CHAPTER - 2

ORGANIC THIOLIGANDS EMPLOYED IN THE PRESENT RESEARCH
CHAPTER - 2

2.1. **METHODS OF PREPARATION AND GENERAL PROPERTIES OF SOME ORGANIC THIOLIGANDS**

The methods of preparation and general properties of the organic reagents used in the present investigation are described below:

2.1.(a) **Preparation and General Properties of Thiocarbohydrazones**

[B60]

Bis (thiophene-2 aldehyde) thiocarbohydrazone and bis (indole-3 aldehyde) thiocarbohydrazone were obtained as condensation products of thiocarbohydrazide with thiophene-2 aldehyde and indole-3 aldehyde respectively, which were prepared as follows:

**Thiocarbohydrazide** [61]:

250 ml of 100 % hydrazine hydrate (5 mole) and 150 ml of water were taken in a one litre three necked round bottomed flask fitted with stirrer, dropping funnel (pressure equiliser type) and a condenser. 76 gms (1 mole) of carbon disulphide were added drop by drop from the dropping funnel to the vigorously agitated hydrazine hydrate solution. After the addition of carbon disulphide the reaction mixture was refluxed on boiling water bath for 30 minutes and cooled in ice bath for half an hour. On cooling, thiocarbohydrazide separated out. It was filtered, washed with ethanol and ether and air dried. The mother liquor was returned to the original
flask and the above procedure of alternate refluxing and cooling was repeated twice. The thiocarbohydrazide obtained from three operations was mixed and recrystallised from water acidified with few drops of concentrated hydrochloric acid. Needle shaped white shining crystals of thiocarbohydrazide were obtained which melt at 168°C.

**Thiophene-2 aldehyde [62]:**

To a solution of 42 gm (0.5 mole) of thiophene and 46 gm (0.64 mole) of dimethyl formamide which was cooled and shaken in a 500 ml flask equipped with a reflux condenser and calcium chloride guard tube, was added slowly 96 gm (0.69 mole) of phosphoryl chloride. The flask was carefully heated on a steam bath until a strong exothermic reaction commenced after which the reaction was modified by cooling in an ice bath until the rapid evolution of hydrochloric acid vapour ceased. The mixture was finally heated on a steam bath for one hour with occasional shaking and then cooled and poured with stirring into a beaker containing 500 gms of cracked ice after which the acidic solution was neutralised with a saturated solution of sodium acetate. The oily liquor was separated and combined with ether extract of the aqueous solution. The ether extract was washed free of all traces of acids with dilute sodium bicarbonate solution, dried over anhydrous sodium sulphate and finally concentrated, vacuum distillation of the resulting red oil gave 2- thiene aldehyde (b.p. 44-45°C at 1.1 mm pressure).
Indole-3 aldehyde [63]:

In a round bottomed three necked flask fitted with an efficient mechanical stirrer, a drying tube and a 125 ml dropping funnel was placed 288 ml of freshly distilled dimethyl formamide. The flask and its contents were cooled in an ice-salt bath for about half an hour and 86 ml of freshly distilled phosphoryl chloride was subsequently added with stirring to the dimethyl formamide over a period of half an hour. The pinkish colour of formylation complex was observed during this step. The 125 ml dropping funnel was replaced with a 200 ml dropping funnel and a solution of 100 gms of indole in 100 ml of dimethyl formamide was added to the yellow solution over a period of one hour during which time the temperature was not allowed to rise above 10°C. After the solution was well mixed the dropping funnel was replaced with a thermometer, and the temperature of the viscous solution was brought to 35°C. The syrup was stirred efficiently at this temperature for one hour for becoming the solution to an opaque canary yellow paste. At the end of the reaction period, 300 gms of cracked ice were added to the paste with careful stirring producing clear cherry red aqueous solution.

