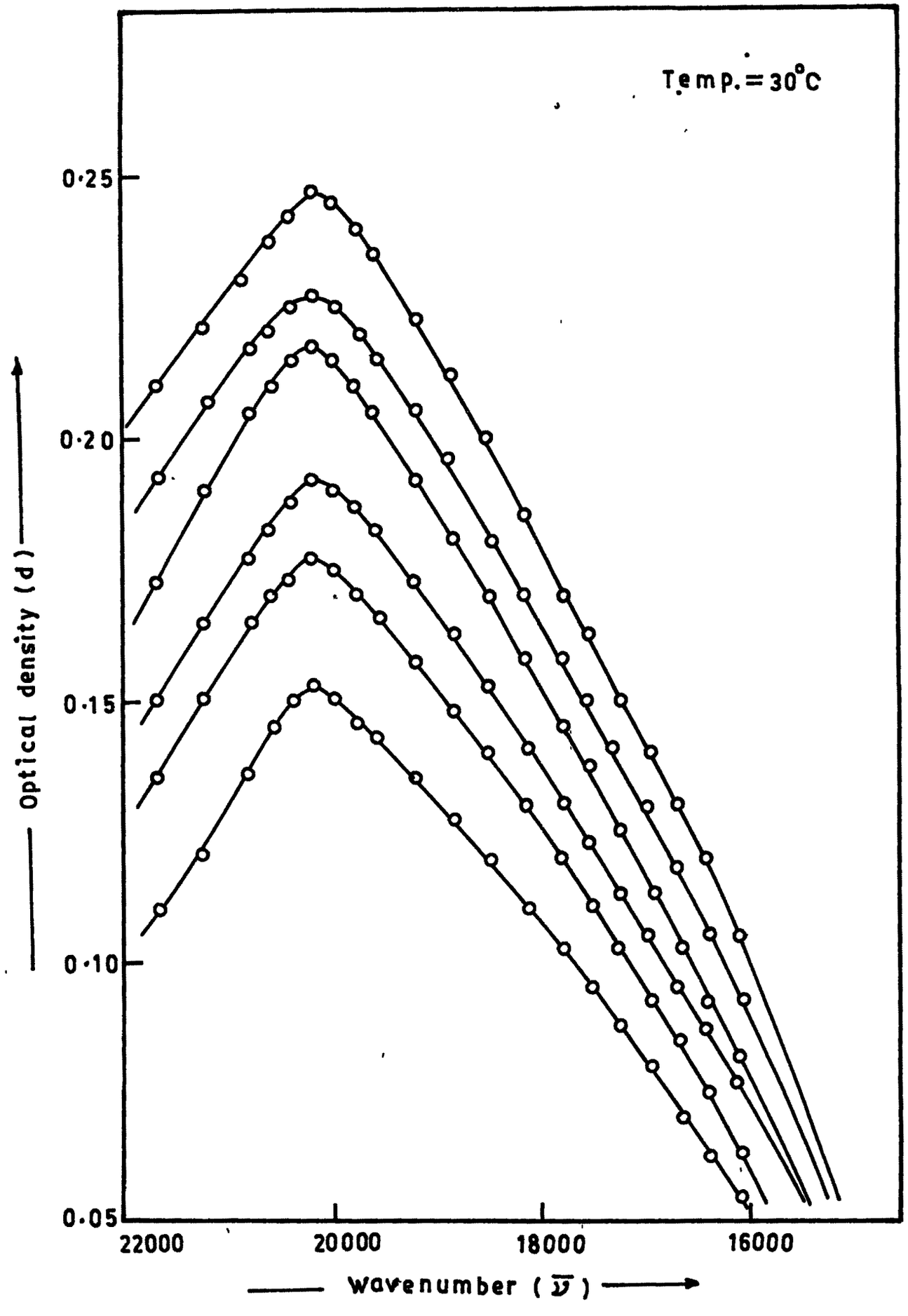
Temp. = 30°C
0·25
0·20
0·15
0·10
0·05
Optical density (d)
22000
20000
18000
16000
Wavenumber ($\bar{\nu}$)

Fig. 3·2

changes in concentrations have little effect on the peak frequency, $\bar{\nu}_{max}$, in each of the complexes studied. Spectral measurements were made with the acceptor concentration of the order of 1.0×10^{-3} M, which was kept constant for each series of measurements having various concentrations of the donor. Spectra were recorded with dichloromethane in the reference cell.

Experimental data were analysed in accordance with equation (1.17). Fig. 3.3 represents the typical plot of $\frac{C_A^o \times C_D^o}{d}$ against $(C_A^o + C_D^o)$ which is the Rose-Drago plot for 1:1 stoichiometric complexes. From the nature of the plot it is clear that the complexes must be other than 1:1 stoichiometry. The experimental data were then analysed in accordance with equation (1.20) which makes an approximation that in the equilibrium

$$A + 2D \rightleftharpoons AD_2$$

only the complex AD_2 absorbs. According to this equation the plots of $\frac{C_A \cdot C_D^{o2}}{d}$ against $C_D^o\,(C_D^o + 4C_A^o)$ were linear. Figs. 3.4 and 3.5 represent typical plots. The slopes and intercepts of these plots are $(\epsilon_\lambda^{AD_2})^{-1}$ and $(K_C^{AD_2} \cdot \epsilon_\lambda^{AD_2})^{-1}$ respectively from which the values of the formation constants, $K_C^{AD_2}$ and the molar absorptivities, $\epsilon_\lambda^{AD_2}$ have been calculated. The method of least squares was used for this purpose. The

Fig.3.3: Rose-Drago plot for 1:1 complex of 2,3-dichloro-1,4-naphthoquinone with o-Ethylaniline in dichloromethane.

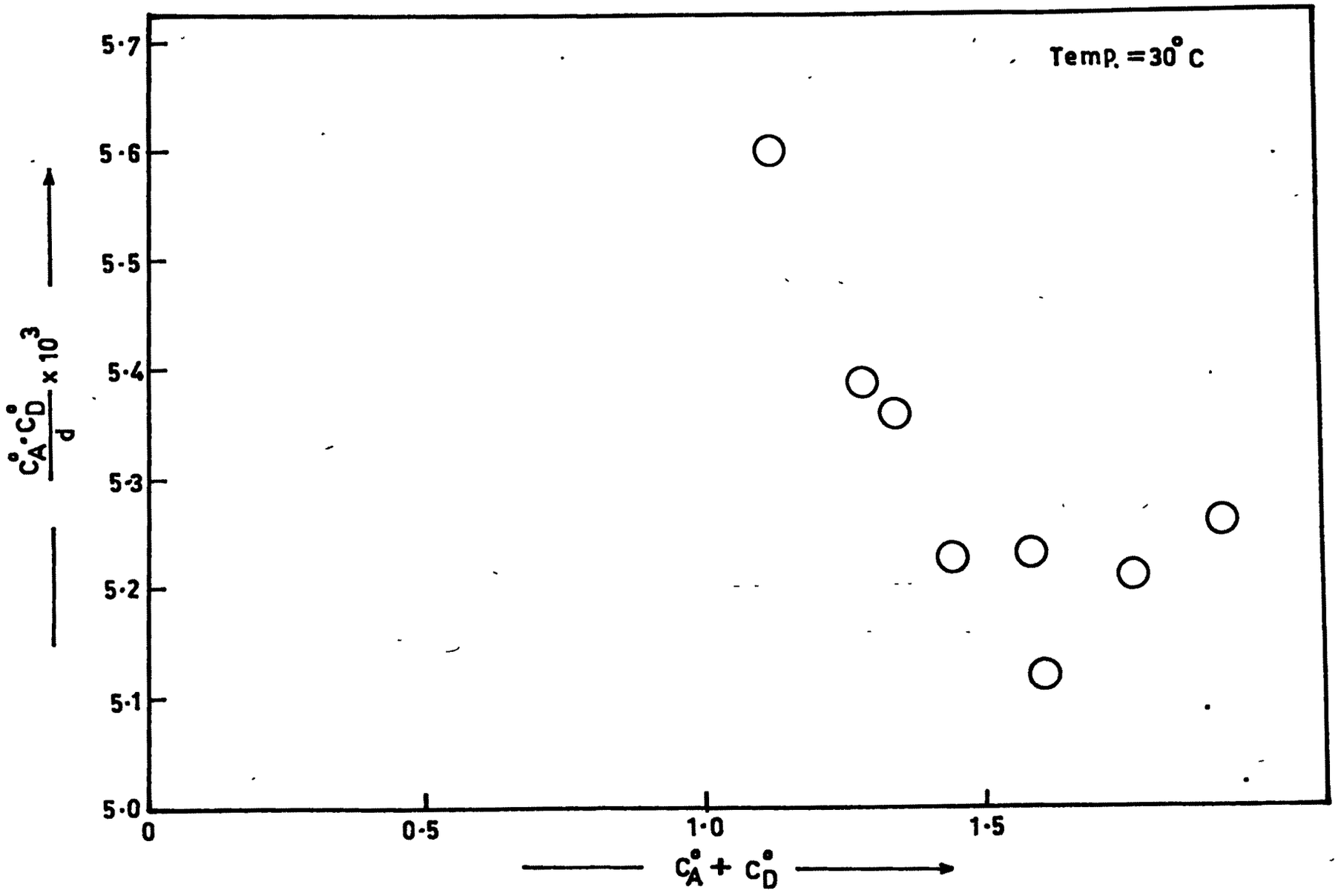
Temp. = 30° C
5·7
5·6
5·5
5·4
5·3
5·2
5·1
5·0
0
0·5
1·0
1·5
$\frac{C_A^\circ \cdot C_D^\circ}{d} \times 10^3$
$C_A^\circ + C_D^\circ$

