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Orginal Research Article

Synthesis, characterization, and thermal degradation of Cu (II) surfactants for sustainable green chemistry

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ABSTRACT

The Cu (II) surfactantsof stearic and palmitic acids were synthesized which are greenish blue in colour and chosen for thermogravimetric and derivative thermal analysis. Their structure has been confirmed by elemental analysis, and mass spectroscopy. Thermogravimetric degradation of Cu (II) palmitate soap was studied for energy of activation. This shows that two step thermal degradation in the range of 423 K to 703 K. Various equations like coats-redfern (CR), horowitz-metzger (HM) and broido equations (BE) were applied to evaluate the energy of activation. Thermal degradation of solid components will be a good and significant method for the removal of the pollutant from the environment. The present study will play an important role for pollution controlling and in the field of green chemistry.

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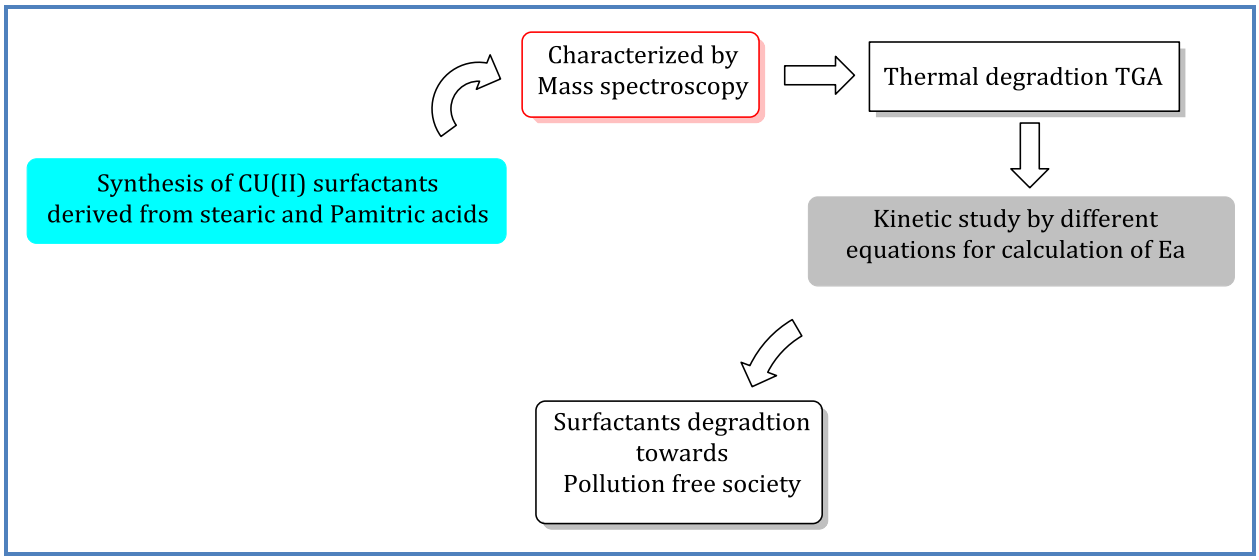
Graphical Abstract



Introduction

It is the prime objective of environmental education to make people aware about the importance of protection and conservation of our environment because indiscriminate release of various pollutants such as surfactants in the environment has created a new facet in the environment pollution [1].

Surfactants most characteristic phenomenon of micellization in the bulk phase, as well as their ability to be accumulated at an interface are of immense theoretical, applied and biological interests as indicated by large number of publication of papers and reviews in last three decades [2].

Particulars information about Cu (II) soaps derived from natural oils, play a vital role in its selection in specific phenomena such as emulsification and also in their use as herbicides, fungicides, pesticides and insecticides etc [3]. Many researcher [4, 5] have studied different spectral techniques like IR, NMR and magnetic instant studies of various complexes containing copper. Mass spectroscopy provides an information about fragmentation process and molecular mass of compound [6, 7].

Thermogravimetry is a valuable technique to establish the kinetic parameters and the oxidative induction period [8, 9]. This led us to synthesize copper (II) palmitate soap to study the thermal properties.

Experimental

Matreials and methods

All chemicals used were of LR/AR grade. Saturated acids were procured directly from the market. Firstly, copper stearate and palmitate soaps were prepared by direct metathesis of corresponding potassium soaps derived from pure Stearic acid and palmitic acid with slight excess of required amount of copper sulphate at 50-55 °C [10]. After washing with hot water and the alcohol, the sample was dried at 80-100 °C and recrystallized with hot benzene.

The Mass Spectra were obtaining from CDIR Lucknow U.P. India. The TGA curves of the samples were obtained on Metter – Toledo system (TGA/SDTA 851e) Module from IIT Powai Mumbai. The analysis was done on STARe software system. TGA was done on nitrogen (N_2) atmosphere between 50 ^{0}C-750 °C at the rate of 10 °C per minute. The results were obtained as plots of weight loss v/s temperature and % weight loss v/s temperature.

