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Thermogravimetric Analysis of Microwave Assisted Novel Macromolecular Complexes of Metal Surfactants

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ABSTRACT

Copper surfactants derived from common fatty acids are found to be eco-friendly, completely biodegradable and nontoxic with significant antiviral, anticancerous, antifungal and antimicrobial properties. Based upon their widest applicability Performa complexes of copper(II) with binuclear ligands were synthesized. The resulting complexes were characterized by elemental analysis, thermo gravimetric analysis, magnetic moment measurements, ^{1}H NMR, IR and ESR spectra and all the data were carefully studied. In the present research work a detailed thermal analysis using TGA technique was done in order to determine their energy of activation by applying equations like Coats-Redfern, Horowitz-Metzger, Broido equation. TGA simply measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere.

Keywords: Thermo gravimetricanalysis, Copper Palmitate, Benzothiazole, Biocidal, Transition Metal Complexes.

INTRODUCTION

Literature review of past coordination chemistry of metallo-nitrogen or sulfur compounds is a source of stimulation to many research workers due to the fact that it possesses unique stereo chemical, magnetic and spectral properties metal complexes of ligands containing nitrogen and sulfur as donor atoms [1-5]. Similarly, the co-ordination chemistry of high oxidation state transition metal complexes is an area of considerable importance because of their biological significance. Now a days, on the other hand surfactants have attracted a considerable attention, as they form a unique class of chemical compounds. These are able to alter surface and interfacial properties and to self associate and solubilize themselves in micelle. Therefore, they tend not only to accumulate at surface but also by their presence change the properties of surface. They are active at interface that can be b/w sol/liq, liq/liq, liq/gas pair of phases. This finally seems that all is the game of solute-solvent interactions taking place [6].

A surfactant molecule is dual in nature and can be categorized into anionic, cationic and nonionic surfactant depending upon their hydrophilic head group. Among Anionic surfactants bearing Copper (II) ions are ideal for investigations because of their valuable characteristics. They are gaining popularity, on account of their immense applicability in industrial, pharmaceutical [7, 8] and medical fields. On account

of their utilitarian effect such as foaming, herbicidal, fungicidal [9], pesticidal, antimicrobial, biocidal [10], anticancerous [11-14] is worth mentioning.

Above said class of surfactants play a vital role in various fields such as rubber industries, paints, varnishes, water proofing and repellency, protection of crops, stabilization of nylon thread, preservation of wood, lubrication etc. All these properties led us to study the micellar features and study the micellar features of copper soaps derived from fatty acids for their maximum possible benefits in agriculture and industries. In view of past interesting results and in continuation of our comprehensive studies on copper complexes with sulfur and nitrogen donating ligands, we report here the preparation of some novel copper complexes.

A detailed Thermo-gravimetric analysis (TGA, a type of thermal analysis) was done to measure the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. TGA measurements were used primarily to determine the composition of soaps and to predict their thermal stability up to elevated temperatures. The use of thermo gravimetric data is mainly for evaluating kinetic parameters of solid state reactions involving weight loss (or gain).

MATERIALS AND METHODS

All chemicals used were of A.R. Grade, substituted aniline used purchased from Merck. Solvents were purified according to standard procedures. Micro analytical data of the compounds was recorded at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. Thin layer chromatography was used to access the purity of the synthesized compounds. The IR spectra of the complexes were obtained as KBR disks in the range 400-4000 cm^{-1} on Perkin Elmer spectrophotometer at CDRI, Lucknow. 1H NMR spectra were recorded at CDRI, Lucknow using $CDCl_3$ as reference. ESR spectra of the complexes were recorded at liquid nitrogen temperature in the X-band region at IIT, Mumbai. Thermo gravimetric analysis was done at IIT, Mumbai. Magnetic susceptibility measurements were conducted at S.P. University, Vallabh Vidhyanagar, Gujrat.

