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ULTRASONIC AND SPECTROSCOPIC INVESTIGATION OF THIOUREA IN NON-AQUEOUS MEDIA

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ABSTRACT

Acoustical and thermo chemical behavior of thiourea in formamide is studied using ultrasonic technique. The Ultrasonic velocity (u), density (ρ) and viscosity (η) measurements have been carried out for the solution at 278, 288, 298, 308, 318 and 328K and at different concentrations. The results arrived from ultrasonic technique yield the various intermolecular interactions occur in the solution. Spectroscopic techniques have been used to identify the various functional groups. The results obtained from spectroscopic studies were correlated with acoustical and thermo chemical properties of the solution.

Keywords: Thiourea(TU), Formamide, Acoustical parameter, Thermo chemical parameter, Tautomeric form, Dimeric structure.

INTRODUCTION

Ultrasonic study on the solution of Thiourea in non-aqueous media provides useful information in understanding the behavior of liquid systems, intramolecular, intermolecular associations and related structural changes. Thioureas are important sulfur and nitrogen containing compounds and they are useful substances in drug research. Some thiourea derivatives possess valuable biological pharmacological activities such as, anti-HIV [1-4] and anticancer properties [5-7]. In addition, urea and thioureas [8-10] have emerged as structurally novel anticonvulsant. Thiourea is mainly used in textile processing [11] and also in the reductive work up of Ozonolysis [12] to give carbonyl compound. Another common application of thiourea is a common sulfur source for making semiconductor calcium sulfide nanoparticle. Use of thiourea is also a measure of change in body water [13]. The role played by the solvent is not a minor one. The presence of a solvent can speed up or slow down a reaction by a factor of 10^{20} [14]. Solvent effects can be more powerful than the effects exerted by any other factor. The solvent formamide is also a constituent of cryoprotectant vitrification mixtures used for cryopreservation of tissues and organs. The current work is to emphasis the solvation effect of thiourea in formamide is studied by calculating various parameters such as Solvation Number(n_h), Apparent Molal Volume(φ_v), Apparent Molal Compressibility(φ_k) Internal Pressure [π_i], Free Volume [V_f] and Intermolecular free Length (L_f). The results obtained from the ultrasonic study as well as spectroscopic study used to analyse various reactions occurring in the solution.

EXPERIMENTAL DETAILS
Ultrasonic Analysis

The chemicals used in the present work are analytical (AR) reagent grade and spectroscopic

(SR) reagent grade of minimum assay of 99.9% obtained from E-Merck. An electrically maintained constant temperature bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperatures. The accuracy in the temperature measurement is ±0.1K. The density of the solution is measured using specific gravity bottle. The viscosity of the solution is measured by the Ostwald's viscometer. Density, viscosity and ultrasonic velocity are determined for thiourea in formamide from 278K to 328K at different molalities using compressibility method. From these obtained data thermo chemical and acoustical parameters are calculated using the following formulae

Solvation Number

$$n_h = \left(\frac{n_s}{n_i}\right)\left[1 - \frac{\beta}{\beta_0}\right] \qquad -------- \quad (1)$$

η - Viscosity of the solution in poise.

β_0 & β are the compressibility of the solvent & solution in cm^2/dynes.

Apparent Molal Volume

$$\varphi_v = \frac{1000}{c_1\rho_0}(\rho_0 - \rho) + \frac{M_1}{\rho_0}\, ml\, mol^{-1} \qquad ------ \quad (2)$$

ρ_0 & ρ are the density of the solvent and solution in gm/cc.

c_1 - The molal concentration M_1 - Molecular weight of the solute in gm.

Apparent Molal Compressibility

$$\varphi_k = \frac{1000}{c_1\rho_0}(\rho_0\beta - \rho\beta_0) + \beta_0\frac{M_1}{\beta_0}\, ml\, mol^{-1}\, cm^2\, dyne^{-1}$$

$$----- \quad (3)$$

c_1 - The molal concentration M_1 - Molecular weight of the solute in gm.

ρ_0 & ρ are the density of the solvent and solution in gm/cc.

β_0 & β are the compressibility of the solvent & solution in cm^2/dynes.

