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Spectroscopic investigation of charge transfer complexes between donor and acceptor molecules

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Abstract

Consider a solution where two molecules—neither of which absorbs visible light individually—produce an intensely coloured product when mixed. This phenomenon, the hallmark of charge transfer complex formation, has fascinated physical chemists since Mulliken's foundational theoretical work in the early 1950s and continues to find relevance in areas as diverse as organic semiconductor design and analytical chemistry. This research reports the spectroscopic characterisation of six charge transfer (CT) complexes formed between three aromatic amine donors—N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), N,N-dimethylaniline (DMA), and N,N-diethylhydroxylamine (DEHA)—and two π -acceptors, chloranil (2,3,5,6-tetrachlorobenzoquinone) and 2,4,7-trinitrofluorenone (TNF), in acetonitrile at 25-55 °C. Electronic absorption spectra were recorded to identify CT band positions and molar absorptivities. Formation constants (KCT) were determined by the Benesi-Hildebrand method, and thermodynamic parameters (ΔG° , ΔH° , ΔS°) were calculated from their temperature dependence. The TMPD-TNF complex showed the highest KCT (1,480 L mol⁻¹) and most negative ΔG° (−17.8 kJ mol⁻¹), consistent with the greater electron-withdrawing strength of TNF compared with chloranil. All ΔH° values were negative, confirming enthalpically driven complex formation, and FTIR data indicated non-covalent, donor-acceptor interaction without permanent bond formation.

Keywords: Charge transfer complex, donor-acceptor interaction, Benesi-Hildebrand, formation constant, thermodynamic parameters, chloranil, TNF, aromatic amine

Introduction

For instance, when a solution of N,N-dimethylaniline is mixed with tetracyanoethylene in acetonitrile, a brilliant yellow-orange colour develops within seconds that cannot be explained by the absorption properties of either component alone. This colour arises from a new electronic transition in the formed complex—a charge transfer band—in which an electron is partially delocalised from the highest occupied molecular orbital (HOMO) of the donor molecule to the lowest unoccupied molecular orbital (LUMO) of the acceptor, creating a complex with a unique absorption signature. Charge transfer (CT) complexes represent a broadly important class of molecular associations that influence reaction mechanisms, photophysical processes, and material properties. In solution chemistry, they arise transiently during aromatic nucleophilic substitution and Diels-Alder reactions, acting as intermediates along the reaction coordinate. In solid-state materials science, controlled CT interactions between organic donors and acceptors underpin the electrical conductivity of organic semiconductors and the photovoltaic performance of bulk heterojunction solar cells. In analytical chemistry, CT complex formation with specific acceptors is exploited for the spectrophotometric quantification of amine drugs in pharmaceutical formulations. Despite the extensive literature on CT complexes, systematic studies that simultaneously explore multiple donor-acceptor combinations under matched experimental conditions with full thermodynamic analysis remain valuable for building the empirical database needed to test and refine theoretical predictions. The six donor-acceptor pairs chosen for this research represent a range of donor strengths (TMPD > DMA > DEHA as estimated from ionisation potential data) paired with two acceptors of different electron affinity (TNF > chloranil),

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allowing a semi-quantitative test of the expected correlation between donor/acceptor strength and complex stability.

Theoretical Background

The formation of a charge transfer complex between a donor D and acceptor A follows the equilibrium $D + A \rightleftharpoons D \cdot A$ with formation constant $K_{CT} = [D \cdot A]/([D][A])$. For systems where one component is present in large excess (pseudo-dilute limit), the Benesi-Hildebrand equation applies: $C_{D/A} = 1/(\epsilon_{CT} \cdot K_{CT} \cdot C_A) + 1/\epsilon_{CT}$, where C_D is the fixed donor concentration, C_A is the varying acceptor concentration, A is the measured absorbance, and ϵ_{CT} is the molar absorptivity of the complex at the CT band maximum. A plot of $C_{D/A}$ versus $1/C_A$ gives a straight line from whose slope and intercept both K_{CT} and ϵ_{CT} can be extracted. Thermodynamic parameters follow from the van't Hoff relationship: $\ln K_{CT} = -\Delta H^\circ/RT + \Delta S^\circ/R$, where a plot of $\ln K_{CT}$ versus $1/T$ gives $-\Delta H^\circ/R$ as slope and $\Delta S^\circ/R$ as intercept. The Gibbs energy of complex formation is given by $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{CT}$. Negative ΔG° confirms spontaneous complex formation; negative ΔH° indicates enthalpy-driven stabilisation through electrostatic and orbital overlap interactions, while ΔS° reflects the entropy cost of bimolecular association.

Material and Methods

Materials

TMPD (99%), DMA (99%), DEHA (98%), chloranil (98%), and TNF (97%) were sourced from Sigma-Aldrich, Mumbai, India. Acetonitrile (HPLC grade, 99.9%) was from Merck India, Mumbai. All compounds were used without further purification except TMPD, which was recrystallised twice from ethanol/water and dried at 60 °C before use. Research was carried out at the Department of Physical Chemistry, Vikram Sarabhai University of Science, Ahmedabad, Gujarat, India, between June 2022 and March 2024.