Scheme 1. Formation of Cu soaps by replacing potassium soap

Results and discussion

The synthesized compound is abbreviated as follows: (*I*) Copper Stearate Soap (CS Soap). (*II*) Copper palmitate Soap (CPSoap). The physical & analytical data of CS and CP soaps are given in Table 1. Elemental analysis was done for soaps for their metal content following standard procedures [11].

Table 1. Analytical and physical data of copper stearate and copper palmitate

Compound	Molecular Weight	M.P. (^{o}C)	Colour	% Found (Calculated)			
				Cu	C	H	O
$C_{36}H_{70}O_4Cu$ (Copper Stearate)	630.42	82	Blue	9.52 [10.07]	67.95 [68.56]	11.01 [11.19]	10.02 [10.15]
$C_{32}H_{62}O_4Cu$ (Copper Palmitate)	573.54	80	Blue	11.01 [11.06]	66.10 [66.91]	10.82 [10.87]	11.03 [11.14]

Mass Spectra

The major peak at m/z obs.(Anal. Calcd.) 626.58 (627.5) and 566.62 (571.5) in the ESI-MS spectrum could be assigned to the molecular ion peak of Cu stearate and Cu palmitae respectively.

The FAB-mass spectra suggested that all the soaps have a dimeric nature. These soaps show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses. The FAB mass spectrum gives additional information about the analyzed species. The spectrum Figure 1 & 2 Shows a series of peak 595.5, 567.6, 539.6, 496.6, 479.5, 451.5, 391.3, and 296.2 corresponding to various fragments of Cu (II) stearate. The FAB mass spectrum gives additional structural information about the analyzed species. The spectrum Figures 3, 4, and 5 shows a series of peak 512.2, 492.4, 391.3, 201.2, 171.1, 117.1 and 89.07 corresponding to various fragments of Cu (II) palmitate [13, 14].

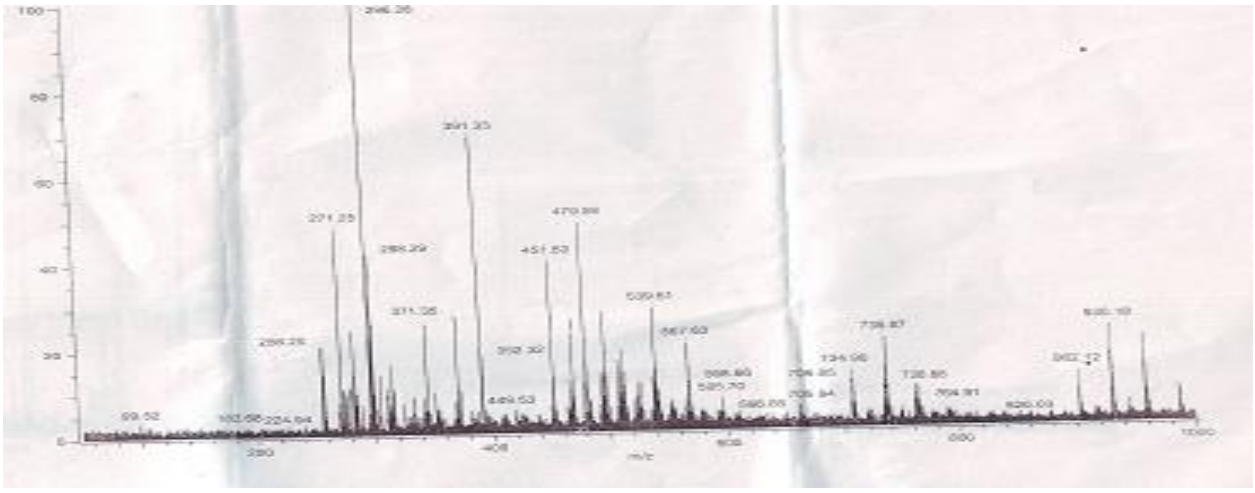


Figure 1. FAB-mass spectra of Cu (II) stearte (A)