Synthesis of Copper Surfactants: Copper palmitate was prepared by mixing one gram of palmitic acid into 25 ml ethyl alcohol, shake the mixture in hot water bath at about 50˚C and then add one drop of phenolphthalein. Prepare a saturated solution of KOH in another beaker and add it into the palmitic acid solution drop by drop until the light pink colour appears. Now again in another beaker prepare a saturated solution of $CuSO_4$ (about 3-4 grams in 5 ml H_2O) and mix it into the above solution with stirring till the blue coloured soap is formed. Filtered and washed with warm water and 10% ethyl alcohol then dried and recrystallised with hot benzene.

Synthesis of substituted 2- amino benzothiazole: Substituted 2-amino benzothiazoles were synthesized using thiocyanation method. In this method (0.1 mol) p- substituted aniline was treated with a mixture of 7.6 g ammonium thiocyanate and 80 ml glacial acetic acid in a 250 ml three necked round bottom flask, with stirrer, dropping funnel and reflux condenser at room temperature for one and half hour. The thiocyanogenation of aryl amine takes place in the presence of thiocyanogen gas, which is generated insitu by the reaction of cupric chloride and ammonium thiocyanate. After cooling the reaction mixture, add 100 ml concentrated HCl, and heat again for half an hour, then cool it and then saturated solution of sodium carbonate (Na_2CO_3) is added to neutralize it, till the solid was formed. The solid separated out was filtered and washed with cold water, dried and recrystallised with ethanol.

Synthesis of complexes: The complex of copper palmitate and benzothiazole was prepared by adding (0.001mol) copper palmitate with (0.002 mol) benzothiazole in 25 – 30 ml ethyl alcohol and mixture was refluxed for about two hours with constant stirring. After cooling the solid separated out was filtered, dried and recrystallised with hot benzene.

RESULTS AND DISCUSSION

All the synthesized complexes are colored and solid in nature, and stable at room temperature. These are insoluble in water but moderately soluble in organic solvents like methanol, ethanol, benzene, DMSO and highly soluble in binary solvent mixtures e.g. methanol + benzene mixture. The analytical and physical data of the complexes are presented in table 1.

The complexes are abbreviated as follows:

1. CP (BTA) CH_3 Copper Palmitate with 2-Amino 6-Methyl benzothiazole - C1
2. CP (BTA) C_2H_5 Copper Palmitate with 2-Amino 6-Ethyl benzothiazole - C2
3. CP (BTA) OCH_3 Copper Palmitate with 2-Amino 6-Methoxy benzothiazole - C3
4. CP (BTA) OC_2H_5 Copper Palmitate with 2-Amino 6-Ethoxy benzothiazole - C4
5. CP (BTA) NO_2 Copper Palmitate with 2-Amino 6-Nitro benzothiazole - C5

Table I : Analytical and Physical Data of the Complexes

Complex	Molecular Formula	Color	M.P. (°C)	C (%)	H (%)	O (%)	N (%)	S (%)	Cu (%)
C1	$C_{80}H_{140}O_8N_4S_2Cu_2$	Brown	270	65.01 (65.08)	9.40 (9.49)	8.61 (8.68)	4.10 (4.34)	3.70 (3.79)	8.55 (8.61)
C2	$C_{81}H_{142}O_8N_4S_2Cu_2$	Black	278	65.21 (65.28)	9.51 (9.54)	8.53 (8.59)	3.71 (3.77)	4.22 (4.29)	8.49 (8.55)
C3	$C_{80}H_{140}O_9N_4S_2Cu_2$	Grey	282	64.32 (64.39)	9.32 (9.38)	9.61 (9.65)	3.68 (3.76)	4.22 (4.29)	8.48 (8.52)
C4	$C_{81}H_{142}O_9N_4S_2Cu_2$	Grayish Black	285	64.52 (64.58)	9.37 (9.43)	9.52 (9.56)	3.69 (3.73)	4.21 (4.26)	8.39 (8.44)
C5	$C_{80}H_{140}O_{10}N_5S_2Cu_2$	Dark Mustard	265	62.89 (62.94)	9.03 (9.09)	10.59 (10.63)	4.60 (4.64)	4.20 (4.25)	8.40 (8.44)