Fig. 3·3

Fig. 3.4: Rose-Drago plot for 2:1 complex of 2,3-dichloro-1,4-naphthoquinone with o-Ethylaniline in dichloromethane.

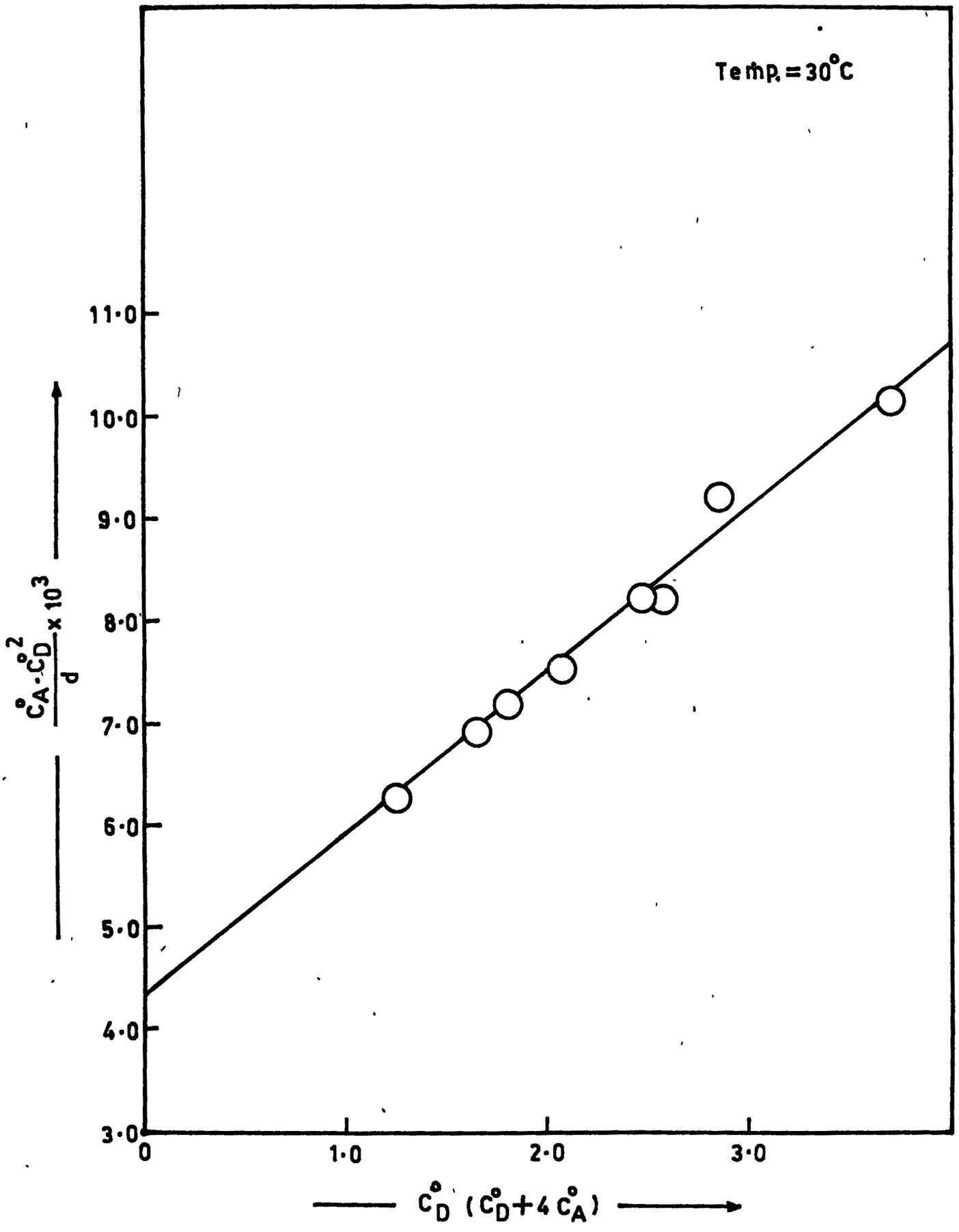
Temp. = 30°C
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
0
1·0
2·0
3·0
$\frac{c_A^\circ - c_D^{\circ 2}}{d} \times 10^3$
$c_D^\circ (c_D^\circ + 4 c_A^\circ)$

Fig. 3·4

Fig. 3.5: Rose-Drago plot for 2:1 complex of 2,3-dichloro-1,4-naphthoquinone with 2,6-dimethylaniline in dichloromethane.

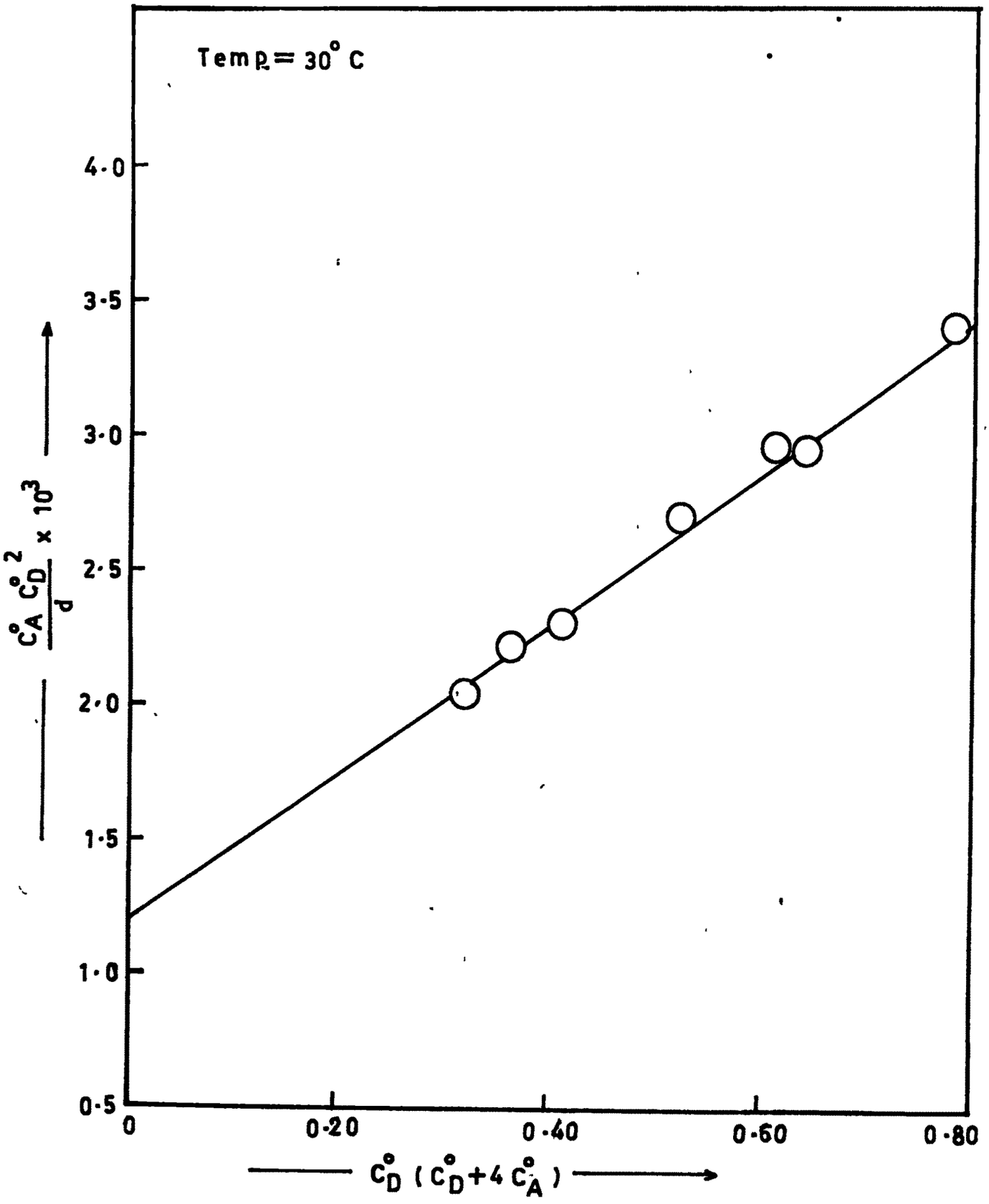
Temp.= 30° C
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
$\frac{C_A^\circ C_D^{\circ 2}}{d} \times 10^3$
0
0·20
0·40
0·60
0·80
$C_D^\circ (C_D^\circ + 4 C_A^\circ)$

Fig. 3·5

Table 3.2

Experimental data for the charge transfer interaction between 2,3-dichloro-1,4-naphthoquinone and o-Ethylaniline in dichloro-methane at different temperatures.

