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## Synthesis and spectrophotometric studies of charge transfer complexes of p-nitroaniline with benzoic acid in different polar solvents

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### HIGHLIGHTS

- A charge transfer or proton transfer complex is synthesized and confirmed by spectral investigations.
- Spectrophotometric studies were made in different polar solvents.
- Benesi-Hildebrand equation in various solvents was used to determine *K*<sub>CT</sub>, *ɛ*<sub>CT</sub>, and *E*<sub>CT</sub> of the CT complex.
- Thermal analysis (TGA–DTA) was also used to confirm the thermal fragmentation and the stability of the CT complex.

### G R A P H I C A L A B S T R A C T

The charge – transfer complex was prepared and characterized by different techniques such as FTIR, <sup>1</sup>HNMR, TGA-DTA. Spectrophotometric studies were also performed in various solvents with different polarity to calculate thermodynamic parameters. Absorption spectra of benzoic acid  $(1 \times 10^{-2} \text{ M})$  in acetone with addition of p-nitro aniline concentrations ranging 0.01–0.05 M are shown with increasing concentrations bottom to top.



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### ABSTRACT

The charge transfer complexes of the donor p-nitroaniline (PNA) with the  $\pi$ -acceptor benzoic acid (BEA) have been studied spectrophotometrically in various solvents such as acetone, ethanol, and methanol at room temperature using an absorption spectrophotometer. The outcome suggests that the formation of the CT-complex is comparatively high in less polar solvent. The stoichiometry of the CT-complex was found to be 1:1. The physical parameters of the CT-complex were evaluated by the Benesi–Hildebrand equation. The data are discussed in terms of the formation constant ( $K_{CT}$ ), molar extinction coefficient ( $\varepsilon_{CT}$ ), Standard Gibbs free energy ( $\Delta G^0$ ), oscillator strength (f), transition dipole moment ( $\mu_{EN}$ ), resonance energy ( $R_N$ ) and ionization potential ( $I_D$ ). The formation constant ( $K_{CT}$ ) of the complex was depends upon the nature of electron acceptor, donor, and polarity of solvents used. It is also observed that a charge transfer molecular complex is stabilized by hydrogen bonding. The formation of the complex has been confirmed by UV–visible, FT-IR, <sup>1</sup>H NMR and TGA/DTA. The structure of the CT-complex is [(PNA)<sup>+</sup> (BEA)<sup>-</sup>]. A general mechanism for its formation of the complex has also been proposed.

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#### Introduction

Molecular interactions between electron donors and electron acceptors are generally associated with the formation of intensely colored charge-transfer complexes, which absorb radiation in the visible region [1]. Charge transfer complexes are formed between electron donors having sufficiently low ionization potential, and electron acceptors having sufficiently high electron affinity. The transfer of an electron from a donor to an acceptor is readily possible in the charge transfer process [2]. Also protonation of the donor to acidic acceptor are generally rout for the ion pair adducts [3–10]. Benzoic acid and its derivatives have been reported to yield charge-transfer complexes [11]. Such a complexation reaction is usually simple, fast, reproducible and reliable.

This paper presents studies of the charge-transfer interaction between p-nitroaniline and benzoic acid in both liquid and solid states. The aim of the work is to determine the reaction stoichiometry, nature of bonding between BEA and PNA, and also some physical parameters. In addition, the nature and structure of the reaction product (CT-complex) in both solution and solid states can be estimated using the spectroscopic techniques like FT-IR, <sup>1</sup>H NMR, TGA–DTA and UV–Vis electronic absorption to obtain the stoichiometry, molecular structure and nature of interaction for the CT-complexes [12–15].

## Experimental

#### Materials

Analytical grade chemicals were used throughout p-nitroaniline (PNA) and Benzoic acid (BEA) was obtained from, CDH. Methanol (Merck), Ethanol (Merck) and Acetone (Merck) were all analytical grade (AR) and used without further purification.