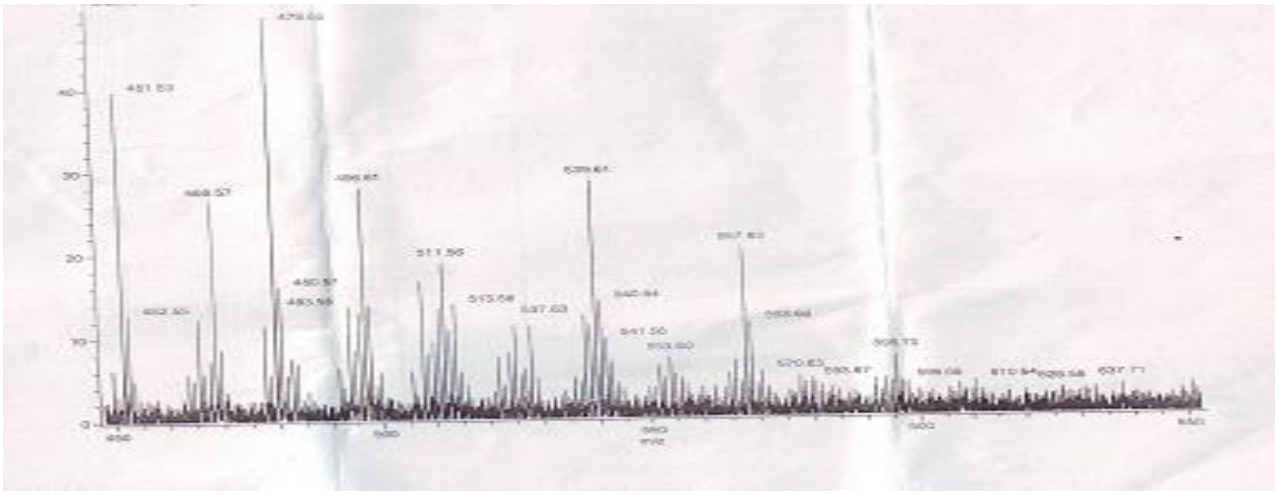


Figure 2. FAB-mass spectra of Cu (II) stearte (A)

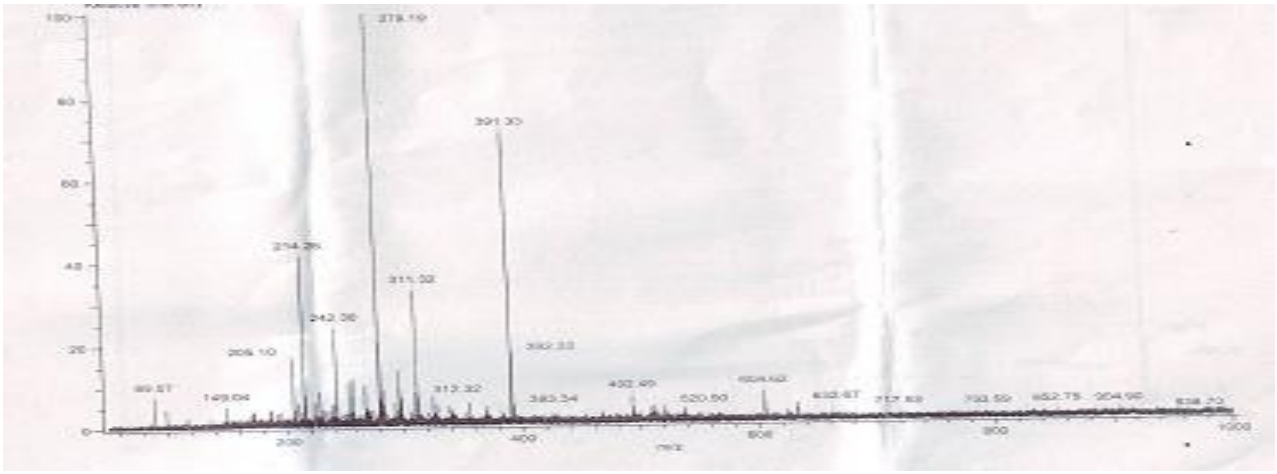


Figure 3. Fragmentation peaks in mass spectra of Cu (II) palmitae (A)