Internal Pressure [π_i]

$$\pi_i = b\, RT\, (k\eta/u)^{1/2} *(\rho^{2/3} / M_{eff}^{7/6})\, atms\, ----- \quad (4)$$

b - Cubic constant (2)

R-Gas constant (8.314×10^7)   T-Temperature k - Constant equal to 4.28×10^9

η - Viscosity of the solution in poise   u- Ultrasonic velocity in cm/sec ρ- Density of the solution in gm/cc M_{eff} - Effective molecular weight of the solution in gm

Free Volume [V_f]

$$V_f = (M_{eff} * u/k\eta)^{3/2}\, cc\, ----- \quad (5)$$

M_{eff} - Effective molecular weight of the solution in gm u - Ultrasonic velocity in cm/sec

k - Constant equal to 4.28×10^9 η - Viscosity of the solution in poise

Intermolecular free Length (L_f)

$$L_f = K\, (\rho)^{-1/2} / u\, \text{Å}\, ----- \quad (6)$$

K – Constant depends on temperature. ρ - Density of the solvent in gm/cc.

u - Ultrasonic velocity in cm/sec.

Spectrum analysis

FTIR spectrum was recorded between 4000 cm^{-1} to 400 cm^{-1} using PERKIN ELEMER SPECTRUM RX1 spectrometer. The UV absorption spectrum of solvent, solute and the solution are also taken.

RESULTS

From the ultrasonic study, the calculated values of various parameters are given in the Table (1) and Table (2). The variations of the parameters with respect to molalities are represented in Figure (1a -1f). The observed spectrum of thiourea, formamide and thiourea in formamide are shown in figure (2a-2c) and observed frequencies are tabulated in table (3).

The UV absorption spectrum of solvent, solute and the solution are shown in figure (3a-3c). The observed peaks are tabulated in table (4).

DISCUSSIONS
Ultrasonic study

The solvation number is positive at high temperatures. At .001m the solution exhibits

positive solvation number for almost all the temperatures. Zero value of solvation number only indicates that no change occurs in the compressibility value of the solvent when the solution is formed. Negative values of solvation number at lower temperatures emphasize that solutions are more compressible than solvent. Positive solvation number of solution suggests that compressibility of the solution at high temperature and at low molalities will be less than that of the solvent. The apparent molal volume (Φv) of thiourea is negative, for all molalities and temperatures. The apparent molal volume (Φv) decreases, as concentration increases, at all temperatures. This supports that there is a weak ion-ion interaction occurring in solution. In thio urea, the apparent molal compressibility (Φk) is found to be negative at 308.15K and 318.15K almost all molalities. The apparent molal volume and apparent molal compressibility have been proven to be a very useful tool in elucidating the structural interaction occurring in solutions.

The acoustical parameters explain the nature and strength of the interaction taking place in the solutions. In the solution, the internal pressure increases up to 0.01m for almost all the temperature. Beyond the 0.01m the internal pressure decreases with respect to molality. This behavior indicates breaking nature of solute in the solvent. The variations in the free volume (V_f) with respect to molalities and temperature of the solutions of thiourea behave in an opposite manner to that of internal pressure as expected.

The results obtained from the present study suggest that the solute- solvent interactions occurring in the solution. This may be due to intermolecular hydrogen bonding present in this system. Intermolecular free length (L_f) is one of the important acoustic parameter in determining the nature of the interaction between the components of the solution. The rise and fall observed in intermolecular free length for all temperatures and molalities in thiourea solution.

This supports the dissociation of molecules occurring in the solution. Thiourea occurs in tautomeric form which is shown in figure (4). In aqueous solution the thione form predominates. Dimeric structure of Formamide is shown in figure (5). Enolic form of formamide is shown in figure (6).

Spectral studies

FT-IR spectroscopy is by far the best way to detect the presence of functional groups in a molecule. The C═O is a strong bond in a carbonyl group. The strong bond due to C═O stretching appears at about 1700cm^{-1}, where it is a seldom obscured by other strong absorptions. In the solvent this strong peak is appeared at 1685 cm^{-1} and in the solution it is right shifted by 2 cm^{-1} i.e. at 1683 cm^{-1}.

In the solvent a peak is appeared at 2771 cm^{-1} and in the solution at 2767 cm^{-1}. It is due to C─H stretching band this in conjugation with carbonyl band is fairly certain evidence for an aldhyde. In the solution at 2391cm^{-1} a peak is observed which is due to asymmetrical stretching mode, since it produces a change in the dipole moment, is IR active. In the solute at 3376 cm^{-1} and at 3177 cm^{-1} peak are observed which represent the different types of N─H stretching band. These peaks classify the types of amide. Tautomeric nature of the solute is confirmed by observing the symmetric and asymmetric N─H stretching vibrations at 3376 cm^{-1} and in 3177 cm^{-1}.

