

## CHAPTER- 3

*Spectrophotometric and spectroscopic studies of charge transfer complexes of m-nitroaniline as an electron donor with picric acid as an electron acceptor in different polar solvents.*

### 3.1. Introduction

Charge transfer complexation is important phenomenon in biochemical and bioelectrochemical energy transfer process [1]. Charge transfer phenomenon was introduced first by Mulliken. The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bonds [2, 3] discussed widely by Foster [4]. Molecular interactions between electron donors and acceptors are generally associated with the formation of intensely colored charge transfer complexes (CTCs) which absorb radiation in the visible region [5]. Molecular complexation and structural recognition are important processes in biological systems, for example, drug action, enzyme catalysis and ion transfers through lipophilic membranes all involve complexation [6]. Charge transfer complexes are currently of great importance since these materials can be utilized as organic semiconductors [7], photocatalysts [8] and dendrimers [9]. They are also important in studying redox processes [10], second order non-linear optical activity [11] and micro emulsion [12].

In this chapter, the studies of formation of CT complex between picric acid (acceptor) and m-nitroaniline (donor). Picric acid forms molecular complexes with aromatic hydrocarbons such as anthracene [13] some aniline derivatives [14] and also with aromatic amines [15-17]. It is also notice that the formation of molecular complexes from two aromatic molecules can arise from the transfer of an electron from a  $\pi$  – molecular orbital of a Lewis base to vacant  $\pi$ - molecular orbital of a Lewis acid, with resonance between this dative structure and the no-band structure stabilizing the complex [18]. He also noted the possibility of complex formation through the donation of an electron from a non-bonding molecular orbital in a Lewis base to a vacant  $\pi$ - orbital of an acceptor ( $n-\pi$ ) [19] with resonance stabilization of the combination.

The interaction of PiOH (picric acid) with MNA (m-nitroaniline) in solvents of different polarity at room temperature have been studied by visible spectra data of CT complex of m-nitroaniline with  $\pi$  acceptor, picric acid in said solvents viz- acetone, ethanol, and methanol and also studied the effect of solvents on the formation of CT complex. The formation constant and  $\lambda_{CT}$  for the CT complex of picric acid with m-nitroaniline in different polar solvents are also determined. The

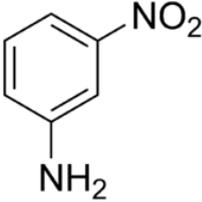
significance of the effects of complexation on spectra has led to a need for studies that attempt to quantify the PiOH/MNA interaction. The purpose of the present work is to investigate this interaction. The concept of CT interaction also offers a platform for explaining the interaction between electronic subsystems of PiOH and MNA and hence widens the scope of the present investigation on understanding the molecular interaction of MNA with  $\pi$  acceptor PiOH.

### 3.2. Chemistry of m-nitroaniline

3- Nitroaniline, also known as meta-nitroaniline and m-nitroaniline, is non-volatile stable solid commonly used as a raw material for dyes. 3-Nitroaniline is aniline carrying a nitro functional group in position 3. It is stable in neutral, acidic or alkaline solutions and is classified as "not readily biodegradable" with "low bioaccumulation potential". It is used as a chemical intermediate for azo coupling component and the dyes disperse yellow and acid blue. This is changed to other substances (dyestuffs and m-nitro phenol) during the dyeing process.

#### 3.2.1 Properties and Definitions

|                           |   |   |
|---------------------------|---|---|
| Molecular Formula         | : | C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>                                 |
| Molecular Weight          | : | 138.14  |
| Melting Point             | : | 114 <sup>0</sup> C  |
| Boiling Point             | : | 306 <sup>0</sup> C  |
| State                     | : | Solid   |
| Vapour Pressure           | : | 3.1E-6 kPa (2.3E-5mmHg) at 25 <sup>0</sup> C  |
| Octanol / Water Partition | : | log Pow = 1.54 at 25 <sup>0</sup> C calculated  |
| Coefficient               |   |   |
| Water Solubility          | : | 1.14g/L   |
| Impurities                | : | The tested chemical could contain<1-3% impurities. Purity of industrial product is unknown. |
| General comments          | : | Non-volatile. Stable in neutral, acidic or alkaline solutions.                              |

| <b>3-Nitroaniline</b>   |                                   |
|---|-----------------------------------|
|  |                                   |
| Other names   | meta-Nitroaniline, m-nitroaniline |
| <b>Properties</b>   |                                   |
| Molecular formula   | $C_6H_6N_2O_2$                    |
| Molar mass  | 138.14 g/mol                      |
| Appearance  | Yellow, Solid                     |
| Melting point   | 114 °C                            |
| Boiling point   | 306 °C                            |
| Acidity ( $pK_a$ )  | 2.47                              |
| <b>Related compounds</b>  |                                   |
| Related compounds   | 2-Nitroaniline, 4-Nitroaniline    |

### 3.2.2 Overall Evaluation

3-nitrobenzenamine is non – volatile stable solid, and the production volume is 13 tonnes/year for 1990, 16 tonnes for 1991, 7 tonnes for 1992 and 0 tonnes for 1993, respectively, in Japan. The production volume in Germany is 454 tonnes for 1972 and 2270 tonnes for 1976. Canada also produced less than 100 tones/year. This chemical is used as raw material for dyestuff in closed system. This chemical is stable in neutral, acidic or alkaline solutions, and is classified as “not readily biodegradable and “low bioaccumulation potential.” The fact that the chemical is moderately toxic to daphnids, slightly toxic to fish and algae implies the environmental risk presumably to be low.

## 3.3. Experimental

### 3.3.1 Materials and Methods

m-nitroaniline (CDH), picric acid (2, 4, 6, tri nitro phenol) (Aldrich) were obtained commercially and used without further purification. Ethanol (Merck analytical grade), acetone (Merck), methanol (Merck) were redistilled prior to their uses.