IR spectral studies: The IR spectrum provides valuable information regarding coordination site of the ligands attached to the metal ion. Selected bands of diagnostic importance of the complexes with relative intensities / peaks are given in table 2. The absorption bands observed in the region 2950- 2970 cm^{-1} and 2917.5 – 2960 cm^{-1} corresponds to C-H symmetric and asymmetric stretching of methyl (- CH_3) and methylene (-CH_3) group of the soap segment present in the complex. Small peak corresponding to –CH_2 twisting and wagging has been observed at 1330-1345 cm^{-1} regions. Methyl and methylene rocking vibrations appears near 1117-1130.8 cm^{-1} and 721-723 cm^{-1}. The absorption band at 1586 cm^{-1} and another band at 1425- 1450 cm^{-1} are due to carboxylate ion COO-, C-O anti symmetric and symmetric stretching respectively. The characteristic band of metal (copper) constituent of soap molecule i.e. (Cu-O) copper oxygen stretching bond has been distinguished at 452 - 470.8 cm^{-1}.

Table 2: IR Spectral Data for Copper (II) Complexes

ABSORPTION BANDS	**CP[BTA]CH_3** (in cm^{-1})	**CP[BTA]C_2H_5** (in cm^{-1})	**CP[BTA]OCH_3** (in cm^{-1})	**CP[BTA]OC_2H_5** (in cm^{-1})	**CP[BTA]NO_2** (in cm^{-1})
CH_3 and CH_2, -C-H Antisym. Stretching	**2917.5**	**2918.0**	**2925.5**	**2955.5**	**2960.2**
CH_3 and CH_2 C-H Sym. Stretching	**2850.0**	**2952.8**	**2958.8**	**2965.0**	**2970.2**
-N-H bending	-	-	**1593**	-	**1597**

COO-, C-O Antisym. Stretching	**1586.7**	**1586.0**	**1586.0**	**1586.0**	**1586.0**
COO-, C-O sym. stretching	**1425.0**	**1450.8**	**1435.5**	**1430.0**	**1438.0**
CH_2, C-H Bending (δ) (twisting and wagging)	**1330**	**1365.0**	**1345.5**	**1340.8**	**1335.0**
CH_3, C-H rocking	**1117**	**1125.2**	**1120.8**	**1130.8**	**1125.9**
CH_2, C-H rocking	**721.2**	**723.5**	**720.8**	**721.5**	**721.0**
Cu-N stretching	**548.0**	**535.2**	**548.2**	**548.6**	**548.8**
Cu-O stretching	**465.2**	**452.8**	**468.2**	**470.8**	**472.3**
NH_2, N-H stretching	**3443.6**	**3480.6**	**3448.8**	**3465.5**	**3450.2**
Ar-C-NO_2 stretching	-	-	-	-	**1448.0**
N-C=S stretching	**1315.0**	**1318.5**	**1320.5**	**1320.0**	**1315.0**
C=S stretching	**1655**	**1660.0**	**1665.8**	**1670.2**	**1674.5**
Ar-C-OCH_3 asym. stretching	-	-	**1240.3**	**1242.5**	-
Ar-C-OCH_3 sym. stretching	-	-	**1020.3**	**1020.7**	-
C-H, Deformation ("oop")	**681.5**	**692.2**	**680.5**	**682.8**	**691.0**

Apart from these bands the following bands was also found corresponding to ligand moiety, display an asymmetrical Ar-O-CH_3 structure bond at 1242 cm^{-1} with symmetrical stretching near 1020 cm^{-1}. In case of CP(BTA)NO_2 a clear peak is observed at 1448 cm^{-1} corresponding to Ar-C-NO_2 vibrations. Both ligands / complexes contain -C=S group attached to a nitrogen atom which gives absorption band in 1655-1674.5 cm^{-1} region. A broad band near 3443 - 3480 cm^{-1} was observed corresponding to -NH stretching of amides. An absorption band observed at 1315-1320 cm^{-1} corresponds to -N-C=S stretching. From IR spectral data, it is evident that ligand acts as a monodentate, bonded to metal ion (copper ion) through primary nitrogen atom of NH_2.The strong band at 1610 cm^{-1}, characteristic of the -NH bending vibration of the – NH_2 group in the free ligand (2-amino 6-methoxy Benzothiazole and 2-amino 6-nitro Benzothiazole) is shifted to lower frequency of 1593-1597 cm^{-1} in the complexes indicated that the primary nitrogen is the coordinating site in the complex. This is further supported by the formation of new bond in the region 535-548 cm^{-1} that is due to Cu - N bonds.

