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TGA Analysis of Transition Metal Complexes Derived from Phenothiazine Ligands

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Abstract: -

Phenothiazine derivatives substituted in the 2 and 7 positions are classed as typical antipsychotics. They have wide applications to reduce hallucinations and delusions associated with psychosis. Due to their characteristic structure they exhibit many valuable analytical properties. They also react with some metal surfactants and form well defined metal complexes. The afore-said ligands of phenothiazines were synthesised by using p-nitroanilines through the Smiles rearrangement and reacts with metal surfactants to form solid complex compound. The synthesised complexes are found to be soluble in the organic solvents and characterized by IR and NMR spectral studies. The electronic spectra and the magnetic moment support the stereochemistry of the complexes, which suggested an octahedral geometry of the metal ion. The thermo gravimetric analysis (TGA) experiments were carried out to explore the thermal stability of the complexes. The thermal behavior of all the metal complexes were studied in the temperature range of 0 to 1100 ^{0}C. The energy of activation was also calculated by applying equations like Coats-Redfern, Horowitz-Metzger and Broido. The use of thermogravimetric data is mainly for evaluating kinetic parameters of solid state reactions involving weight loss or gain.

Key words: phenothiazine, cobalt oleate, thermo gravimetric analysis, metal surfactants, metal complexes.

Introduction: -

Phenothiazine is an organic compound that occurs in various anticholinergic and antihistaminic drugs. It has the formula $S(C_6H_4)_2NH$. This yellow tricyclic compound is soluble in acetic acid, benzene, and ether. The compound is related to the thiazine-class of heterocyclic compounds. Derivatives of the parent compound find wide use as drugs[1] because having biological active properties. Phenothiazine derivatives[5] characterized by a tricyclic aromatic ring with sulfur and nitrogen atoms and substituents in the 2 and 10 or 3 and 7 positions. Phenothiazine derivatives known as tranquilizers[2], neuroleptics[2], antiphychotropic, antiinfective[6], anticholinergic antimalarial[7] and antihistaminic drugs[1].They are industrial antioxidant[8], antimicrobial[9], thermal stabilizers, pesticides[10], polymeric indicators, and used as dyes and pigments. Structural modifications made on the parent structure has resulted to the reports on the successful synthesis of many congeners both linear and angular phenothiazine compounds[10]. Certain phenothiazine derivatives can be determined by electroanalytic methods[11] and are also useful to cure human leukaemia[12].Since the pharmacological activities of phenothiazine are attributed to the basic nitrogen of the ring which donates electron to the biological receptors by charge transfer mechanism. Owing to their multifold applications we synthesised complexes of above ligands, which are ecofriendly and completely biodegradable[8].

TGA-FT-IR TGA-MS TGA-GC/MS

Fig: 1- Image depicting a TGA instruments

Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. This technique can be used to evaluate the thermal stability of a material, in a desired temperature range, if a species is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace.

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss ofvolatiles (such as moisture).TGA is useful to study the kinetics of decomposition process and is termed as Thermal Analysis Kinetics (TAK). Thermal Analysis Kinetics (TAK) seeks to quantitatively analyse the relationships between temperature and physical properties (e.g., the mass change as a function of time) measured by the thermal analysis techniques. The development of TAK is based on chemical thermodynamics, chemical kinetics and thermal analysis techniques. By analysing data obtained by thermal analysis techniques, TAK is able to provide kinetic parameters, estimate the thermal stability and life span of materials, and the best operationconditions of polymers, quantitatively describe the reaction rate and reaction mechanisms, and provide supporting information for estimating properties of energetic materials and combustibles13.It is capable of quantitatively characterizing reactions and phase change processes, determining the most probable reaction mechanisms, and extracting activation energies and pre-exponential factors of solid state reactions. There are various methods of kinetic analysis, here we are using Coats-Redfern method and Broido method to evaluate the value of activation energy, to compare degradation process.

