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Kinetics and thermodynamics of thermal degradation and antimicrobial activity of zinc phenothiazine oleate complex

Abstract

The role of metals in organic synthesis has been well known from the beginning of the development of synthetic procedure in organic Chemistry. Heterocyclic complexes have attracted increasing interest because of their role in the understanding of molecular process occurring in biochemistry and coordination chemistry. The Nitrogen donor aromatic ligand constitutes an important and interesting class of drugs / dyes not only for synthetic investigation but also for their usefulness to resist diseases. Colloidal systems are extremely wide spread in nature and are of great practical importance in our daily life. Surfactants are very useful in modern engineering and pharmaceuticals due to formation of micelles in solutions and high surface activity. Present work has been initiated with a view to obtain a profile as to the nature and structure of complex of phenothiazine with zinc oleate in different non-aqueous solvents that are of great significance in explaining their characteristics under different conditions. The present work reveals synthesis of zinc soap and its complex with phenothiazine ligand. For this synthesis the para substituted aniline was selected as the most suitable initial compound. An analytical and spectral study (IR, NMR) of this complex has been done. In order to know their thermal stability, thermogravimetric analysis has been done. A biocidal activity of complex has been carried to access their comparative toxicity.

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1. Introduction

The interrelationship of transition metal with nitrogen-sulphur donor macrocycles has been the subject of a range of studies. There were a number of studies to find synthetic, kinetic, thermodynamic and structural aspects of complex formation with a range of metal ions [1-2]. The transition metal complex with nitrogen donor ligand has allure cogent attention as catalyst and also due to diagnostic and therapeutic medical application. The metal soaps in polar and non -polar solvents have various uses in fields of applications like foaming, wetting, emulsification etc. due to their surface active properties [3-4]. Surface active agents have vital components and play a significant role in biological systems. The nitrogen donor ligands such as phenyl thiourea,

phenothiazine, benzothiazole etc. have been serving as the basis of the variety of drugs/dyes for over five decades. Phenothiazine compounds and its derivatives are found useful as drugs, industrial antioxidant, thermal stabilizer, pesticides, polymer indicator, dyes and pigments [5-6]. The pharmacological activities of phenothiazine is been attributed to the basic nitrogen of the ring which donate electrons to biological receptors by charge transfer mechanism. Zinc is an essential trace element. It is found throughout the human body in a variety of tissues, such as skin, bone, liver, muscle or brain. zinc (II) complex of carboxylates appeared to have good antibacterial activity; e.g., a strong inhibitive effect was noticed towards E. coli and S. Aureus [7-8]. In the search for zinc (II) complex of known antimicrobial drugs strong antibacterial activity has been achieved; e.g. the interaction between zinc and the gyrase inhibitor ciprofloxacin and various nitrogen-donor ligand has been studied and the complex was found more potent than the drugs alone [9].Of course, many notable physico-chemical properties of metal soaps have been reported [10]. However, only scanty references are available as to the physico-chemical properties of complex of metal soap with nitrogen donating ligand in mixed solvent. Also it is believed that biological activity is often enhanced on complexation [11-12]. In the present study, we synthesized the complex in the hope that they may possess potential biological activities. In this present paper we report the characteristic nature and biologically active metal and applications of the biologically active metal complex of nitrogen donor ligand. We report the synthesis, characterization, structural insight, thermal decomposition, and biochemical studies of Zn (II) oleate complex obtained with substituted phenothiazine.

2. Experimental

2.1 Preparation of substituted phenothiazine:

3.32 g (0.01 mole) of 2-amino 5-nitro benzenethiol, 0.4 g (0.01 mole) sodium hydroxide and 2.02 g (0.01 mole) 2,4 dibromo 1-nitrobenzene in absolute alcohol (25 ml) were refluxed for 1-2 h. Mixture was cooled and filtered. Residue was washed with hot water and 80% ethanol and recrystallized in acetone (Figure 1).

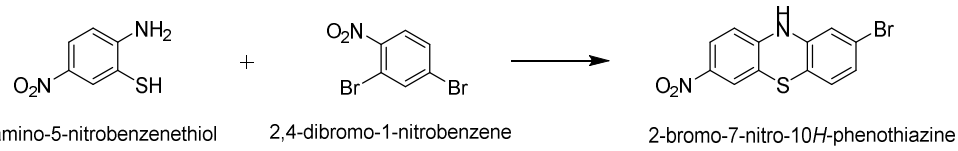

Figure 1: Synthesis of ligand

2.2 Preparation of metal (Zn) surfactants:

Metal oleate was prepared by mixing one gram of oleic acid into 25ml ethyl alcohol, shake the mixture in hot water bath about 50°C and then add one drop of phenolphthalein. Prepare a saturated solution of KOH in another beaker and add it into the oleic acid solution drop by drop until the light pink colour appears. Now again in another beaker prepare a saturated solution of $ZnSO_4$ (3-4 g in 5 ml of water) and mix it into the above solution with constant stirring till a coloured soap (white colour for zinc oleate) is formed. Filter and wash it with warm water and 10 % ethyl alcohol, then dried and recrystallized with hot benzene (Figure 2).

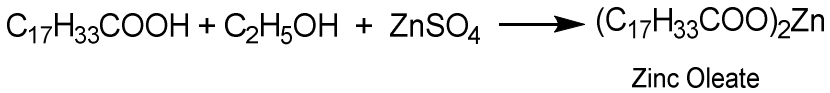

Figure 2: Synthesis of metal (Zinc) oleate surfactant

2.3 Preparation of Metal (Zn) complex:

The complex of metal oleate (zinc oleate) and phenothiazine was prepared by adding (0.001 mole) zinc oleate with (0.002 mole) phenothiazine in 25-30 ml ethyl alcohol and the mixture was refluxed for about two hours with constant stirring. After cooling the solid separate out was filtered, dried and recrystallized with hot benzene (Figure 3). The physical and analytical data of synthesized complex are shown in Table 1.