$\bar{\nu}_{max}$ = 21270 cm^{-1}; $C_A^o = 1.0 \times 10^{-3} M$

Sr. No.	C_D^o M.	d O.D.	$C_D^o[C_D^o+4\ C_A^o]$	$\frac{C_A^o.C_D^{o2}}{d}.10^3$	$C_A^o + C_D^o$	$\frac{C_A^o.C_D^o}{d}.10^3$
1	2	3	4	5	6	7
i) Temperature: 25°C						
1	1.12	0.2450	1.2589	5.1200	1.121	4.5714
2	1.21	0.2700	1.4689	5.4226	1.211	4.4815
3	1.28	0.2825	1.6435	5.7996	1.281	4.5309
4	1.35	0.3000	1.8279	6.0750	1.351	4.5000
5	1.44	0.3200	2.0794	6.4800	1.441	4.5000
6	1.60	0.3550	2.5664	7.2112	1.601	4.5070
7	1.76	0.3875	3.1046	7.9938	1.761	4.5419
8	1.92	0.4175	3.6941	8.8297	1.921	4.5988

contd.

Table 3.2 contd.

1	2	3	4	5	6	7
			ii) Temperature: 28°C			
1	1.12	0.225	1.259	5.575	1.121	4.9777
2	1.21	0.245	1.469	5.976	1.211	4.9387
3	1.28	0.270	1.643	6.068	1.281	4.7407
4	1.35	0.2825	1.828	6.451	1.351	4.7787
5	1.44	0.3050	2.079	6.798	1.441	4.7213
6	1.60	0.3200	2.566	8.000	1.601	5.0000
7	1.76	0.3550	3.105	8.725	1.761	4.9577
8	1.92	0.3875	3.694	9.513	1.921	4.9548
			iii) Temperature: 30°C			
1	1.12	0.2000	1.2589	6.2690	1.121	5.6000
2	1.28	0.2375	1.6435	6.8985	1.281	5.3894
3	1.34	0.2500	1.8010	7.1824	1.341	5.3600
4	1.44	0.2750	2.0790	7.5403	1.441	5.2363
5	1.57	0.3075	2.4720	8.0159	1.571	5.1057
6	1.60	0.3125	2.5660	8.1920	1.601	5.1200
7	1.76	0.3375	3.1046	9.1780	1.761	5.2148
8	1.92	0.3650	3.6941	10.0997	1.921	5.2602

Table 3.3

Experimental data for the charge transfer interaction between 2,3-dichloro-1,4-naphthoquinone and 2,6-dimethylaniline in dichloromethane at different temperatures.

$\bar{\nu}_{max}$ = 20200 cm^{-1}; C_A^o = 1.0 x 10^{-3} M

Sr. No.	C_D^o M.	d O.D.	$C_D^o[C_D^o+4\ C_A^o]$	$\frac{C_A^o.C_D^{o2}}{d}.10^3$	$C_A^o + C_D^o$	$\frac{C_A^o.C_D^o}{d}.10^3$
1	2	3	4	5	6	7
i) Temperature: 25°C						
1	0.48	0.1600	0.2323	1.440	0.481	3.000
2	0.56	0.1800	0.3158	1.742	0.561	3.111
3	0.64	0.1925	0.4122	2.122	0.641	3.316
4	0.72	0.2175	0.5213	2.367	0.721	3.287
5	0.80	0.2300	0.6432	2.783	0.801	3.478
6	0.84	0.2450	0.7089	2.880	0.841	3.428
7	0.88	0.2550	0.7779	3.038	0.881	3.451
8	0.96	0.2725	0.9254	3.401	0.961	3.542

contd.

Table 3.3 contd.

1	2	3	4	5	6	7
			ii) Temperature: 28°C			
1	0.48	0.1525	0.2323	1.5108	0.481	3.1475
2	0.56	0.1725	0.3158	1.8179	0.561	3.2464
3.	0.64	0.1850	0.4122	2.2140	0.641	3.4594
4	0.72	0.2150	0.5213	2.4111	0.721	3.3488
5	0.80	0.2325	0.6432	2.7527	0.801	3.4408
6	0.84	0.2475	0.7089	2.8509	0.841	3.3939
7	0.88	0.2550	0.7779	3.0368	0.881	3.4510
8	0.96	0.2750	0.9254	3.3512	0.961	3.4909
			iii) Temperature: 30°C			
1	0.56	0.1525	0.3158	2.0564	0.561	3.6721
2	0.60	0.1625	0.3624	2.2222	0.601	3.7037
3	0.64	0.1775	0.4122	2.3076	0.641	3.6056
4	0.72	0.1925	0.5213	2.6929	0.721	3.7403
5	0.78	0.2050	0.6146	2.9678	0.781	3.8049
6	0.80	0.2175	0.6432	2.9425	0.801	3.6782
7	0.88	0.2275	0.7779	3.4039	0.881	3.8681
8	0.96	0.2475	0.9254	3.7236	0.961	3.8788

experimental data for all these plots are given in tables 3.2 and 3.3. The formation constants and molar absorptivities have been listed in Table 3.4.

Table 3.4

Computed values of formation constants, $K_C^{AD_2}$ and molar absorptivities, $\epsilon_\lambda^{AD_2}$, of 2,3-dichloro-1,4-naphthoquinone complexes with o-Ethylaniline and 2,6-dimethylaniline in dichloromethane at different temperatures.

Sr. No.	Temperature °C	Formation constant $K_C^{AD_2}$ litre^2 mole^{-1}	Molar absorptivity, $\epsilon_\lambda^{AD_2}$, litre mole^{-1} cm^{-1}
		(i) o-Ethylaniline	
1	25	0.468	656.3
2	28	0.490	595.2
3	30	0.360	641.6
		(ii) 2,6-dimethylaniline	
1	25	3.170	350.5
2	28	2.543	385.2
3	30	2.312	360.6

Fig. 3.6: Modified van't Hoff plot for 2,3-dichloro-1,4-naphthoquinone complex with 2,6-dimethylaniline in dichloromethane.