Material and Methods: -

All chemicals used were of A. R. grade, substituted aniline, purchased from Merck, and were used as received. Solvents were purified according to standard procedures14,23.

Preparation of 2-bromo-7-nitrophenothiazines:

3.32 grams (0.01 mol) of benzenethiol, 0.4 grams (0.01 mol) sodium hydroxide and 2.02 gram (0.01 mol) bromonitrobenzene in absolute alcohol (25 ml) were refluxed for 1-2 hours. Mixture was cooled and filtered. Residue was washed with hot water and 80% ethanol, then dried and crystallised from acetone.

Preparation of Metal surfactants:

Cobalt/ Nickel oleate was prepared by mixing one gram of oleic acid into 25ml ethyl alcohol, shake the mixture in hot water bath about 50oC 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 color appears.

Now again in another beaker prepare a saturated solution of $CoCl_2$/ $NiCl_2$ (about 3-4 grams in 5 ml of water) and mix it into the above solution with constant stirring till a purple/green colored soap is formed. Filter and wash it with warm water and 10 % ethyl alcohol, then dried and recrystallised with hot benzene.

$$2C_{17}H_{33}COOH + NiCl_2 \xrightarrow{C_2H_5OH} (C_{17}H_{33}COO)_2Ni$$

$$2C_{17}H_{33}COOH + CoCl_2 \xrightarrow{C_2H_5OH} (C_{17}H_{33}COO)_2Co$$

Preparation of Complexes:

The complexes of cobalt oleate/ nickel oleate and phenothiazines were prepared by adding 0.62 gm (0.001 mol) cobalt/nickel oleate with 0.65gm (0.002 mol) phenothiazine in 25-30 ml ethyl alcohol and the mixture was refluxed for about two hours with constant stirring. After cooling the solid separated out was filtered, dried and recrystallised with hot benzene.

$$2(C_{17}H_{33}C00)_2Co + C_{12}H_7O_2N_2SB\,r \xrightarrow{C_2H_5OH} C_{96}H_{146}O_{12}Co_2N_4S_2Br_2$$

$$2(C_{17}H_{33}C00)_2Ni + C_{12}H_7O_2N_2SB\,r \xrightarrow{C_2H_5OH} C_{96}H_{146}O_{12}Co_2N_4S_2Br_2$$

Table I :- Analytical and Physical data of 2-bromo-7-nitrophenothiazine ligand

Compound	Molecular Weight (gm)	M.P. (^oC)	Color	% Found (Calculated)					
				C	H	O	N	S	Br
$C_{12}H_7O_2N_2SBr$	323.16438	230	Black	44.82 (44.60)	2.06 (2.18)	9.68 (9.90)	8.82 (8.67)	9.78 (9.92)	24.84 (24.73)

Table II :- Analytical and Physical data of Metal Surfactants

Compound	Molecular Weight (gm)	M.P. (^oC)	Color	% Found (Calculated)			
				C	H	O	Metal
$C_{36}H_{66}O_4Co$	621.8384	232	Purple	69.82 (69.53)	10.33 (10.69)	10.86 (10.29)	09.28 (09.48)
$C_{36}H_{66}O_4Ni$	621.5986	224	Green	69.76 (69.56)	10.60 (10.70)	10.50 (10.30)	9.14 (9.44)

Table III:- Analytical and Physical data of Metal complexes

Compound	Mol. Weight (gm)	M.P. (^oC)	Color	% Found (Calculated)						
				C	H	O	N	S	Br	Co/ Ni
$C_{96}H_{146}O_{12}Co_2N_4S_2Br_2$	1890.0056	285	Dark Brown	60.97 (61.01)	7.54 (7.79)	10.44 (10.16)	2.68 (2.96)	3.50 (3.39)	8.73 (8.45)	6.14 (6.24)
$C_{96}H_{146}O_{12}Ni_2N_4S_2Br_2$	1889.5260	248	Dark Brown	60.92 (61.02)	7.88 (7.79)	10.26 (10.16)	2.86 (2.97)	3.24 (3.39)	8.56 (8.46)	6.28 (6.21)

Result and Discussion: -

The synthesized complexesare colored and solid in nature, stable at room temperature. They are insoluble in water but moderately soluble in organic solvents like methanol, ethanol, benzene and highly soluble in binary solvent mixture. The analytical data of ligands and complexes are recorded in table as given in the end.