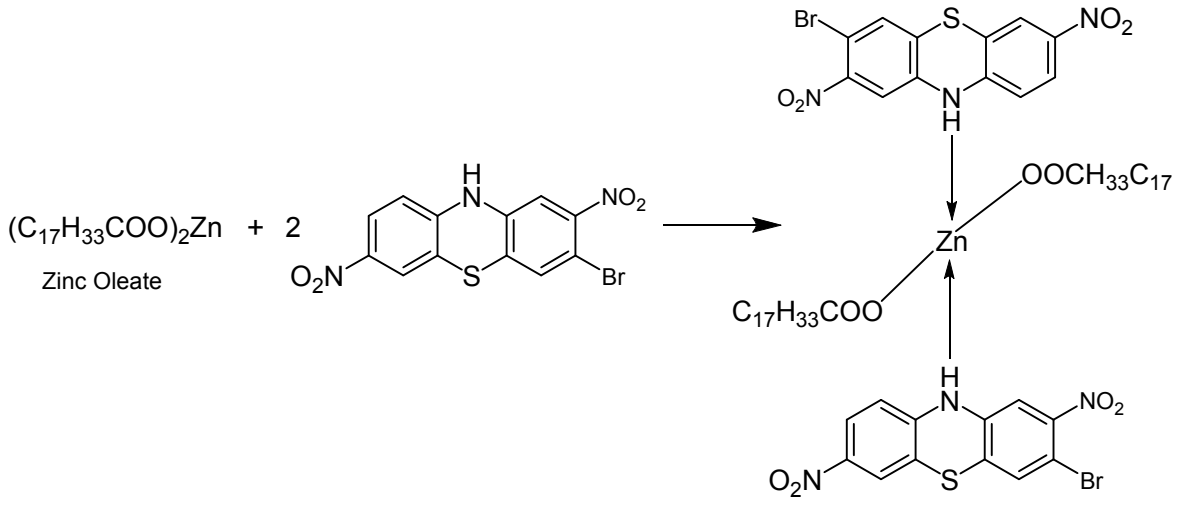

Figure 3: Synthesis of Zinc oleate phenothiazine complex

Table 1: Analytical and physical data of Zinc oleate phenothiazine complex

Compound	M.W.	M.P. (°C)	Colour	% Found (Calculated)						
				C	H	O	N	S	Br	Zn
$C_{60}H_{80}O_8N_4S_2Br_2Zn$	1274.53	245	Gray White	56.4 [56.5]	6.3 [6.3]	10.06[10.0]	4.26 [4.39]	5.14 [5.04]	12.46 [12.54]	5.28 [5.13]

2.4 Characterization:

2.41 IR Spectra:

The spectral measurements (IR, NMR) and elemental analysiswere carried out at the MNIT Jaipur Rajasthan.The IR spectrum of the complex was obtained as KBr discs in the range 400-4000 cm^{-1} on Perkin Elmer spectrophotometer.

2.42 TGA studies:

The TGA curves of the samples were obtained on Metter – Toledo system Module. The analysis was done on STARe software system. TGA was done on nitrogen (N_2) atmosphere between 0^0C – 1100^0C at the rate of 10^0C per minute. The results were obtained as plots of weight loss v/s temperature and weight loss v/s time (Figures. 4-7).

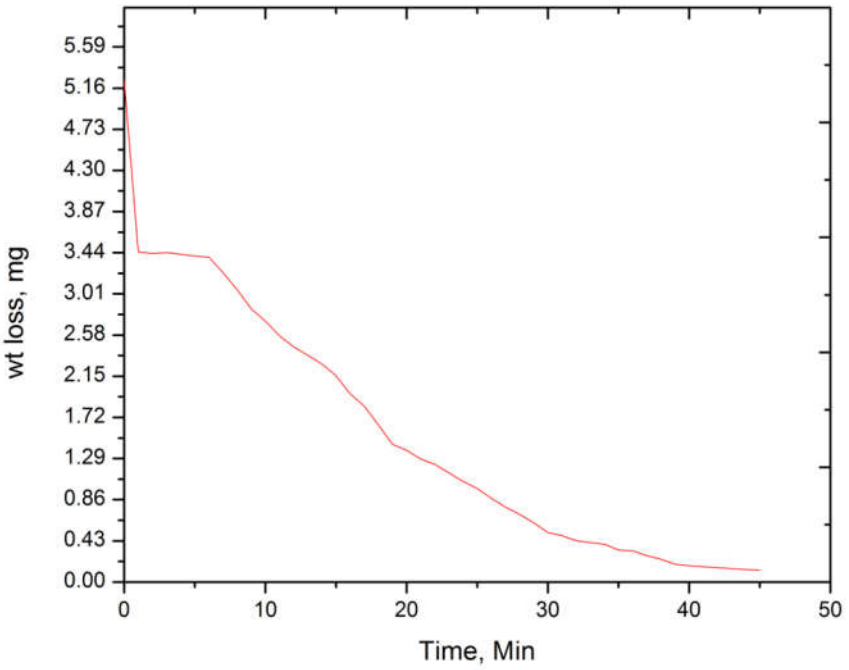

Figure 4: Thermogram between time v/s wt. loss (mg.) for Zinc oleate phenothiazine complex