In the solution a peak is observed at 1589 cm^{-1}. This involves coupling of the N─H bending and C─N stretching vibration. Resonance effect occurs in carbonyl absorptions due to replacement. In solvent resonance effect predominates than the inductive effect. This effect increases C═O bond length and reduces the frequency of absorption, which effect is confirmed by observing a peak at 1685 cm^{-1} in the solvent and in the solution which is further decreased by 2cm^{-1} i.e. at 1683cm^{-1}. A new band occurs at 1598 cm^{-1}. This is due to H- bonding via >C=O of solvent and NH$_2$ of solute

destroying the dimeric structure of pure solvent. When a carbonyl group of amide is involved in hydrogen bonding its stretching frequency is lowered [15], which is observed in the solution at $1683cm^{-1}$ by lowered $2cm^{-1}$ from $1685cm^{-1}$ in the solvent. Rao and Vengataraghavan [16] correlated data on their spectra of thiocarbonyl derivatives in the literature and concluded that strong vibrational coupling was operative in the case of nitrogen containing thiocarbonyl derivatives and that the C═S vibrations are not located. From that observation it is confirmed that thiourea in non-aqueous media the thiol form predominates. These bands appear consistently in the region of $1570cm^{-1}$ to $1397cm^{-1}$, $1420cm^{-1}$ to $1260cm^{-1}$ and $1140cm^{-1}$ to $940cm^{-1}$ in the IR spectrum because of mixed vibrations of ─N─C═S moiety. These bands are appeared in the solution at $1468cm^{-1}$, 1390 cm^{-1}, $1050cm^{-1}$ respectively. All these spectral changes may be attributed to the presence of hydrogen bonding patterns, which are shown in figure (7a) and (7b).

UV Spectroscopic study

In the solvent, transition occurs between non-bonding atomic orbital and antibonding orbitals. The non-bonding electrons are held more loosely than σ bonding electrons and consequently undergo transitions at comparatively longer wavelengths. These transitions occur with compounds containing double bonds involving hetro-atoms bearing unshared pair(s) of electrons. This type of transition is important feature of the spectra of aldehydes and ketones and is sensitive to substitution on the chromophore structure. In the solvent, peak observed at 201nm shows the $\pi \rightarrow \pi^*$ type of transition and 243nm shows the n→π*type of transition. This type of transition is always less intense because the electron in the n orbital are situated perpendicular to the plane of π bond and consequently the probability of the jump of an electron from n to π* orbital is very low. In the solute the peaks are observed from 190nm onwards. Number of peaks observed in

the range of 270nm, 273nm, 277nm, 286nm. It shows the n→π* transition occurs in the solute. The position of $\pi \rightarrow \pi^*$ transitions in carbonyl compounds vary with the nature of the solvent used. As the polarity of the solvent increases, the $\pi \rightarrow \pi^*$ bands undergo a bathochromic (red) shift and the n→π* undergo a gradual hypsochromic shift.

The $\pi \rightarrow \pi^*$ band shifts to longer wavelength in a more polar solvent because the $\pi \rightarrow \pi^*$ transition have a polar excited state which would normally be stabilized by hydrogen bonding in more polar solvents. This lowers the energy gap between π and π* levels and consequently increases the wavelength of π →π* band. In the case of n→π* band lowers the energy of n orbital because of hydrogen bonding.

CONCLUSION

Thiourea occurs in tautomeric forms. In the present study, from the acoustic properties of the solution of thiourea shows that there is a linear variation occurring in the solution. These changes reveal the fact that there is a weak interaction exists between the solute and solvent and breaking nature of the solute in solvent. The variations observed in intermolecular free length also confirm the dissociation of molecules occurring in the solution. From the spectral analysis various functional groups were identified. Tautomeric nature of solute is conformed. The dimeric structure of formamide is changed due to solvation with thiourea. Results obtained from the acoustical studies such as (i) breaking nature of solute in solvent (ii) Intermolecular hydrogen bonding are also confirmed by the spectroscopic studies.

