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Spectrophotometric Studies of Charge Transfer Complex between *p*-Chloranil and Certain Aromatic Amines at 302 K

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Spectrophotometric studies of charge transfer complexation between *p*-chloranil and aromatic amines like N,N-dimethyl amine, N-methyl amine, *o*-toluidine, benzyl amine and diphenyl amine have been carried out in chioroform medium. All the complexes show charge transfer band in the visible region and they form 1 : 1 complexes of *n*-π type. The relevant spectral parameters for the charge transfer complexes like association constant, Gibb's free energy, molar extincion coefficient, ionisation potential and resonance energy were calculated. A comparative study on the evaluation of association constant is investigated by modified B-H, Scott and F-H-W equations, besides proposing a semiempirical McConnel equation.

INTRODUCTION

The presence of different functionalities as substituents in organic molecules modifies the electronic charge distribution and hence in some molecules availability of electrons is increased (donor) while in others it is decreased (acceptor). When these molecules come into contact either directly or through suitable solvent, appreciable interaction occurs between the donor and the acceptor leading to perceptible colouration, because of charge transfer or electron donor-acceptor complex[1, 2]. The components of the complex are presumably held together by forces arising from a no bond resonance involving dispersion, with a structure in which there is donation of electrons from one molecule to another. This leads to excited states not corresponding to higher electronic levels in either component separately but however it is characteristic of the complex as a whole. Hence the electronic transition between these states results in absorption in visible or near visible region of the electromagnetic spectrum. In view of the diverse applications of charge transfer complexes in semi-conductor7s[3, 4], hormone drug activities[5–8] in cell mediated metabolism and more important so in nonlinear optics[9–11], considerable interest was shown in the recent past which culminated in several monographs[12–16].

EXPERIMENTAL

The chemicals used in the study are N,N-dimethylamine (NNDMA) (E. Merck), N-methylamine (NMA) (Schurchardt, Zur Synthesis), benzylamine (BAM) (SD's Fine Chemicals), *o*-toluidine (OTE) (Ranbaxy Laboratories) diphenyl amine (DPA) (E. Merck), chloroform (CF) (Glaxo Laboratories) and chloranil (CAL) (Scissco Chemical Industries) which were purified by standard methods[17].

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The donors are polar and the solvent has appreciable polarisability. The absorption spectrum of the pure compounds, *viz.*, NNDMA, DMA, OTE, BAM, DPA and CAL in chloroform solvent was recorded in a double beam spectrometer (Shimadzu UV-Vis 160, Japan) using chloroform as reference.

The λ_{max} was found to be 255.4, 249.6, 247.5, 259.6, 286.6 and 292.5 nm respectively. The charge transfer band, λ_{CT}, for NNDMA-CAL, NMA-CAL, OTE-CAL, BAM-CAL and DPA-CAL occurs at 652.5, 599.5, 561.2, 532 and 656 nm respectively. Since λ_{CT} is well resolved and distinct from λ_{max}, spectrophotometric studies prove to be a convenient means to investigate. Stock solutions of the donors and acceptors were prepared and a series of solution mixtures for each donor-acceptor system was pepared in such a way that the donor concentration is by far greater than the acceptor concentration as demanded by the theory, while at the same time keeping the total volume of the solution constant. The absorbance (d) for each concentration and for each system was monitored at the respective λ_{CT}. The absorbance values for each system and for each concentration are shown in Table-1.

TABLE-1

Solvent: Chloroform; Temperature 302 K

NNDMA-CAL		NMA-CAL		OTE-CAL		DPA-CAL		BAM-CAL	
$C_A^0 = 1.518$ mM		$C_A^0 = 1.396$ mM		$C_A^0 = 0.931$ mM		$C_A^0 = 0.898$ mM		$C_A^0 = 0.101$ mM	
C_D^0	d	C_D^0	d	C_D^0	d	C_D^0	d	C_D^0	d
0.250	0.689	0.250	0.760	0.249	0.349	0.247	0.200	0.301	0.243
0.375	0.907	0.375	0.993	0.373	0.473	0.370	0.273	0.451	0.346
0.500	1.090	0.500	1.186	0.498	0.563	0.494	0.349	0.602	0.250
0.625	1.267	0.626	1.339	0.622	0.646	0.617	0.411	0.903	0.256
0.745	1.394	0.751	1.488	0.747	0.715	0.740	0.464	1.204	0.262
0.875	1.516	0.876	1.579	0.871	0.772	0.863	0.512	1.505	0.268
0.999	1.603	1.000	1.725	0.995	0.848	0.987	0.573	1.805	0.274
1.125	1.711	1.126	1.772	1.120	0.891	1.111	0.612	—	—
1.250	1.781	1.251	1.915	1.244	0.954	1.234	0.659	—	—

C_A^0 and C_D^0 are initial conc. of donor and acceptor.