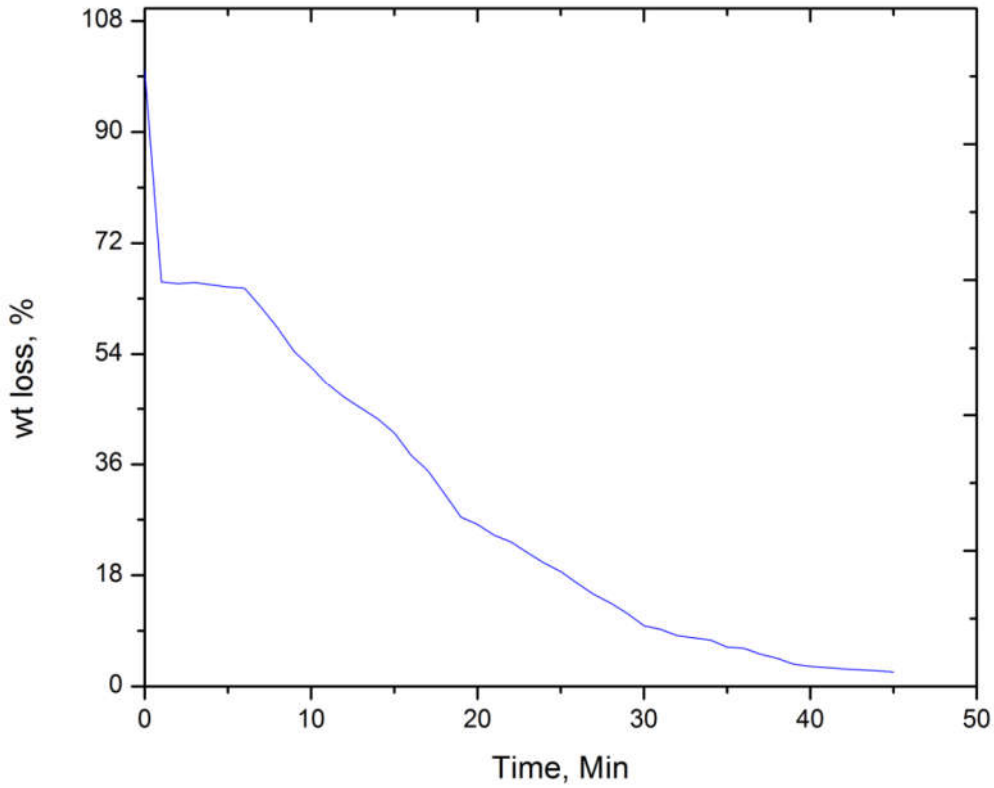

Figure 5: Thermogram between time v/s wt. loss (%.) for Zinc oleate phenothiazine complex

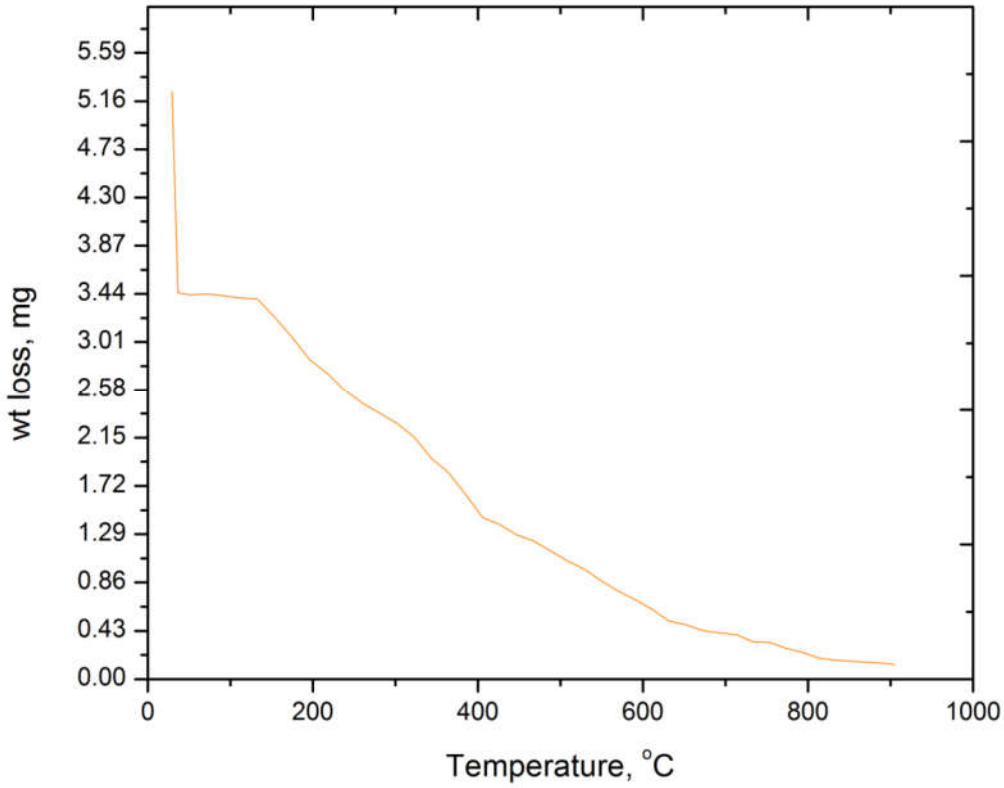

Figure 6: Thermogram between temperature v/s wt. loss (mg) for Zinc oleate phenothiazine complex