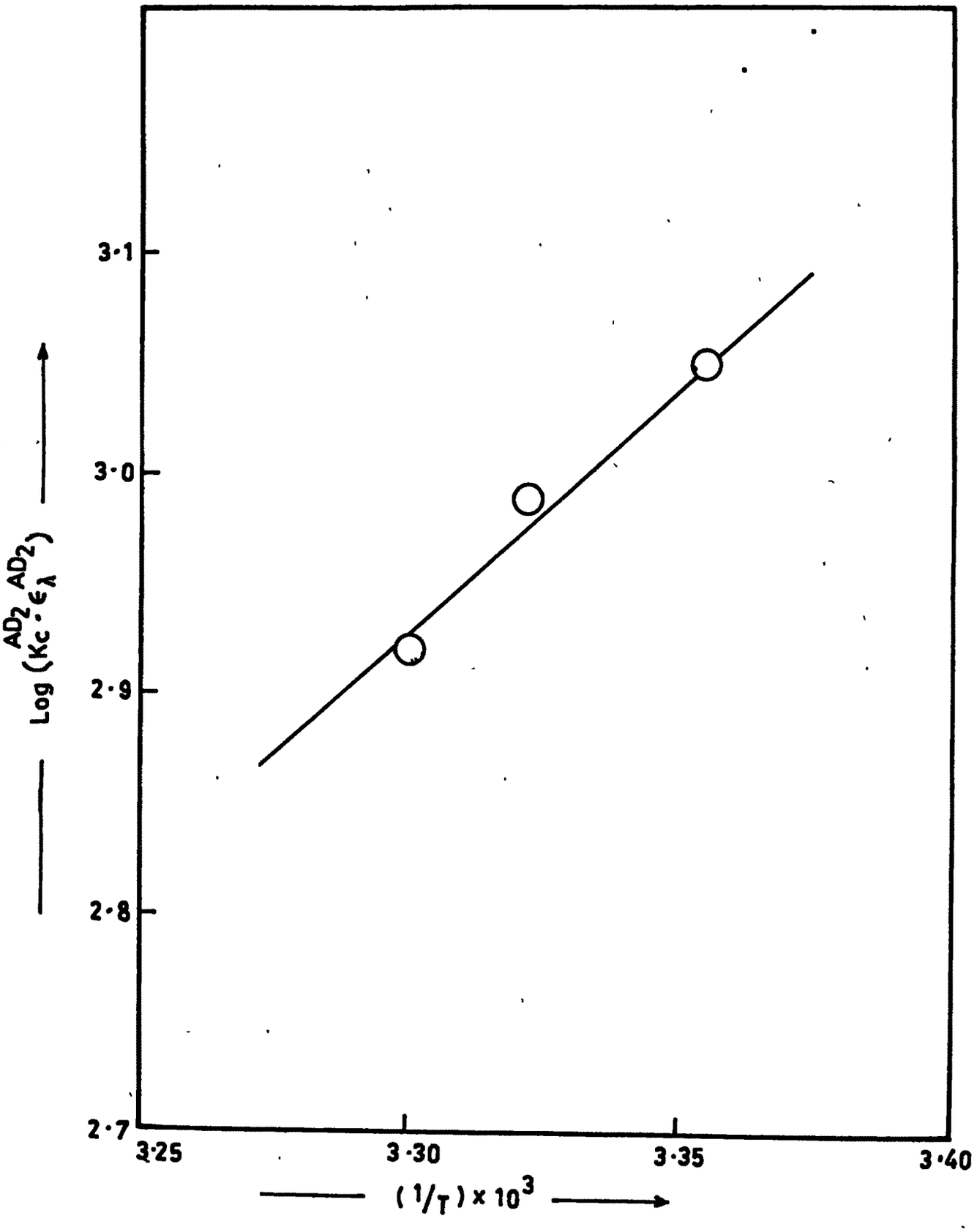
3·1
3·0
2·9
2·8
2·7
3·25
3·30
3·35
3·40
Log ($K_c^{AD_2} \cdot \epsilon_\lambda^{AD_2}$)
$(1/T) \times 10^3$

Fig. 3·6

b) Donor-acceptor equilibria involving 2,3-dichloro-5-nitro-1,4-naphthoquinone acceptor

The acceptor was prepared as explained in Chapter-II. o-Ethylaniline and 2,6-dimethyl aniline were used as electron donors. On mixing the solutions of donors with the solutions of acceptors in dichloromethane characteristic colours were developed indicating the formation of complexes in each case. These complexes are characterised by intermolecular charge transfer absorption bands appearing in the visible region. Typical charge transfer spectra are shown in Figs. 3.7 and 3.8. The charge transfer absorption bands appear in the region where neither the donor nor the acceptor species absorb. The peak frequencies $\bar{\nu}_{max}$, of these complexes are given in table 3.5.

Table 3.5

Peak frequencies, $\bar{\nu}_{max}$, of the complexes of 2,3-dichloro-5-nitro-1,4-naphthoquinone with o-Ethylaniline and 2,6-dimethylaniline in dichloromethane.

Sr.No.	Donor	λ_{max} (nm)	$\bar{\nu}_{max}$ (cm^{-1})
1	o-Ethylaniline	525	19,040
2	2,6-dimethylaniline	560	17,850

Concentration of the acceptor was about 1.0×10^{-3} M

Fig. 3.7: Absorption spectra of 2,3-dichloro-5-nitro-1,4-naphthoquinone complex with o-Ethylaniline in dichloromethane at various concentrations of o-Ethylaniline. The concentration of the acceptor is constant. In all the runs $C_D^o \gg C_A^o$.

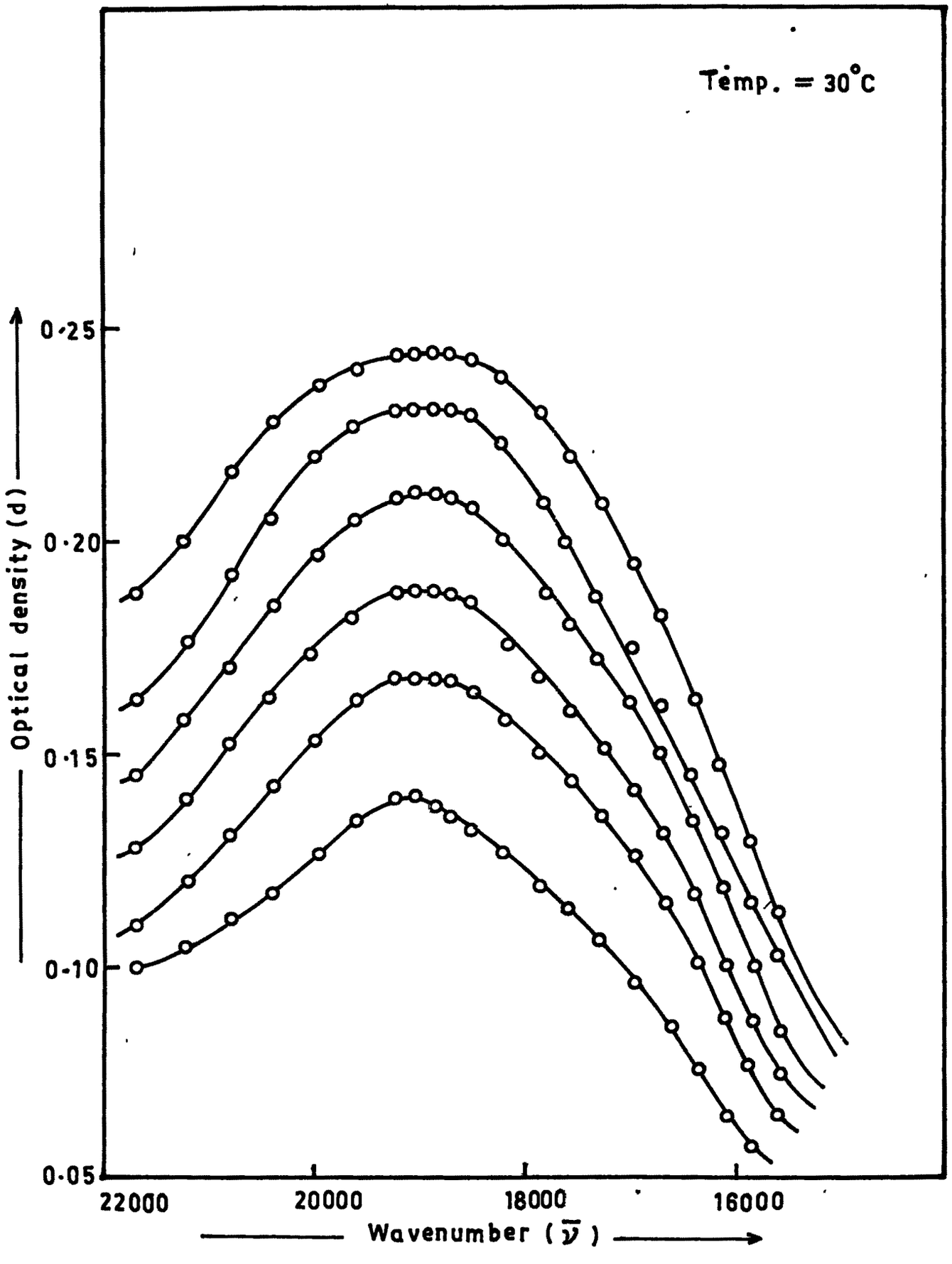
Temp. = 30°C
Optical density (d)
0·25
0·20
0·15
0·10
0·05
22000
20000
18000
16000
Wavenumber ($\bar{\nu}$)

Fig. 3·7

3908
A

Fig. 3.8: Absorption spectra of 2,3-dichloro-5-nitro-1,4-naphthoquinone complex with 2,6-dimethylaniline in dichloromethane at various concentrations of the donor. The concentration of the acceptor is constant. In all the runs $C_D^o \gg C_A^o$.