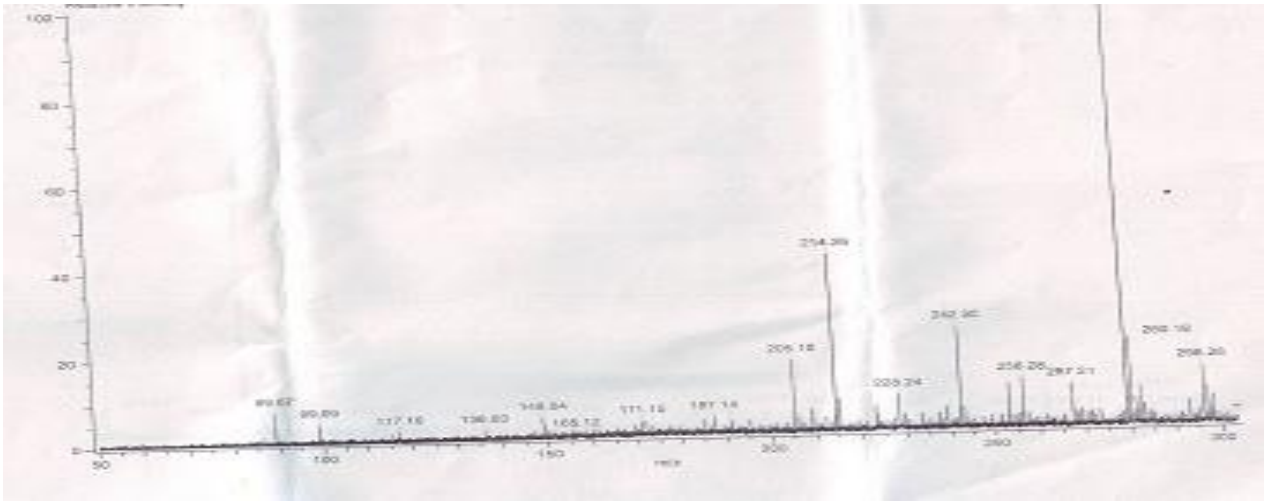


Figure 4. Fragmentation peaks in mass spectra of Cu (II) palmitae (B)

Thermal decomposition

The results from thermogravimetric analysis are usually reported in the form of curves relating the mass lost from the material against temperature (Figure 5, 6). The TGA curves plotted for CP that the decomposition of the complexes takes place in two steps, in temperature range of 423K to 703K. The copper soaps decompose into parent ketones, cupric oxide and carbon dioxide. For this system, the weight of final residue is observed to be in agreement with the theoretically calculated weight of metal oxide from the molecular formula of the corresponding soap. It is suggested that the long chain fatty acids produce volatile compounds, which are constantly removed by vapour generated during heating [15]. The DTA curve shows in Figure 7 reveals that endothermic reaction.

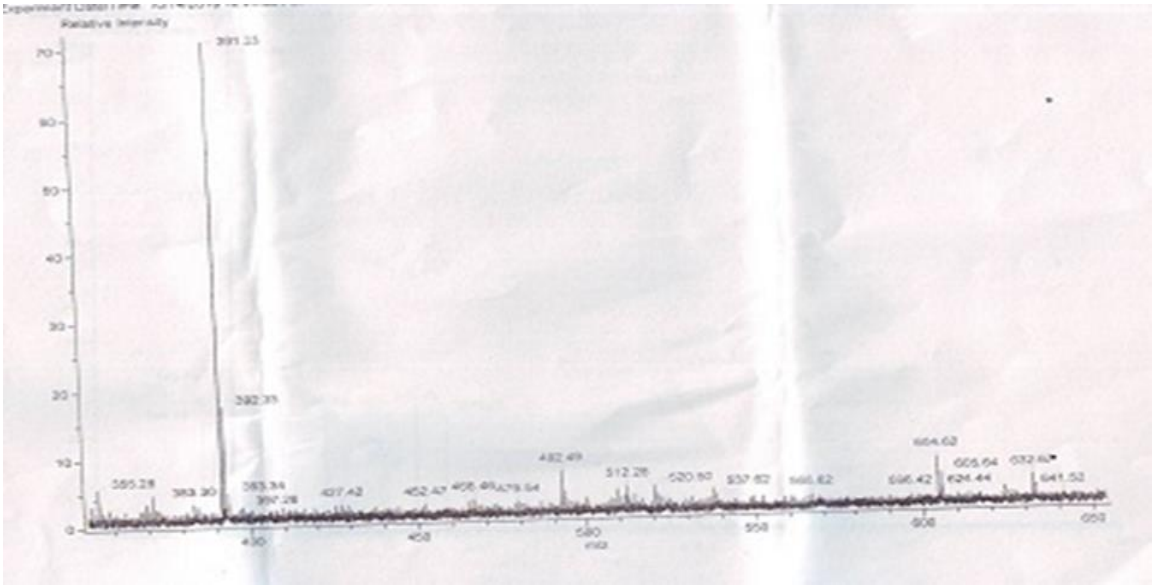


Figure 5. Fragmentation peaks in mass spectra of Cu (II) palmitate (C)