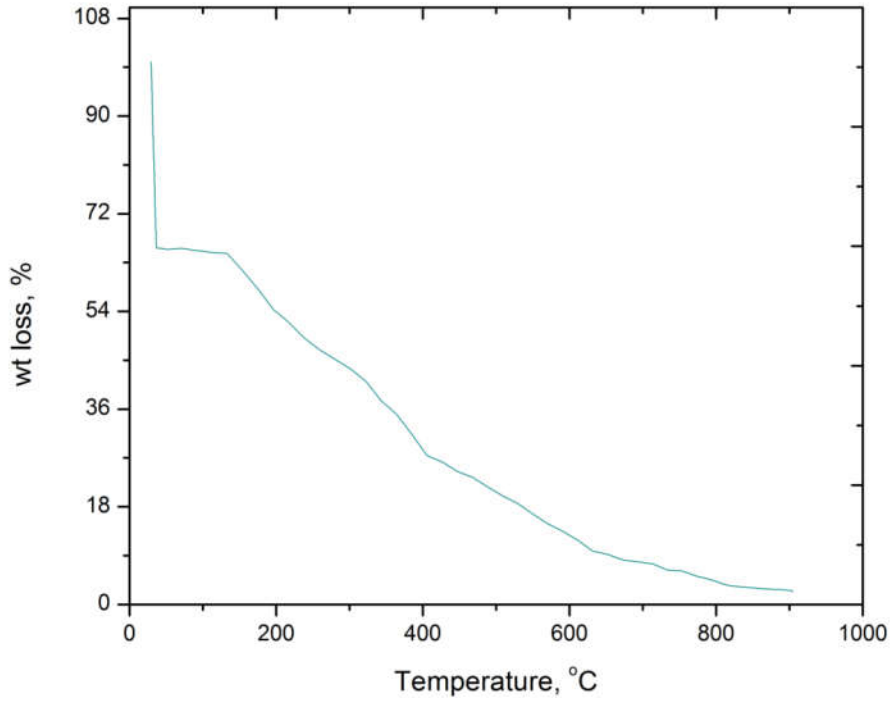

Figure 7: Thermogram between temperature v/s wt. loss (%) for Zinc oleate phenothiazine complex

2.5 Biological studies [13]

Step 1: Processing of the sample. The unknown compound is re-suspended in DMSO in mass concentration (w/v)

Step 2: Antimicrobial Susceptibility Testing (Kirby-Bauer and Stokes' methods. [14]

I. Hinton susceptibility test: Savoured Dextrose Agar (antifungal screening) is the only susceptibility test medium that have been validated by NCCLS.

II. McFarland turbidity standard: A McFarland 0.5 standard was prepared and used.

III. Preparation of inoculum: This procedure was exactly same as earlier reported methods [15].

IV. Loading the plate with Positive, negative control and sample The working supply of antibiotic (streptomycin, positive control) must be stored at 4 °C 50 µl of the antibiotic suspension was dispensed in the well labelled with C (control), (R, negative control), sample (S) to the plates as earliest.

V. Recording and interpreting results After the Loading of C, S, R on the plate, invert the plate and incubate at 35°C for 16 to 18 hrs. After incubation, diameter of the zones of inhibition taken.

3. Results and Discussion

3.1 IR Spectral Studies:

The IR spectra provide valuable information regarding coordination site of the ligand attached to the metal ion. The absorption bands observed in the region 2924 cm^{-1} and 2852 cm^{-1} corresponds to C-H symmetric and asymmetric stretching of methyl (-CH_3) and methylene (-CH_2) group of the soap segment present in the complex. Small peak corresponding to –CH_2 twisting and wagging has been observed at 1325 cm^{-1} region. Methyl and methylene rocking vibrations appears near 1118 cm^{-1} and 751 cm^{-1} and another band at 1401 cm^{-1} are due to carboxylate ion COO-, C-O antisymmetric and symmetric stretching respectively. It shows the presence of fatty acid group of metal soap. A ring stretching (skeletal bands) observed at 1601 cm^{-1} shows a heteroaromaticring system [15]. Another strong band near 1460 cm^{-1} indicates the presence of nitro group in aromatic system of ligand. Small peaks corresponding to-C-S- vibrations have been observed in the region of 751 cm^{-1}.

The ν(Ar-N) frequency in the complex are observed around 1300-1340 cm^{1}whichis lower than that observed in free ligand and this evidence supports to the coordination of phenothiazine nitrogen. Involvement of phenothiazine nitrogen in the complexion is also supported by the presence of a new band at 502 cm^{-1}, assignable to ν(M-N) for Zn (II) complex. From IR spectral data, it is evident that ligand act as a monodented, bonded to metal ion (Zn) threw secondary nitrogen atom of NH. The band near 1560 cm^{-1} characteristic of N-H bending vibration to the N-H group in the free ligand is shifted to lower frequency of 1539 cm^{-1} in the complex indicate that the secondary nitrogen is the coordinating site in the complex [16]. The IR spectra of free ligands shows characteristic bands due to lactam ν(C=O) in the region 1601 cm^{-1} and ν(C-S-C) in the region 619 cm^{-1}, these band were not shifted in the IR spectra of the complex, indicating the non-participation of carbonyl oxygen and sulphur in coordination (Figure 8).