NMR spectral studies: The ^1H NMR spectra of free ligands and corresponding complexes have been compared and determine the bonding. The signals were assigned on the basis of chemical shifts, spin-spin interaction and their effect on substitution.

Table 3: NMR Spectral Data For Copper (II) Complexes

COMPLEX → / PEAKS ↓	CP(BTA)CH_3 (in δ)	CP(BTA)C_2H_5 (in δ)	CP(BTA)OCH_3 (in δ)	CP(BTA)OC_2H_5 (in δ)	CP(BTA)NO_2 (in δ)
-CH_3-CH_2-R	0.882	0.885	0.887	0.887	0.889
-CH_2-CH_2-R	1.254	1.256	1.250	1.252	1.250
CH_2-COO^-	1.682	1.685	1.685	1.689	1.689
CH_3-Ar	2.173	-	-	-	-

NH_2 (Broadened Peak)	3.95	3.92	3.95	3.94	3.90
Aromatic Proton	7.252	7.250	7.252	7.256	7.250
Tautomeric – NH_2 (Weak Signal)	7.862	7.865	7.864	7.864	7.860

A perusal of the spectra (Table 3) of copper complexes shows signals of aliphatic $–CH_3$ proton attached to $–CH_2$-R group in the range of δ 0.882-0.889, $-CH_2$ proton attached to $–CH_2$- R group shows signals at δ 1.250-1.256. A broadened peak is observed at δ 3.90 - .3.95 indicating to $–NH_2$ proton. This peak indicates the co-ordination through the – NH_2 group of Benzothiazole segment to the metal (copper) atom of the soap segment.

ESR spectral studies: The g-tensor value of the copper complex can be used to derive the ground state. In octahedral complexes, the unpaired electron may lie in the dx^2- y^2 or dz^2 orbital. The Spin Hamiltonian parameters for the copper complexes are calculated from the spectra. g- tensor values (for both complexes) are g|| > g| > g0 suggest that complexes has distorted octahedral geometry with unpaired electron lying in dx^2-y^2 orbital. The ESR parameters of the complexes coincide well with the related systems, which suggest that the complexes have octahedral geometry and the systems are axially symmetric. In the axial spectra, the g-values are related with exchange interaction coupling constant (G) by the expression, G = g|| -2/ g □- 2 According to Hathaway, if the G value is larger than four, the exchange interaction is negligible because the local tetragonal axes are aligned parallel or slightly misaligned. It its value is less than four, the exchange interaction is considerable and the local tetragonal axes are misaligned. For the present copper complex, it is higher than 4, which suggests that the local tetragonal axes are aligned parallel or slightly misaligned and consistent with a $dx^2 – y^2$ ground state. From the forgoing discussion it is concluded that the ligands react with copper (II) palmitate to form the metal complexes. Also the aforesaid spectral data clear that the coordination number is six for copper ion in dimeric complexes of the type Cu_2 $(C_{15}H_{31}COO)_4$ L_2 have been proposed.

Thermo Gravimetric Analysis (TGA) : In TGA the sample mass is monitored as it is subjected to a temperature program. The atmosphere is controlled and includes either oxidizing (oxygen/air) or inert conditions. To measure weight loss or gain, TGA uses heat to force reactions and physical changes in materials. The thermal behavior of Cu (II) complexes, including stability ranges, percentage of weight loss, percentage of residue obtained after decomposition process using thermogravimetry has been studied. The thermogravimetry curves of first four complexes were recorded in the temperature range of 3500 °C to 5000 °C, in an atmosphere of nitrogen. Complexes undergo decomposition in one stage, which show about 90.5 % decomposition. The final weight loss observed agress with the value calculated for the conversion of the complex to its oxide, CuO. The percentage of the cupric oxide (8.40 %) found by the TG data is in good agreement with the theoretical data (9.66 %). The thermal behavior of $CP[BTA]NO_2$ was analyzed by TGA in the atmosphere of nitrogen in temperature range of 1000 °C to 1100 °C. Synthesized complex undergo decomposition, corresponding to the elimination of saturated fatty acid (Palmitic acid) as parent ketone, ligand and carbon dioxide. The weight of the residue (10.09%) correspondence to the formation of the stable cupric oxide agrees well with calculated value (9.61%) The energy of activation (Eact) for all the complexes was measured by Coats-Redfern (equation 14), Horowitz-Metzer (equation 15) and Broido (equation 16). The results of these equations are summed in table 4.