This solution was mixed with 100 ml of water and the mixture was transferred to a 3-l three necked flask containing 200 gms of crushed ice and fitted with an efficient mechanical stirrer and a separatory funnel containing solution of 375 gm (9.4 mole) of sodium hydroxide in one litre water. The aqueous base was added
dropwise with stirring until about one third of it has been added. The remaining two-third was added rapidly with efficient stirring and the resulting suspension was heated rapidly to the boiling point and allowed to cool to room temperature after which it was placed in a refrigerator overnight. The precipitate was collected on a filter and suspended in water. Most of the inorganic material dissolved and the product was then collected on a filter washed with water and air dried, yielding about 120 gm indol-3 aldehyde, m.p. 196-197°C.

i) Bis (thiophene-2 aldehydo) thiocarbohydrazone :

The thiocarbohydrazone of thiophene-2 aldehyde (BTATCH) was prepared by adding two moles of thiophene-2 aldehyde slowly to an aqueous hydrochloric acid solution of thiocarbohydrazide (1 mole) in a round bottomed flask with constant shaking. The reaction started immediately at room temperature with the separation of slightly yellowish flocculent precipitate of bis (thiophene-2 aldehydo) thiocarbohydrazone. The precipitate was filtered off and washed with ethanol and ether and recrystallised from ethanol, dried at room temperature and stored in a desiccator. BTATCH which was formed as a white flaky crystalline compound, melts at 183°C. The compound is highly stable at room temperature without any decomposition even after one year of storing in a desiccator. The reagent is insoluble in water, moderately soluble in alcohol and highly soluble in dimethyl formamide. Elemental analysis of the compound
(C = 44.49 %, H = 3.30 %, N = 18.94 %, S = 32.60 %) agrees with the formula C_{11}H_{10}N_{4}S_{3} (C = 44.89 %, H = 3.40 %, N = 19.04 %, S = 32.65 %).

ii) Bis (indole-3 aldehydo) thiocarbohydrazone:

The thiocarbohydrazone of indole-3 aldehyde was prepared by the method as described above, the only exception was that crystalline indole-3 aldehyde in ethanol was taken in place of thiophene-2 aldehyde. A yellow precipitate of bis (indole-3 aldehydo) thiocarbohydrazone was obtained and was recrystallised from dimethyl formamide-water mixture. Bis (indole-3 aldehydo) thiocarbohydrazone forms yellow, flaky crystals, which melt at 220°C with decomposition. The compound is highly stable, insoluble in water, poorly soluble in ethanol, but highly soluble in dimethyl formamide.

2.1.(b) Preparation and General Properties of Substituted Thioureas

I. Acyl substituted thioureas. General method of preparation:

All the acyl substituted thioureas of the type R-NH-C=NH C-R were prepared by the following general procedure as described by R. Charonnat and F. Le. Perdriel [64]. Ammonium thiocyanate (0.1 mole) was dissolved in acetone and 0.1 mole of the respective acylating agent (RCOCl) was added slowly with constant shaking. The mixture was refluxed for 10 minutes on a hot water bath and most of the
acetone was removed by distillation. The residue was added slowly in crushed ice taken in a beaker with constant stirring when the reagent solidified. The crude reagent was filtered and recrystallised from ethanol. The following acyl substituted thioureas were prepared and described below:

i) N-α-Naphthyl-N¹-benzoyl thiourea:

α-naphthyl amine and benzoyl chloride were taken as the starting materials. The recrystallised compound is insoluble in water and moderately soluble in ethanol. Melting point of the compound is 166°C. The compound is stable towards heat, light and air.

ii) N-Parahydroxy phenyl-N¹-benzoyl thiourea:

Using benzoyl chloride and β-hydroxy aniline as the starting material the organic reagent was prepared. The recrystallised reagent (m.p. 162°C) was obtained as white powdered crystals. It is insoluble in water, highly soluble in ethanol and stable towards heat, light and air.

iii) N-Paramethyl-phenyl-N¹-benzoyl thiourea:

The organic reagent was obtained as light yellow needle shaped shining crystals using benzoyl chloride and paramethyl aniline as the starting materials. The recrystallised reagent (m.p. 157°C) is stable towards heat, light and air. It is poorly soluble in water and moderately soluble in ethanol.
iv) N-Paramethoxy-phenyl-N'-benzoyl thiourea:

The organic reagent was prepared from 4-methoxy aniline and benzoyl chloride. The reagent was obtained as shining white crystals, insoluble in water, moderately soluble in ethanol and stable towards heat, light and air. The melting point of the reagent is 160°C.

v) N-3-Pyridyl-N'-benzoyl thiourea:

The reagent was prepared by using 3-amino-pyridine and benzoyl chloride. The recrystallised reagent is white crystal with a yellow tinge and highly soluble in ethanol and melts at 165°C. It is stable towards heat, light and air.

II. Disubstituted thioureas-General method of preparation [65]:

0.2 mole of R-NH₂ in ethanol and 0.1 mole of carbon disulphide were mixed with a little (20% of the weight of carbon disulphide) powdered potassium hydroxide and taken in a round bottom flask. The content was refluxed for eight hours on an electrical water bath. The whole system was set up on a fume cupboard. When the reaction was completed, the content of the flask almost solidified. Excess carbon disulphide was distilled off and the residue in the flask was shaken with dilute hydrochloric acid to remove any amine (R-NH₂) present. It was filtered and washed with dilute hydrochloric acid. The crude product was recrystallised from rectified spirit.
i) N, N'-diparamethoxy phenyl thiourea:

The organic reagent was prepared from para methoxy aniline and carbon disulphide. The recrystallised white crystals are insoluble in water and moderately soluble in hot-ethanol. The compound is stable towards heat, light and air.

ii) N, N'-dipyridyl thiourea:

This organic compound was prepared by using 2-amino pyridine and carbon disulphide as the starting materials.

The recrystallised reagent (m.p. 146°C) was obtained as shining nice white needle shaped crystals. It is poorly soluble in water, highly soluble in ethanol and stable towards heat, light and air. Elemental analysis of the compound (C = 57.68 %, N = 24.04 %, H = 4.49 %, S = 13.92 %) is in good agreement with the formula C_{11}H_{10}N_{4}S (C = 57.39 %, H = 4.348 %, N = 24.34 %, S = 13.91 %).

2.2. PROPERTIES OF CHELATES FORMED BY THE ORGANIC THIOLIGANDS WITH PLATINUM METALS

2.2.(a) Chelates Formed by Thioarbohydrazones:

i) Chelates of bis (thiophene-2 aldehyde) thioarbohydrazone (BTATCH) with platinum metals:

BTATCH, the thioarbohydrazone of thiophene-2 aldehyde posses
excellent chelating abilities with all the platinum metals and the characteristics of the chelates are summarised below:

**TABLE 2.1.**

**PROPERTIES OF THE CHELATES FORMED BY BIS (THIOPHENE-2 ALDEHYDO) THIOCARBOHYDRAZONE WITH PLATINUM METALS**

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Condition for complex formation</th>
<th>Colour of the complex/ $\lambda_{\text{max}}$ (nm)</th>
<th>Solubility in ethanol</th>
<th>Extractable in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(III)</td>
<td>Hot and dilute hydrochloric and 0.3 - 0.7 (N)</td>
<td>Pink 540</td>
<td>Soluble</td>
<td>not extractable</td>
</tr>
<tr>
<td>Rh(III)</td>
<td>Hot acetate buffer medium</td>
<td>yellow 385</td>
<td>soluble</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>Dilute hydrochloric acid/Na-acetate buffer medium at room temperature 2-5 pH</td>
<td>yellow 385-390</td>
<td>soluble</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>Os(VI)</td>
<td>Hot acetate buffer medium 5.5-6.0pH</td>
<td>Brown 390-395</td>
<td>soluble</td>
<td>ethyl acetate chloroform: ethanol</td>
</tr>
<tr>
<td>Ir(III)</td>
<td>Hot acetate buffer medium 5.6-6.6pH</td>
<td>yellow 380</td>
<td>soluble</td>
<td>ethyl acetate ethanol</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>Hot acetate buffer</td>
<td>Reddish brown 410</td>
<td>soluble</td>
<td>ethyl acetate</td>
</tr>
</tbody>
</table>
Bis (thiophene-2 aldehydo) thiocarbohydrazone may serve as an ideal analytical reagent for the determination of platinum metals due to the following reasons:

i) The complex formation reactions could be made selective by proper control of pH, temperature etc.

ii) The reagent produces sensitive colour reactions with the platinum metals and most of the platinum metal complexes exhibits their \( \lambda_{\text{max}} \) in visible region. Interferences from other metals can be avoided with easy practice.

The spectrophotometric determination of ruthenium(III) and iridium(III) with the above reagent is discussed in Chapter 3.

ii) Chelates of bis (indole-3 aldehydo) thiocarbohydrazone with platinum metals:

The results of the preliminary study of the reactions between the platinum metals and the reagent are shown in Table 2.2.
## Table 2.2

Properties of the Chelates Formed by Bis (Indole-3 Aldehydo) Thio Carbollhydrazone with the Platinum Metals

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Condition for complex formation</th>
<th>Colour of the complex</th>
<th>Extractable in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(III)</td>
<td>Dilute hot hydrochloric acid medium</td>
<td>Red</td>
<td>not extractable</td>
</tr>
<tr>
<td>Rh(III)</td>
<td>Hot acetate medium</td>
<td>Brown</td>
<td>not extractable</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>Acetate medium at room temperature</td>
<td>Yellow</td>
<td>Extractable in ethyl acetate</td>
</tr>
<tr>
<td>Os(VI)</td>
<td>Hot acetate medium</td>
<td>Deep green</td>
<td>Isobutyl methyl ketone</td>
</tr>
<tr>
<td>Ir(III)</td>
<td>In hot dilute hydrochloric acid medium</td>
<td>Orange red</td>
<td>not extractable</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>Hot acetate medium</td>
<td>Green</td>
<td>Isobutyl methyl ketone</td>
</tr>
</tbody>
</table>

Although the colour reactions as shown in Table 2.2. are favourable but the organic thioligand is very much insoluble in water and ethanol and the compound itself is coloured in both the acid and acetate media. The reagent is found to be unsuitable for the spectrophotometric determination of the platinum metals.

2.2.(b) Chelates formed by Substituted Thioureas with Platinum Metals
I. Platinum metal chelates of acyl substituted thioureas:

The following acyl substituted thioureas react with the platinum metals and form coloured complexes:

i) N-α-naphthyl-N'-benzoyl thiourea

ii) N-para-hydroxyphenyl-N'-benzoyl thiourea

iii) N-paramethylphenyl-N'-benzoyl thiourea

iv) N-para-methoxyphenyl-N'-benzoyl thiourea

v) N-β-pyridyl-N'-benzoyl thiourea.

In view of their poor sensitivity and selectivity, the analytical applications of the above reagents have not been studied further.

II. Chelates formed by disubstituted thioureas with platinum metals:

i) Chelates of N, N'-diparamethoxy phenyl thiourea:

The results of the preliminary studies on the reactions between the platinum metals and the above thioligand are shown in Table 2.3.
It can be seen from Table 2.3 that the thioligand forms coloured platinum metal complexes under different conditions. However, it can not be recommended as an analytical reagent for the said metals because of its poor solubility and sensitivity.
**ii) Chelates of N, N'-dipyridyl thiourea with platinum metals:**

N, N'-Dipyridyl thiourea possesses excellent chelating abilities with all the platinum metals and the properties of those chelates are summarised below:

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Condition of complex formation</th>
<th>Colour of the complex</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Extractable in</th>
<th>Composition expressed as the molar ratio of the reagent and metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(III)</td>
<td>Hot acetate buffer medium 3.7-5.5 pH</td>
<td>Yellowish brown</td>
<td>350</td>
<td>Chloroform: ethanol</td>
<td>3:1</td>
</tr>
<tr>
<td>Rh(III)</td>
<td>Hot acetate buffer medium 4.7-6.6 pH</td>
<td>Yellow</td>
<td>335</td>
<td>Chloroform</td>
<td>3:1</td>
</tr>
<tr>
<td>Pt(II)</td>
<td>Acetate buffer medium of room temperature 4.4-5.6 pH</td>
<td>Yellow</td>
<td>330</td>
<td>Chloroform</td>
<td>2:1</td>
</tr>
<tr>
<td>Os(VI)</td>
<td>Hot acetate buffer medium 3.6-5.8 pH</td>
<td>Green</td>
<td>355</td>
<td>Chloroform: ethanol</td>
<td>2:1</td>
</tr>
<tr>
<td>Ir(III)</td>
<td>Hot acetate buffer medium 5.0-6.4 pH</td>
<td>Yellow</td>
<td>335</td>
<td>Chloroform: ethanol</td>
<td>3:1</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>Hot dilute hydrochloric acid medium</td>
<td>Brown</td>
<td>340</td>
<td>Chloroform: ethanol</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Hot acetate buffer medium</td>
<td>Yellow</td>
<td>350</td>
<td>Chloroform: ethanol</td>
<td>-</td>
</tr>
</tbody>
</table>
N, N'-dipyridyl thiourea may be recommended as an ideal analytical reagent for the spectrophotometric determination of platinum metals owing to the following reasons:

i) The complex formation reactions can be made selective by proper control of acidity, temperature, masking agent etc.

ii) The complexes are highly coloured and are easily extractable in organic solvents.

iii) The colour reactions are highly sensitive.

iv) The chelates are highly stable under reaction conditions and are in definite composition.

The detailed analytical studies have been described in Chapter 4.

Though the reagent N, N'-dipyridyl thioureas (D.Py.T) forms extractable coloured complexes with all the platinum metals e.g. ruthenium(III), rhodium(III), palladium(II), osmium(VI), iridium(III) and platinum(IV) but detailed analytical study of ruthenium(III) and platinum are not entitled here. Because the reagent, forms a brown complex with ruthenium (λ\text{max} at 350 nm (u.v. region) and in comparison with the firstly mentioned reagent, BTATCH, it is less selective in determination of ruthenium, and is discarded. The reagent (D.Py.T) forms a brown complex with platinum(IV) in dilute hydrochloric acid medium (0.5-1 M) and
yellow complex in hot acetate buffer medium, but the first method suffer from lack of sensitivity (molar absorptivity is the order of $\sim 10^3$ L mole$^{-1}$ cm$^{-1}$), while the other method is satisfactory when sensitivity is concerned but cannot be recommended due to its poor selectivity. Thorough analysis of rhodium(III), palladium (II), osmium(VI), iridium(III) are performed with great success.

2.3. ULTRAVIOLET AND INFRARED ABSORPTION SPECTRA OF THE ORGANIC THIOligands

The present investigation is based on the colour reactions between platinum metal ions and the organic thioligands. It is, therefore, desirable to discuss the spectral characteristics of these reagents:

1) Ultraviolet Absorption Spectra of the Thioligands:

A Carl-Zeiss FMQ II model spectrophotometer was used for measuring the transmittance of the organic compounds.

a) Bis (thiophene-2 aldehyde) thiocarbohydrazone (BTATCH):

The absorption spectrum of BTATCH in ethanol shown in Fig. 2.1. exhibits two absorption maxima at 260 nm and 335 nm.