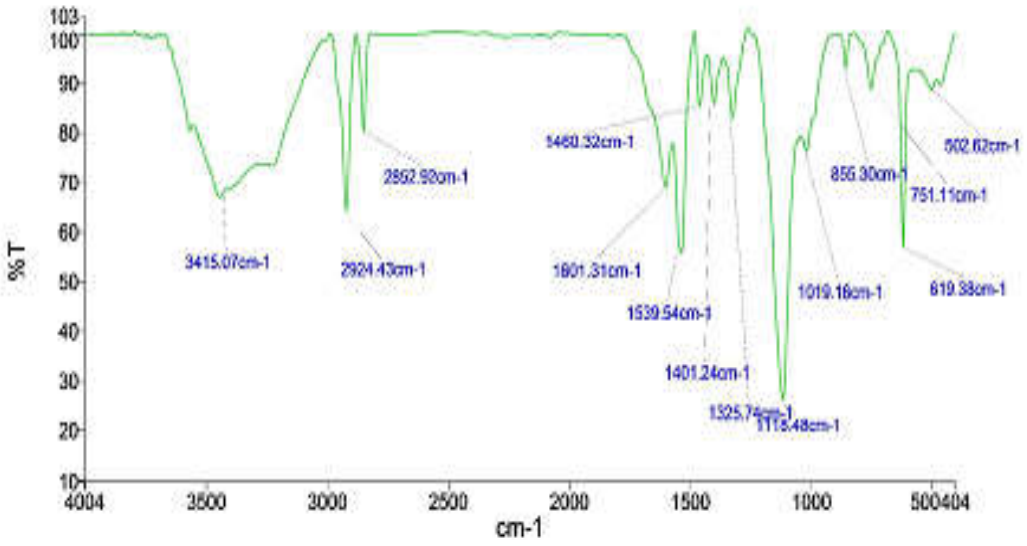

Figure 8: IR spectra of zinc oleate phenothiazine complex

3.2 NMR studies

The ligand to metal bonding is further supported by ^1H NMR spectra. The complex showed broadened peak at δ 3.65-3.70 ranges due to the protons [17]. This peak indicates the co-ordination through the –NH group of phenothiazine to the metal (zinc) atom of the soap segment. In addition to the above signal, resonance corresponding to CH_3 and CH_2 protons attached to $-CH_2$-R groups is also observed in δ 0.90 and δ 1.22 regions (Figure 9).

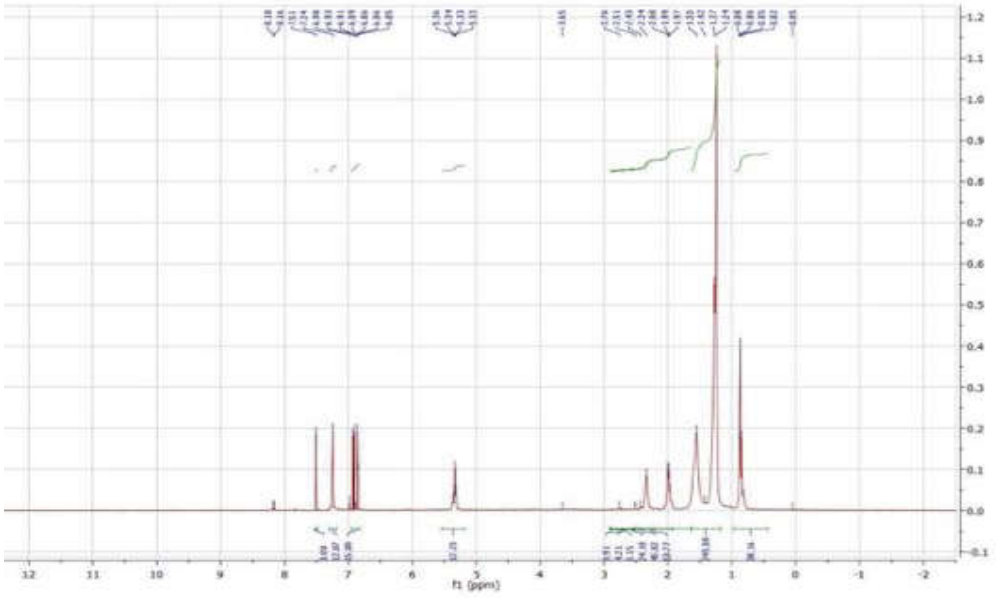

Figure 9: NMR spectra of zinc oleate phenothiazine complex

3.2 TGA Studies:

Kinetic studies of thermal decomposition become very useful in calculating the important parameters like activation energy (Ea), enthalpy change (ΔH), entropy change (ΔS), change in free energy (ΔG) etc., which directly govern the factors of thermal stability of any complexes [18]. The energy of activation (Ea) for the complex was measured by Coats-Redfern, Horowitz – Metzger equation and Broido equation [19-20].

Coats and Redfern derived the equation

$$\frac{\log[-\log(1-\alpha)]}{T^2\alpha E} = \frac{\log AR}{E(1-2RT)} - \frac{E}{2.303RT} \qquad (1)$$

Where 'α' stands for the fraction of soap decomposed, 'n' for the order of the reaction, 'K' for the rate constant, 'E' for the energy of activation of the reaction, 'R' the gas constant (R = 8.314 J mol^{-1} K) and 'A' for the pre – exponential or frequency factor and is usually assigned to be independent of absolute temperature 'T'.

The values of energy of activation using Coats–Redfern equation for each of the three steps for the referred systems have been evaluated from the linear plots of 'log {[– log (1-α)] / T^2} v/s 1/T'. The values of activation energies evaluated from the slope of these plots are recorded in Table 2 and are observed to be in following order shown in Figure 10.