$$\frac{\log f(\alpha)}{T^2} = \frac{\log AR}{aE}\left(1-\frac{2RT}{E}\right) - \frac{E}{2.303RT} \qquad \text{(Equation – 14)}$$

$$\ln[\ln(1-\alpha)^{-1}] = \frac{E.Q}{}$$

RT^2 (Equation – 15)

$$\ln [\ln(1/y)] = -\frac{E}{RT} + C \quad \text{(Equation – 16)}$$

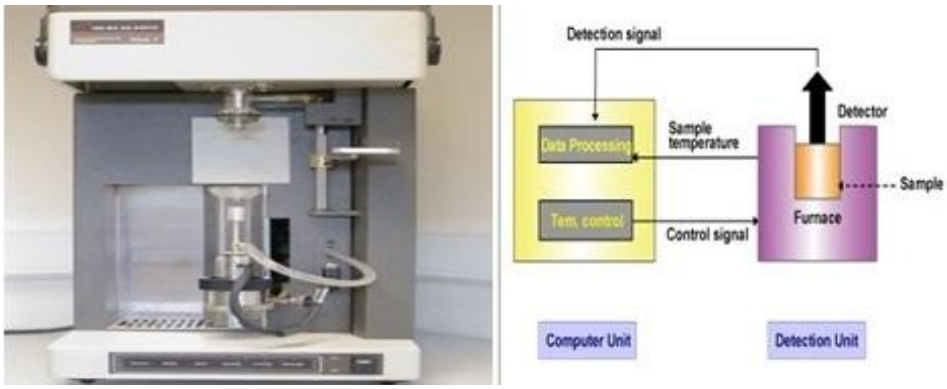

Fig.1. Image depicting a TGA instrument and flow chart of its system unit

Table 4. Energy of Activation for the Decomposition Reaction Using Various Equations

COMPLEX	COATS REDFERN EQN	HOROWITZ METZER EQN	BROIDO EQN
$CP(BTA)CH_3$	60.78	68.90	66.00
$CP(BTA)C_2H_5$	60.80	68.85	65.50
$CP(BTA)OCH_3$	62.85	70.20	68.85
$CP(BTA)OC_2H_5$	62.82	72.86	69.65
$CP(BTA)NO_2$	10.25	10.62	20.50

Plots Of % Weight V/S Temperature Depicting Thermal Degradation of Synthesized Complexes: The plots are shown in figures 2-6.