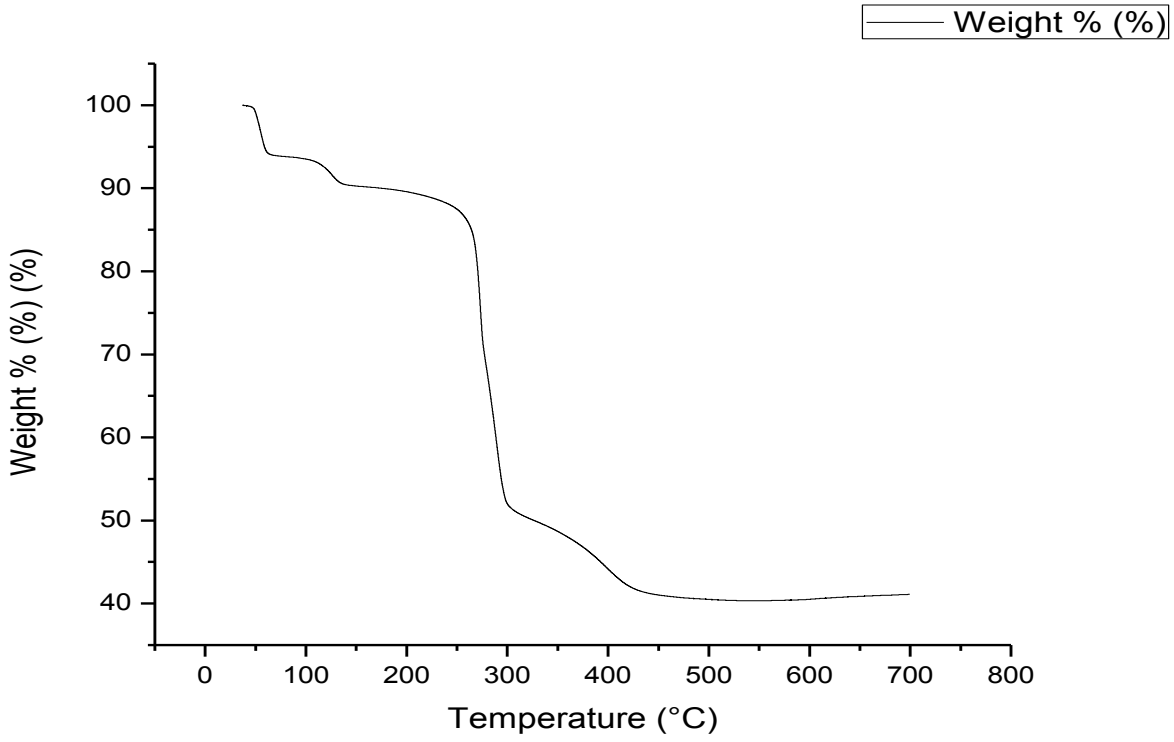


Figure 6. (A) Fragmentation peaks in mass spectra of Cu (II) palmitate (C). (B) Plot of % weight loss *v/s* temperature depicting thermal degradation of copper palmitate soap