IR Spectra:

The IR spectrum provides valuable information regarding coordination site of the ligand attached to the metal ion14,15. The absorption bands observed in the region 2921-2118 cm-1 and 2852-2849 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 1350-1390 cm-1 regions. Methyl and methylene rocking vibrations appears near 1102-1112 cm-1 and 725 cm-1

and another band at 1460- 1470 cm-1 are due to carboxylate ion COO-, C-O antisymmetric and symmetric stretching respectively. The characteristic band of metal (cobalt/nickel) constituent of soap molecule. A broad band observed at 3405-3480 cm-1 corresponding to –N-H stretching of amides. Also, ring stretching (skeletal bands) observed at 1600-1430 cm-1 shows a heteroaromatic ring system.

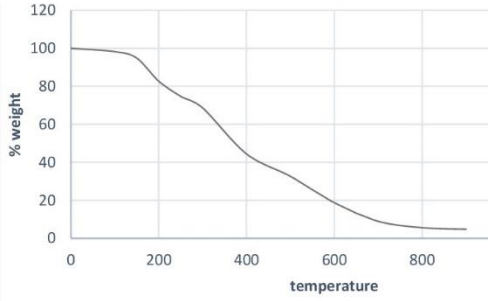
A strong band near 1490-1460 cm-1 and 100-1380 cm-1 indicates the presence of nitro group in aromatic system of ligand. Small peaks corresponding to-C-S- vibrations have been observed in the region of 750-610 cm-1. Involvement of phenothiazine nitrogen in the complexation is supported by the presence of a new band at 458-436 cm-1, assignable to ν(M-N) for Ni(II) and Co (II) complexes. From IR spectral data, it is evident that ligand act as a monodented, bonded to metal ion (cobalt/nickel ion) through 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 1543-1539 cm-1 in the complex indicate that the secondary nitrogen is the coordinating site in the complex16.

NMR spectral analysis:

The 1HNMR spectra of free ligand and corresponding complexes has been compared and determine the bonding. The signalswere assignedbased on chemical shifts, spin-spin interaction and their effects on substitution. Signals on 7.3 δ shows the presence of aromatic C-H in the compound. Also peaks on 8.2 δ,7.8 δ shows the presence of a –I group (here $–NO_2$) in the molecule. A broad peak is observed at 3.5 δ indicating to –N-H proton. This peak indicates the coordination through the NH group of phenothiazine molecule to the metal atom of soap segment.

Thermo Gravimetric Analysis (TGA)17,18 :-

In TGA the sample mass is monitored as at is subjected to a temperature program. The atmosphere also controlled as using either oxidizing (oxygen/ air) or inertcondition (in presence of organ, nitrogen and helium etc.). In TGA we measure weight loss or gain, for this purpose TGA uses heat to force reaction and physical changes in materials19. Various scientist has done TGA studies to evaluate various kinetic parameters for metal soap of cobalt and nickel20.



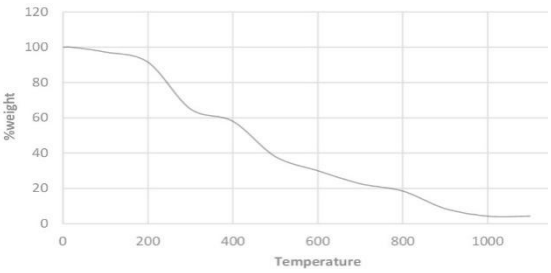


Fig :2- TGA of Ni-Complex

Fig :3- TGA of Co-Complex

By TGA we study the stability ranges, percentage of weight loss, percentage of residue obtained after decomposition process21,22. The thermogravimetry curve of complexes were recorded in the temperature range of 100 0C to 1100 0C, in an atmosphere of nitrogen. Complexes undergo decomposition in one stage, which shows about 90.0 % decomposition. The final weight loss observed aggress with the value calculated for the conversion of the complexes to its oxide (CoO/NiO). The percentage of the CoO and NiO (3-4%)found by TG data is a good agreement with the theoretical data.