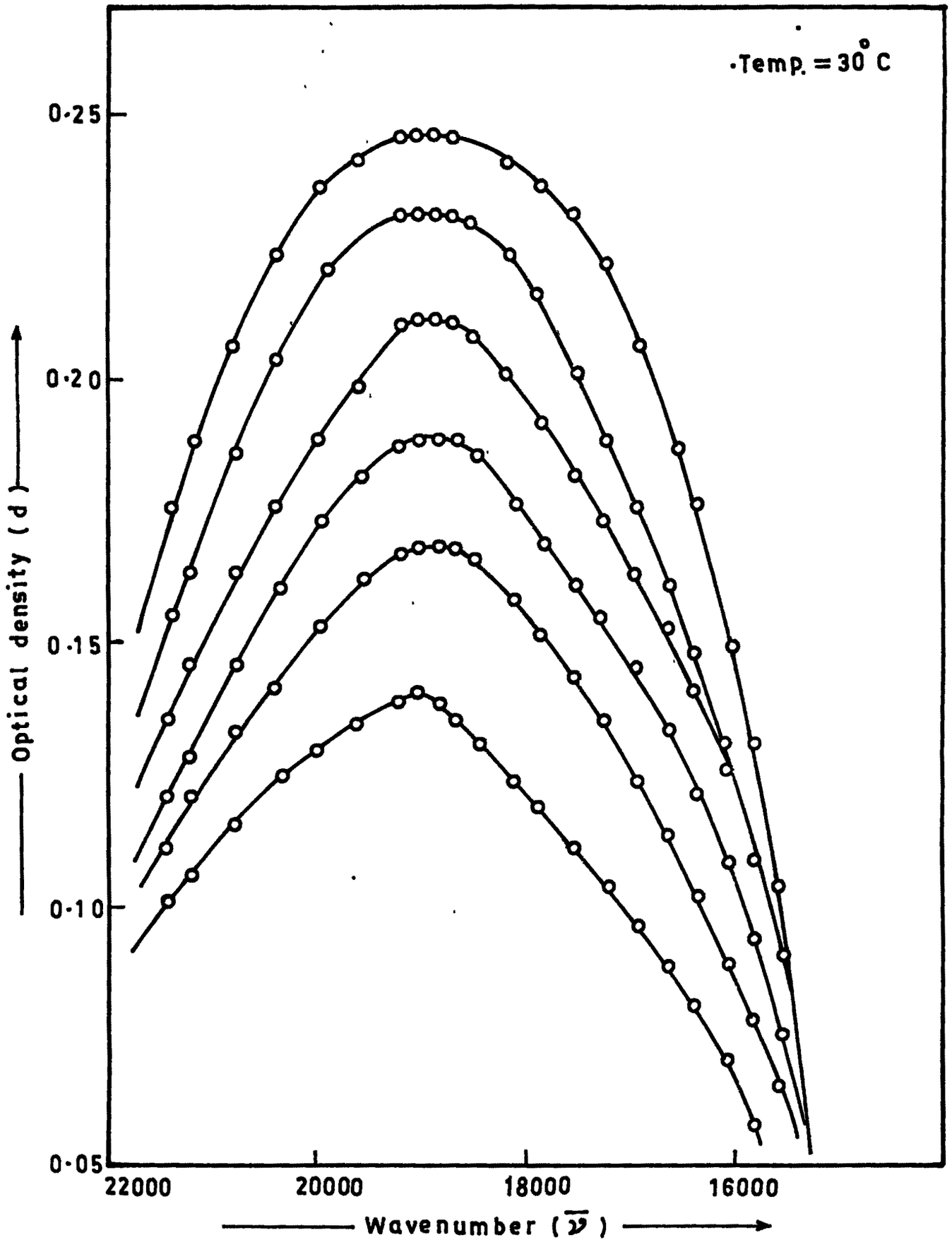
Temp. = 30° C
0·25
0·20
0·15
0·10
0·05
Optical density (d)
22000
20000
18000
16000
Wavenumber ($\bar{\nu}$)

Fig. 3·8

which was kept constant whereas the concentration of the donor was varied in each series of measurements. Concentration of the donor was much higher than the concentration of the acceptor. Spectra were recorded at different temperatures. Experimental data showed that the absorption peak frequencies, $\bar{\nu}_{max}$, values are almost unaffected by changes in temperature and concentration of the donor. Dichloromethane solvent was used in the reference cell.

The data were analysed in accordance with equation (1.17) which gives Rose-Drago plots for 1:1 stoichiometric complexes. Fig. 3.9 shows typical Rose-Drago plot for 1:1 stoichiometric complexes of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 2,6-dimethylaniline in dichloromethane. Non-linearity of the plots clearly indicates the existence of complexes other than 1:1 stoichiometry. The data were then analysed in accordance with the equation (1.20) which gives Rose-Drago plot for 2:1 (donor-acceptor) stoichiometric complexes. Typical plots are shown in Figs. 3.10 and 3.11. The linearity of the plots suggests that there exists only 2:1 stoichiometric complex. Formation constants, $K_C^{AD_2}$ and molar absorptivities $\epsilon_\lambda^{AD_2}$ have been computed from these plots. The values of $K_C^{AD_2}$ and $\epsilon_\lambda^{AD_2}$ have been listed in Table 3.6. These values were calculated by using the method of least squares. The experimental data in respect of Figs. 3.9, 3.10 and 3.11 are given in Tables 3.7 and 3.8.

Fig. 3.9: Rose-Drago plot for 1:1 complex of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 2,6-dimethylaniline in dichloromethane.

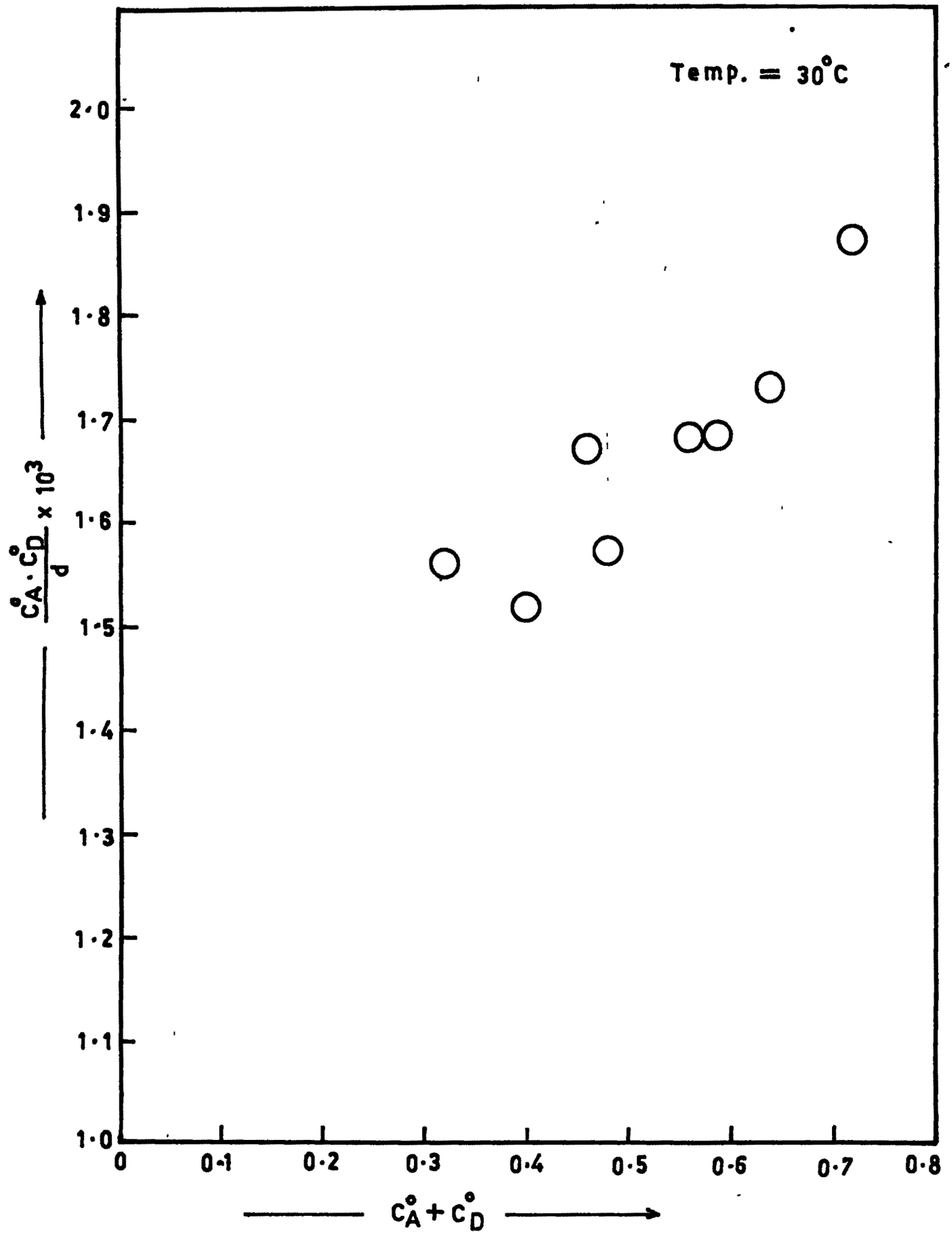
Temp. = 30°C
2·0
1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
$\frac{c_A^\circ \cdot c_D^\circ}{d} \times 10^3$
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
$c_A^\circ + c_D^\circ$

Fig. 3·9

Fig. 3.10: Rose-Drago plot for 2:1 complex of 2,3-dichloro-5-nitro-1,4-naphthoquinone with o-Ethylaniline in dichloromethane.