RESULTS AND DISCUSSION

Analyses of the data for all the five systems were investigated by the equations proposed by modified Benesi-Hildebrand[18] (B-H), Foster-Hammick-Wardley[19] (F-H-W) and Scott[20]. The plots for all the systems are given in Figures 1–3. The plots clearly predict the charge transfer complex stoichiometery to be 1 : 1. This is in good agreement with the theory. Further the experimental results clearly reveal absence of higher order complexes as borne out by F-H-W plots, since the plots, *viz.*, d/C_D^0 versus d and $(d/C_D^0)^2$ versus d are curves (unpublished work). It has been inferred that the complex formed is of n-π type. The association constant, K_c^{AD} and

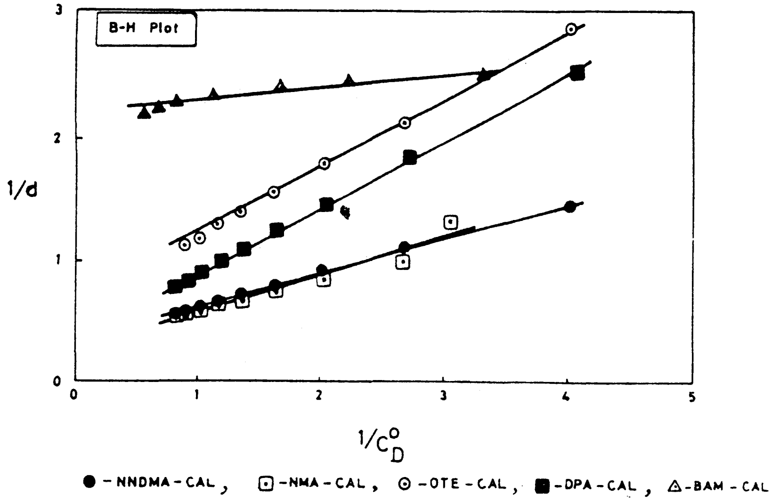

Fig. 1

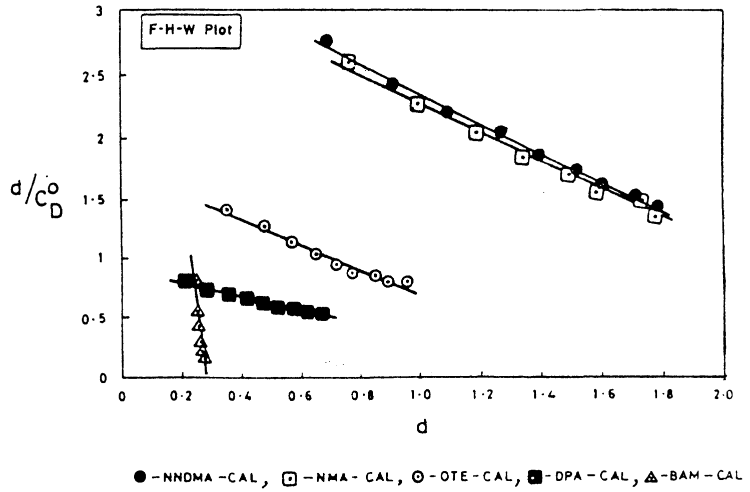

Fig. 2

molar extinction coefficient, $\varepsilon_{max}^{\lambda}$, were calculated from the experimental data and are shown in Table-2. Analysis by LS (Least Square) fitting for each system gives a fairly linear correlation with a significient correlation coefficient, $|r| = 0.99$. Analysis of the result shows that there is a close agreement among K_c^{AD} and $\varepsilon_{max}^{\lambda}$ from all the three methods. The plot of charge transfer energy (E_{CT}) versus the literature value of the ionisation potential (I_P) is found linear as shown in Figure 4. This clearly validates the McConnell equation[21]. The calculated ionisation potential agrees with the literature value and hence a semiempirical equation, *viz.*, $E_{CT} = 1.338\, I_P + 7.772$ has been suggested for the systems studied for the said