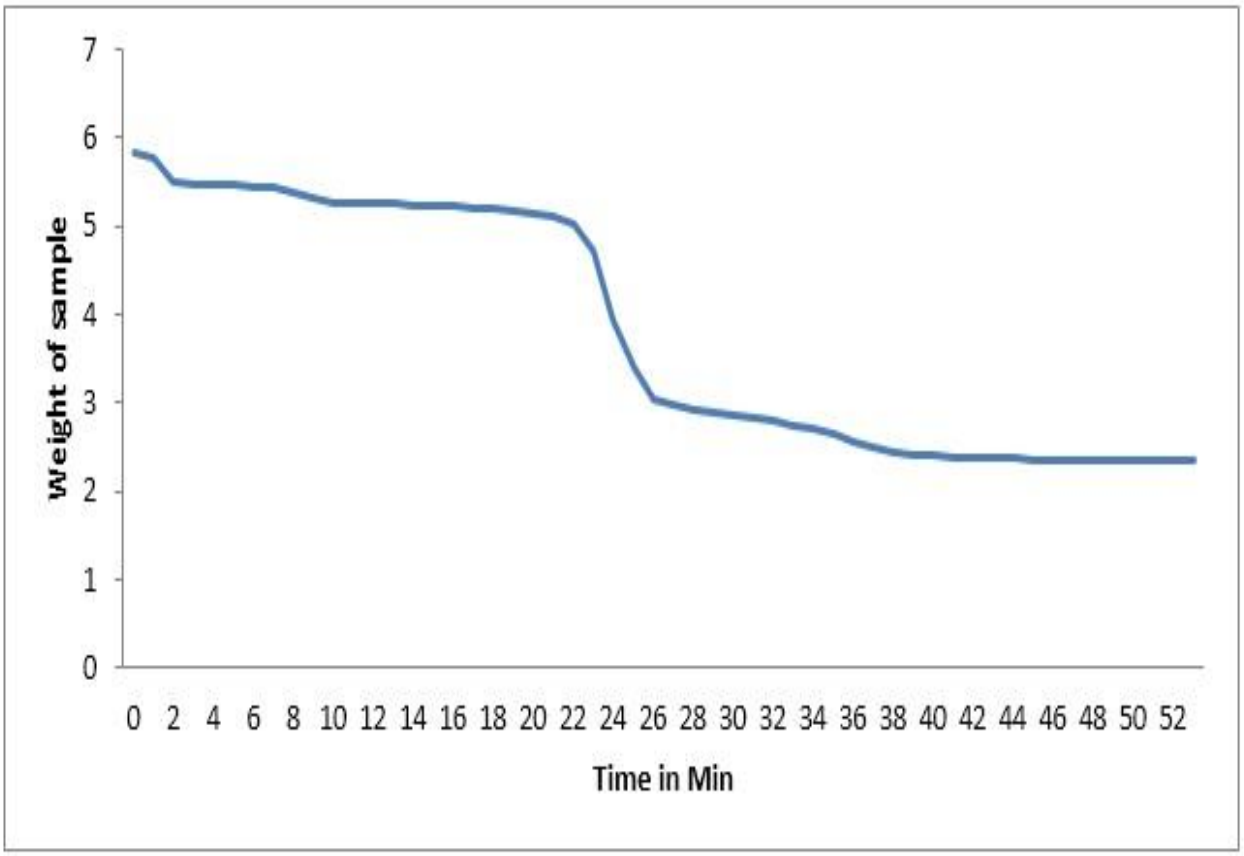


Figure 7. Plot of % weight loss in mg. *v/s* temperature depicting thermal degradation of copper palmitate soap

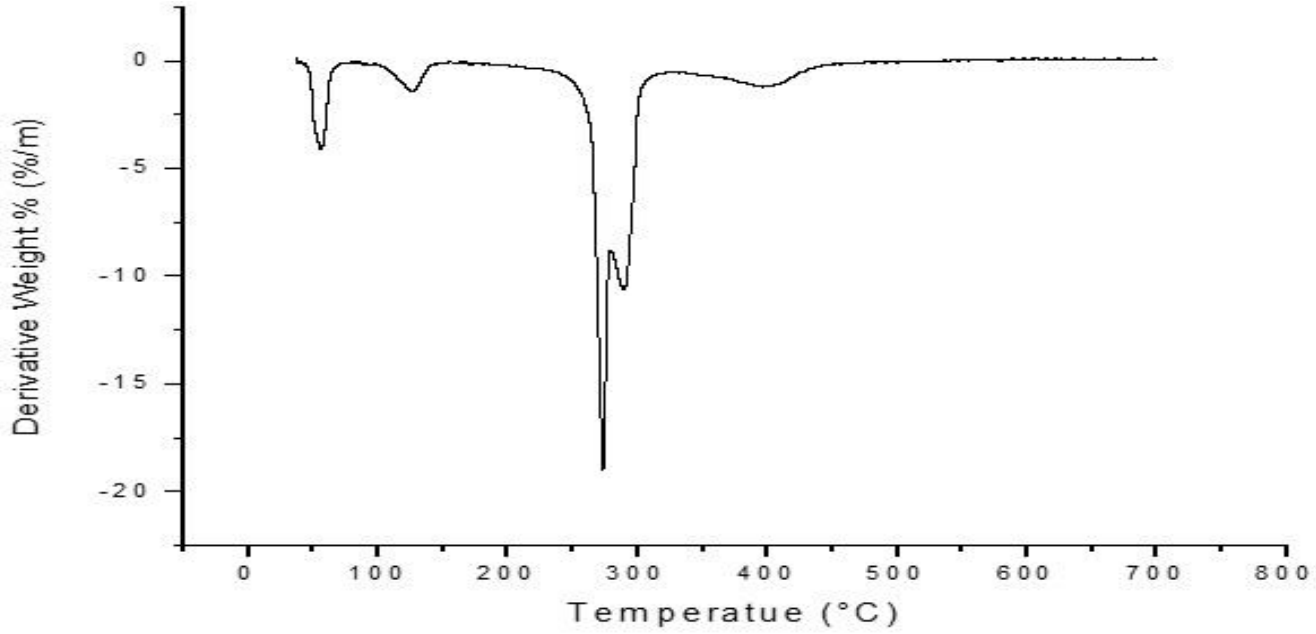


Figure 8. Plot of DTA curve of copper palmitate soap

Kinetic Parameters

Coats-Redfern [1] equation, Horowitz-Metzger [3] equation and Broido [4] equations have been applied to evaluate the energy of activation (E) for thermal degradation of copper palmitate soap molecule. Of the various methods of kinetic analysis, Coats-Redfernequation has been found to be the most appropriate in calculating the energy of activation. Coats and Redfern derived the equation [16].

$$\log f(\alpha) = \log AR\,(1 - 2RT) - E \quad (1)$$

$$T^2\, aE \quad E \quad 2.303RT$$

Where 'a' is the linear rate of heating and $f(\alpha) = -\log(1-\alpha)$ for n=1
Hence, this equation can be rewritten as –

$$\log[-\log(1-\alpha)] = \log AR\,(1 - 2RT) - E \quad (2)$$

$$T^2\, aE \qquad E \qquad 2.303RT$$

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) 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 two steps for CS system has been evaluated from the linear plots of 'log {[– log (1-α)] / T2} 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 7.