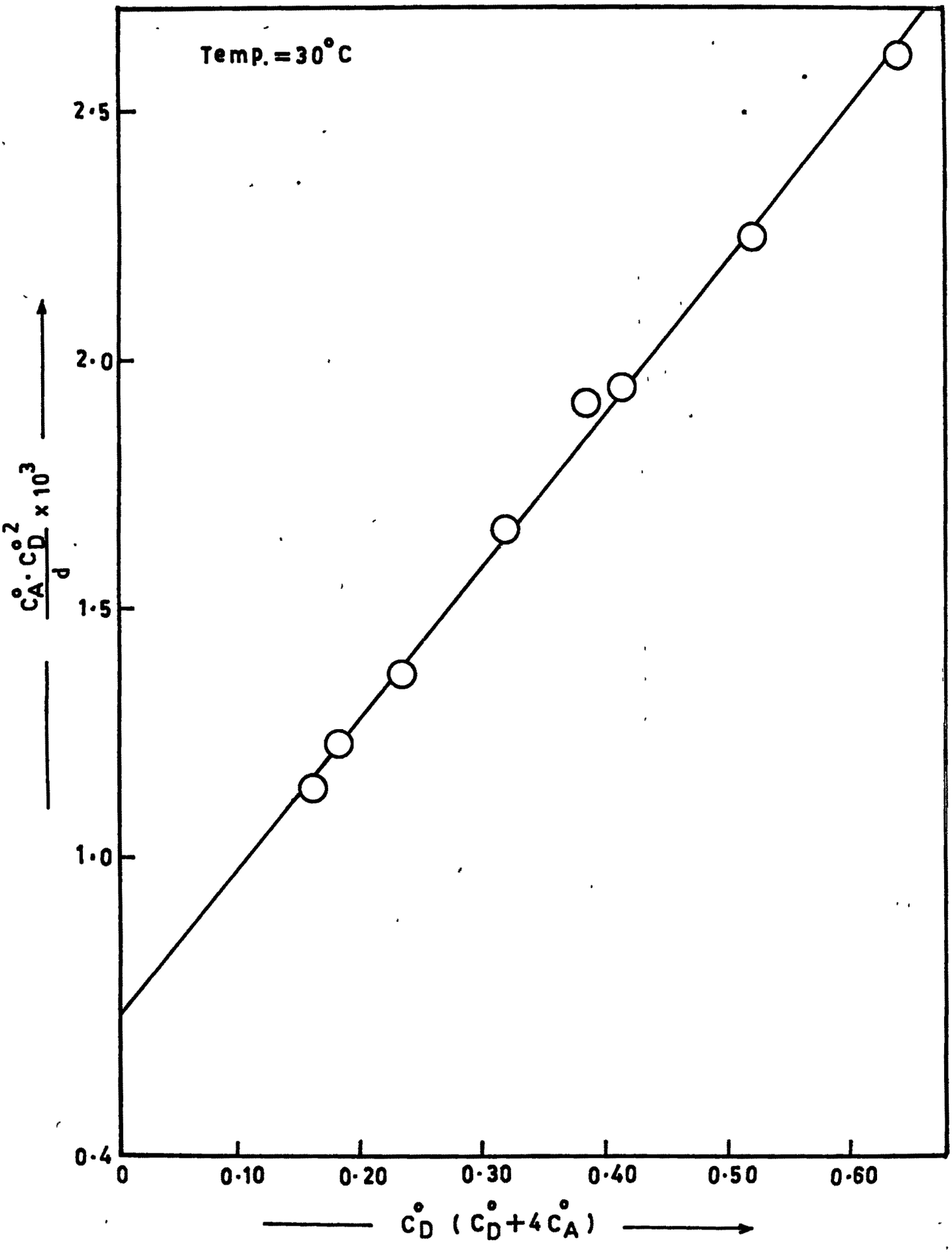
Temp. = 30°C
2·5
2·0
1·5
1·0
0·4
$\frac{C_A^\circ \cdot C_D^{\circ 2}}{d} \times 10^3$
0
0·10
0·20
0·30
0·40
0·50
0·60
$C_D^\circ\ (C_D^\circ + 4C_A^\circ)$

Fig. 3·10

Fig. 3.11: Rose-Drago plot for 2:1 complex of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 2,6-dimethylaniline in dichloromethane.

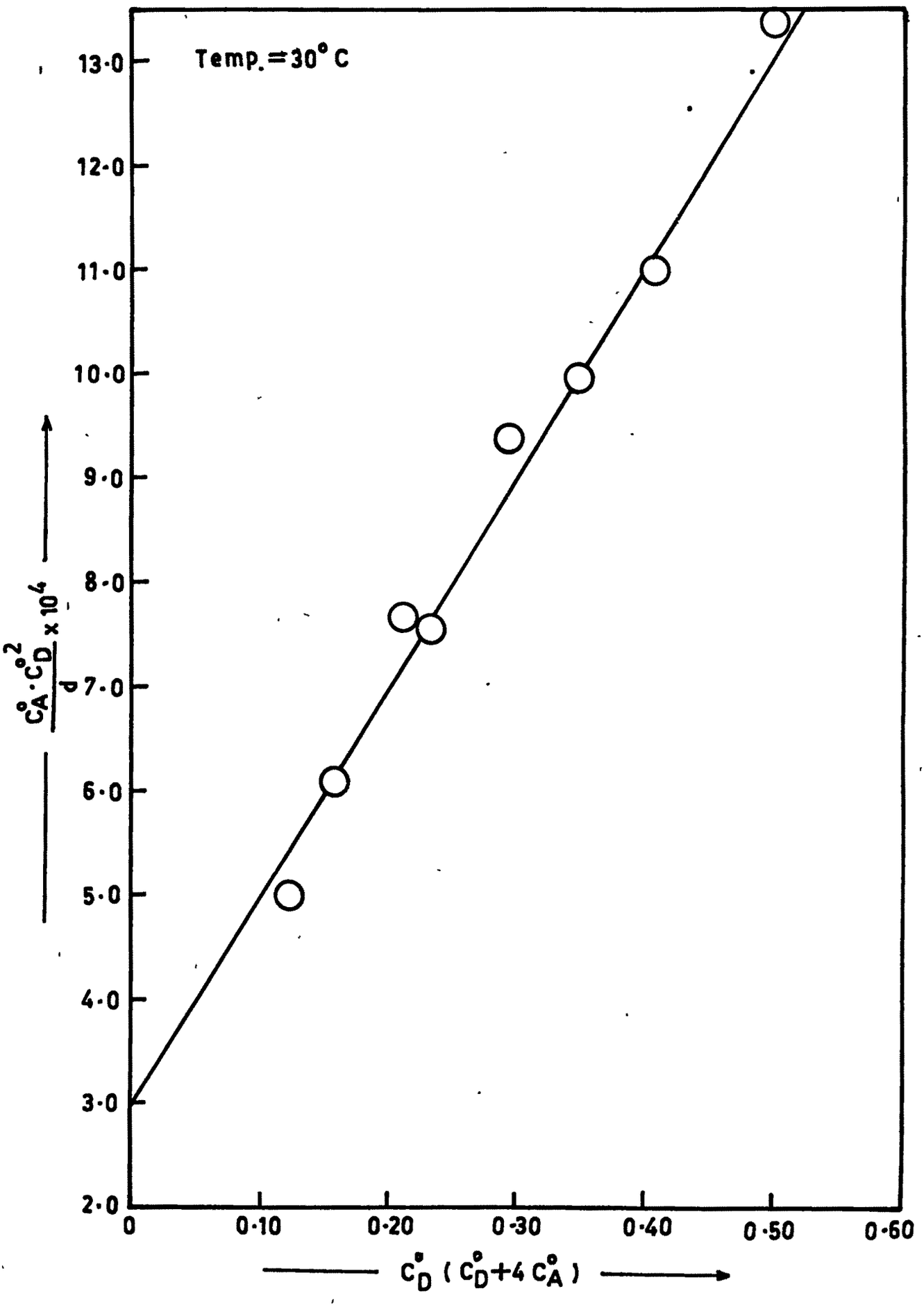
Temp.=30° C
13·0
12·0
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
$\frac{C_A^\circ \cdot C_D^{\circ 2}}{d} \times 10^4$
0
0·10
0·20
0·30
0·40
0·50
0·60
$C_D^\circ\ (C_D^\circ + 4\,C_A^\circ)$

Fig. 3·11

Table 3.6

Computed values of formation constants, $K_C^{AD_2}$, and the molar absorptivities, ϵ^{AD_2} of 2,3-dichloro-5-nitro-1,4-naphthoquinone complexes with o-Ethylaniline and 2,6-dimethylaniline in dichloromethane at different temperatures.