#### Preparation of standard solutions

Solutions of donor of different concentrations, 0.01 M, 0.02 M, 0.03 M, 0.04 M, and 0.05 M, were prepared in different volumetric flask by dissolving accurately weighed p-nitroaniline in different solvents such as acetone, ethanol and methanol.

A standard solution of acceptor, benzoic acid (0.01 M concentration), was prepared by dissolving accurately weighed of acceptor in above solvents in different volumetric flasks.

#### Synthesis of solid CT-complex

Analar R grade samples of p-nitroaniline and benzoic acid were employed for the synthesis of the title compound. Equimolar solutions of the two reactants were separately prepared in methanol and mixed together. The resulting solution was stirred well for about thirty minutes.

The precipitated adduct was filtered off and repeatedly recrystallised from methanol to enhance the degree of purity of the synthesized compound.

#### Analyses

The electronic absorption spectra of the donor p-nitroaniline, acceptor benzoic acid and the resulting complex in acetone, ethanol and methanol were recorded in the visible range 400–600 nm using a spectrophotometer ELICO SL 177 scanning mini spectrophotometer with a 1 cm quartz cell path length. The FT-IR spectra of the reactants and the resulting CT-complex were recorded with the help of FT-IR spectrometer INTERSPEC-2020 (spectra lab UK) measured in KBr pellets. The nuclear magnetic resonance, <sup>1</sup>H

#### **Results and discussion**

#### Observation of CT-bands

A 3 ml volume of donor and acceptor were scanned separately through a spectrophotometric titration [16] at room temperature with their wavelength of maximum absorption 230 nm for benzoic acid, 400 nm for p-nitroaniline in acetone, 340 nm for blank solvent (acetone) and 410 nm for CT-complex of .01 M PNA and .01 M BEA in acetone are shown in Fig. 1. The reaction mixture of donor (10 ml) and acceptor (10 ml) in different solvents viz, acetone, ethanol and methanol formed a yellow colored charge transfer complex. The concentration of the donor in the reaction mixture was kept greater than acceptor,  $[D_0] \gg [A_0]$  [17,18] and changed over a wide range of concentration from 0.01 M to 0.05 M while concentration of  $\pi$ -acceptor (benzoic acid) was kept fixed [17] at 0.01 M in each solvents, these produced solutions with donor: acceptor molar ratios varying from 1:1 to 5:1. These concentrations ratios were used to straight line diagram for determination of the formation constants of CT-complex as separate shown in Table 3

The spectrum of solution of 0.01 M BEA, and 0.01 M PNA in different solvents were recorded with solvents as reference, the longest wavelength peak was considered as CT-peak [19]. The change of the absorption intensity to higher value for all complexes in this study was detected with added donor and was investigated as shown in Table 3. These measurements were based on the CT-absorption bands exhibited by the spectra of the organizations described on above and are represented in Figs. 2–4. In all systems studied, the absorption spectra are of similar nature except for the position of the absorption maxima ( $\lambda_{CT}$ ) of the complexes. The CT-complex absorption spectra were analyzed by fitting to the Gaussian function;

$$v = v_0 + [A/w_0/(\pi/2)]e^{[-2(x-x_c)^2/w^2]}$$



**Fig. 1.** Absorption spectra of (A) .01 M Benzoic acid. (B) Blank solvent (Acetone). (C) .01 M p-nitro aniline. (D) CT-complex of .01 M PNA and .01 M BEA in acetone.

#### Table 1

Gaussian curve analysis for the CT-complex in spectrum of BEA with PNA in different polar solvents.