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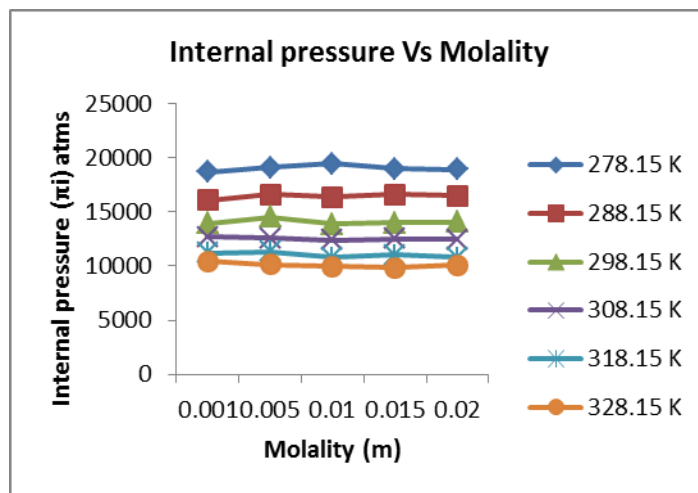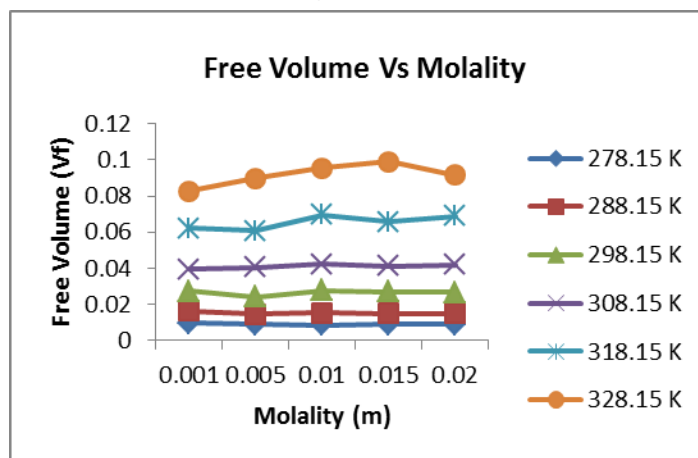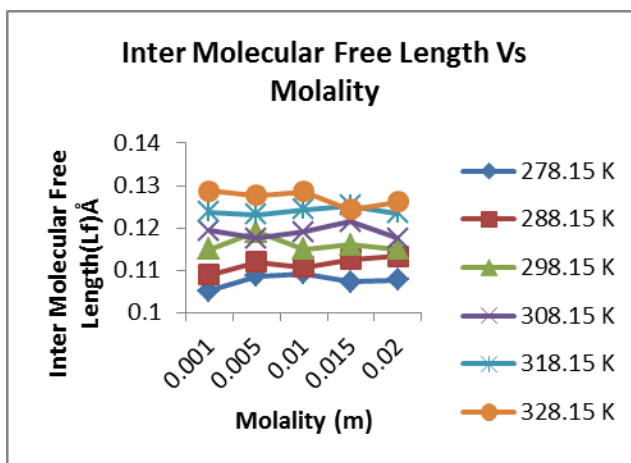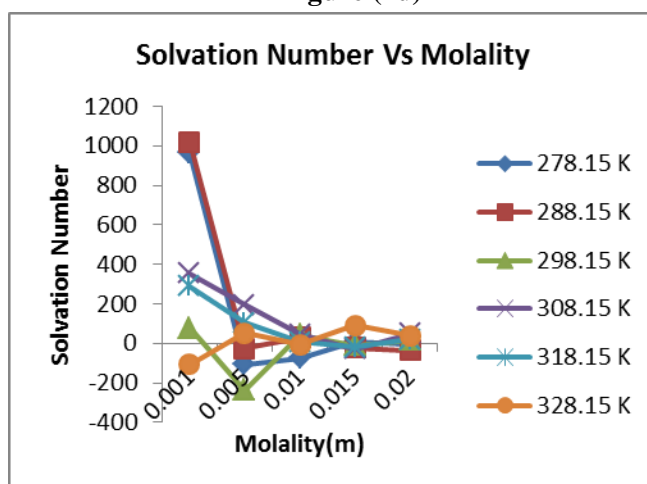
Figure (1a)

Figure (1b)

Figure (1c)

Figure (1d)

