IR Spectral and Thermal Behavior of Cerium Myristate and Cerium Palmitate

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Abstract: IR Spectral and Thermogravimetric Analysis were used to illustrate the structure of Cerium Myristate and Palmitate in solid state. IR results makes know that the fatty acid exists with dimeric structure through intermolecular hydrogen bonding and cerium soaps were ionic in nature. Thermal Analysis was carried out by using Freeman–Carroll's and Horowitz - Metzger Equations. Decomposition of soaps was kinetically of zero order and their energy of activation increases with increasing chain length of soaps.

Key words: Cerium Myristate, Cerium Palmitate, IR Spectra and Thermogravimetric Analysis.

Introduction

Combination of metals with monobasic carboxylic acids which are generally insoluble in water and soluble in non polar solvents are called as metal soaps. Their stability, chemical reactivity, volatility and availability lend them as material of extensive profitable importance. Interest in studies of metal soaps has been boosted by its applications in diversified fields [1-7] as antioxidants, emulsifiers, ink driers, paints, polymer stabilizers, coating agents, lubricants, fuel additives, fungicides and also in photothermogravimetry. Metal soaps of lanthanide metals were synthesized for the first time by Mishra et al (1963). Darshana et al (2015) studied structure of Samarium and Praseodymium soaps in solid state using X-ray, IR and TGA. Similar parameters on Terbium Laurate have been studied by Kamal et al (2016). M.S. Khirwar (2016) studied the Thermogravimetric Analysis of Yttrium Soaps in solid state .

In contrst to earlier studies, attempts have been made to investigate the structure of cerium soaps (myristate and palmitate) in solid state through IR Spectral and Thermgravimetric Analysis

MATERIAL AND METHODS

AnalaR grade cerium nitrate, myristic acid, palmitic acid, methanol, benzene, and ethanol, (purity 99.9% received from Indian Rare Earth Limited, Kerala) were used in the present investigation. The classical method of direct metathesis was employed. This involves treating of potassium soaps by pouring a slight stochiometric excess of aqueous metal salt solution into the clear dispersion at raised temperature with vigorous stirring. After initial drying in an air oven 50-60^{0}C, final drying was carried out under reduced pressure. The precipitates was filtered off and washed with hot distilled water and acetone.

Infrared Absorption Spectra of myristic acid, palmitic acid and corresponding potassium and cerium myristate and palmitate were recorded with a Thermo Nicolet Avtar “370” spectrophotometer in the region 4000-400cm^{-1} using potassium bromide disc method.

Thermogravimetric analysis of cerium myristate and palmitate were undertaken at heating the samples from 50^{0}C to 930^{0}C at constant rate of heating (20^{0}C/min) under nitrogen atmosphere in a Diamond TGDTA Temperature Scan.

RESULTS AND DISCUSSION

The infrared spectral bands (Fig.1 & 2) and their tentative assignments for cerium myristate and palmitate were assigned and compared with corresponding fatty acid (myristic and palmitic acid) and potassium myristate and potassium palmitate. (Table-1 & 2)

Table -1
Frequencies (cm^{-1}) of Absorption Maxima with their Assignments of Myristic acid, Potassium Myristate, and Cerium Myristate.

S. No	Assignment	Myristic Acid	Potassium Myristate	Cerium Myristate
1	CH_2, C-H asym stretch	2920vs	2920vs	2920vs
2	CH_2, C-H sym stretch	2855s	2640vw	2851s
3	O-H stretch	2640vw	2640vw	
4	C=O stretch	1700vs		
5	COO^-, C-O asym stretch	_	1550vs	1599 s
6	CH_2 deform	1465ms	1460ms	1435m
7	C-O strech + O-H in plane deform	1430ms	1445ms	
8	COO- ,C-O sym stretch		1420 s	1461 s
9	CH_2 (adjacent to COOH group)	1405vs		
10	CH_3 sym deform		1380m	
11	Progressive bands (CH_2, twist and wag)	1350-1190w	1340-1100w	1300 m
12	CH_3 rocking	1120-1065vw	1105-1120w	
13	OH out- of- plane deform	940m		
14	CH_2 rocking	735-725 ms	755-725ms	723 m
15	COOH bending mode	690ms	700ms	
16	COOH wagging mode	550ms		

Table- 2

Frequencies (cm^{-1}) of Absorption maxima with their Assignments of Palmitic acid, Potassium Palmitate and Cerium Palmitate.

S.No	Assignment	Palmitic Acid	Potassium Palmitate	Cerium Palmitate
1	CH_2, C-H asym stretch	2910vs	2920vs	2919 s
2	CH_2, C-H sym stretch	2850s	2850s	2850 s
3	O-H stretch	2650v		
4	C=O stretch	1700vs		
5	COO^-, C-O asym stretch	_	1550vs	1575s
6	CH_2 deform	1460ms	1460ms	1464 s
7	C-O strech + O-H in plane deform	1450ms	1450ms	
8	COO- ,C-O sym stretch		1430m	1464 s
9	CH_2 (adjacent to COOH group)	1410ms		
10	CH_3 sym deform		1380ms	
11	Progressive bands (CH_2, twist and wag)	1350-1100w	1325-1190w	1198m
12	CH_3 rocking	1110w	1110w	
13	OH out- of- plane deform	930vw		
14	CH_2 rocking	720w	720ms	723s
15	COOH bending mode	690w		
16	COOH wagging mode	550s		

Key to abbreviations
vs = very strong
ms = medium strong
w = weak
s = strong
m = medium
vw = very weak

The studies indicate that characteristic frequencies in the spectra of fatty acids (myristic and palmitic acids) are 2640 cm^{-1} and 2650 cm^{-1} (O-H stretching vibrations), 1700 cm^{-1} (C=O stretching vibrations), 1430 cm^{-1} and 1450 cm^{-1} (O-H in plane bending and C-O stretching) and at 940 cm^{-1} and 930 cm^{-1} (out of plane bending of O-H group) indicates the presence of carboxyl group in the form of dimeric structure is studied by Dyer(1969) and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acid. The absorption maxima near 690 and 550 cm^{-1} in the spectra of fatty acids are associated with carboxyl group bending and wagging modes and are independent of the chain length of the fatty acid radical.