Systems	Solvent	Α	W	χς	Y <sub>0</sub>
BEA + PNA BEA + PNA	Acetone Ethanol	$2.75 \pm 0.730$ $5.33 \pm 3.730$	52.53 ± 12.49 154.78 ± 68.35	405.78 ± 7.47 385.65 ± 46.77	$\begin{array}{c} 0.00976 \pm 0.0015 \\ 0.0044 \pm 0.00318 \end{array}$
BEA + PNA	Methanol	$3.24 \pm 0.278$	42.69 ± 3.95	419.21 ± 1.67	0.0107 ± 0.00142

#### Table 2

CT-complex absorption maxima ( $\lambda_{CT}$ ), transition energies ( $hv_{CT}$ ), of the BEA + PNA complexes, experimentally determined values of ionization potentials ( $I_D$ ), oscillator strength (f), dipole moments ( $\mu_{EN}$ ), and resonance energies ( $R_N$ ) of complexes.

Systems	Solvent	$\lambda_{CT}$ (nm)	$hv_{CT}$ (eV)	$I_D$ (eV)	$f imes 10^5$	$\mu_{EN}$ (Debye)	$[R_N]$ (eV)
BEA + PNA	Acetone	405.78	3.06	9.52	4.62	0.429	0.0016
BEA + PNA	Ethanol	385.65	3.22	9.72	1.34	0.426	0.0016
BEA + PNA	Methanol	419.21	2.96	9.40	1.20	0.770	0.0056

#### Table 3

Data for spectrophotometric determination of stoichiometry, absorption maxima ( $\lambda_{CT}$ ), and association constants ( $K_{CT}$ ), molar absorptivities ( $\varepsilon_{CT}$ ), of CT-complex of BEA and PNA in acetone, ethanol, and methanol at 298 K.

Systems	Solvent	Temp (K)	$[D]_0$ in M	[A] <sub>0</sub> in M	Absorbance at $\lambda_{CT}$ (nm)	$\lambda_{CT}$ (nm)	$K_{CT}$ (l mol <sup>-1</sup> )	$\epsilon_{CT} (1  \mathrm{mol}^{-1}  \mathrm{cm}^{-1})$
BEA + PNA	Acetone	298	0.01	0.01	0.064	410	18,550	40.8
			0.02		0.104			
			0.03		0.139			
			0.04		0.176			
			0.05		0.218			
BEA + PNA	Ethanol	298	0.01	0.01	0.043	415	11,870	40.1
			0.02		0.073			
			0.03		0.103			
			0.04		0.129			
			0.05		0.161			
BEA + PNA	Methanol	298	0.01	0.01	0.080	420	6410	131
			0.02		0.138			
			0.03		0.197			
			0.04		0.265			
			0.05		0.397			



**Fig. 2.** Absorption spectra of benzoic acid  $(1 \times 10^{-2} \text{ M})$  in acetone with addition of p-nitro aniline concentrations ranging 0.01–0.05 M are shown with increasing concentrations bottom to top.



**Fig. 3.** Absorption spectra of benzoic acid  $(1 \times 10^{-2} \text{M})$  in ethanol with addition of p-nitro aniline concentrations ranging 0.01–0.05 M are shown with increasing concentrations bottom to top.

#### Determination of Ionization potentials of the donor

The ionization potentials of the donor  $(I_D)$  in the charge transfer complexes were calculated using empirical equation derived from Aloisi and Piganatro [20]

where *x* and *y* denote wavelength and absorbance, respectively. The results of the Gaussian analysis for all systems under study are shown in Table 1. The wavelengths at these new absorption maxima ( $\lambda_{CT} = \chi_c$ ) and the corresponding transition energies ( $\hbar v$ ) are summarized in Table 2



**Fig. 4.** Absorption spectra of benzoic acid  $(1 \times 10^{-2} \text{ M})$  in methanol with addition of p-nitroaniline concentrations ranging 0.01–0.05 M are shown with increasing concentrations bottom to top.

$$I_D(\text{eV}) = 5.76 + 1.53 \times 10^{-4} v_{CT} \tag{1}$$

where  $v_{CT}$  is the wave number in cm<sup>-1</sup> of the complex were determined in different solvents, viz, acetone, ethanol and methanol.

