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Thermo gravimetric Analysis of Copper (II) soaps Derived from Groundnut (*Arachis hypogaea*) and Sesame (*Sesamum indicum*) Edible Oils

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ABSTRACT

The semi solid Copper (II) soaps derived from Groundnut (*Arachis hypogaea*) oil and Sesame (*Sesamum indicum*) oil have been synthesized and characterized by elemental analysis IR and NMR spectroscopy. IR and NMR spectroscopic studies have been also done earlier. These soaps are eco-friendly and biodegradable. The copper soaps derived from these oils have been thermally analyzed using TGA technique to determine their energy of activation. These Copper (II) soaps show single step thermal degradation corresponding to saturated, monounsaturated and polyunsaturated fatty acid components of the edible oils. Various equations like Coats-Redfern, Horowitz-Metzger and Broido equations were applied to evaluate the energy of activation. The values of energy of activation are observed to be in the following orders for both soaps : CG > CS. CG is observed to be more stable than CS soap due to its higher activation energy.

Keywords: Copper Groundnut soap, Copper Sesame soap, TGA, Coats-Redfern, Horowitz-Metzger and Broido equation, energy of activation.

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INTRODUCTION

Anionic surfactants bearing Copper (II) ions are ideal for investigations because of their valuable characteristics – foaming, wetting, detergency, emulsification etc [1-4].

The Copper (II) soaps in polar and non-polar solvents having remarkable interest and find their uses in various fields of applications like foaming, wetting, emulsification and lubrication etc due to the surface-active properties of soaps [5]. Viscometric studies at various temperature, apparent molar, volume ultrasound surface tension and antifungal activities related with micellar features of copper soaps in various organic solvents have been studied by Sharma et al [6-8]

Metallic soaps which are derived from Groundnut (*Arachis hypogaea*) and Sesame (*Sesamum indicum*) oils are commercially important as they find use in diverse applications such as dries in paint or inks, components of lubricating greases, catalysts and water proofing agents [9-14] .

Edible oils like Groundnut (*Arachis hypogaea*) and Sesame (*Sesamum indicum*) oils are being used for preparation of bio-diesel fuel. Spectral studies (IR & NMR) to confirm and analyze structural informations, geometry of soaps of Copper (II) Groundnut and Copper (II) Sesame have already been done in our laboratory and reported earlier.

Thermo-gravimetric analysis (TGA) is a thermal analysis technique which measures 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 are used primarily to determine the composition of soaps and to predict their thermal stability up to elevated temperatures. The use of thermo-gravimetric data to evaluate kinetic parameters of solid-state reactions involving weight loss (or gain) has been investigated by a number of workers [15-17].

EXPERIMENTAL

All the chemicals were of AR grade. Solvents were purified according to standard procedures before use. Elemental analysis was done for soaps for their metal content following the standard procedures [1,2,18].

Benzene was dehydrated by storage over sodium wire for 2-3 days and by refluxing for about twenty hours, it was then distilled and redistillation was carried out azeotropically and ethanol [17].

Copper soaps were prepared by refluxing the edible oils (i.e. Groundnut and Sesame oils) extracted from kernels and purified two-three times following the standard procedure) with ethyl alcohol and 2N KOH solution for about 4h (Direct Metathesis). The neutralization of excess KOH was done by slow addition of 0.5N HCL. Saturated solution of copper sulphate was then added to it for conversion of neutralized potassium soap into their corresponding copper

soap. After washing copper soap with hot water the samples were dried. The soap was recrystallised using hot benzene.

$$RCOOH \xrightarrow[EtOH]{KOH} RCOOK \xrightarrow{Cu^{+2}} (RCOO)_2Cu$$

In general the two soaps obtained are dark green in colour. The soap are highly soluble in benzene as well as methanol-benzene system but insoluble in water. Both the soaps are stable at room temperature and their physical parameter like saponification value (S.V.), saponification equivalent (S.E.) and molecular weight is given in earlier studies.

Thermo-gravimetry has been employed to study the kinetics of thermal decomposition of Copper-Groundnut soap(CG) and Copper-Sesame soap (CS). The TGA curves were obtained by Perkin Elmer Thermal Analysis apparatus from SAIF, IIT-Powai, Mumbai. TGA was done atmosphere between 0^0 C - 600^0C at the rate of 10^0C per minute.

RESULT AND DISCUSSIONS

The synthesized compounds are abbreviated as follows :-

1. Copper Groundnut Soap (CG)
2. Copper Sesame Soap (CS)

IR and NMR spectral analysis of these soaps reported earlier.