Figure (1e)
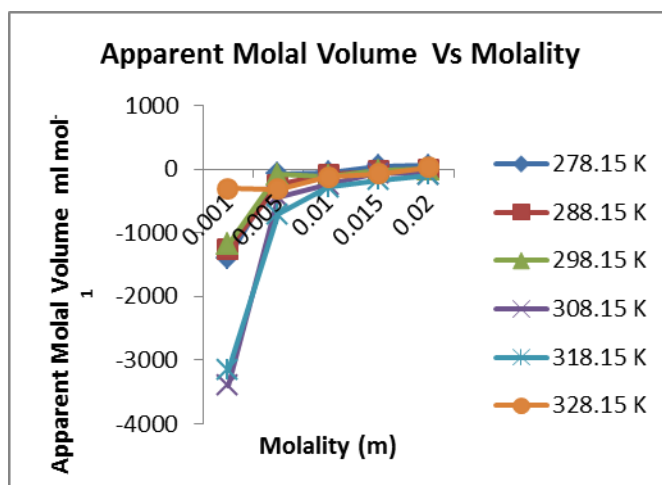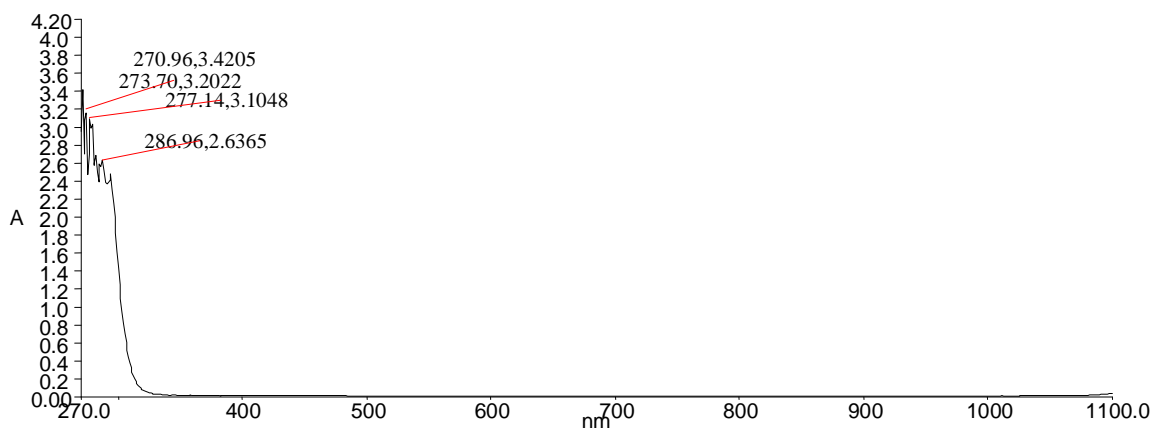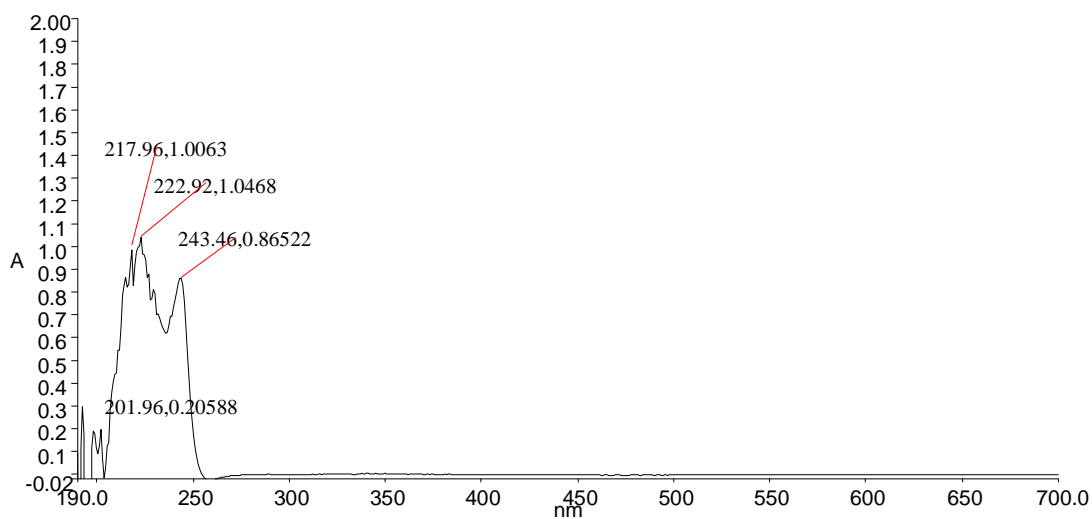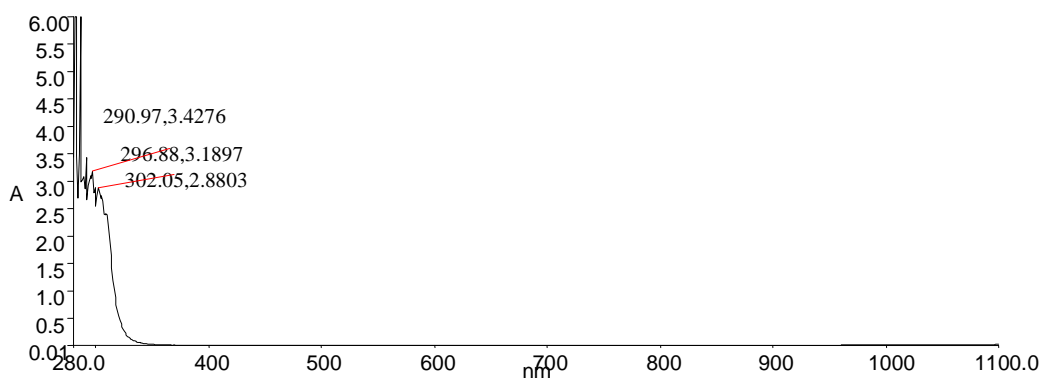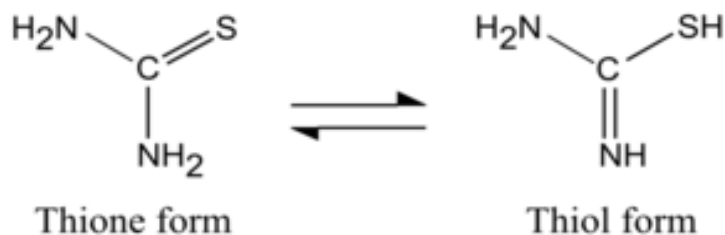