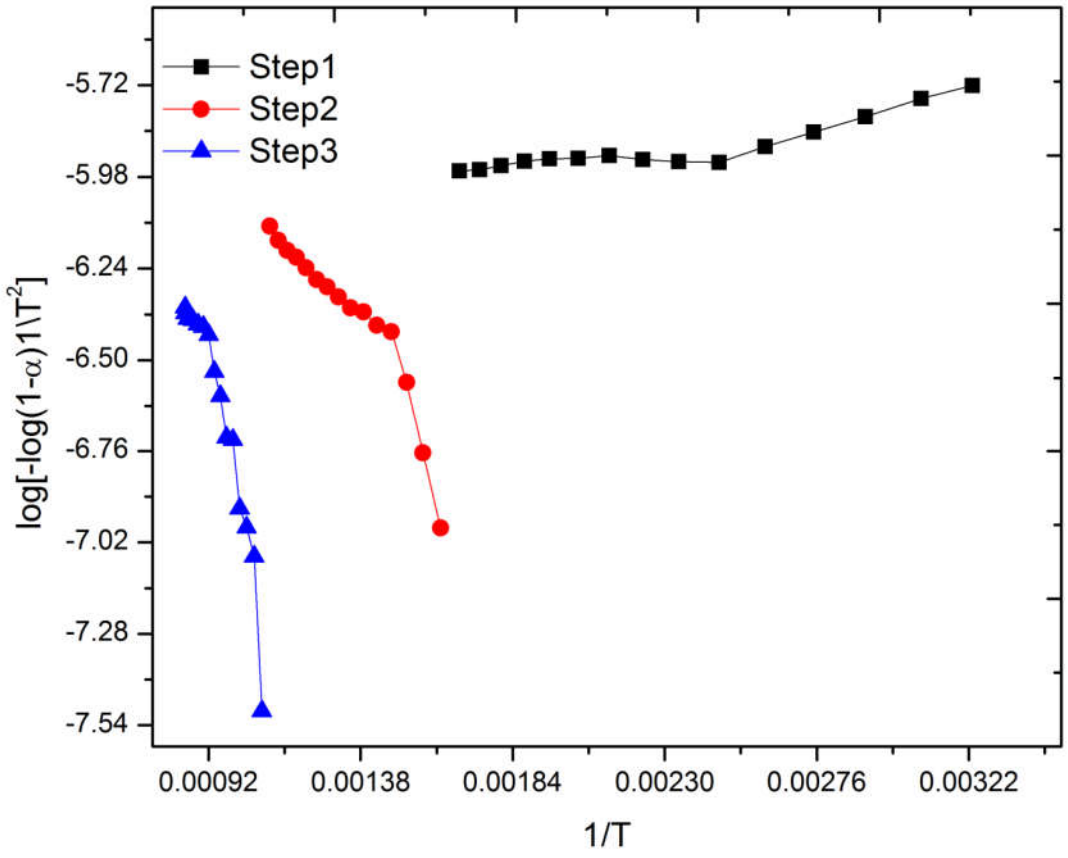

Figure 10: Plots of CRE for zinc oleate phenothiazine complex

Step III > Step II > Step I.

Horowitz – Metzger equation has been used to evaluate the value of 'E' according to the following equation:

$$\ln[\ln(1-\alpha)-1] = \frac{E\theta}{RT_s^2} \quad (2)$$

Where 'α' is the fraction of soap decomposed at time 't', 'T_s' is the temperature at which the rate of decomposition is maximum and 'θ' is equal to (T – T_s). The energy of activation as recorded in Table 2 are obtained from the slope of the plot between ln[ln (1– α)$^{-1}$] v/s θ. For Horowitz – Metzger equation the values of each step are in the order shown in Figure 11.

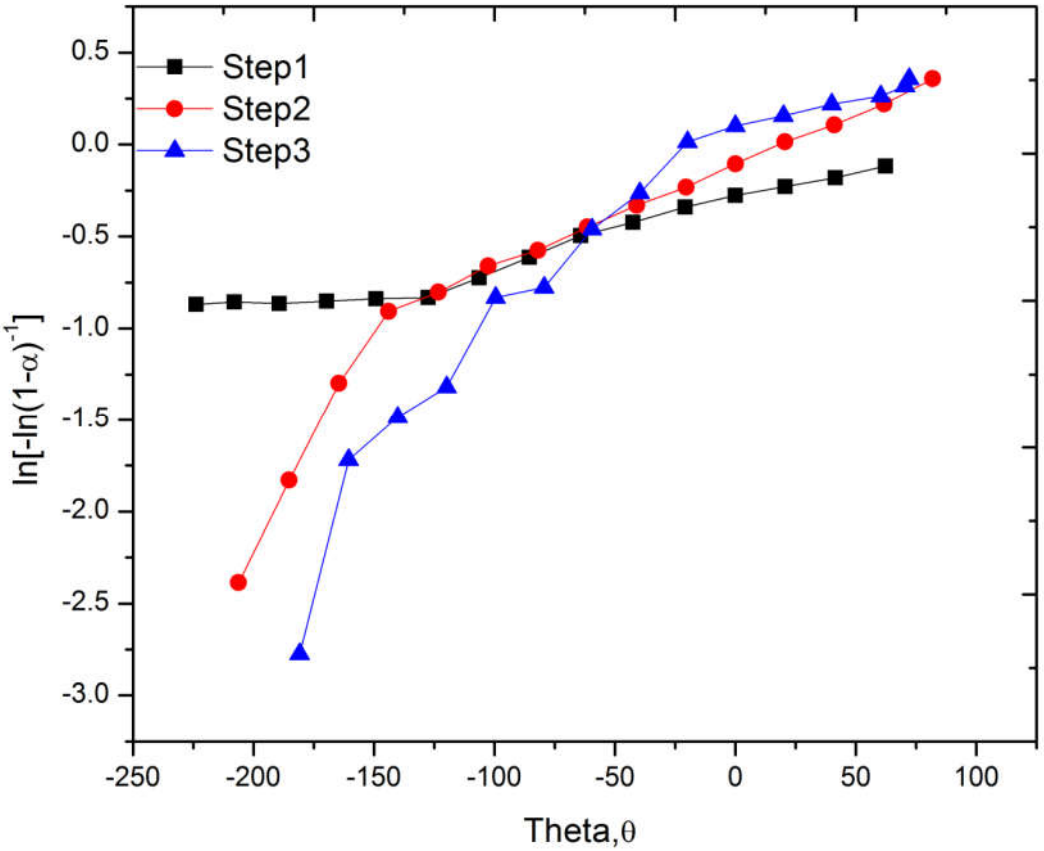

Figure 11: Plots of HME for zinc oleate phenothiazine complex

Step III > Step II > Step I

The energy of activation for the stepwise thermal decomposition of referred system has also been calculated by using Broido's equation which is as follows:

$$\ln[\ln(1/y)] = -E + \frac{C}{RT} \quad (3)$$

Where 'y' is fraction of weight at temperature 'T', 'E' is the activation energy and 'R' is the gas constant in J mol^{-1} K^{-1}. The energy of activation for each step is calculated from the slope of plot between ln [ln (1/y)] and (1/T). The values of activation energies for different steps of thermal decomposition of Zinc phenothiazine complex are recorded in Table 2 and are found to be in the following order and also shown in Figure 12.