# Determination of oscillator strength, (*f*), and transition dipole moment, $(\mu_{EN})$

From the CT-absorption spectra, one can determine oscillator strength. The value of oscillator strength f is estimated using the formula

$$f = 4.32 \times 10^{-9} \int \varepsilon_{CT} d\nu \tag{2}$$

where  $\int \varepsilon_{CT} dv$  is the area under the curve of the extinction coefficient of the absorption band in question vs. frequency. To a first estimate,

$$f = 4.32 \times 10^{-9} \varepsilon_{\rm CT} \Delta V_{1/2} \tag{3}$$

where  $\varepsilon_{CT}$  is the maximum extinction coefficient of the band and  $\Delta v_{1/2}$  is the half-width, i.e., the width of the band at half the maximum extinction. The observed oscillator strengths of the CT-bands are summarized in Table 2.

The extinction coefficient is associated to the transition dipole by

$$\mu_{\rm FN} = 0.0952 [\varepsilon_{\rm CT} \Delta v_{1/2} / \Delta v]^{1/2} \tag{4}$$

where  $\Delta v \simeq v$  at  $\varepsilon_{CT}$ . The estimated values of ( $\mu_{EN}$ ) for the complex are reported in Table 2.

#### Determination of resonance energy $(R_N)$

Briegleb and Czekalla [21] theoretically derived the relation

$$\varepsilon_{\rm CT} = 7.7 \times 10^{-4} / [\&v_{\rm CT} / [R_{\rm N}] - 3.5] \tag{5}$$

where  $\varepsilon_{CT}$  is the molar extinction coefficient of the complex at the maximum of the CT absorption,  $\nu_{CT}$  is the frequency of the CT-peak and  $(R_N)$  is the resonance energy of the complex in the ground state, which, indeed is a contributing factor to the stability constant of the complex (a ground state property). The values of  $(R_N)$  for the complexes under study have been given in Table 2.

Determination of standard free energy changes ( $\Delta G^0$ ) and energy ( $E_{CT}$ ) of the  $\pi$ - $\pi^*$  interaction between donor and acceptor

The standard free energy changes of complexation ( $\Delta G^0$ ) were estimated from the association constants by following the equation derived by Martin et al. [22].

$$\Delta G^0 = -2.303 \, RT \log K_{CT} \tag{6}$$

where  $\Delta G^0$  is the free energy change of the CT-complexes (kJ mol<sup>-1</sup>), *R* is the gas constant (8.314 J mol<sup>-1</sup> K), *T* is the temperature in Kelvin degrees (273 + °C) and  $K_{CT}$  is the association constant of the complexes (l mol<sup>-1</sup>) in different solvents at room temperature.

The energy ( $E_{CT}$ ) of the  $\pi$ - $\pi$ \* interaction between the donor (PNA), and acceptor (BEA), is calculated using the following equation derived by Briegleb [23].

$$E_{\rm CT} = 1243.667 / \lambda_{\rm CT \ nm} \tag{7}$$

The calculated values of ( $E_{CT}$ ) given in Table 4, where  $\lambda_{CT}$  is the wavelength of the CT band.

Spectrophotometric study of formation constants of the charge transfer Complexes of in different polar solvents

Stoichiometries and the formation constants of the charge transfer complex of p-nitroaniline with benzoic acid have been determined in different polar solvents, acetone, ethanol and methanol at room temperature using Benesi–Hildebrand equation [24,25]. The spectrophotometric data were used to estimate the values of formation constants, ( $K_{CT}$ ) of the complexes. The changes in the absorbance upon addition of PNA of a solution of BEA of fixed concentration follow the Benesi–Hildebrand [24,25] equation in the form.