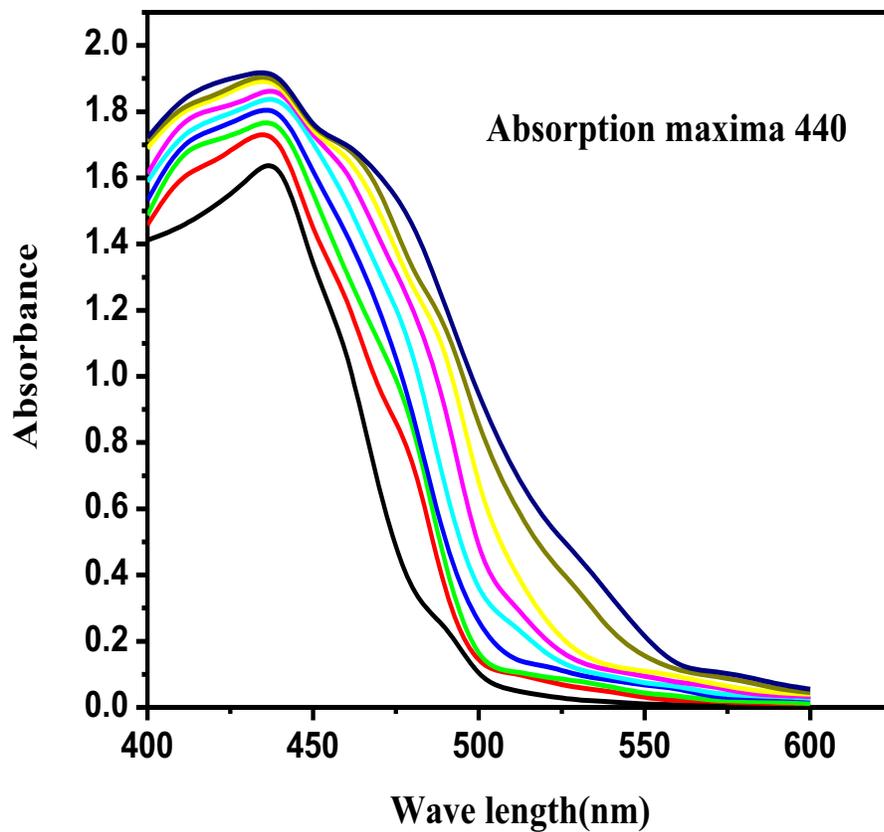
### 3.3.2 Preparation of standard solutions

Solutions of donor of different concentrations, .01 M, .015 M, .02 M, .03 M, .05 M, 0.1 M, 0.2 M, 0.3 M, and 0.5 M were prepared in different volumetric flask by dissolving accurately weighed m-nitroaniline in different solvents such as acetone, ethanol and methanol.

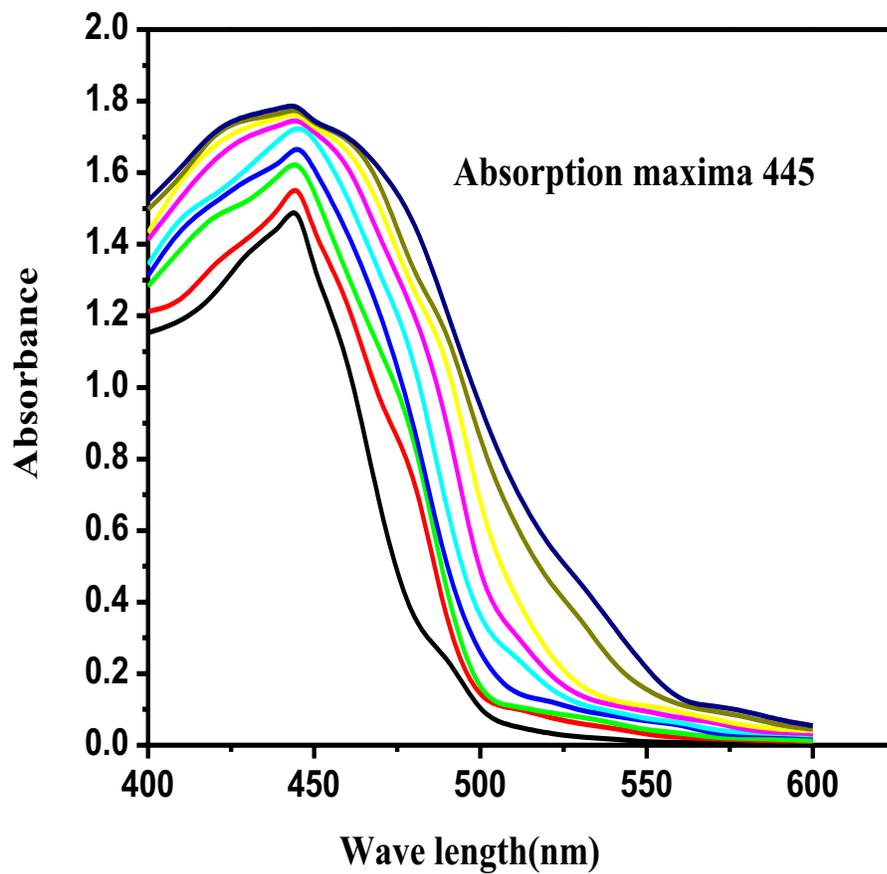
A standard solution of acceptor, picric acid of (0.01 M) concentration was prepared by dissolving accurate weight of acceptor in above solvents in different volumetric flask. The electronic absorption spectra of the donor m-nitroaniline, acceptor picric acid and the resulting complex in acetone, ethanol and methanol were recorded in the visible range 400nm–600nm using a spectrophotometer ELICO SL 177 scanning mini spectrophotometer with a 1cm quartz cell path length, are shown in Figs. (1, 2 & 3).