Determination of Kinetic Parameters:

Kinetic studies of thermal decomposition become very useful in calculating the important parameters like activation energy (E_a), enthalpy change (ΔH), entropy change (ΔS), change in free energy (ΔG) etc., which directly govern the factors of thermal stability of any complexes. Thermal decomposition kinetics was proposed by Flynn. Freeman and Carrol published their method of kinetic analysis of thermoanalytical data. The energy of activation (E_a) for all the complexes were measured by Coats-Redfern and Broido equation.

Broido's Method for Analysis of TGA Data:

In TGA method, when a complex is heated it starts degradation and it is assumed that the degradation products are volatile. The progress of degradation is observed by continues weighing of sample.

According to Broido the weight of sample (W_t) subjected to thermal analysis at any time (t) is related to the fraction of the number of initial molecules not yet decomposed (y) by the equation: -

$$Y = \frac{N}{N0} = \frac{Wt - W\infty}{W0 - W\infty}$$

Where,

N = No. of molecules at the end of pyrolysis

N0 = No. of molecules initially present

Wt = Active weight of material at any time t

$W\infty$ = Weight of material at the end of pyrolysis

$W0$ = Weight of material taken initially

Broido used following relationship for the calculation of activation energy as-

$$ln\left[ln\left(\frac{1}{y}\right)\right] = -\frac{\mathrm{E_a}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}}\right) + \text{Constant}$$

By the slope of $ln\left[ln\left(\frac{1}{y}\right)\right]$ vs $\frac{1}{\mathrm{T}}$, we calculate the value of activation energy ($\mathrm{E_a}$) for both nickel complex and cobalt complex.

Coats-Redfern Method for analysis of TGA data:

In this method we use following kinetic equation:

$$ln\left[\frac{-ln(1-\alpha)}{T^2}\right] = ln\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT}$$

or, $log\left[\frac{-log\,(1-\alpha)}{T^2}\right] = log\left[\frac{AR}{\beta\, E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.303\,RT}$

Where α is extent of reaction expressed by

$$\alpha = \frac{m_0 - m}{m_0 - m_f}$$

where m_0= initial weight of compound

m_f= final weight of compound

m = weight of compound at any temperature (t)

The above equation is the Coats-Redfern method. To calculate the activation energy, we plot a curve between log[-log(1-α)/T2] and 1/T.

In the present investigation we use Broido method and Coats-Redfern method to determineenergy of activation (Ea) for complex using TGA pattern.

Conclusion:-

In this paper the novel ligand named 2-nitrophenothiazine and its metal complexes with cobalt and nickelhave been synthesised and characterised by spectral and analytical data. From thermogram and table IV, it can be concluded that degradation of the complexes involves three steps, in which the first step included the degradation of fatty acid i.e. oleic acid, starts around 200 0C. The second step includes degradation of phenothiazine ligand around 3000C to 400 0C. Finally, after 8000C to 900 0C, the third step goes in which we found that the TGA graph tends to be constant.Activation energy can be calculated by the plots from both methods. From the perusal of table-IV, the activation energy of Nickel complex with phenothiazine is greater than that of Cobalt complex with phenothiazine.

Table (IV):- Activation Energy of Complexes

S. No.	Metal Complex	Activation energy (Calmole-1K-1) Coats-Redfern Method	Activation energy (Calmole-1K-1) Broido Method
1.	Co-Complex	2537.33	5045.04
2.	Ni-Complex	3268.75	5643.00

So, the activation energy order will be – Ni complex > Co complex

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