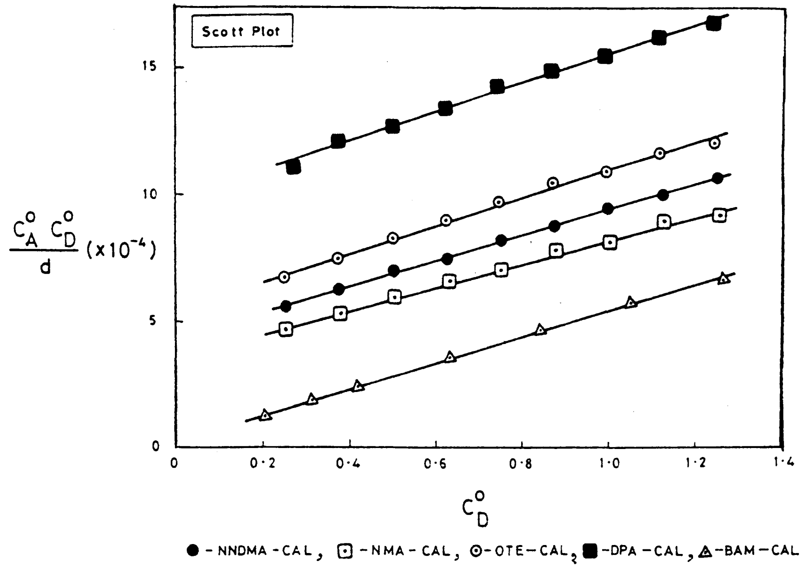

Fig. 3

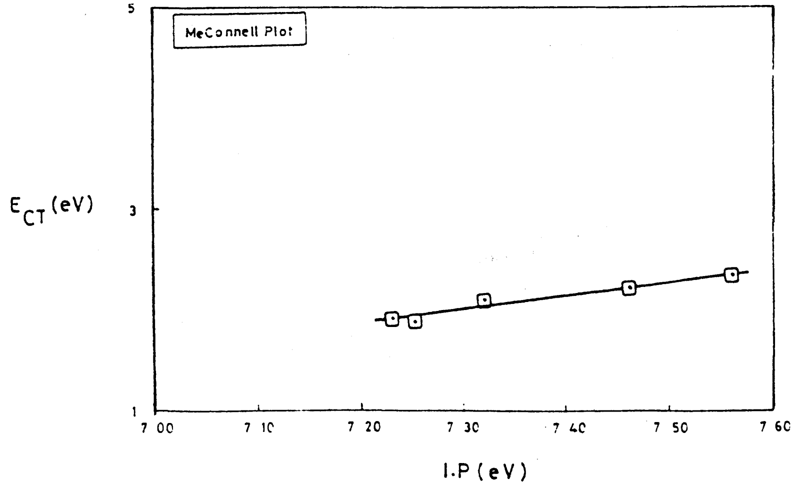

Fig. 4

acceptor. It has been found that the charge transfer energy increases with ionisation potential as reported by Roy and Seal[22]. The interesting observation is that the donor basicity (pK_a) for the systems DPA, OTE, NMA, NNDMA, and BAM increases in the order $0.8 < 4.38 < 4.84 < 5.15 < 9.35$ while the CT band does not shift to longer wavelength. The resonance energy[23], R_N, and Gibb's free energy change are computed from the mean values obtained from the said three methods and are shown in Table-3. The molar extinction coefficient of the donor exhibits decreasing trend which indicates[24] that the donor character increases in the order BAM < NMA < NNDMA < DPA < OTE.

TABLE-2

System	Ionisation potential donor		F-H-W	Scott	B-H	F-H-W	Scott	B-H
	$(I_P)_L$	$(I_P)_C$	K_C^{AD}			ε_λ^{AD}		
NNDMA-CAL	7.23	7.23	1.225	1.238	1.183	1960	1919	1921
NMA-CAL	7.32	7.36	1.397	1.367	1.873	1855	2101	2085
OTE-CAL	7.46	7.43	1.406	1.047	1.080	1747	1777	1466
DPA-CAL	7.22	7.46	0.630	0.577	0.587	1723	1744	1639
BAM-CAL	7.56	7.55	16.180	14.710	18.800	2738	2775	2697

$(I_P)_L$—Literature value and $(I_P)_C$—calculated value of the donor ionisation potentials (eV), K_C^{AD} ($dm^3\ mol^{-1}$) and ε_λ^{AD} ($10^{-1}\ m^2\ mol^{-1}$).

TABLE-3

System	CT energy (eV)	Free energy change $\langle \Delta G \rangle$ kJ mol^{-1}	Resonance energy $\langle R_N \rangle$ kJ mol^{-1}	Molar extinction coeff. $\langle \varepsilon_\lambda^{AD} \rangle$	Association constant $\langle K_C^{AD} \rangle$
NNDMA-CAL	1.90	–0.489	4.614	1933	1.215
NMA-CAL	2.07	–1.094	5.232	2014	1.546
OTE-CAL	2.21	–0.411	4.616	1663	1.178
DPA-CAL	1.89	1.291	4.033	1702	0.598
BAM-CAL	2.32	–7.049	7.998	2737	16.560

Conclusion

From the present study it appears that the nature and position of the substituents in the donor, steric effect in the CT complex, electronic influence and solvent polarisability play a prominent role in governing the formation and stability of the electron donor complexes. Further it is possible to calculate the association constant and molar extinction coefficient and other related thermodynamic and spectral parameters without recourse to much complicated equations like Ketelaar[25], Rose-Drago[26] and hill climbing technique of Rosenbrook[27].

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