### 3.3.3 Synthesis of CT complex

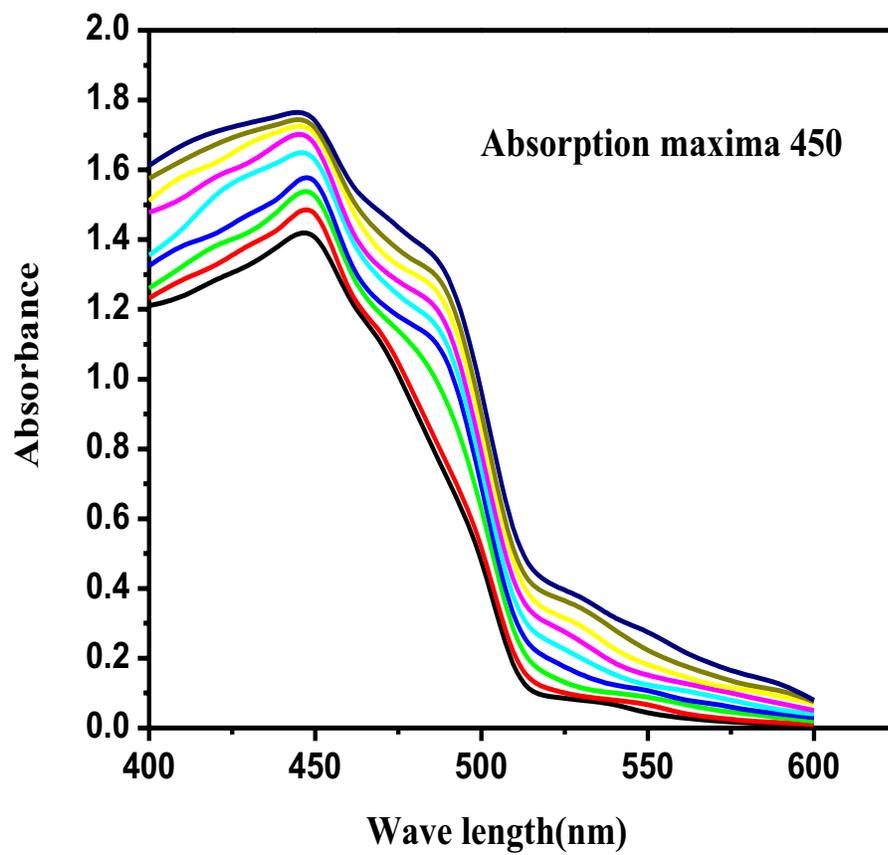
Picric acid, (solid) was mixed with m- nitroaniline, (solid) in agate mortar in the stoichiometric ratio 1:1. The start of the reaction was indicated by a color change



**Fig. 1.** Absorption spectra of picric acid ( $1 \times 10^{-2}$  M) in acetone with addition of m-nitroaniline concentrations ranging 0.01 M to 0.5 M are shown with increasing concentrations bottom to top.



**Fig. 2.** Absorption spectra of picric acid ( $1 \times 10^{-2}$  M) in ethanol with addition of m- nitroaniline concentrations ranging 0.01 M to 0.5 M are shown with increasing concentrations bottom to top.



**Fig. 3.** Absorption spectra of picric acid ( $1 \times 10^{-2}$  M) in methanol with addition of m- nitroaniline concentrations ranging 0.01 M to 0.5 M are shown with increasing concentrations bottom to top.

(dark-yellow). The mixture was thoroughly mixed and kept in oven below their mp. For a week, occasionally mixed during this period .The reaction product was washed several times with benzene to remove untreated components. The color of the final product was dark yellow. The product was dried and kept in a desiccator.

#### *3.3.4 Reaction product from solution*

The saturated solution of picric acid and m-nitroaniline in acetone were mixed and crystallized from benzene. The solution was kept at room temperature for 16 days, giving yellow colored crystals.

#### *3.3.5 Solid state reaction in capillary (reactants in contact)*

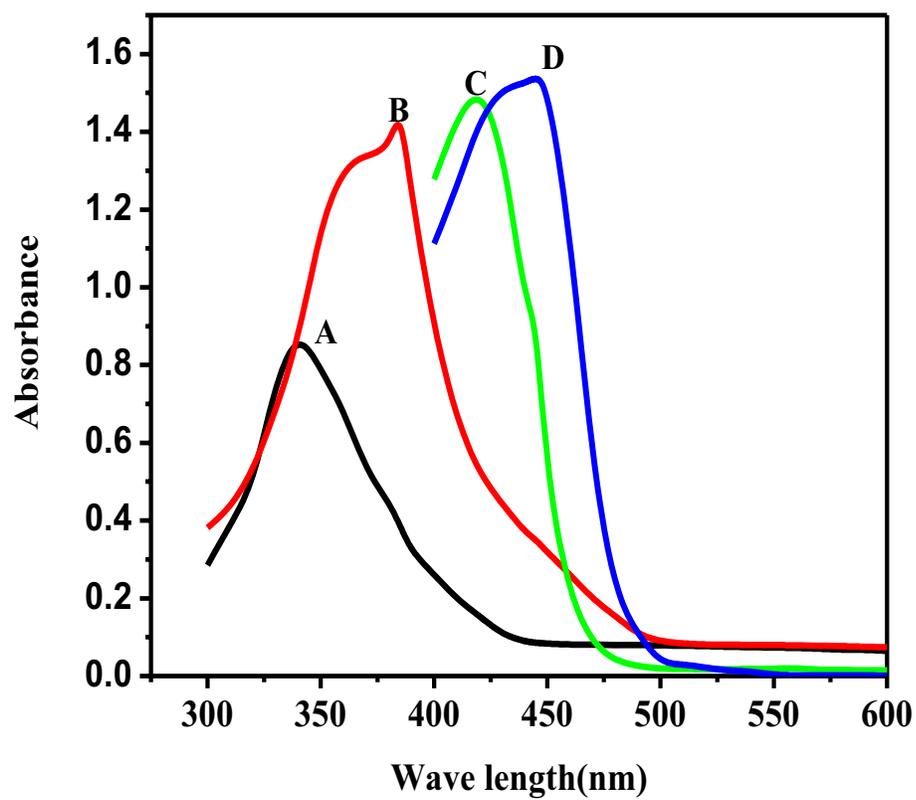
A Pyrex glass capillary having inner diameter (0.186cm) and length about 5cm was used for this purpose one end of the capillary was sealed, half of the capillary was filled with m- nitroaniline of particle size below 100 mesh, for uniform packing, each capillary was tapped for 5 min. the surface was smoothened with the help of a thin glass rod. The remaining half of the capillary was filled with picric acid (particle size < 100 mesh) in such a way that the two components came in close contact. After filling the capillary, the other end was also sealed and kept in oven below their mp. At the junction of the two components, the reaction started with a color change (dark yellow), and grew in the side of picric acid.

FTIR spectra of picric acid , m-nitroaniline and the reaction product obtained from solid state reaction between acceptor and donor were recorded with the help of FTIR spectrometer INTERSPEC – 2020 (spectra lab U.K.) measured in KBr pellets.

#### *3.3.6 Observation of CT bands*

A 3ml volume of donor and 3 ml volume of acceptor were scanned separately through a spectrophotometric titration [20] at room temperature with their wavelength of maximum absorption, which were: 380 nm for picric acid, 420 nm for m-nitroaniline in acetone and for blank solvent (acetone) 340 nm shown in Fig. 4.