Step II >Step I

Mention may also be made of the fact that although decomposition is continuous with respect to time and temperature, yet Freeman – Caroll method is not applicable, as the plots of '[log (dw / dt)] / [log Wr]v/s 1/T' do not pass through the origin confirming that the order of reaction is not zero. To confirm the energy of activation, Horowitz – Metzger equation has been used to evaluate the value of 'E' according to the following equation [17].

$$\ln[\ln(1 - \alpha)^{-1}] = E.\theta \quad (3)$$

$$RT_s^2$$

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 $\ln[\ln (1- \alpha)^{-1}]$ v/s θ. For Horowitz–Metzger equation the values of each step are in the order shown in Figure 8.

Step II > Step I

The energy of activation for the stepwise thermal decomposition of all the referred systems has also been calculated by using Broido's equation which is as follows [18].

$$\ln [\ln (1/y)] = - E + C \quad (4)$$

$$RT$$

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 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 ofare recorded in Table 2 and are found to be in the following order and also shown in Figure 9.

Step II > Step I

A perusal of Table 2 reveals that for all the referred systems, the value of activation energy is higher for the second step and smaller for the first step, irrespective of the equation applied i.e. the stepwise energy of activation follows the order:

Step II > Step I

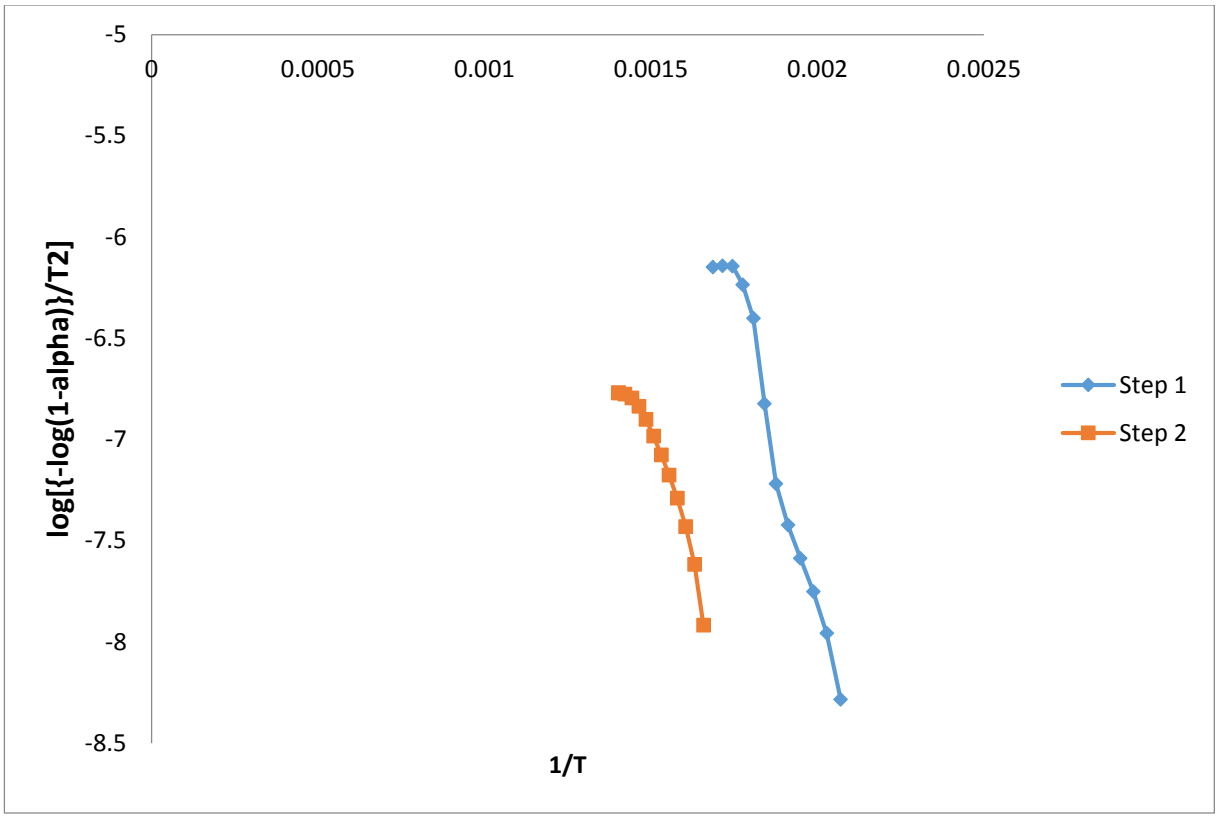


Figure 9. Plots of different steps for coats and redfern equation

Table 2. Energy of activations (In kJ/mole^{-1}) for the decomposiyion reaction of copper palmitate soap

Soap ↓ / Step and equation →	Coats – Redfern		Horowitz – Metzger		Broido	
	I	II	I	II	I	II
Cu Palmitate	43.9	139.8	74.3	120.9	73.3	158.3