The heterocyclic compound, thiophene, due to the presence of low energy d-orbital on the sulphur atom possesses aromatic character and hence the spectrum of the above compound, a derivative
of thiophene, may be compared with the spectrum of benzene derivatives. The absorption maxima which appears at 260 nm 
\( \sim 10^5 \text{ L mole}^{-1} \text{ cm}^{-1} \) may be compared with the band at 255 nm in pure benzene. This bathochromic shift may be due to loss in symmetry through substitution. The second peak appearing at 335 nm 
\( \sim 10^5 \text{ L mole}^{-1} \text{ cm}^{-1} \) may be due to extension of conjugation [66, 67] as exhibited by thiosemicarbazone. This band may be assigned to be due to \( n - \pi^* \) transitions [68] considering the shifting of absorption maxima in different polar solvents.

b) \( N, N'\)-dipyridyl thiourea (D. Py. T):

Fig. 2.2. represents the absorption spectra of \( N, N'\)-dipyridyl thiourea, the spectrum of pyridine derivative may be compared with that of benzene derivative (considering the hetero atom as \(-\text{CH} = \text{CH}-\) group in benzene). The absorption spectrum in this case exhibits two maximal absorption peaks. One at 263 nm \( \sim 10^4 \text{ L mole}^{-1} \text{ cm}^{-1} \) possibly arises from \( n - \pi^* \) transition and another at 300 – 305 nm 
\( \sim 10^4 \text{ L mole}^{-1} \text{ cm}^{-1} \) may be assigned to be due to \( n - \pi^* \) transition because the peak is shifted to shorter wavelength in solvents of increasing polarities [68].

ii) Infrared Absorption Spectra of the Thioligands:

A Perkin-Elmer 597 infrared spectrophotometer was used for measuring the absorbances of the organic compounds in potassium bromide phase.
Fig. 2.1 Absorbance curve of Bis-(thiophene-2-aldehyde)-thiocarbohydrazone in ethanol.

\[ \text{[Bis-(thiophene-2-aldehyde)-thiocarbohydrazone]} = 1 \times 10^{-6} \text{(M)} \]
Fig. 2.2 Absorbance curve of N,N'-Dipyridylthiourea in ethanol.

\([N,N'-\text{Dipyridyl thiourea}] = 2 \times 10^5 \text{(M)}\)
a) Bis (thiophene-2 aldehydo) thiocarbohydrazone (BTATCH):

The infrared absorption spectrum of BTATCH is shown in Fig. 2.3.

The nature of the main characteristic bands due to contents of the various functional groups is discussed here. The absorption bands at 3250 cm$^{-1}$ and 2960 cm$^{-1}$ appeared to be due to presence of -N-H and -CH stretching frequency respectively. The weak band appeared at 1600 cm$^{-1}$ may be due to -C=N stretching frequency [71]. Here CNH stretching frequency may be corresponds to the band at 1550 cm$^{-1}$ (involving both -NH bending and -CN stretching).

Much difficulties arise in characterising the -C=S absorption band. Because in organic thioamides, assignments for the proposed absorption band have ranged from 1570 cm$^{-1}$ to 690 cm$^{-1}$ and there has been much controversy on this range. The available data have been widely reviewed by Rao et al. [69] and by Jenson and Neilson [70]. The band appeared at 1500 cm$^{-1}$ correspond to amide - II frequency. The bands between 1265 cm$^{-1}$ and 1225 cm$^{-1}$ may be assigned due to amide - I band. The frequency of 1380 cm$^{-1}$ may be due to C-N stretching vibration. The strong band appeared at 725 cm$^{-1}$ may be assigned due to aromatic moiety present in the compound. All of these bands are in well agreement with the band observed in thiocarbohydrazide and explained by Kurzer and Wilkinson[71a].
Fig. 2.3 IR absorption curve of Bis(thiophene-2-aldehyde) thiocarboxydrazone in KBr phase.
b) **N, N'-dipyridyl thiourea**