For preparing the reaction mixture 10 ml donor and 10 ml acceptor mixed together in different solvents viz - acetone, ethanol and methanol. A dark yellow color charge transfer complex was formed in each solvent (The complex for each of the reaction mixture stood overnight at room temperature to form stable couple



**Fig. 4.** Absorption spectra of (A) Blank solvent (acetone), (B) Picric acid .01 M, (C) m- nitroaniline.01 M, (D) CTC of MNA .01 M and PiOH .01 M in acetone.

before analysis at the maximum absorbance 440 nm for acetone, 445 nm for ethanol and 450 nm for methanol).

The concentration of the donor in the reaction mixture was kept greater than acceptor,  $[D_0] \gg [A_0]$  [21, 22] and changed over a wide range of concentration from 0.01 M to 0.5 M while concentration of  $\pi$ - acceptor(picric acid) was kept fixed [21] at 0.01 M in each solvents, these produced solutions with donor: acceptor molar ratios varying from 1:1 to 50:1, these concentrations ratios were used to straight line diagram for determination of the formation constants of CTC.

To obtain the CT bands, the spectrum of solution of 0.01 M PiOH, and 0.01 M MNA in different solvents were recorded with solvents used as a reference, it is observed that new absorption peak appear in the visible region. In some cases multiple peaks were obtained, the longest wavelength peak was considered as CT peak [23]. The change of the absorption intensity to higher for all complexes in this study when adding the donor was detected and investigated are shown in Table 3.

These measurements were based on the CT absorption bands exhibited by the spectra of the systems which were above mentioned and given in Figs. [1, 2 & 3]. In all the system studied, the absorption spectra are of similar nature except for the position of absorption maxima  $\lambda_{CT}$  of the complex. The CT absorption spectra were analysed by fitting to the Gaussian function  $y = y_0 + [A/w\sqrt{(\pi/2)}] \exp [-2(x-x_c)^2/w^2]$  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 ( $\lambda_{CT} = x_c$ ) and the corresponding transition energies (hv) are summarized in Table 2.

### 3.3.7 Determination of Ionization potentials of the donor

The ionization potentials of the donor ( $I_D$ ) in the charge transfer complexes are calculated using empirical equation derived by Aloisi and Piganatro [24]

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

where  $\nu_{CT}$  is the wave number in  $\text{cm}^{-1}$  corresponding to the CT band formed between donor and acceptor(PiOH).

**Table 1** Gaussian curve analysis for the CT in spectrum of PiOH with MNA  
different polar solvents

| Systems                | Area of the curve (A) | Width of the curve (W) | Centre of the curve ( $x_c$ ) | $Y_0$                 |
|------------------------|-----------------------|------------------------|-------------------------------|-----------------------|
| PiOH+MNA<br>(Acetone)  | $141.92 \pm 7.70$     | $67.00 \pm 3.57$       | $425.58 \pm 1.51$             | $-0.00512 \pm 0.0281$ |
| PiOH+MNA<br>(Ethanol)  | $121.95 \pm 7.50$     | $64.44 \pm 3.77$       | $430.63 \pm 1.49$             | $-0.0052 \pm 0.03162$ |
| PiOH+MNA<br>(Methanol) | $162.63 \pm 11.58$    | $88.30 \pm 5.53$       | $434.44 \pm 2.13$             | $0.01969 \pm 0.03815$ |

**Table 2 CT absorption maxima ( $\lambda_{CT}$ ), transition energies ( $h\nu_{CT}$ ), of the PiOH complexes, experimentally determined values of ionization potentials ( $I_D$ ), oscillator strength ( $f$ ), dipole moments ( $\mu_{EN}$ ), and resonance energies ( $R_N$ ) of complexes**

| <b>Systems</b>         | <b><math>\lambda_{CT}</math> (nm)</b> | <b><math>h\nu_{CT}</math> (eV)</b> | <b><math>I_D</math> (eV)</b> | <b><math>f \times 10^5</math></b> | <b><math>\mu_{EN}</math> (Debye)</b> | <b><math>R_N</math></b> |
|------------------------|---------------------------------------|------------------------------------|------------------------------|-----------------------------------|--------------------------------------|-------------------------|
| PiOH+MNA<br>(Acetone)  | 425.58                                | 2.92                               | 9.34                         | 2.77                              | 0.932                                | 0.0072                  |
| PiOH+MNA<br>(Ethanol)  | 430.63                                | 2.88                               | 9.30                         | 2.49                              | 0.900                                | 0.0066                  |
| PiOH+MNA<br>(Methanol) | 434.44                                | 2.86                               | 9.27                         | 3.37                              | 0.894                                | 0.0065                  |

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

From the CT absorption spectra, one can extract oscillator strength. The oscillator strength  $f$  is estimated using the formula

$$f = 4.32 \times 10^{-9} \int \epsilon_{CT} dv \quad (2)$$

extinction coefficient of the band and  $\Delta\nu_{1/2}$  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.

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

$$f = 4.32 \times 10^{-9} \epsilon_{CT} \Delta\nu_{1/2} \quad (3)$$

where  $\epsilon_{CT}$  is the maximum

The extinction coefficient is related to the transition dipole by

$$\mu_{EN} = 0.0952 [\epsilon_{CT} \Delta\nu_{1/2} / \Delta\nu]^{1/2} \quad (4)$$

where  $\Delta\nu \approx \nu$  at  $\epsilon_{CT}$  and  $\mu_{EN}$  is defined as  $-e \int \psi_{ex} \sum_i r_i \psi_g d\tau$ .  $\mu_{EN}$  for the complexes of PiOH with MNA are given in Table 2

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

Briegleb and Czekalla [25] theoretically derived the relation

$$\epsilon_{CT} = 7.7 \times 10^4 / [h\nu_{CT} / [R_N] - 3.5] \quad (5)$$

where  $\epsilon_{CT}$  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, obviously 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.

