

Spectroscopic study on Thiourea and Thiosemicarbazide in Non-aqueous media

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Abstract: The spectroscopic methods of the different regions of the Electromagnetic spectrum are the most powerful and useful techniques available for the understanding of molecular structure, nature of bonding between atoms, confirmation analysis, symmetry of molecules, ions in crystals and so forth. The high resolution IR spectroscopic studies have recently received a great thrust due to the advent of advanced Fourier transform spectrometers. In the present investigation the spectral changes are studied in the vibrational spectra of thiourea, thiosemi carbazide in non aqueous solvent. The H_2N stretching vibrations observed at $3371cm^{-1}$, $3259cm^{-1}$, & $3156cm^{-1}$ indicated that 3 different types of NH_2 groups arising out of tautomeric form. The results obtained from the present study confirm that the solute – solvent interactions occurring in the solution is through intermolecular H- bonding.

Keywords – Dimeric structure, Hydrogen bonding, Thiosemicarbazide, Thiourea.

I. Introduction

Progress in the area of non-linear optics (NLO) depends upon the development of new materials. When compared with the inorganic materials, organic and materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response time and good optical properties [1-3]. The advent of the instrumental methods like infrared has now made the task of an organic chemist comparatively simpler [4] although the IR spectrum is characteristic of the entire molecule. Fourier transform Infrared Spectrometry (FTIR) has been extensively developed over the past decade and provides a number of advantages. The Organo sulfur compounds have variety of applications in industries. It is mainly used in textile processing [5] and also in the reductive work up of Ozonolysis [6] to give carbonyl compound. They are also used as building blocks to pyrimidine derivatives. Thiourea condenses with β -dicarbonyl compounds [7]. Thiourea is a reagent in organic synthesis to pharmaceuticals like thiobarbituric acid and sulfathiazole. Thiosemicarbazide has been shown to be good ligand for range of metals, including zinc, mercury, cadmium and nickel [8,9] Thiosemicarbazide is a thiourea derivative. It is used in the preparation of antibacterial compounds. In the present investigation the FTIR spectral studies are carried out in non – aqueous solutions of thiourea(Thiourea solvated in formamide) & thiosemicarbazide (Thiosemicarbazide in formamide) in order to probe the effect of H – bonding in the solvation process.

II. Experimental Technique

Thiourea & Thio semicarbazide (AR Merc) were used in non - aqueous medium. Solutions of saturation molalities were prepared by weighing in electronic balance and an accuracy of (0.001gm) were stored in vaccum decicator until use. The Fourier transform infrared was carried out between $4000cm^{-1}$ to $400cm^{-1}$ by recording the spectrum using PERKIN ELMER SPECTRUM RXI spectrometer.

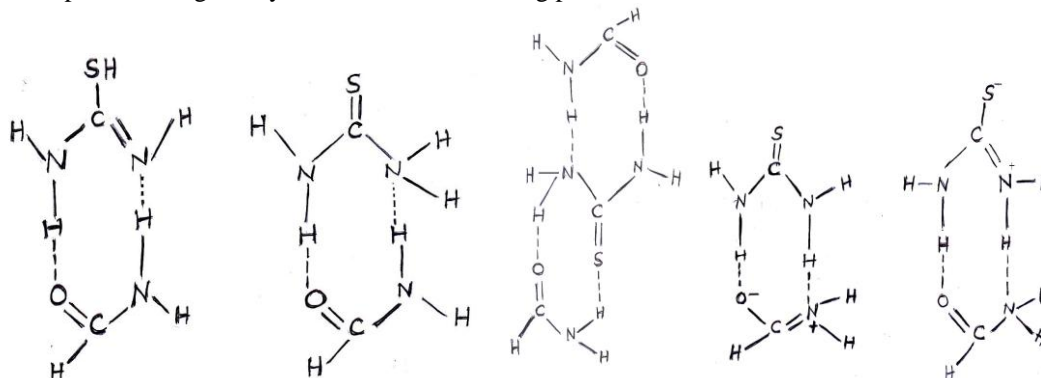
III. Results And Discussion

1.1 FTIR Study – THIOUREA (TU)

The spectrum of formamide (solvent) and thiourea(solute) is shown in fig. (1) and (2).The observed frequencies are tabulated. In the spectrum of thiourea, the vibrations found at $3371cm^{-1}$, $3260cm^{-1}$, & $3156cm^{-1}$ indicate that the three different types of NH_2 groups arising out of tautomeric form. The peaks at $2684cm^{-1}$, $2354 cm^{-1}$ besides small shoulders upto $2100 cm^{-1}$ are indicative of ammonium & iminium salt like structure. A sharp peak at $1585 cm^{-1}$ arises due to thioamide (C=S) asymmetric stretching vibration while the symmetric vibrations may be located at $1449 cm^{-1}$. A broad band at $1088 cm^{-1}$ is due to C-S vibrations. The sharp peak at $729 cm^{-1}$ is assigned to the S-H bending vibration. C-N bending vibration and NH bending vibration found at $627 cm^{-1}$ and at $493 cm^{-1}$ respectively.