Figure(1f)
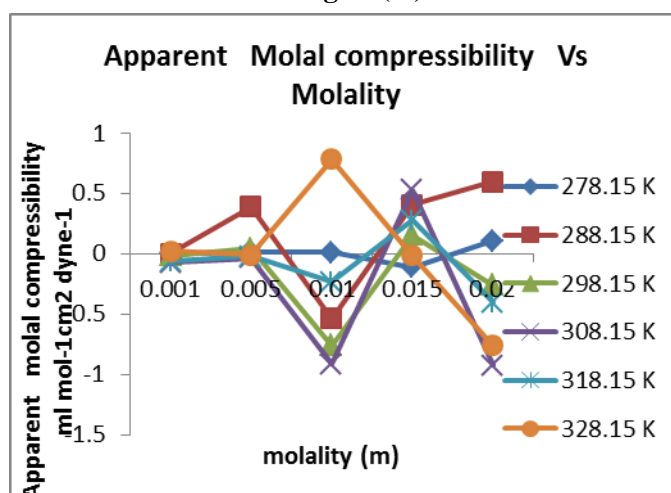
Figure (2a) FTIR Spectrum of Thiourea
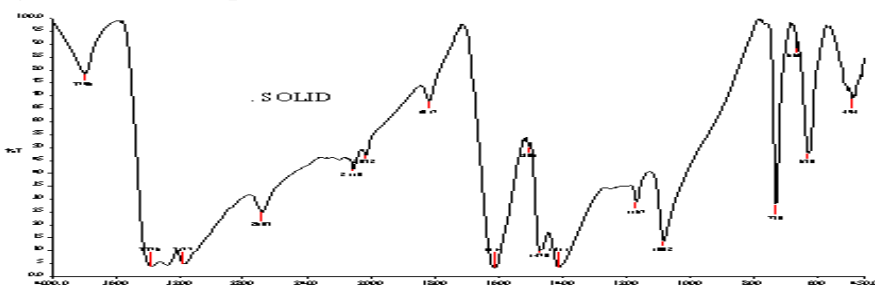
Figure (2b)   FTIR   Spectrum of Formamide
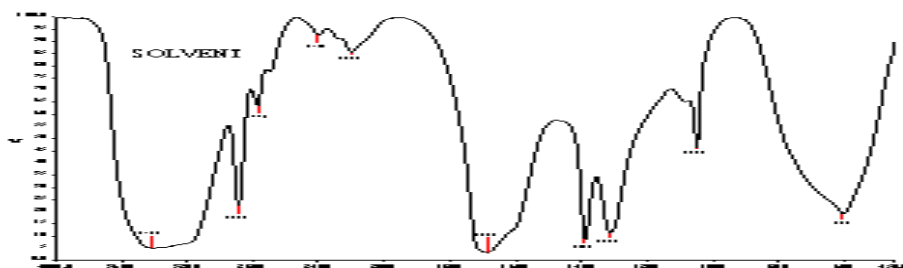
Figure (2c)   FTIR   Spectrum of Thiourea in Formamide
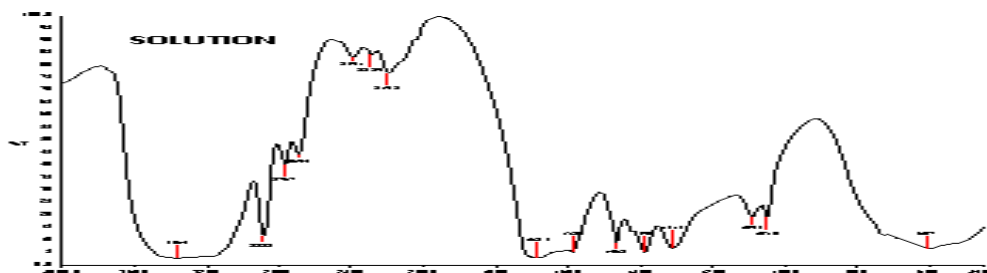
Figure (3a) UV Spectrum of Thiourea