### 3.3.10 Determination of Standard free energy changes ( $\Delta G^\circ$ ) and transition energy ( $E_{CT}$ ), of the $\pi$ - $\pi^*$ interaction between donor and acceptor

The standard free energy changes of complexation ( $\Delta G^\circ$ ) were calculated from the association constants by the following equation derived by Martin, Swarbrick and Cammarata [26]

$$\Delta G^\circ = -2.303 RT \log K_{CT} \quad (6)$$

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

The energy ( $E_{CT}$ ) of the  $\pi$  - $\pi^*$  interaction between donor (MNA) and acceptor (PiOH), is calculated using the following equation derived by G. Briegleb and Z. Angew [27]

The calculated values of  $E_{CT}$  given in Table 5

$$E_{CT} = \frac{1243.667}{\lambda_{CT} \text{ nm}} \quad (7)$$

where  $\lambda_{CT}$  is the wavelength of the CT band

## 3.4. Result and discussion

### 3.4.1 Spectrophotometric study of formation constants of the charge transfer complexes of PiOH/MNA in different polar solvents

Stoichiometries and the formation constants of the charge transfer complex of m-nitroaniline with picric acid have been determined in different polar solvents viz- acetone, ethanol and methanol at room temperature using Benesi–Hildebrand equation [28, 29]. The spectrophotometric data were employed to calculate the values of formation constants,  $K_{CT}$  of the complex. The changes in the absorbance

upon addition of MNA to a solution of PiOH of fixed concentration follow the Benesi- Hildebrand [28, 29] equation in the form

$$[A]_o / [A] = (1 / K_{CT}\epsilon_{CT}) \times 1 / [D]_o + 1/\epsilon_{CT} \quad (8)$$

where  $[D]_o$  and  $[A]_o$  are the concentrations of the m-nitroaniline donor, and picric 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  $\epsilon_{CT}$  is the molar extinction coefficient, is not quite that of complex Eq.(8) [28, 29] is valid under the condition  $[D]_o \gg [A]_o$  [21, 22] for 1:1 donor-acceptor complexes. The concentration of the donor (MNA) was changed over a wide range from 0.01M to 0.5M while concentration of  $\pi$  acceptor PiOH was kept fixed at 0.01M in each reaction mixture. These produced solution with donor: acceptor molar ratio varying from 1:1 to 50:1, experimental data are given in Table 3.

The Benesi – Hildebrand [28, 29] method is an approximation that has been used many times and gives decent results. But the extinction coefficient is really a different one between the complex and free species that absorbs at the same wavelength. 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 MNA. The typical absorbance data for charge transfer complexes of MNA with PiOH in different polar solvents at room temperature are reported in Table 1 & 3. In all systems very good linear plots according to Eq. (7) [28, 29] are obtained, shown in Figs. 5, 6, 7. Formation constants for the complex 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 than 0.995. Plots of  $[A]_o / [A]$  against  $1 / [D]_o$  were found to be linear in all systems in Figs. 5, 6 & 7 showing 1:1 charge transfer complex, i.e. the straight lines are obtained with the slopes  $1/K_{CT}\epsilon_{CT}$  and these results prove the formation of the 1:1 CTC. From slope  $1/K_{CT}\epsilon_{CT}$  and intercept,  $1/\epsilon_{CT}$ ,  $K_{CT}$  and  $\epsilon_{CT}$  of the complex were calculated.

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

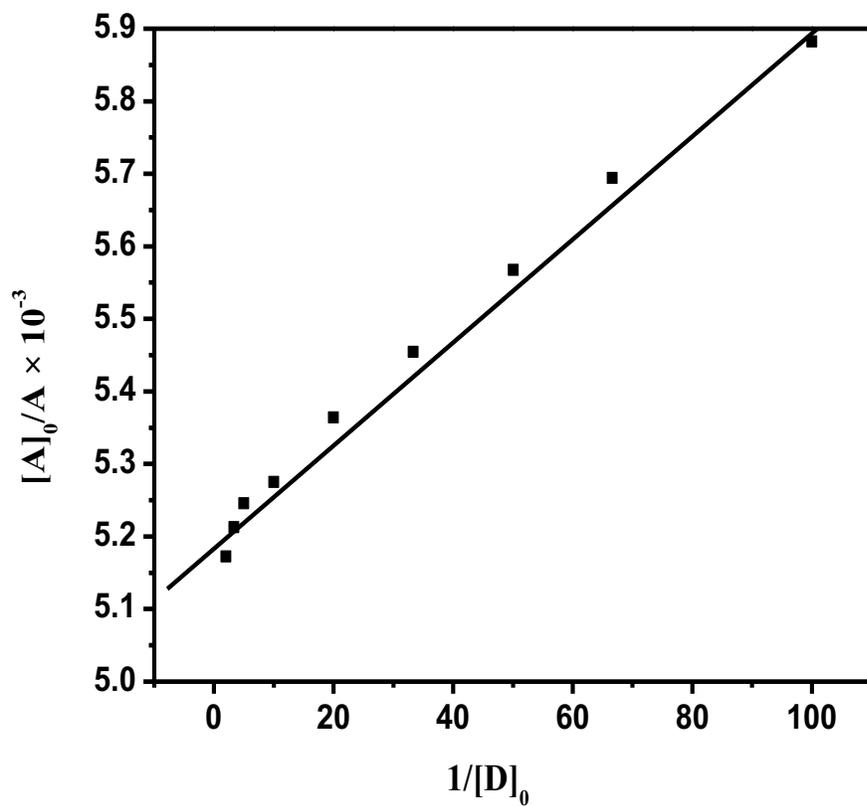
The experimental results of the CT interaction between picric acid with m-nitro aniline in different polar solvents shown in Table 3. The values of association constants ( $K_{CT}$ ) are  $729 \text{ l mol}^{-1}$  in acetone,  $569 \text{ l mol}^{-1}$  in ethanol, and  $470 \text{ l mol}^{-1}$  in methanol and the values of molar extinction coefficient ( $\epsilon_{CT}$ ) are  $192 \text{ l mol}^{-1}\text{cm}^{-1}$  in acetone,  $179 \text{ l mol}^{-1}\text{cm}^{-1}$  in ethanol, and  $177 \text{ l mol}^{-1}\text{cm}^{-1}$  in methanol. 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 increases significantly from methanol to acetone with decreasing solvents polarity. Moreover, the increase in  $K_{CT}$  values with decreasing solvents polarity, may also be due to the fact that, CTC should be stabilized in less polar solvent (30). Dissociation of the complexes into  $D^+ \text{ --- } A^-$  radicals have been found to occur in the ground state.

It means that the CTC should be strong in less polar solvent than polar solvent. The red shift occurred accordingly in CTC complex caused by polarity change from using acetone to methanol.