Thermo-gravimetric Analysis

Thermo-gravimetric Analysis method for kinetic analysis is reported here. This technique which measures the weight change in a soap as a function of temperature and time, in a controlled environment. This technique is very useful to investigate the thermal stability of a soap, or to investigate its behavior in different atmospheres (e.g. inert or oxidizing). The technique can be used in the examination of absorptive surfaces together with the nature and processes involved in the thermal decomposition and oxidation process [19]. TGA is useful to determine characteristics of soaps to determine degradation temperatures, absorbed moisture content of soaps, determines temperature and weight change of decomposition reactions and determine the kinetics of a reaction based on weight changes.

The exact information as to the nature and structure of the complexes are of great importance for their use in industries and for explaining their characteristics under different conditions [20-25]. TGA technique to determine their energy of activation various equations like Coats-Redfern, Horowitz-Metzger and Broido equations were applied to evaluate the energy of activation [26-28]. Thermo gravimetric has been employed to study the kinetics of thermal decomposition of CG and CS. TGA was done on nitrogen (N_2) atmosphere between

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25^0C - 600^0C at the rate of 10^0 C per minute. The results from Thermo-gravimetric analysis are usually reported in the form of curves relating the mass lost from the sample against temperature. The curves shows the loss in weight that occurred at different temperatures, as different types of water are lost from the surface.

The results of Thermo-gravimetric analysis of these soaps (CG and CS) show that the final residue is metal oxide. A plot of the weight loss of the sample w % v/s time t for these soaps that initially the soap decomposes slowly and then rapidly and finally becomes almost constant (Fig.- 1& Fig.- 2). The slight leap in the beginning of the every curve may be due to the breaking of the uncoordinated water molecule attached to the soaps.