$$[A]_0/A = (1/K_{CT}\varepsilon_{CT}) \times 1/[D]_0 + 1/\varepsilon_{CT}$$
(8)

where  $[D]_0$  and  $[A]_0$  are the concentrations of the p-nitroaniline donor, and benzoic acid acceptor, respectively, A is the absorbance of the donor–acceptor mixture at  $\lambda_{CT}$ , against the solvents as reference,  $(K_{CT})$  is the formation constant and  $\varepsilon_{CT}$  is the molar extinction coefficient, is not quite that of complex. Eq. (8) [24,25] is valid under the condition  $[D]_0 \gg [A]_0$  [17,18] for 1:1 donor–acceptor complexes. The concentration of the p-nitroaniline (PNA) was varied over a wide range from 0.01 M to 0.05 M while the concentration of  $\pi$ -acceptor BEA was kept fixed at 0.01 M in each reaction mixture. These produced solutions with a donor: acceptor molar ratios varying from 1:1 to 5:1 experimental data were given in Table 3.

The Benesi–Hildebrand [24,25] method produced good results. The intensity in the visible region of the absorption bands, measured against the solvent as reference, increases with increased in the polarity and addition of the PNA. The typical absorbance data for charge transfer complexes of PNA with BEA in different polar solvents at room temperature were reported in Tables 1 and 3. In all systems, linear plots, were obtained according to Eq. (7) [24,25] and are shown in Figs. 5-7. Formation constant for the complexes in different polar solvents at room temperature determined from the BH plots are summarized in Table 3. The correlation coefficients of all such plots were above 0.99. Plots of  $[A]_0/$ A against  $1/[D]_0$  were found to be linear in all systems in Figs. 5–7 showing 1:1 charge transfer complexes, i.e. the straight lines are obtained with the slopes,  $1/K_{CT\varepsilon_{CT}}$ . These results suggest the formation of 1:1 CT-complexes. From slope  $1/K_{CT\epsilon_{CT}}$  and intercept,  $1/\epsilon_{CT}$ ,  $K_{CT}$  and  $\varepsilon_{CT}$  of the CT-complex was calculated in different polar solvents.

#### Table 4

Association constant ( $K_{CT}$ ), correlation coefficients (r) and standard free energy changes ( $\Delta G^0$ ), transition energy ( $E_{CT}$ ), and absorption maxima ( $\lambda_{CT}$ ) of BEA + PNA complexes obtained from Benesi–Hildebrand plots.

Systems	Solvent	$K_{CT}$ (l mol <sup>-1</sup> )	$\lambda_{CT}(\mathbf{nm})$	$-\Delta G^0$ (kJ mol <sup>-1</sup> )	r	$E_{CT}$ (eV)	$I_D$ (eV)
BEA + PNA BEA + PNA	Acetone Ethanol	18,550 11.870	410 415	24.306 23.222	0.995 0.998	3.03 2.99	9.49 9.44
BEA + PNA	Methanol	6410	420	21.682	0.993	2.96	9.40



**Fig. 5.** Relation between  $[A]_0/A$  and  $1/[D]_0$  of BEA + PNA in acetone.



**Fig. 6.** Relation between  $[A]_0/A$  and  $1/[D]_0$  of BEA + PNA in ethanol.

#### Effect of solvents on the formation of CT-complexes

The experimental results of the CT interaction between BEA with PNA in different polar solvents reveal the values of association constant  $K_{CT}$ , in acetone (18,550 1 mol<sup>-1</sup>), ethanol (11,870 1 mol<sup>-1</sup>) and methanol (6410 1 mol<sup>-1</sup>) and the values of molar extinction coefficient  $\varepsilon_{CT}$  in acetone (40.8 1 mol<sup>-1</sup> cm<sup>-1</sup>), ethanol (40.1 1 mol<sup>-1</sup> cm<sup>-1</sup>) and methanol (131 1 mol<sup>-1</sup> cm<sup>-1</sup>). The spectroscopic properties were markedly affected by the variation in solvent polarity in which measurements were carried out. In the present investigation, the  $K_{CT}$  values increase significantly from methanol to acetone with decreasing solvent polarity. Moreover, the increase in  $K_{CT}$  values with decreasing solvent polarity may also be due to the fact that, the CT-complex should be stabilized in less