Table 2: Kinetic parameter, energy of activation for the decomposition reaction of complex

Compound	Steps	C.R.E.	H.M.E.	B.E.
Complex	I	29.81	12.55	8.650
	II	43.95	31.25	28.18
	III	78.41	65.54	66.93

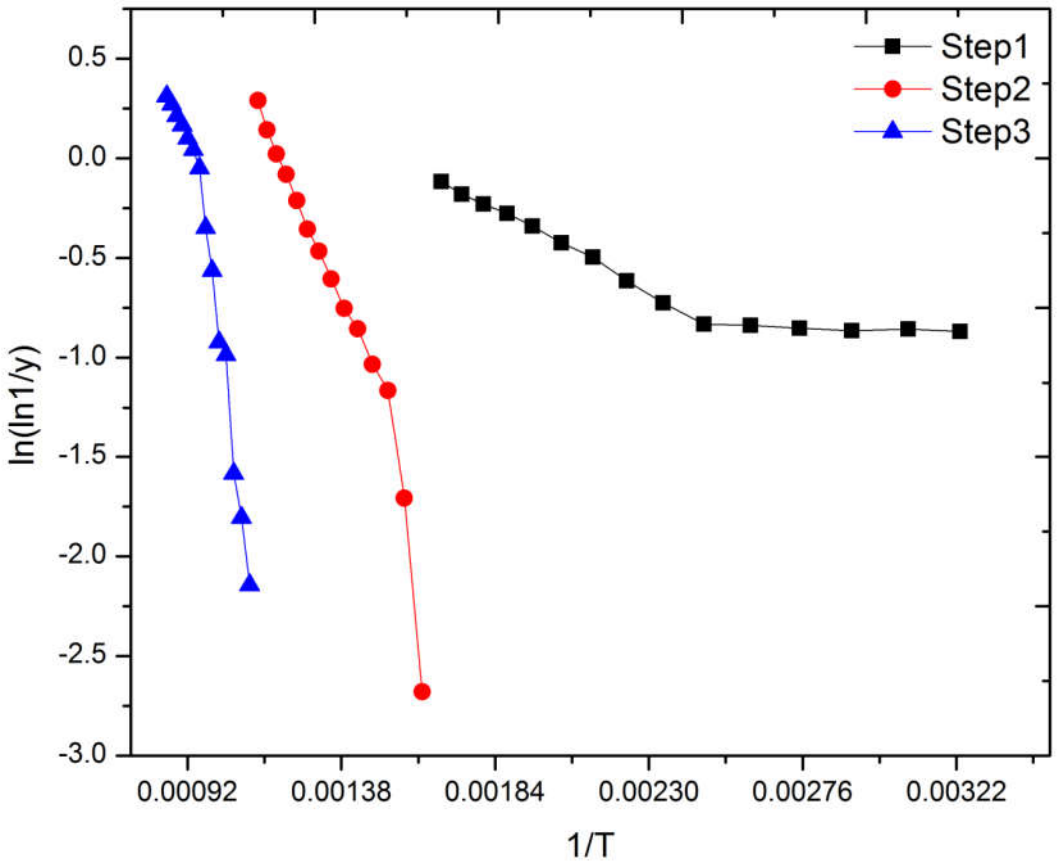

Figure 12: Plots of BE for zinc oleate phenothiazine complex

Step III > Step II > Step I

A perusal of Table 2 reveals that for the referred system, the value of activation energy is highest for the third step and smallest for the first step, irrespective of the equation applied signifying that complex molecule degrade first in metal surfactant (Step-3) than metal surfactant degrade in its ligand (Step-2) and then ligand degrade in its elements (Step-1). Step 3 has higher activation energy compare to other two steps due to complex molecule has higher molecular weight than co-responding metal surfactant and ligand [21-22]. The complex molecule has negative entropy, which indicates that the decomposition reactions proceed with a lower rate than the normal ones. The negative value of entropy also indicates that the activated complex has a more ordered and more rigid structure than the reactants or intermediates [23-24].The negative values of the entropies of activation are compensated by the values of enthalpies of activation, leading to almost the same values for the free energy of activation (Table 3).

Table 3: Thermodynamic parameters for the decomposition reaction of complex

Step	Z (s^{-1})	ΔS* ($J\ K^{-1}\ mol^{-1}$)	ΔH* ($kJ\ mol^{-1}$)	ΔG* ($kJ\ mol^{-1}$)
I	9.87x10-8	-383.91	25.38	230.30
II	1.89x10-6	-305.49	37.12	288.23
III	0.2330	-268.26	69.23	365.44

3.3 Biological Studies:

The study aims to evaluate the bioactivity of synthesized complex against test organisms. [25-26]. Antimicrobial sensitivity was performed for synthesized complexon Muller Hinton Agaragainst *Candida abicans*, *Aspergillusniger, Trichodermaressi and Penicillun* by Kirby-Bauer Stokes' method [27-28] Results obtained using Itraconazole (5 mg (w/v)) as antifungal agent control (C) and for negative reference Ethanol/Methanol (R) are mentioned in Table 4 and Figure 13-14. Activity index = zone of inhibition of sample[S]/zone of inhibition of reference [R] and the activity can be found out by:

Table 4: Descriptive statics results of antifungal activities of zinc phenothiazine complex

Fungi	Concentration (mg/ml)	Count	Av. % Inhibition	Std. Error
Candida Albicans	20	3	14.23	0.06
Aspergillus niger		3	11.47	0.22
Trichodermaressi		3	14.47	0.21
Candida Albicans	40	3	12.47	0.20
Aspergillus niger		3	17.63	0.30
Penicillun		3	10.57	0.26
Candida Albicans	60	3	10.73	0.41
Trichodermaressi		3	17.57	0.36
Penicillun		3	10.63	0.16
Candida Albicans	80	3	13.60	0.28
Trichodermaressi		3	18.73	0.06