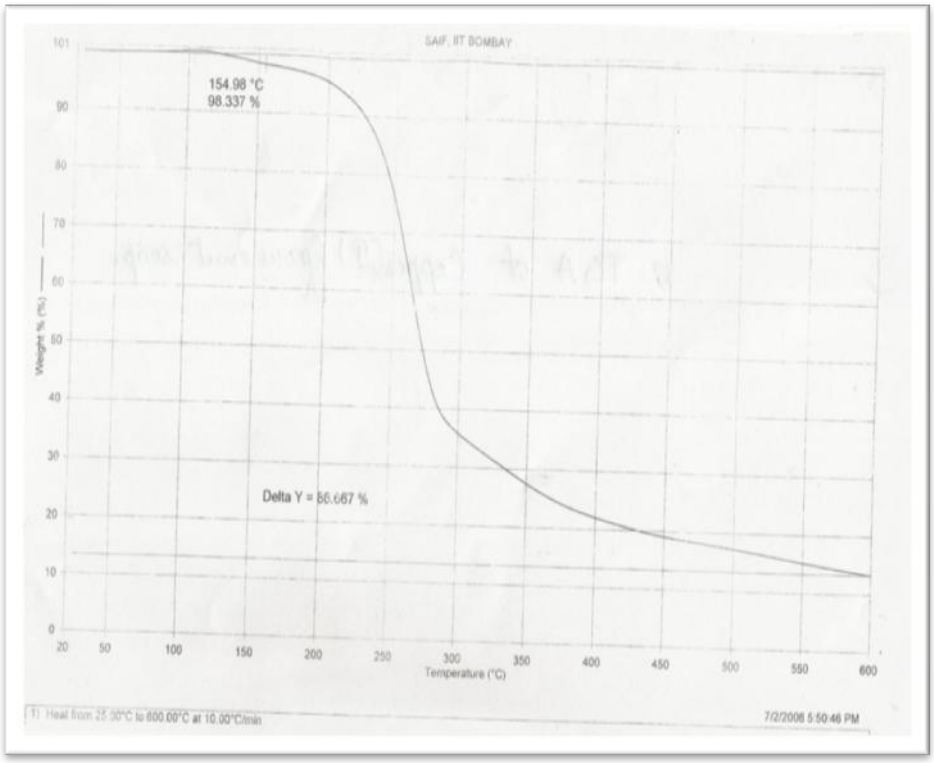

Fig 1: TGA of CG

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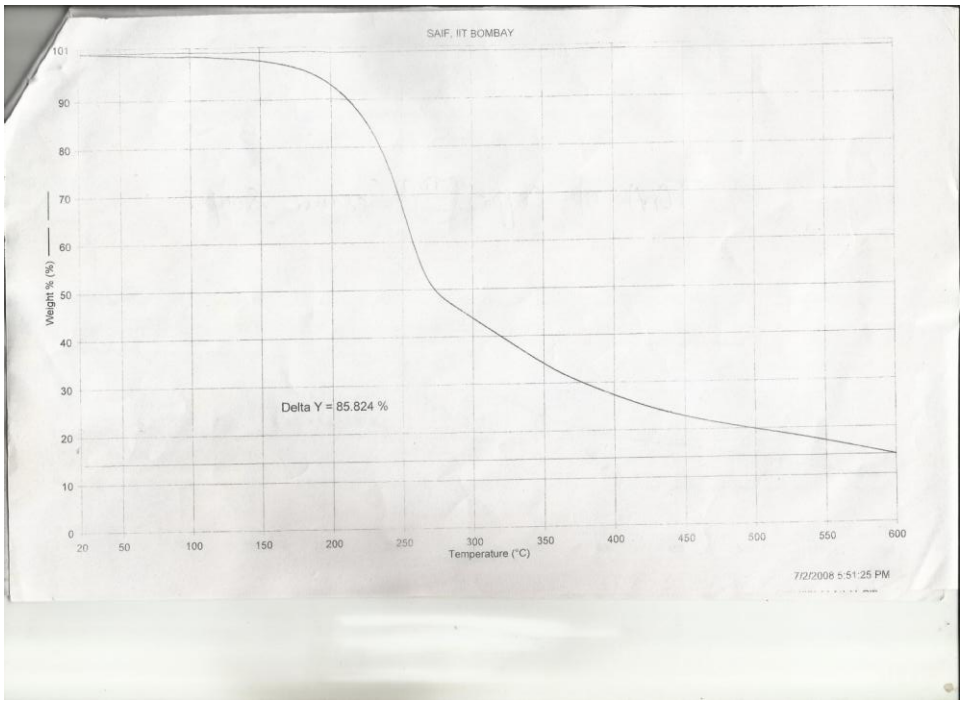

Fig. 2 – TGA of CS

Kinetic Parameters: These results have been applied on various equations like Coats – Redfern equation Horowitz – Metzger equation and Broido equation to evaluate the energy of activation (E) for thermal degradation of these soaps. Of the various methods of kinetic analysis, Coats-Redfern [26] equation has been found to be the most appropriate in calculating the energy of activation.

For n = 1, this equation can be written as –

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

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 $mol^{-1}K^{-1}$) and 'A' for the pre-exponential or frequency factor and is usually assigned to be independent of absolute temperature 'T'. The plots of '{[-log (1- α)] / T^2} v/s 1/T' are linear and the values of activation energies evaluated from the slope of these plots are recorded in Table- 1. The values are observed to be in the following order for these soaps CG>CS.

Table 1: Energy of Activation (in KJ Mole $^{-1}$) for the decomposition reaction of copper soaps derived from Groundnut oil and Sesame oil using various equations.

Soaps	C.R.E.	H.M.E.	B.E.
CG	85.74	104.86	81.68
CS	75.78	101.98	71.62

To confirm the energy of activation Horowitz-Metzger [27] equation has been used to evaluate the value of 'E'. The Horowitz-Metzger equation is as follows.

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

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 is obtained from the slope of the plot between 'ln[ln(1- α)$^{-1}$] v/s θ'. For Horowitz-Metzger equation the values of each soaps are repored in Table- 1 and are found to be in the order CG>CS.

The energy of activation for the thermal decomposition of these soaps have also been calculated by using Broido's [28] equations which is as follows :

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

where 'y' is fraction of weight at temperature 'T', 'E' is the activation energy and 'R' is the gas constant in joule mol^{-1}K^{-1}. The value of activation energy is of these soaps are recorded in Table -1 and are found to be in the following order CG>CS.

A perusal of Table- 1 reveals that the value of activation energy is higher for the CG and smaller for the CS. There was a good correlation between the activation energies evaluated by various equations and approximation methods however the values obtained by the approximation methods were higher than the values obtained by integration methods which can be ascribed the different mathematical treatment of the methods. In general CG is derived from Groundnut oil shows higher thermal stability due to higher content of saturated fatty acids and MUFA. The higher PUFA content of CS makes it less stable and needs lesser energy to degrade.

This may be concluded by the above studies that CS soap may be easily degradable as compare to soap CG naturally biologically and thermally. The products prepared by Groundnut and Sesame should be promoted and encouraged due to their significance and degradability.

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