**Fig. 7.** Relation between  $[A]_0/A$  and  $1/[D]_0$  of BEA + PNA in methanol.



Fig. 8. FTIR spectrum of (A) Complex of BEA and PNA, (B) acceptor BEA and (C) donor PNA.

polar solvent [26]. This is supposed to refer to the decrease of energy of electrostatic interactions within the complex. Dissociation of the complexes into  $D^+-A^-$  radicals have been found to occur in the ground state [27]. It means the formation of the CT-complex should be strong in less polar solvent than more polar solvent.

The influence of solvent polarity on spectroscopic and thermodynamic properties of molecular electron-donor–acceptor (EDA) complexes is discussed. The data given in Table 3, show that BEA interacts more strongly with PNA in acetone among the other two solvents. The experimentally determined values of oscillator strength, (*f*) in acetone ( $4.62 \times 10^{-5}$ ), ethanol ( $1.34 \times 10^{-5}$ ) and methanol ( $1.20 \times 10^{-5}$ ), and the values of transition dipole

#### Table 5

Characteristic infrared frequencies  $(\mathrm{cm}^{-1})$  and tentative assignments for BEA, PNA and their complex.

BEA	PNA	Complex	Assignments
3067w,br	3480s	3484s	v(O—H), BEA, hydrogen bonding b/w
-	3356s,br	3361s	-OH-H-NH
	3220s,br	3223s	ν(N—H), PNA
3004w,br		-	v <sub>as</sub> (C—H), CH3 + CH <sub>3</sub>
2833br	3108w	3076w	$v(C-H)$ , aromatic $v(^{+}NH)$
2674br	1923w	2834w	
	1747w	2679w	
1690vs	1635ms	1688s	-C=0
1603vs	-	1633vs	$v_{as}(NO_2)PNA$
1579vs	1591vs	1589ms	v(C=C), aromatic
	-	-	$\delta$ def (N-H), +NH <sub>2</sub> ring
-			Breathing bands
-	1474s	1474vs	C—H deformation
1496ms	1442s	1423ms	
1420s	1398vs	1320vs	$v(C-C)$ , $v_sNO_2$ , PNA
1321vs	1302w	1292vs	$v_{as}(C-N)$
-			
1289vs	-	-	v(CO)
1182ms	1183w	1181ms	
1127ms	1110br	1110ms	$v_s(C-N)$
1071vs	-	1070m	
928ms	998s	1030vs	δ (C—H) in plane bending
809w	842sharp	999w	$\delta_{rock}$ , +NH <sub>2</sub>
		935s	CH <sub>2 rock</sub> skeletal
-		844s	Vibrations
	754vs	753m	C—H out of plane
706ms	698vs	662ms	Bending
-	534ms	543sh	
666vs	490ms	495br	C—H wagging
547w	-	-	
428s	418sharp	420ms	CNC deformation

S, strong, w, weak; m, medium, sh, shoulder, v, very; vs, very strong, br, broad; v, stretching; vs, symmetrical stretching;  $v_{as}$ , asymmetrical stretching.

moment, ( $\mu_{EN}$ ) in acetone (0.0429 Debyes) ethanol (0.426 Debyes) and methanol (0.770 Debyes), and values of resonance energy ( $R_N$ ) in acetone (0.0016 eV), ethanol (0.0016 eV), and methanol

(0.0056 eV), given in Table 2, indicate that complex should be stable in less polar solvent (acetone).

The parameters, thus obtained are represented in Table 4, and these values show that complexation is thermodynamically favored proved. The free energy change of the complexation also reveals that the CT-complex formation between donor (PNA) and acceptor (BEA) is of exothermic in nature. The values of  $\Delta G^0$  in acetone (-24.306 kJ mol<sup>-1</sup>), ethanol (-16.204 kJ mol<sup>-1</sup>), and methanol (-15.291 kJ mol<sup>-1</sup>) given in Table 4, generally become more negative as the association constants for molecular complex increases.