1.2 FTIR- THE SOLUTION OF THIOUREA IN FORMAMIDE:

The solution spectrum is shown in fig. (3) In the solution the solvent peak at 3416cm^{-1} has shifted to 3372cm^{-1} towards lower energy side by 44cm^{-1} . Besides a series of stretching vibrations are observed at 3267cm^{-1} , 3163cm^{-1} , 2888cm^{-1} , 2688cm^{-1} and at 2204cm^{-1} . These vibration frequencies are confirmed the presence of both the solute [NH] and solvent peaks [CH] and [C=NH]. The sharp peak of bands at 1697cm^{-1} and 1550cm^{-1} in the solvent spectrum have disappeared and a new band occurs at 1598cm^{-1} . This peak has arisen due to H- bonding between $>\text{C}=\text{O}$ of solvent and NH_2 of solute destroying the dimeric structure of pure solvent. The $>\text{C}=\text{S}$ vibration at 1584cm^{-1} is shifted to higher energy by 14cm^{-1} . A higher energy shift of 10cm^{-1} occurs at 1399cm^{-1} peak and dramatic change in this band region may be attributed to solute- solvent interaction in $>\text{C}=\text{N}-\text{H}$ site. A new peak arises at 1077cm^{-1} due to C-S stretching mode of the solute. The 729cm^{-1} 627cm^{-1} are due to bending vibrations of the solute shifted to lower energy region of the solution compared to the salt spectrum. In this region the 494cm^{-1} has shifted to higher energy region by 1cm^{-1} . All these spectral changes may be due to the H-bonding pattern which shown below



1.3 FTIR - THIOSEMI CARBAZIDE (TSC)

The salt spectrum of TSC is shown in fig. (4) The series of vibrations in the region 3365cm^{-1} to 3169cm^{-1} are due to different types of NH_2 and NH groups. The absorption frequencies found at 1616cm^{-1} and 1516cm^{-1} are due to $>\text{C}=\text{S}-\text{NH}$ functional groups. ie. asymmetric and symmetric stretching vibrations of thio amide I & II bands. At 1273cm^{-1} & 1155cm^{-1} C=N bending and C-S stretching vibrations occur. The C-S, NH_2 and NH bending vibrations are found at 993cm^{-1} , 792cm^{-1} , 649cm^{-1} and 576cm^{-1} respectively.

1.4 FTIR - THIOSEMICARBAZIDE IN FORMAMIDE (TSC)

The solution spectrum of TSC in formamide is shown in fig. (5), which is similar to the solvent rather than to the salt. This indicates the predominant amount of formamide compared to solute molecules. A lower energy shift of 3400cm^{-1} band by 16cm^{-1} is observed. It is due to the weakening of C=O-NH bonds in the solvent. Broadening of this peak which is quite smooth may be due to the binding of NH of formamide to another group in the solute. The four small shoulders like peaks in the region 2407cm^{-1} to 2064cm^{-1} have become well defined in the solution spectra indicating the presence of strong solute – solvent interactions. A broad peak centered at 1619cm^{-1} encompasses both the amide I of formamide and thioamide I band of TSC. The intense peak is characteristics of strong solute - solvent interaction at $>\text{C}=\text{O}$ & $>\text{C}=\text{S}$ groups. This peak has shifted to lower energy region by 79cm^{-1} indicating $>\text{C}-\text{O}$ more single bond character during donor – acceptor interaction. Similarly the amide II vibration has also shifted to lower energy by 22cm^{-1} indicating lengthening of bonds. At 997cm^{-1} , 787cm^{-1} , the solute vibrations are observed. The former is higher energy shift by 3.6cm^{-1} , while the later peak is lower energy shift by 4.5cm^{-1} which is the indication of strong binding. The solute – solvent interaction through inter molecular H bonding are given below.