Figure 13: Photos of Zn phenothiazine complex plates showing inhibition zones

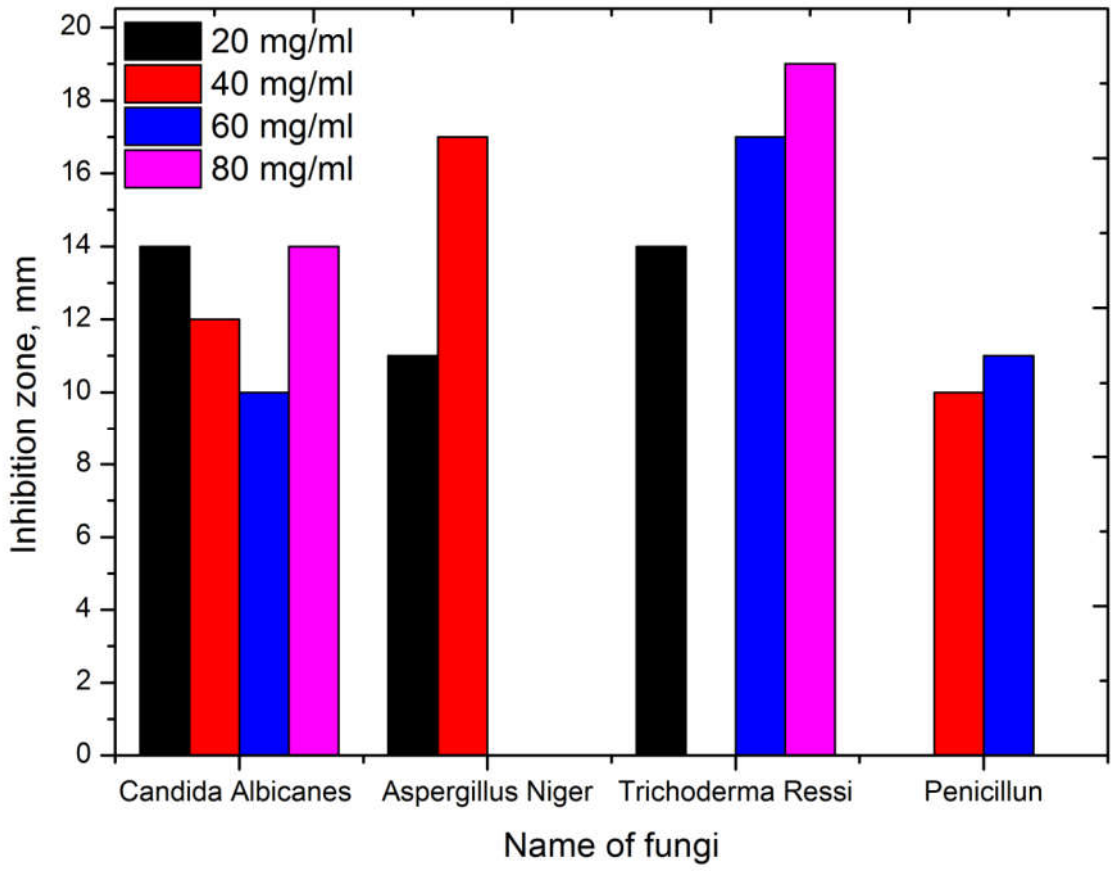

Figure 14: Antimicrobial results of Zn phenothiazine complex over various fungi

Activity = activity index × 10 If the Zone of Inhibition is < 13 = it means that the extract is inactive, 13 – 18 = it means that the extract is bioactive, > 18 = it means that the extract is highly active [29]. The results of ANOVA for the antifungal activities synthesized complex are shown in Table 5. The predicted R^2 are in reasonable agreement and closer to 1.0. [30], this confirms that the experimental data are well satisfactory. The descriptive statics results of synthesized complex also confirm satisfactory results in triplet.

Table 5: ANOVA results of antifungal activities of zinc phenothiazine complex

Concentration of complex (mg/ml)	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*	R^2
20	16.71	2	8.35	53.33	0.00015	5.14	0.995
40	92.04	2	46.02	178.53	0.00000	5.14	0.992
60	94.78	2	47.39	151.24	0.00001	5.14	0.996
80	39.53	1	39.53	230.25	0.00011	7.71	0.997

4. Conclusion

The extensive use of surfactants has created a new problem in environment because they are either slowly biodegraded or do not biodegrade. Therefore it is necessary to search out an alternate and quicker method for the treatment of these pollutants. Thermal Methods (TGA) it provides significant information about the removal of the natural surfactant segments from the environment. TGA degradation of zinc phenothiazine complex determines energy of activation in this study. The results of thermogravimetric analysis reveal that referred system undergo stepwise thermal degradation in three steps corresponding to the decomposition of complex molecule, metal surfactant and ligandin to its elemental part in the temperature range of 150^0C–850^0C. Various equations like Coats-Redfern (CR), Horowitz-Metzger (HM) and Broido equations (BE) were applied to evaluate the kinetic and thermodynamic parameters for thermal degradation of complex. An antifungal activity reveals that the complex under study shows very good affinity towards various fungi namely *Candida abicans*, *Aspergillusniger, Trichodermaressi, and Penicillun.* This study is very important for pollution controlling and in the field of Green Chemistry. It is concluded from this work that zinc phenothiazine complex are recommended as therapeutic compounds. In the present study the synthesized complex are checked to inhibit the growth of various fungi and observed that synthesized complex shows very good antifungal activities.

5. Acknowledgement

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