### FT-IR spectra of CT-complex and reactants

FT-IR spectra of the p-nitro aniline (donor), benzoic acid (acceptor) and their CT-complex were shown in Fig. 8. While their assignments of the characteristic FT-IR spectral bands were reported in Table 5. The formation of the charge transfer complex during the reaction of PNA with BEA is strongly evidenced by the presence of the main characteristic infrared bands of the donor and acceptor in the spectrum of the product. However, the bands of the donor are shifted to lower frequencies while that of the acceptor are shifted to the higher frequencies. There are changes in their intensities compared with that of the free donor and acceptor. This shift has been attributed to the charge transfer from donor to acceptor upon the complexation. These changes may be attributed to the expected symmetry and electronic structure modifications in both donor and acceptor units in the product thus formed relative to the free molecules. The -OH peak has disappeared in the spectrum of the CT-complex, whereas in free BEA this was observed at  $3004 \text{ cm}^{-1}$  (weak, broad). The disappearance of the –OH peak in the CT-complex has been ascribed to the proton transfer from the acceptor to the donor or transfer of lone pair electrons the donor to acceptor leading to an intermolecular hydrogen bonding as reported previously [15,28], so as to the new band observed at 3484 cm<sup>-1</sup> (strong) and is due to the  $\upsilon$  (N<sup>+</sup>-H···O<sup>-</sup>) while the



Fig. 9. <sup>1</sup>H NMR spectrum of CT complex.



Scheme 1. Mechanism for interaction between p-nitro aniline with benzoic acid.

N–H stretching vibration is kept at  $3361 \text{ cm}^{-1}$  (strong) and  $3223 \text{ cm}^{-1}$  (strong) which is normally kept at  $3300 \text{ cm}^{-1}$  (medium) and  $3199 \text{ cm}^{-1}$  (medium weak). The band at  $3076 \text{ cm}^{-1}$ (weak) is due to the aromatic C-H stretching vibration. The -NH<sub>2</sub> deformation mode is observed by the absorption at 1633 cm<sup>-1</sup> (very strong) in CT complex, whereas in free PNA this was observed at 1635 cm<sup>-1</sup> (medium strong). This band overlaps with the aromatic C=C stretching vibrations. Thus, it has been understood that the shift to the lower frequency of donor in the spectrum of the CT-complex is due to the formation of the CT-complex [28]. The  $-NO_2$  group are observed at 1589 cm<sup>-1</sup> (medium strong) in the CT complex, whereas in free PNA this was observed at 1591 cm<sup>-1</sup> (very strong). The absorption at 1633 cm<sup>-1</sup> and 1474 cm<sup>-1</sup>are due to the aromatic C=C stretching vibrations. The C–H in and out plane vibration is observed at  $1070 \text{ cm}^{-1}$ ,  $753 \text{ cm}^{-1}$  and  $935 \text{ cm}^{-1}$  respectively.

#### <sup>1</sup>H NMR spectrum of CT-complex

<sup>1</sup>H NMR spectrum of the CT-complex were studied in CDCl<sub>3</sub> and shown in Fig. 9. In the nuclear magnetic resonance <sup>1</sup>H NMR spectrum of CT-complex the proton of carboxylic group of benzoic acid is absent while in free benzoic acid this proton occurred at  $\delta$  = 12.09 ppm and p-nitro aniline ring system were specified in the region  $\delta$  = 8.05–6.60 ppm for p-nitro aniline. All the observed peaks in the spectrum of the individual reactants are also celebrated in the spectrum of CT-complex except -OH peak, suggesting that the disappearance of -OH peak in the spectrum of CT-complex is due to the formation of <sup>+</sup>N-H<sub>3</sub> ion through hydrogen bonding between --OH group of benzoic acid, --NH<sub>2</sub> group of p-nitro aniline [29]. The –OH proton is assigned at  $\delta$  = 12.09 ppm in free benzoic acid, which has been united in the bunch of aromatic protons of p-nitro aniline moiety in the region  $\delta$  = 8.05–6.60 ppm. This up field shift in frequency has been attributed to an increase in electron density on the benzoic acid part of the CT-complex due to transfer of protons from benzoic acid to