The Fig. 2.4 represents the infrared absorption spectrum of N, N'-dipyridyl thiourea. Using the references of Belamy [72] and Nakanisi [73], the main characteristic bands which arise due to the functional groups discussed here. The bands between 1500 and 1600 cm\(^{-1}\) are highly characteristic of the aromatic ring itself. The bands between 1470 cm\(^{-1}\) and 1435 cm\(^{-1}\) correspond to amide II frequency. The strong band at 1470 cm\(^{-1}\) may be assigned to C-N stretching mode. The frequency at 1350 cm\(^{-1}\) may also be due to C-N stretching frequency. And the band at 1310 cm\(^{-1}\) may be represented the mixed vibration of CN and NH mode and from the observed bands at 1140, 1185 cm\(^{-1}\), we may assigned the presence of C=S stretching frequencies. The strong band appeared at 760 cm\(^{-1}\) may be explained as the out of plane C-H bending absorption of monosubstituted pyridine [72].

### 2.4. DISSOCIATION CONSTANTS OF THE ORGANIC THIOLIGANDS

It has been pointed out in Chapter -1, that the greater the basic strength of any ligand, the greater is the stability of its metal complexes. In order to have an idea about the basicity of the ligand, the dissociation constant of N, N'-dipyridyl thiourea has been determined potentiometrically in 50 % ethanol, but that of Bis (thiophene-2 aldehyde) thiocarbohydrazone could not be obtained because of its low solubility.
Fig. 2-4. IR absorption curve of N,N-Dipyridyl thiourea in KBr phase.
Dissociation constant of N, N'-dipyridyl thiourea by Bjerrum's half $\bar{n}_H^+$ method [74]:

N, N'-dipyridyl thiourea is considered as weak monobasic acid. In a solution of weak acid, say HA, there is an equilibrium between the ions and the undissociated molecules, which can be represented as follows:

$$HA \rightleftharpoons H^+ + A^-$$

The dissociation constant ($k_a$) for a monobasic acid should be,

$$k_a = \frac{[H^+][A^-]}{[HA]} \quad (I)$$

where the terms in the brackets represent concentrations in dilute solutions.

The ligands were titrated against standard alkali solution and the pH values were recorded. The $\bar{n}_H^+$ values were then calculated from the following equation:

$$\bar{n}_H^+ = \frac{\text{Total concentration of } H^+ \text{ ion present} - \text{H}^+ \text{ ion liberated}}{\text{Total concentration of ligand}}$$

$$= \frac{C_A + E + [OH^-] - [H^+] - C_B}{C_A} \quad (II)$$

From the knowledge of the concentration of the ligand ($C_A$), free acid present ($E$) if added, and amount of standard alkali added ($C_B$),
together with pH value of the medium and ionic product of water 
($K_w$), the quantity $n^+$ can be calculated. For values of $n^+ < 1$, 
the ligand may be titrated with standard alkali and the equation 
(II) reduces to the form,

$$
\bar{n}^+ = \frac{C_k + [\text{OH}^-] - [H^+] - C_B}{C_k}
$$

(III)

The dissociation constant $k_a$, can be subsequently derived by 
conventional Bjerrum's method, i.e. by plotting $\bar{n}^+$ against pH 
of the medium. The $K_a$ value (negative logarithm of dissociation 
constant) was the computed from the pH value corresponding to 
$\bar{n}^+ = 0.50$.

EXPERIMENTAL

Apparatus:

A systronics expanded-scale pH meter (type 331), equipped 
with glass and calomel electrodes, was used for all pH measurements.