Sr. No.	Temperature °C	Formation constant, $K_C^{AD_2}$ litre^2 mole^{-2}	Molar absorptivity, $\epsilon_\lambda^{AD_2}$ litre mole^{-1}cm^{-1}
		(i) o-Ethylaniline	
1	23	7.533	380.4
2	25	6.504	357.5
3	28	5.806	332.7
4	30	4.983	327.3
		(ii) 2,6-dimethylaniline	
1	23	6.208	598.8
2	25	6.530	549.4
3	28	6.288	537.6
4	30	6.880	506.3

Thermodynamic quantities such as free energy, ethalpy and entropy of formation of these complexes were computed by using the method of least squares. For this purpose modified van't Hoff plots i.e., log ($K_C^{AD_2}.\epsilon_\lambda^{AD_2}$) Vs T^{-1} were made.

Table 3.7

Experimental data for the charge transfer interaction between 2,3-dichloro-5-nitro-1,4-naphthoquinone and o-Ethylaniline in dichloromethane at different temperatures.

$\bar{\nu}_{max}$ = 19040 cm^{-1}; C^o = 1.0 x 10^{-3}M.

Sr. No.	C_D^o M.	d O.D.	$C_D^o[C_D^o+4\ C_A^o]$	$\frac{C_A^o.C_D^{o2}}{d}.10^4$	$C_A^o + C_D^o$	$\frac{C_A^o.C_D^o}{d}.10^3$
1	2	3	4	5	6	7
		i) Temperature: 23°C				
1.	0.40	0.2200	0.1616	7.272	0.401	1.8182
2	0.48	0.2375	0.2323	9.701	0.481	2.0210
3	0.53	0.2550	0.2830	11.015	0.531	2.0784
4	0.56	0.2625	0.3158	11.946	0.561	2.1333
5	0.64	0.2800	0.4122	14.628	0.641	2.2857
6	0.70	0.2950	0.4928	16.610	0.701	2.3729
7	0.72	0.3000	0.5213	17.280	0.721	2.4000
8	0.80	0.3200	0.6432	20.000	0.801	2.5000
		ii) Temperature 25°C				
1	0.40	0.1850	0.1616	8.648	0.401	2.1621
2	0.48	0.2125	0.2323	10.842	0.481	2.2588
3	0.53	0.2300	0.2830	12.213	0.531	2.3043
4	0.56	0.2375	0.3158	13.204	0.561	2.3578
5	0.64	0.2575	0.4122	15.906	0.641	2.4854
6	0.70	0.2700	0.4928	18.148	0.701	2.5926
7	0.72	0.2750	0.5213	19.023	0.721	2.6181
8	0.80	0.2925	0.6432	22.068	0.801	2.7350

contd..

Table 3.7 contd.

1	2	3	4	5	6	7
			iii) Temperature: 28°C			
1	0.40	0.1700	0.1616	9.412	0.401	2.3529
2	0.48	0.1900	0.2323	12.126	0.481	2.5263
3	0.53	0.2025	0.2830	13.872	0.531	2.6173
4	0.56	0.2100	0.3158	14.933	0.561	2.6666
5	0.64	0.2300	0.4122	17.808	0.641	2.7826
6	0.70	0.2425	0.4928	20.206	0.701	2.8866
7	0.72	0.2475	0.5213	20.945	0.721	2.9091
8	0.80	0.2675	0.6432	23.925	0.801	2.9906
			iv) Temperature: 30°C			
1	0.40	0.1400	0.1616	11.428	0.401	2.8571
2	0.43	0.1500	0.1866	12.327	0.431	2.8666
3	0.48	0.1675	0.2323	13.755	0.481	2.8656
4	0.56	0.1875	0.3158	16.725	0.561	2.9800
5	0.62	0.2000	0.3869	19.220	0.621	3.1000
6	0.64	0.2100	0.4122	19.504	0.641	3.0476
7	0.72	0.2300	0.5213	22.539	0.721	3.0315
8	0.80	0.2450	0.6432	26.120	0.801	2.9629

Table 3.8

Experimental data for the charge transfer-interaction between 2,3-dichloro-5-nitro-1,4-naphthoquinone and 2,6-dimethylaniline in dichloromethane at different temperatures.

$\bar{\nu}_{max}$ = 17850 cm^{-1}; C_A^o = 1.0 x 10^{-3}M.

Sr. No.	C_D^o M.	d O.D.	$C_D^o[C_D^o+4\ C_A^o]$	$\frac{C_A^o.C_D^{o\,2}}{d}.10^4$	$C_A^o + C_D^o$	$\frac{C_A^o.C_D^o}{d}.10^3$
1	2	3	4	5	6	7
		i) Temperature: 23°C				
1	0.32	0.2575	0.1037	3.977	0.321	1.242
2	0.40	0.2975	0.1616	5.378	0.401	1.344
3	0.44	0.3250	0.1954	5.957	0.441	1.354
4	0.48	0.3400	0.2323	6.776	0.481	1.412
5	0.56	0.3775	0.3158	8.307	0.561	1.483
6	0.64	0.4150	0.4122	9.870	0.641	1.542
7	0.72	0.4500	0.5213	11.520	0.721	1.600
8	0.78	0.4875	0.6115	12.480	0.781	1.600
		ii) Temperatire: 26°C				
1	0.32	0.2250	0.1037	4.551	0.321	1.4220
2	0.40	0.2875	0.1616	5.565	0.401	1.3913
3	0.44	0.3000	0.1954	6.453	0.441	1.4666
4	0.48	0.3300	0.2323	6.981	0.481	1.4545
5	0.56	0.3650	0.3158	8.533	0.561	1.5342
6	0.64	0.3925	0.4122	10.778	0.641	1.6305
7	0.72	0.4175	0.5213	12.416	0.721	1.7245
8	0.78	0.4500	0.6115	13.520	0.781	1.7333

contd..

Table 3.8 contd.

1	2	3	4	5	6	7
			iii) Temperature: 28°C			
1	0.32	0.2150	0.1037	4.763	0.321	1.488
2	0.40	0.2750	0.1616	5.818	0.401	1.454
3	0.44	0.2875	0.1954	6.734	0.441	1.530
4	0.48	0.3175	0.2323	7.257	0.481	1.512
5	0.56	0.3475	0.3158	9.024	0.561	1.611
6	0.64	0.3800	0.4122	10.779	0.641	1.684
7	0.72	0.4025	0.5213	12.879	0.721	1.789
8	0.78	0.4325	0.6115	14.067	0.781	1.803
			iv) Temperature: 30°C			
1	0.32	0.2050	0.1037	4.995	0.321	1.5609
2	0.40	0.2625	0.1616	6.095	0.401	1.5238
3	0.46	0.2750	0.2134	7.695	0.461	1.6727
4	0.48	0.3050	0.2323	7.554	0.481	1.5737
5	0.56	0.3325	0.3158	9.431	0.561	1.6842
6	0.59	0.3500	0.3505	9.946	0.591	1.6857
7	0.64	0.3700	0.4122	11.070	0.641	1.7297
8	0.72	0.3850	0.5213	13.464	0.721	1.8701

Typical plots are shown in Figs. 3.6 and 3.12. The values of ΔG^{o}, ΔH^{o} and ΔS^{o} have been listed in Table 3.9. The data for modified vant's Hoff plots are given in Table 3.10.