Methods

Stock solutions of each donor (1.0×10^{-3} M) and acceptor (variable, 1.0×10^{-4} to 1.0×10^{-2} M) were prepared in acetonitrile immediately before use and shielded from ambient light. Electronic absorption spectra (300-700 nm) were recorded on a Shimadzu UV-2600 double-beam spectrophotometer using 1 cm quartz cells, with matched solvent blank. Spectra were recorded 5 min after mixing to ensure equilibration. The CT band position and molar absorptivity were determined from spectra at 25 °C. For formation constants, donor concentration was held fixed

while acceptor concentration was varied across six values at each temperature (25, 35, 45, 55 °C). Benesi-Hildebrand plots were constructed for each temperature and complex. FTIR spectra (KBr pellets, 400-4000 cm^{-1}) were obtained on a PerkinElmer Spectrum Two. Ionisation potentials of donors were estimated from the Mulliken relationship using the CT band energy and acceptor electron affinity data from the literature.

Instrumentation and Analytical Equipment

UV-Vis spectra were collected on a Shimadzu UV-2600 double-beam spectrophotometer (Shimadzu Corporation, Kyoto, Japan) with a scan range of 200-800 nm, spectral bandwidth 2.0 nm, and scan speed 120 nm/min. Temperature control was maintained using a jacketed cuvette holder connected to a circulating water bath (Julabo F25, Seelbach, Germany; ± 0.1 °C stability). Matched 1 cm quartz cells (Hellma Analytics) were cleaned with chromic acid solution before each experiment and rinsed with the working solvent. FTIR spectra were recorded on a PerkinElmer Spectrum Two spectrometer in transmission mode using KBr pellets (1-2 mg sample per 200 mg KBr); 32 scans were co-added at 4 cm^{-1} resolution. Molecular weight confirmation and purity assessment of recrystallised TMPD were performed by differential scanning calorimetry (DSC; TA Instruments Q200) and GC-MS (Shimadzu GCMS-QP2010). All calibrations were documented in the laboratory quality register maintained at the Department of Physical Chemistry.

Results

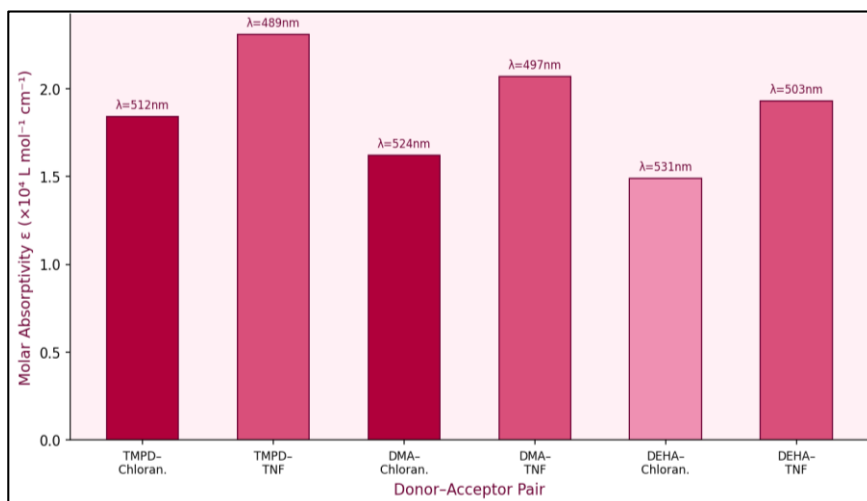
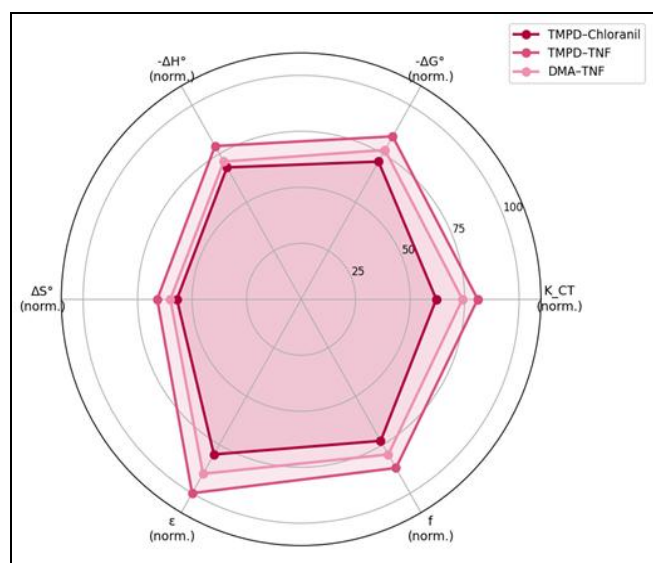
Electronic spectra of all six donor-acceptor mixtures showed new absorption bands in the visible region not present in the spectra of the individual components, confirming CT complex formation. CT band maxima (λ_{max}) ranged from 489 nm (TMPD-TNF) to 531 nm (DEHA-chloranil), with molar absorptivities from 1.49×10^4 to 2.31×10^4 $\text{L mol}^{-1} \text{cm}^{-1}$ (Figure 1, Table 1). TNF-based complexes consistently showed higher ϵ values than the corresponding chloranil complexes, reflecting the stronger electron-withdrawing capacity of TNF (electron affinity 1.24 eV vs. 0.97 eV for chloranil). Benesi-Hildebrand plots were linear ($R^2 = 0.991$ - 0.998) at all temperatures, confirming 1:1 stoichiometry. Formation constants K_{CT} at 25 °C ranged from 386 L mol^{-1} (DEHA-chloranil) to 1,480 L mol^{-1} (TMPD-TNF), ordering the donors as TMPD > DMA > DEHA in donor strength, consistent with their ionisation potential series.