Reagents and Chemicals:

Reagent solution:

$N, N'$-dipyridyl thiourea:

Doubly recrystallised reagent was dissolved in spectroscopic 
grade ethanol to prepare exactly a $1.0 \times 10^{-2}$ M solution.
Sodium hydroxide solution:

Solution of sodium hydroxide was prepared by dissolving pellets of pure sodium hydroxide (E.M.) in carbon dioxide free double distilled water and dilute solutions of different strengths were prepared. The solutions were standaridised against standard oxalic acid solution.

Sodium perchlorate solution:

Sodium perchlorate (E.M.) was purified by crystallisation and a definite amount of salt was dissolved in double distilled water in order to prepare a 0.1 M sodium perchlorate solution. All chemicals used were of analytical grade.

Procedure:

Potentiometric titrations were carried out with these ligands in 50:50 (v/v) water-ethanol mixture against standard sodium hydroxide to find out the dissociation constant of the reagent. A measured amount of the reagent solution was taken in a 50 ml pyrex beaker and the temperature was thermostatically maintained at 31 ± 0.5°C. A supporting electrolyte like sodium perchlorate solution was added to maintain the ionic strength 0.025 M. The measurements in all the cases were carried out at this constant ionic strength of 0.025 M. After each addition of standard sodium hydroxide from a microburette, pH of the solution was read with the help of a pH-meter, equipped with glass and calomel electrode. Stirring was carried out with a magnetic stirrer which was switched off during
the measurement of pH of the solution. During titrations ethanol was added in appropriate amounts so as to maintain water-ethanol ratio (v/v) constant. The pH-meter was standarised against buffer solutions of pH 4.0 (phthalate buffer) and 9.27 (borate buffer) and 7.0 before titrations and was checked after each set of titrations with the same buffer.

Results:

The concentration correction at each steps of titration due to change in volume of the solutions are incorporated in the results represented in the Table 2.5, as well as in Fig. 2.5.

**TABLE - 2.5.**

DISSOCIATION CONSTANT OF N, N'-DIPYRIDYL THIOUREA

<table>
<thead>
<tr>
<th>Alkali (0.025 M) added in ml.</th>
<th>pH</th>
<th>$n_H^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.92</td>
<td>9.99</td>
</tr>
<tr>
<td>0.09</td>
<td>8.60</td>
<td>9.97</td>
</tr>
<tr>
<td>0.21</td>
<td>9.30</td>
<td>9.93</td>
</tr>
<tr>
<td>0.35</td>
<td>9.72</td>
<td>9.90</td>
</tr>
<tr>
<td>0.54</td>
<td>9.88</td>
<td>9.86</td>
</tr>
<tr>
<td>0.70</td>
<td>10.02</td>
<td>9.80</td>
</tr>
</tbody>
</table>
TABLE 2.5 (CONTD.)

<table>
<thead>
<tr>
<th>Alkali (0.025 M) added in ml.</th>
<th>pH</th>
<th>$\bar{n}H^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.83</td>
<td>10.14</td>
<td>.78</td>
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<tr>
<td>.96</td>
<td>10.20</td>
<td>.75</td>
</tr>
<tr>
<td>1.15</td>
<td>10.26</td>
<td>.71</td>
</tr>
<tr>
<td>1.53</td>
<td>10.42</td>
<td>.61</td>
</tr>
<tr>
<td>1.68</td>
<td>10.52</td>
<td>.58</td>
</tr>
<tr>
<td>1.88</td>
<td>10.60</td>
<td>.545</td>
</tr>
<tr>
<td>2.16</td>
<td>10.68</td>
<td>.45</td>
</tr>
<tr>
<td>2.33</td>
<td>10.70</td>
<td>.268</td>
</tr>
<tr>
<td>2.82</td>
<td>10.80</td>
<td>.005</td>
</tr>
</tbody>
</table>

The pK$_a$ value of $N, N'$-dipyridyl thiourea was calculated from the graph shown in the Fig. 2.5. And it is $\approx 10.60$. 
Fig. 2.5 πH–pH curve of N,N'-Dipyridyl thiourea in 50% ethanol.