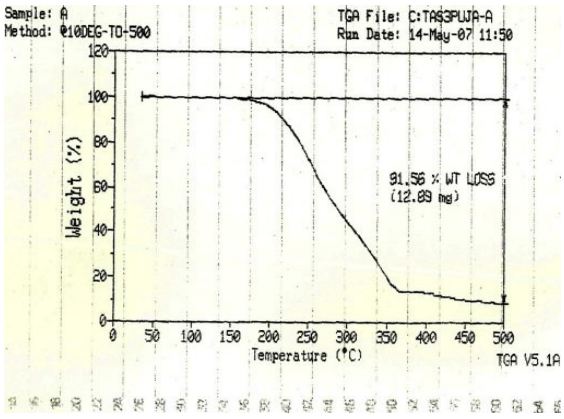

Fig.2 Thermal degradation of $CP(BTA)OCH_3$

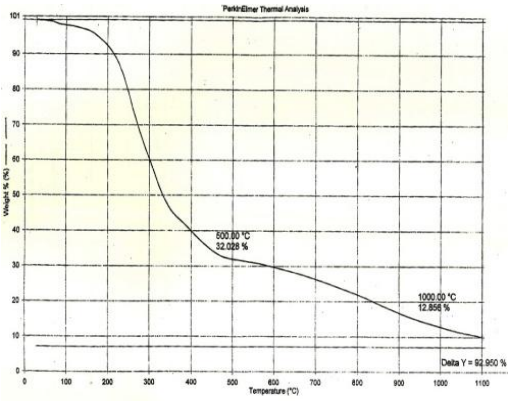

Fig.3 Thermal degradation of $CP(BTA)OC_2H_5$

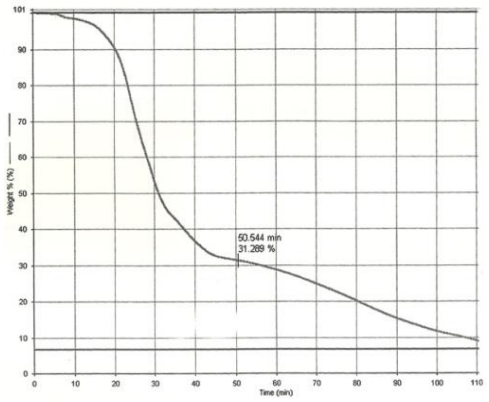

Fig.4 Thermal degradation of $CP(BTA)CH_3$

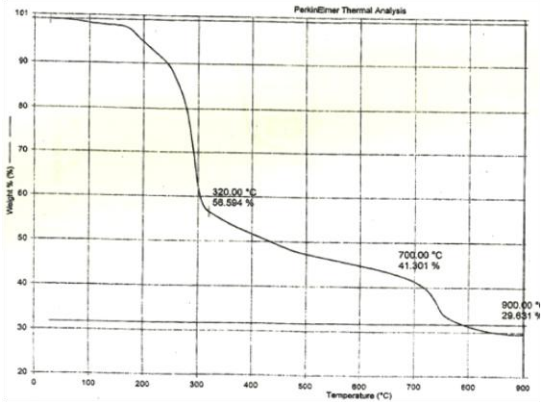

Fig.5 Thermal degradation of $CP(BTA)NO_2$

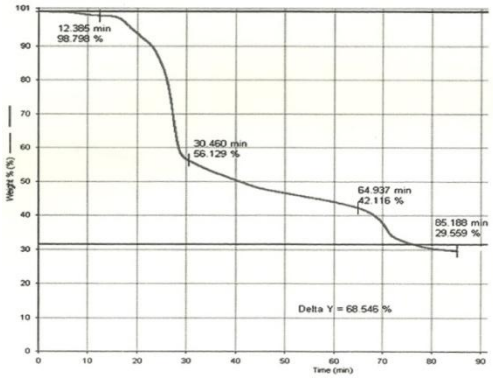

Fig.6 Thermal degradation of $CP(BTA)C_2H_5$

APPLICATIONS

TGA results of synthesized copper (II) complexes are useful primarily to determine the composition of soaps and to predict their thermal stability up to elevated temperatures. The use of thermo gravimetric data is mainly for evaluating kinetic parameters of solid state reactions involving weight loss (or gain).

CONCLUSIONS

From the thermogram and table no. 4, it can be concluded that $CP(BTA)NO_2$ complex needs longer time and higher temperature to completely decompose as compared to all the four complexes. Also, it is clear from table no. 4 that among the first four complexes, methoxy and ethoxy group containing complexes take less time and temperature for complete decomposition as compared to those containing methyl and ethyl groups. Thus, the present research work makes an attempt to prepare complexes from metal and azole ring compounds and it is found that the beneficial effects of the synthesized pharmaceuticals are much more than narrowly mentioned. In this paper novel ligands and complexes containing $-CH_3$, $-OCH_3$, $-C_2H_5$, $-OC_2H_5$, $-NO_2$ group are prepared and characterized by analytical data. Their thermal behavior and energy of activation were compared to conclude that the time and temperature taken by the complexes are as follows-

$CP(BTA)NO_2 > CP(BTA)CH_3 > CP(BTA)C_2H_5 > CP(BTA)OC_2H_5 > CP(BTA)OCH_3$

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