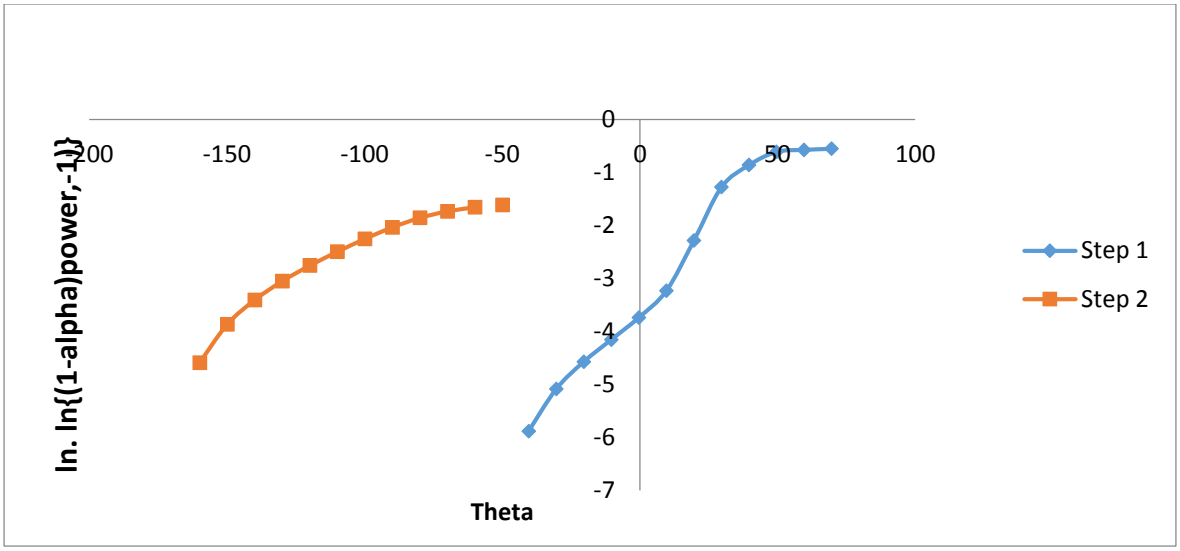


Figure 10. Plots of different steps for Horowitz – Metzger equation

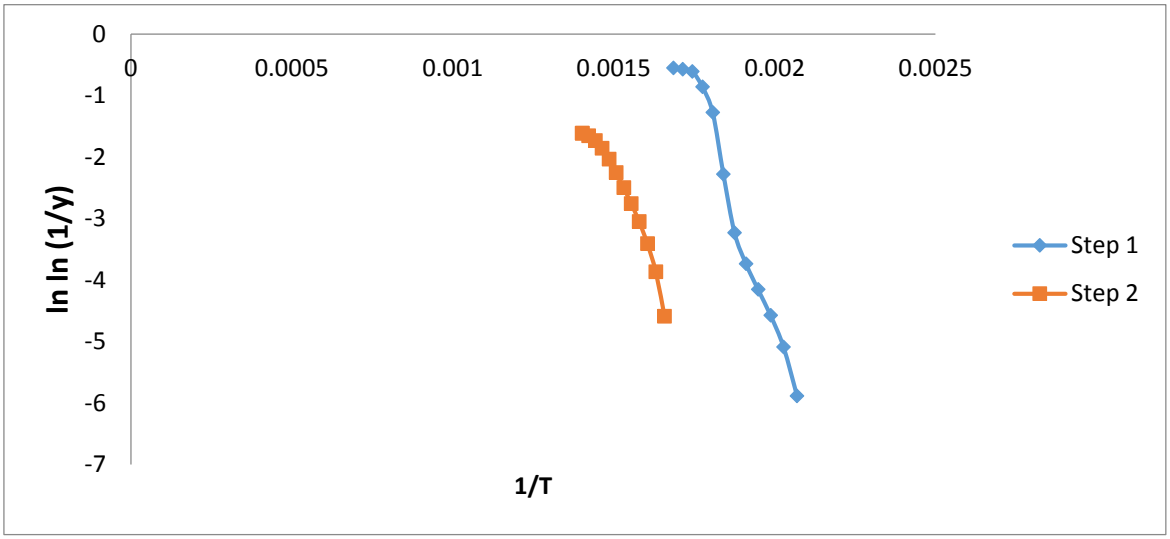


Figure 11. Plots of different steps for broido'sequation

There was a good correlation between the activation energies evaluated by various integration and approximation methods, however, the values obtained by the approximation methods were higher than the values obtained by integration methods, which can be ascribed to the different mathematical treatments of the methods.

Conclusion

The extensive use of surfactants, insecticides and pesticides has created a new problem in environment because they are either slowly biodegraded or do not biodegrade at all. Therefore it is necessary to search out an alternate and quicker method for the treatment of these pollutants.

Thermaldegradation of solid components procured after drying the polluted solid waste will be a good and significant method for the removal of the natural soap segments from the environment. This study will play an important role for pollution controlling and in the field of green chemistry.

Acknowledgments

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