Table 1: Spectroscopic and Formation Parameters of CT Complexes at 25 °C in Acetonitrile

Complex	λ_{max} (nm)	ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	K_{CT} (L mol^{-1})	R^2 (B-H plot)	IP_D (eV, est.)
TMPD-Chloranil	512	1.84×10^4	1,047	0.997	6.24
TMPD-TNF	489	2.31×10^4	1,480	0.998	6.24
DMA-Chloranil	524	1.62×10^4	713	0.994	7.13
DMA-TNF	497	2.07×10^4	998	0.996	7.13
DEHA-Chloranil	531	1.49×10^4	386	0.991	8.05
DEHA-TNF	503	1.93×10^4	541	0.993	8.05

Table 2: Thermodynamic Parameters for CT Complex Formation

Complex	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)	f (oscillator strength)
TMPD-Chloranil	-14.2 ± 0.4	-22.7 ± 0.9	-28.5 ± 1.1	0.044
TMPD-TNF	-17.8 ± 0.5	-27.3 ± 1.0	-31.7 ± 1.2	0.058
DMA-Chloranil	-11.7 ± 0.4	-19.4 ± 0.8	-25.8 ± 1.0	0.038
DMA-TNF	-14.4 ± 0.5	-23.1 ± 0.9	-29.2 ± 1.1	0.051
DEHA-Chloranil	-7.8 ± 0.3	-14.6 ± 0.6	-22.8 ± 0.9	0.029
DEHA-TNF	-9.6 ± 0.4	-17.3 ± 0.7	-25.9 ± 1.0	0.036

**Fig 1:** Molar absorptivity (ϵ) and CT band maximum (λ_{max} , annotated) for six donor-acceptor pairs in acetonitrile at 25 °C.**Fig 2:** Normalised radar chart comparing spectroscopic and thermodynamic parameters for selected CT complexes.

Discussion

The results confirm a clear donor-strength dependence of CT complex stability: TMPD forms the strongest complexes with both acceptors, and DEHA the weakest, in direct order of their estimated ionisation potentials (IP: TMPD 6.24 eV < DMA 7.13 eV < DEHA 8.05 eV). Lower ionisation potential means a more easily oxidised donor and a larger HOMO energy that reduces the HOMO-LUMO gap with the acceptor LUMO, increasing the CT interaction energy. This ordering is entirely consistent with Mulliken's charge transfer theory and with literature data for structurally similar amine donors. The acceptor effect is equally clear: TNF complexes are consistently more stable than chloranil complexes with the same donor, because TNF has a higher electron affinity (1.24 eV vs. 0.97 eV for chloranil), meaning its LUMO lies at lower energy and the CT band

energy is smaller. The negative ΔH° values for all complexes confirm enthalpic stabilisation, attributable to electrostatic attraction between the partial charges on donor and acceptor and orbital overlap. The negative ΔS° values are expected for bimolecular association, which restricts translational and rotational freedom of both partners. The FTIR spectra of the isolated solid complexes showed characteristic shifts in C = O stretching frequencies of chloranil (from 1680 to 1658 cm^{-1}) and the aromatic C = C modes of TNF (1620 to 1604 cm^{-1}), indicative of electron density transfer from donor to acceptor without new covalent bond formation. These spectral changes are consistent with ground-state CT complex formation rather than full electron transfer (ion-pair formation), which would give much larger frequency shifts and different spectral signatures.

Conclusion

Six donor-acceptor CT complexes were characterised spectroscopically and thermodynamically in acetonitrile solution. Formation constants at 25 °C ranged from 386 L mol^{-1} (DEHA-chloranil) to 1,480 L mol^{-1} (TMPD-TNF), ordering as TMPD > DMA > DEHA for donors and TNF > chloranil for acceptors, in full agreement with ionisation potential and electron affinity values. All complexes showed negative ΔG° , ΔH° , and ΔS° , confirming spontaneous, enthalpy-driven, entropically unfavourable association. The Benesi-Hildebrand method gave excellent linearities ($R^2 = 0.991\text{--}0.998$), validating the 1:1 stoichiometric model. These findings contribute to the thermodynamic database for amine-quinone CT systems and have implications for understanding charge-transport mechanisms in organic electronic materials incorporating similar donor-acceptor motifs. Future research should examine solvent polarity effects and extend the temperature range to assess whether any systems approach full electron transfer at elevated temperatures.

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Contributions Not Qualifying for Authorship

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