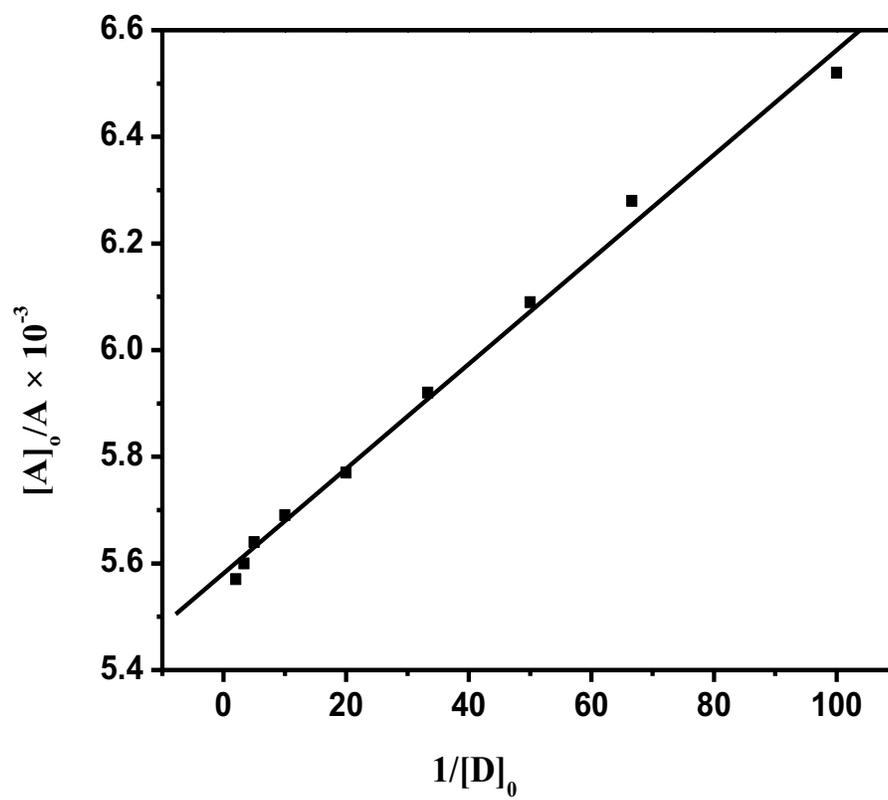
However the data given in Table 3 shows that PiOH interacts more strongly with MNA in acetone than that of the other two solvents. The experimentally determined values of the oscillator strength ( $f$ ) are  $2.77 \times 10^{-5}$  in acetone,  $2.49 \times 10^{-5}$  in ethanol, and  $3.37 \times 10^{-5}$  in methanol, and the values of transition dipole moment ( $\mu_{EN}$ ) are: 0.932(Debye) in acetone, 0.900 (Debye) in ethanol, and 0.894 (Debye) in methanol and values of resonance energy ( $R_N$ ) are: 0.0072 in acetone, 0.0066 in ethanol, and 0.0065 methanol, are given in Table 2. The data indicate that complex should be stable in a less polar solvent (acetone) than the other two solvents (ethanol and methanol). The very low values of  $f$  indicate that CT complex studied here have almost neutral character in its ground state.

**Table 3 Data for spectrophotometric determination of stoichiometry, absorption maxima ( $\lambda_{CT}$ ), and association constants ( $K_{CT}$ ), molar absorptivities ( $\epsilon_{CT}$ ), of CTC of PiOH and MNA in acetone, ethanol, and methanol at 298 K**

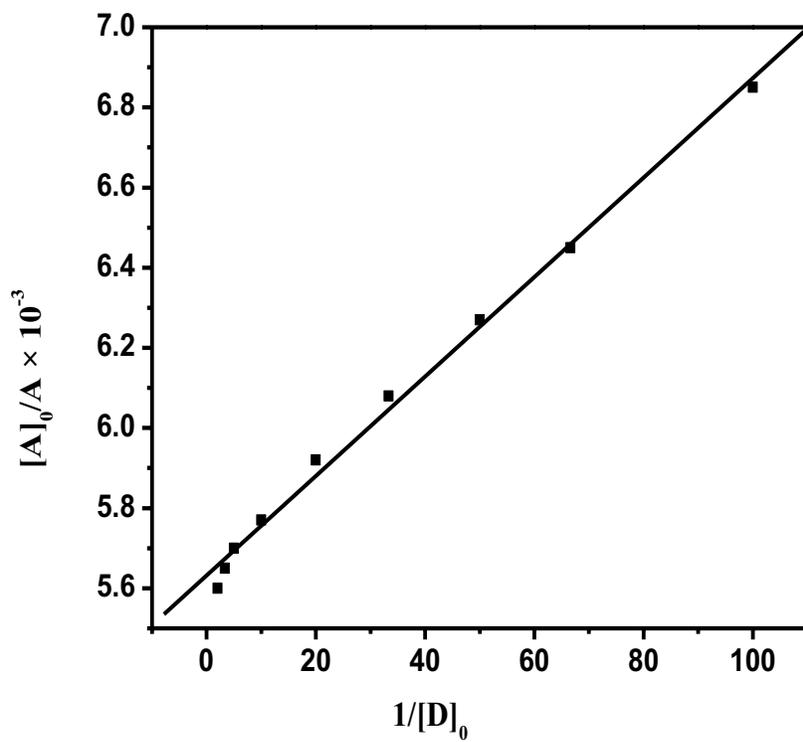
| Systems             | Temperature (K) | Donor concentration in M | [A] <sub>0</sub> in M | Absorbance at $\lambda_{CT}$ (nm) | $\lambda_{CT}$ (nm) | $K_{CT}$ (l mol <sup>-1</sup> ) | $\epsilon_{CT}$ (l mol <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|-----------------|--------------------------|-----------------------|-----------------------------------|---------------------|---------------------------------|---|
| PiOH/MNA (Acetone)  | 298             | 0.01                     | 0.01                  | 1.698                             | 440                 | 729                             | 192   |
|                     |                 | 0.015                    |                       | 1.756                             |                     |                                 |   |
|                     |                 | 0.02                     |                       | 1.798                             |                     |                                 |   |
|                     |                 | 0.03                     |                       | 1.832                             |                     |                                 |   |
|                     |                 | 0.05                     |                       | 1.865                             |                     |                                 |   |
|                     |                 | 0.1                      |                       | 1.895                             |                     |                                 |   |
|                     |                 | 0.2                      |                       | 1.905                             |                     |                                 |   |
|                     |                 | 0.3                      |                       | 1.918                             |                     |                                 |   |
|                     |                 | 0.5                      |                       | 1.932                             |                     |                                 |   |
| PiOH/MNA (Ethanol)  | 298             | 0.01                     | 0.01                  | 1.532                             | 445                 | 569                             | 179   |
|                     |                 | 0.015                    |                       | 1.592                             |                     |                                 |   |
|                     |                 | 0.02                     |                       | 1.642                             |                     |                                 |   |
|                     |                 | 0.03                     |                       | 1.689                             |                     |                                 |   |
|                     |                 | 0.05                     |                       | 1.733                             |                     |                                 |   |
|                     |                 | 0.1                      |                       | 1.755                             |                     |                                 |   |
|                     |                 | 0.2                      |                       | 1.772                             |                     |                                 |   |
|                     |                 | 0.3                      |                       | 1.785                             |                     |                                 |   |
|                     |                 | 0.5                      |                       | 1.795                             |                     |                                 |   |
| PiOH/MNA (Methanol) | 298             | 0.01                     | 0.01                  | 1.458                             | 450                 | 470                             | 177   |
|                     |                 | 0.015                    |                       | 1.548                             |                     |                                 |   |
|                     |                 | 0.02                     |                       | 1.593                             |                     |                                 |   |
|                     |                 | 0.03                     |                       | 1.643                             |                     |                                 |   |
|                     |                 | 0.05                     |                       | 1.689                             |                     |                                 |   |
|                     |                 | 0.1                      |                       | 1.732                             |                     |                                 |   |
|                     |                 | 0.2                      |                       | 1.752                             |                     |                                 |   |
|                     |                 | 0.3                      |                       | 1.768                             |                     |                                 |   |
|                     |                 | 0.5                      |                       | 1.785                             |                     |                                 |   |