Table 3.9

Free energies ΔG^{o}, enthalpies, ΔH^{o}, and entropies, ΔS^{o} of formation of complexes between 2,3-dichloro-5-nitro-1, 4-naphthoquinone and o-Ethylaniline and 2,6-dimethylaniline in dichloromethane at 303 ^{o}K

Sr. No.	System	$-\Delta G^{o}$ Kcal $mole^{-1}$	$-\Delta H^{o}$ Kcal $mole^{-1}$	$-\Delta S^{o}$ Cal deg^{-1} $mole^{-1}$
1)	2,3-dichloro-5-nitro-1,4-naphthoquinone + o-Ethylaniline	0.967	15.73	48.7
2)	2,3-dichloro-5-nitro-1,4-naphthoquinone + 2,6-dimethylaniline	1.161	11.40	33.8

The oscillator strength (f) which is a measure of the integrated intensity of the charge transfer band and the transition dipole, $\mu_{(EN)}$, were computed by using equations (1.9) and (1.10) respectively, viz.,

Fig. 3.12: Modified van't Hoff plot for 2,3-dichloro-5-nitro-1,4-naphthoquinone with o-Ethylaniline in dichloromethane.

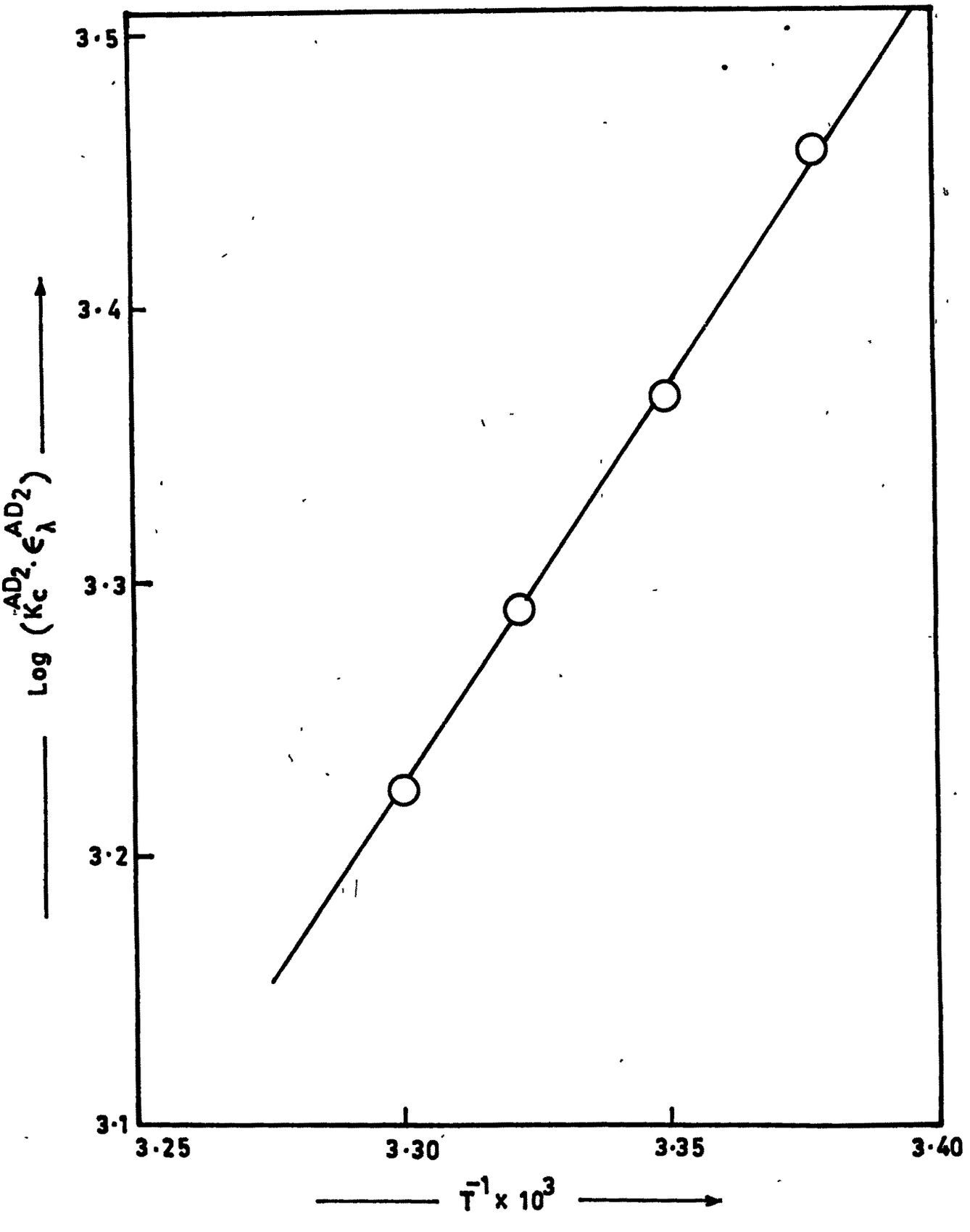
3·5
3·4
3·3
3·2
3·1
Log ($K_c^{AD_2} \cdot \epsilon_\lambda^{AD_2}$)
3·25
3·30
3·35
3·40
$T^{-1} \times 10^3$

Fig. 3·12

Table 3.10

Data for the modified van't Hoff plots.

Sr. No.	Temp. T.K.	$\frac{1}{T} \times 10^3$	$K_C^{AD_2} \cdot \epsilon_\lambda^{AD_2}$	$\log (K_C^{AD_2} \cdot \epsilon_\lambda^{AD_2})$
	i) 2,3-dichloro-1,4-naphthoquinone-2,6-dimethylaniline system.			
1	298	3.355	1130.0	3.0531
2	301	3.322	979.6	2.9911
3	303	3.300	833.7	2.9210
	ii) 2,3-dichloro-5-nitro-1,4-naphthoquinone-o-Ethylaniline system.			
1	296	3.378	2865.0	3.4572
2	298	3.356	2325.0	3.3664
3	301	3.322	1931.0	3.2860
4	303	3.300	1631.0	3.2125

$$f \simeq 4.32 \times 10^{-9} \times \epsilon_{max} \cdot \Delta\bar{\nu}_{1/2}$$

and

$$\mu_{(EN)} \simeq 0.0958 \left(\frac{\epsilon_{max} \cdot \Delta\bar{\nu}_{1/2}}{\bar{\nu}_{max}} \right)^{1/2}$$

where ϵ_{max} is the molar absorptivity, $\Delta\bar{\nu}_{1/2}$ is the half band width and $\bar{\nu}_{max}$ is the peak frequency of the charge transfer absorption band. Oscillator strengths, half band widths and transition dipole for two systems of 2,3-dichloro-5-nitro-1,4-naphthoquinone are given in Tables 3.11 and 3.12.

Table 3.11

Oscillator strength (f), half band width, ($\Delta\bar{\nu}_{1/2}$), and transition dipole (μ_{EN}) of 2,3-dichloro-5-nitro-1,4-naphthoquinone and o-Ethylaniline charge transfer interaction in dichloromethane at 30°C

$\bar{\nu}_{max}$ = 19040 cm^{-1}, ϵ_{max} = 327.3 litre $mole^{-1}cm^{-1}$

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

Sr. No.	C_D^o M.	$\Delta\bar{\nu}_{1/2}$ cm^{-1}	f x 10^3	$\mu_{(EN)}$ (Debye)
1	0.40	4,100	5.797	0.804
2	0.48	5,000	7.070	0.888
3	0.56	5,200	7.352	0.906
4	0.64	5,300	7.494	0.914
5	0.72	5,400	7.635	0.923
6	0.80	5,700	8.059	0.948

Average half band width, $\Delta\bar{\nu}_{1/2}$ = 5117

Average oscillator strength, f = 7.201

Average transition dipole $\mu_{(EN)}$ = 0.897

Table 3.12

Oscillator strength (f), half band width ($\Delta\bar{\nu}_{1/2}$), and transition dipole (μ_{EN}) of 2,3-dichloro-5-nitro-1,4-naphthoquinone and 2,6-dimethylaniline charge transfer interaction in dichloromethane at 30°C.

$\bar{\nu}_{max}$ = 17,850 cm^{-1}, ϵ_{max} = 506.3 litre $mole^{-1}$ cm^{-1}

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

Sr. No.	C_D^o M	$\Delta\bar{\nu}_{1/2}$ cm^{-1}	f x 10^3	$\mu_{(EN)}$ (Debye)
1	0.32	4,650	1.017	1.099
2	0.40	5,000	1.094	1.141
3	0.48	5,150	1.127	1.157
4	0.56	5,300	1.159	1.174
5	0.64	5,400	1.182	1.185
6	0.72	5,700	1.247	1.217

Average half band width, $\Delta\bar{\nu}_{1/2}$ = 5191

Average oscillator strength, f = 1.187

Average transition dipole $\mu_{(EN)}$ = 1.162