Figure (3b) UV Spectrum of Formamide

Figure (3c) UV Spectrum of Thiourea in Formamide

Figure (4)   Tautomeric form of Thiourea

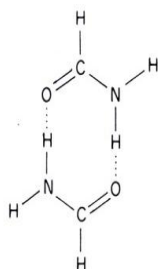Thione form   Thiol form
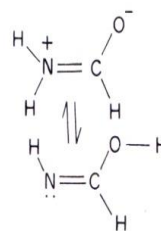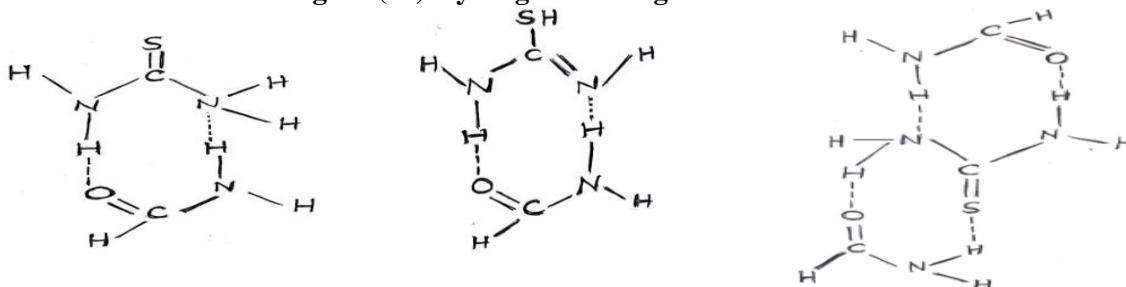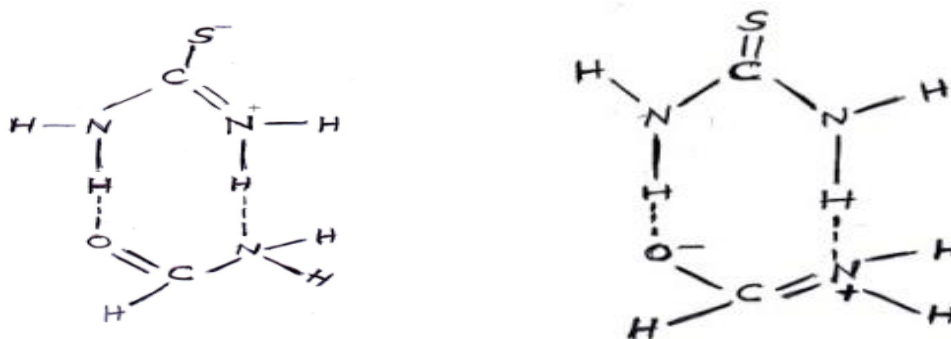
Figure(5) Dimeric structure of formamide   **Figure(6) Enolic form of formamide**