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



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



**Fig. 7.** Relation between  $[A]_0/A$  and  $1/[D]_0$  of PiOH and MNA in methanol

The parameters thus obtained are represented in Table 4 and these values show that complexation is thermodynamically favored. The free energy change of the complexation also reveals that the CTC formation between used donor (MNA) and acceptor (PiOH) is of exothermic in nature. The values of ( $\Delta G^0$ ) are -16.318 ( $\text{kJmol}^{-1}$ ) in acetone, -15.691( $\text{kJmol}^{-1}$ ) in ethanol and -15.234 ( $\text{kJmol}^{-1}$ ) in methanol and are also shown in Table 4.

Free energies changes are generally more negative as the association constants of the molecular complex increases. As the bond between the components becomes stronger and thus the components are subjected to more physical strain or loss of freedom, the values of  $\Delta G^0$  become more negative.

The ionization potentials  $I_D$  (eV) of the donor can be calculated using the experimentally determined  $\lambda_{CT}$  of the CTC from Eq. (1) (24). The calculated values of ( $I_D$ ) are 9.23 (eV) in acetone, 9.19 (eV) in ethanol and 9.15 (eV) in methanol of PiOH/MNA system and they are shown in Table 5. The approximate consistency of  $I_D$  values indicates that the ionization potential has a negligibly small effect on  $K_{CT}$  values.

#### 3.4.3 Comparative study of FT- IR spectra of CT complex and reactants

FT-IR spectra of the free acceptor and donor as well as the formed CT complex are given in Fig. 8 and their bands assignments reported in Table 6. However the appearances of a group of FT-IR spectral bands in the spectra of CT complex support the conclusion that a deformation of the electronic environment of m-nitroaniline has occurred by accepting a proton from PiOH. The shift of the FT-IR bands of the acceptor to lower wave numbers and those of the donor part to higher values reflects a donor to acceptor charge transfer of  $\pi$ - $\pi^*$  interaction, i.e.  $D_{HOMO} \rightarrow A_{LUMO}$  transition [32].

The FT-IR spectrum of the complex of PiOH and MNA in Fig 8. Shows the presence of characteristic absorption bands due to the varied forced constants in the donor and the acceptor species on account of the prevalent charge transfer mechanism. This makes the crystals of this type more ionic than other organic crystals. The asymmetric and symmetric stretching vibrations of the  $-\text{NO}_2$  group are observed at  $1536.52 \text{ cm}^{-1}$  and  $1344.13 \text{ cm}^{-1}$  respectively. Normally the asymmetric stretching vibration of the  $-\text{NO}_2$  group is sensitive to polar influences and the electronic states of the species. Therefore, it has been realized that the shift to lower

**Table 4 Association constant ( $K_{CT}$ ), correlation coefficients (r) and Standard free energy changes ( $\Delta G^0$ ) of PiOH/MNA complexes obtained from Benesi-Hildebrand plots**

| Systems                | $K_{CT}$<br>( $l\text{mol}^{-1}$ ) | $-\Delta G^0(298\text{K})$<br>( $\text{kJmol}^{-1}$ ) | r     |
|------------------------|------------------------------------|---|-------|
| PiOH/MNA<br>(Acetone)  | 729                                | 16.318  | 0.995 |
| PiOH/MNA<br>(Ethanol ) | 569                                | 15.691  | 0.996 |
| PiOH/MNA<br>(Methanol) | 470                                | 15.234  | 0.997 |

**Table 5** The CTC transition energies ( $E_{CT}$ ), CTC absorption maxima ( $\lambda_{CT}$ ), and Ionization potential ( $I_D$ ) of donor of in different polar solvents