Solute-Solvent interaction of thiosemicarbazide with formamide

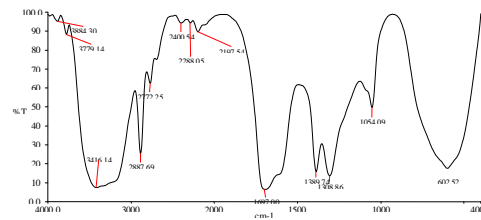
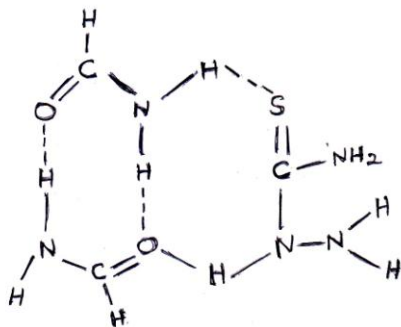


Fig.1 FTIR Spectrum of Formamide

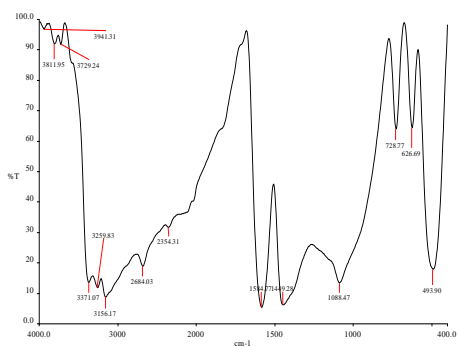


Fig.2 FTIR Spectrum of Thiourea

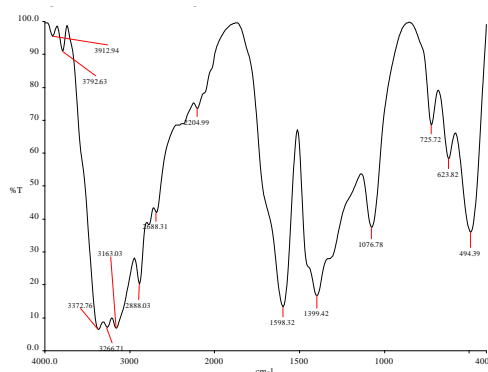


Fig.3 FTIR Spectrum of Thiourea in Formamide

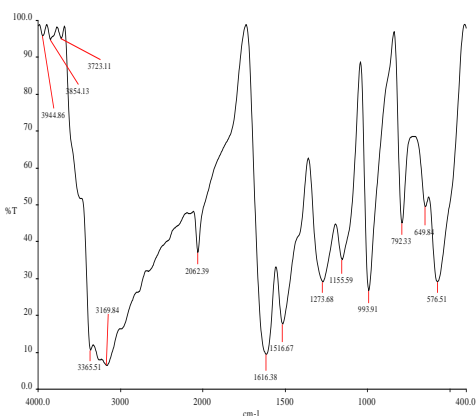


Fig.4 FTIR Spectrum of Thiosemicarbazide

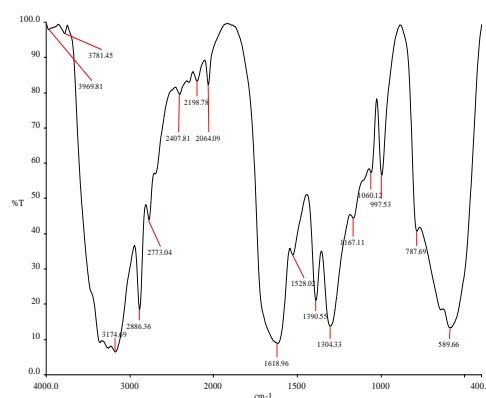


Fig.5 FTIR Spectrum of Thiosemicarbazide in Formamide

TABLE - 1 A comparative study of FTIR spectral results

Band Assignment	Wave Number cm^{-1}				
	Formamide	Thio urea	Thio urea with Formamide	TSC	TSC with Formamide
ν_{NH}	3416	3371	3372	3366	3400(sh)
ν_{CH}	2888	3260	3267	3169	2886
	2772	3156	3163	2400–	2773
	2600 – 2500(sh)	2684	2888	2300(sh)	2600(sh)
	2400	2354	2688	2062(sh)	2408
$\nu_{\text{C=N}}$	2288	2100	2205	1616	2300-2200(sh)
	2197	1700 –	1598	1517	1618
$\nu_{\text{C=S}}$	1697	1600(sh)	1377	1356(sh)	1528
$\nu_{\text{C-S}}$	1550(sh)	1584	1400–	1273	1391
	1390,1309	1449	1300(sh)	993	1304
	1054	1088	726	792	1060
ν_{CH}	603	729	624	650	997
		627	494	577	787
		494			590

IV. Conclusion

From this spectral analysis various functional groups are identified. The dimeric structure of formamide is changed due to solvation with thiourea. Strong solute-solvent interaction occurs in TSC with formamide. This study also confirmed that the solute- solvent interactions occurring in the solutions is through intermolecular H-bonding.

Acknowledgement

Authors acknowledge the immense help received from the scholars whose articles are cited and included in references of this manuscript. The authors also grateful to authors/editors/publishers of all those articles, journals and books from where the literature for this article has been reviewed and discussed.

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