Figure (7a) Hydrogen bonding in neutral form

Figure (7b) Hydrogen bonding in ionic form

Table -1: Thermo chemical parameters of Thiourea in formamide

Parameters	Molality(m)	Temperature					
		278.15 K	288.15 K	298.15 K	308.15 K	318.15 K	328.15 K
Solvation number	.001	963.59	1019.16	79.10	354.36	288.15	-107.22
	.005	-106.77	-27.37	-236.12	195.18	104.44	53.09
	.01	-74.87	29.61	41.31	45.67	6.99	-7.616
	.015	7.46	-23.97	-9.24	-30.51	-18.10	90.35
	.02	-5.16	-34.83	14.91	49.39	19.94	39.99
Apparent Molal Volume ml mol^{-1}	.001	-1391.46	-1254.77	-1189.06	-3402.77	-3159.36	-306.35
	.005	-72.78	-242.00	-87.88	-436.75	-713.57	-313.01
	.01	-52.22	-88.75	-113.75	-247.01	-284.79	-126.53
	.015	49.80	-31.32	-23.09	-68.79	-171.94	-72.72
	.02	54.13	-9.45	-2.50	-90.13	-92.61	22.59
Apparent molal compressibility ml mol-1cm2 dyne-1	.001	-0.001688	-0.00018	-0.0179	-0.0762	-0.0656	0.0195352
	.005	0.0177695	0.3906	0.041	-0.0360	-0.0222	-0.0113941
	.01	0.0124562	-0.54	-0.761	-0.915	-0.236	0.48469
	.015	-0.10981	0.4027	0.154	0.5285	0.2748	-0.0176403
	.02	0.104672	0.5975	-0.262	-0.927	-0.407	-0.760961

Table -2: Acoustical parameters of Thiourea in formamide

Parameters	Molality (m)	Temperature					
		278.15 K	288.15 K	298.15 K	308.15 K	318.15 K	328.15 K
Internal pressure (π_i) atms	.001	18674.7	16095.2	13945.0	12696.8	11215.8	10453.0
	.005	19111.1	16626.2	14500.3	12563.8	11306.5	10172.1
	.01	19430.3	16365.1	13862.2	12415.9	10792.2	9973.9
	.015	18996.3	16593.8	14008.8	12488.3	11003.7	9847.9
	.02	18937.0	16508.4	14040.6	12444.4	10821.9	10103.7
Free Volume (V_f) cc	.001	0.00944	0.01620	0.02723	0.03941	0.06198	0.08258
	.005	0.00880	0.01470	0.02419	0.04060	0.06056	0.08984
	.01	0.00838	0.01541	0.02773	0.04210	0.06957	0.09528
	.015	0.00895	0.01477	0.02684	0.04128	0.06562	0.09898
	.02	0.00903	0.01500	0.02665	0.04178	0.06892	0.09143
Inter Molecular Free Length(L_f)Å	.001	0.1051	0.1089	0.115	0.1193	0.1237	0.1287
	.005	0.1087	0.1119	0.119	0.1176	0.1231	0.1276
	.01	0.1092	0.1108	0.115	0.119	0.1243	0.1286
	.015	0.1072	0.1125	0.116	0.1215	0.1253	0.1244
	.02	0.1077	0.1133	0.115	0.1176	0.1234	0.1261

Table – 3: Observed Peaks in FTIR spectrum - Wave number cm^{-1}

Band Assignment	Formamide	Thiourea	Thiourea in Formamide
νN-H	3422	3376 3177	3364
νC-H	2889 2771 2402	2683 2110 2032	2888 2767 2694 2391 2289
νC=N	2198		2198
νC=O	1685	1614	1683
νC-N		1506	1589
νC=S	1390 1313 1051	1470 1411 1167 1082	1468 1390 1313 1093 1050
δC-H	605	730 666 630 494	607

Table- 4: UV spectrum analysis

Formamide	Type of transition
201.96, 217.96, 222.92, 243.46	π→π*
Thiourea	
270.96,273.70,277.14, 286.96	n→π*
Thiourea in Formamide	
290.97, 296.88, 302.05	n→π*