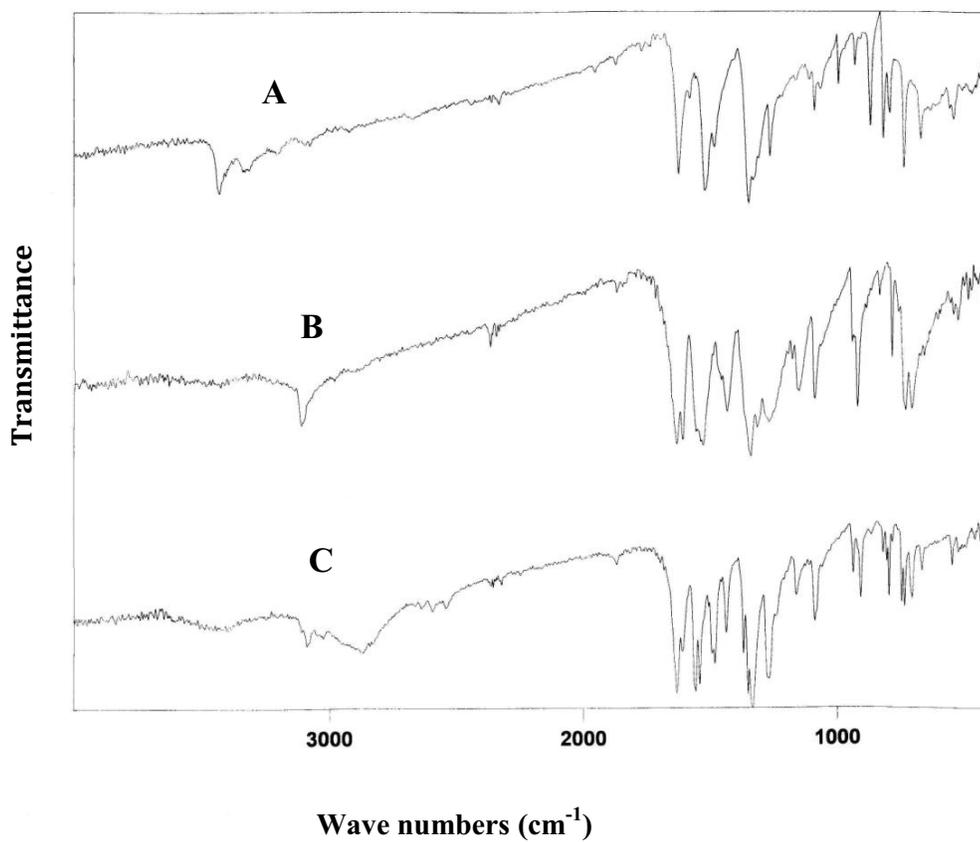
| <b>Systems</b>         | <b><math>E_{CT}</math> (eV)</b> | <b><math>\lambda_{CT}</math> (nm)</b> | <b><math>I_D</math> (eV)</b> |
|------------------------|---------------------------------|---------------------------------------|------------------------------|
| PiOH/MNA<br>( Acetone) | 2.82                            | 440                                   | 9.23                         |
| PiOH/MNA<br>(Ethanol)  | 2.79                            | 445                                   | 9.19                         |
| PiOH/MNA<br>(Methanol) | 2.76                            | 450                                   | 9.15                         |

**Table6**

**Characteristic infrared frequencies (cm<sup>-1</sup>) and tentative assignments for PiOH, MNA and their complex.**

| PiOH                | MNA                 | Complex             | Assignments   |
|---------------------|---------------------|---------------------|---|
| 3108s,br            | 3433sharp           | 3253ms              | v(O-H) ,H bonded                                    |
| -                   | 3322br              | -                   | v (N-H)   |
| -                   | 3190sh              | 3090ms              | v (C-H)   |
| 2875 w              | 2664sh              | 2857br              | v <sub>s</sub> (C-H)                                |
| -                   | -                   | -                   |   |
| 1630vs              | -                   | -                   | v <sub>as</sub> (C-H)                               |
| 1606ms              | 1621 v <sub>s</sub> | 1632ms              | v <sub>as</sub> NO <sub>2</sub>                     |
| 1529 br             | 1585sh              | 1608sh              | v(C=C)  |
| -                   | 1519br              | 1536br              | δ def (N-H), +NH <sub>2</sub> ring breathing bands  |
| -                   | 1484sh              | 1425 v <sub>s</sub> | C-H deformation                                     |
| 1437ms              | -                   | -                   |   |
| -                   | 1342w               | 1344br              | v(C-C), v <sub>s</sub> NO <sub>2</sub>              |
| 1341v <sub>s</sub>  | 1322sh              | -                   | v(C-N)  |
| 1275 v <sub>s</sub> | 1261 v <sub>s</sub> | 1278w               | v(C-O)  |
| 1154ms              | 1048 v <sub>s</sub> | 1148ms              | (C-H) in plane bending                              |
| 1083ms              | -                   | 1171ms              |   |
| -                   | -                   | 1090ms              |   |
| 916ms               | 993ms               | 913ms               | δ <sub>rock</sub> , +NH <sub>2</sub>                |
| 830w                | 922 sharp           | 892sh               |   |
| 779sharp            | 866sharp            | 842ms               | CH <sub>2</sub> <sub>rock</sub> skeletal vibrations |
| -                   | 811v <sub>s</sub>   | 807ms               |   |
| -                   | 735v <sub>s</sub>   | 781v <sub>s</sub>   |   |
| 734ms               | 664v <sub>s</sub>   | 731v <sub>s</sub>   | C-H out of plane bending                            |
| 703ms               | -                   | 704ms               |   |

S, strong, w, weak; m, medium, sh shoulder, v, very; vs very strong, br broad; v, stretching; v<sub>s</sub>, symmetrical stretching; v<sub>as</sub> asymmetrical stretching.



In the spectra of CT- complex of m-nitroaniline and picric acid, MNA almost completely consumed evidence of H- bonding and -OH intensity decreased and position of the peak also shifted.

frequency of  $\nu_{\text{asym}} \text{NO}_2$  vibration ( $1536.52\text{cm}^{-1}$ ) in the spectrum of the complex compared with free picric acid ( $1606\text{cm}^{-1}$ ) is due to the increased electron density on the picric acid moiety owing to the charge transfer interaction in the complex [33].

### Conclusions

From the foregoing discussion, it may be concluded that the UV -Vis spectrophotometric method for the study of CTC of picric acid with m-nitroaniline reveals that it forms 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,  $K_{\text{CT}}$  and molar extinction coefficients  $\epsilon_{\text{CT}}$  of all systems were evaluated by the Benesi - Hildebrand method. The values of association constant of the CTC decrease with increasing solvent polarity, due to the destabilization of CTC in polar solvents and then the dissociation of the complex into  $\text{D}^+ \text{A}^-$ . The interaction between the donor and acceptor was found to be  $\pi$ - $\pi^*$  transitions by the formation of radical ion pairs. The spectroscopic and thermodynamic parameters of the complexes were found to be solvents dependent. The values of the oscillator strengths ( $f$ ) transition dipole moments ( $\mu_{\text{EN}}$ ) resonance energies ( $R_{\text{N}}$ ) and standard free energies ( $\Delta G^\circ$ ) have been estimated for the PiOH/MNA systems in different polar solvents. The results show that the investigated 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 spectrum shows that the complex was formed by transferring a proton from the acceptor (PiOH) to the donor (MNA).

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