Fig. 10. TGA–DTA curves (A) p-nitro aniline, (B) benzoic acid and (C) complex of BEA + PNA.

p-nitro aniline. The doublet 'peaks at  $\delta$  = 8.12 ppm and triplet peaks at  $\delta$  = 7.62 ppm are assigned to the rest of protons are in the same kind in the benzoic acid moiety in the CT-complex. The formation of a hydrogen bond bridge between —NH proton of p-nitro aniline and —OH proton of benzoic acid is supported by the significant downfield shift of the NH peaks relative to pure compounds provide convincing evidence for the association of molecules [30]. Mechanism and structure of the CT-complex of acceptor and donor is given in Scheme 1.

# Comparative study of thermograms for benzoic acid, p-nitroaniline and their CT-complex

The comparative study of thermograms for benzoic acid, p-nitroaniline and their CT-complex were carried out by DTG-60H thermal analysis in a nitrogen atmosphere with a flow rate of 30 ml min<sup>-1</sup> and heating rate  $25 \,^{\circ}$ C min<sup>-1</sup> in the temperature range 20–400 °C showing in Fig. 10(a-c). The reference was a 10 mg alumina powder. Thermo gravimetric (TGA) and differential thermo gravimetric (DTA) analysis were carried out using in the temperature range of 0–400 °C using 10.299 mg, 7.914 mg, and

4.926 mg for benzoic acid, p-nitroaniline, CT-complex, respectively in order to confirm the charge transfer interaction and thermal stability of the CT-complex.

The thermogram of the donor (PNA) exhibit it decomposes in one step at 256 °C with weight loss of close to 89.75% and acceptor shows two decomposition steps at 180 °C and 315 °C with a weight loss of approximately 89.038% and 12.001%, respectively, with a complete loss in each case, at higher decomposition temperature for donor and acceptor in CT complex compared with free donor and acceptor (shown in Fig. 10). The CT complex of BEA and PNA exhibits two decomposition steps at 178 °C and 247 °C with weight loss 98.620% and 3.370% respectively. The decomposition at 247 °C with weight losses 3.370% is probably due to the donor (PNA). This has been attributed to the formation of CT-complex and its stability compared to its constituents.

#### Conclusions

The UV-Vis spectrophotometric method for the study of the CT-complex of benzoic acid with p-nitro aniline ascertains the formation of 1:1 (A:D) complex in all three solvents, viz-acetone, ethanol and methanol. In all systems the stoichiometry is unaltered by changing the solvent. The association constants,  $(K_{CT})$  and molar extinction coefficients  $(\varepsilon_{CT})$ , of all systems were assessed by the Benesi-Hildebrand method. The spectroscopic and thermodynamic parameters of the CT-complexes were found to be dependent on polarity of the solvents. Since the values of oscillator strengths, (f) transition dipole moments ( $\mu_{EN}$ ), resonance energies,  $(R_N)$  and standard free energies,  $(\Delta G^0)$ , have been estimated for the BEA/PNA systems in different polar solvents. The outcomes demonstrate that the investigated CT-complex is stable. exothermic and spontaneous. From the trends in the CT absorption bands, the ionization potentials of the donor molecules have been estimated. The FT-IR and <sup>1</sup>H NMR spectrum shows that the charge transfer complex formed between BEA and PNA is stabilized by hydrogen bonding which exists, formed between -OH group of benzoic acid and hydrogen atom of the amino group of p-nitro aniline.

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