The infrared spectra of potassium and cerium myristate and palmitate illustrate noticeable difference with the spectra of corresponding fatty acids in some spectral region. A number of characteristic vibrations of free fatty acids were found completely absent in their respective regions in the spectra of their corresponding soaps. The loss of carboxyl frequency (1700 cm^{-1}) in the spectra of soaps indicate that there may be a complete resonance in the two C-O bonds of the carboxyl groups of the soap molecule. The two C-O bonds become identical with their force constants assuming an intermediate value between those of normal double and single bonds.

The appearance of two absorption bands of the carboxyl group corresponding to the symmetric and asymmetric vibrations of two carboxylate ions studied by Koga et.al.(1961)& Duavl et. Al(1942) lies in the vicinity of 1420-1475 cm^{-1} and 1512-1600 cm^{-1}, respectively in the spectra of potassium and cerium myristate and palmitate instead of one band near 1700 cm^{-1} confirms the formation of soaps and indicates that these soaps have an ionic character. The absorption with strong intensity absorbed in the vicinity of 725-720 cm^{-1} in the spectra of these soaps are associated with the rocking vibration of a chain of successive methylene groups – $(CH_2)_n$ and are sensitive to the crystallization of soap. These soaps do not show absorption maxima in the region 3600-3590 cm^{-1} which confirms the absence of water of crystallization

A perusal of data collected in Table-1 and Table 2 indicates that the myristic acid and palmitic acid exist with dimeric structure through intermolecular hydrogen bonding between carboxylic groups of two fatty acid molecules whereas corosponding potassium and cerium soaps were ionic in nature.

THERMOGRAVIMETRIC ANALYSIS

The results of Thermogravimetric Analysis of cerium myristate and palmitate are given in (Figs. 3& 4.)It has been analyzed that final residues are the metal oxides and the weights of the residues are approximately equal to the theoretically calculated weights of metal oxides from the molecular formula of corresponding metal soaps. Therefore the decomposition of cerium myristate and palmitate can be expressed by the equations (1) and (2).

$$2Ce(C_{13}H_{27}COO)_3 \rightarrow 3C_{13}H_{27}COC_{13}H_{27}+Ce_2O_3+3CO_2 \qquad \ldots(1)$$

$$Th(C_{15}H_{31}COO)_4 \rightarrow 2C_{15}H_{31}COC_{15}H_{31}+ThO_2+2CO_2 \qquad \ldots(2)$$

This decomposition leads to format of ketone which is detected in the form of white crystalline powder condensed at the cold part of sample. Thermogravimetric Analysis shows that these soaps decompose significantly up to 110^0C slowly between 110 and 320^0C then very rapidly up to 480^0C and finally show very small change with further increase in temperature.

The energy of activation and order of reaction using Freeman and Carroll's (1958) rate expression has been calculated for the thermal decomposition of these soaps, where soaps disappeared continuously with the constant rate of increase in temperature and with passage of time period. In thermal decomposition of metal soaps one of the product being gaseous and Freeman–Carroll's expression can be expressed as:-

$$\Delta\frac{\left\{\log\left(\frac{dw}{dt}\right)\right\}}{\{\Delta(\log W_r)\}} = \frac{E}{2.303R} - \frac{\Delta\left(\frac{1}{T}\right)}{\Delta(\log W_r)} + n \qquad \ldots(3)$$

where, E= Energy of activation ,n=order of reaction, T= temperature on absolute scale,W_r= difference between the total loss in weight and loss in weight at time t , i.e. W_o- W_t.dw/dt = rate of weight loss obtained from the loss in weight of soaps and the loss at predetermined time.

The activation energy for thermal decomposition process of cerium myristate and palmitate has been calculated from the slope of the plots of $\Delta\frac{\left\{\log\left(\frac{dw}{dt}\right)\right\}}{\{\Delta(\log W_r)\}}$ verses$\frac{\Delta\left(\frac{1}{T}\right)}{\Delta(\log W_r)}$. The order of reaction for the thermal decomposition of soaps has found almost zero and the values of energy of activation for thermal decomposition for cerium myristate and palmitate are 43.26 and 43.89KJ mol^{-1} respectively.

Horowitz – Metzger(1963). also provided a method for the evaluation of energy of activation for the thermal decomposition of these metal soaps. Horowitz - Metzger equation can be represented as:-

$$\text{In}[(1-\alpha)^{-1}] = \frac{E}{RT_s^2}.\theta \qquad (4)$$

where ,

α = fraction of soap decomposed at time, t, E= energy of activation,Ts = temperature on absolute scale at which the rate of decomposition is maximum, and θ = T-Ts. The values of activation energies for the soaps has been calculated from the slope of the plot of ln[ln (1-α)-1] verses θ are 42.34 KJ mol^{-1} for cerium myristate and 42.90 KJ mol^{-1} for cerium palmitate.

The values of activation energy calculated from Freeman–Carroll's and Horowitz – Metzger equations were in good agreement. The above discussion leads to the conclusion that the surface of cerium soap molecule was fully covered by the product, the rate of decomposition becomes constant and the process is kinetically of zero order and the activation energies fo the soaps increases with the chain length.

Conclusion

The results of IR spectral analysis show that fatty acid exists in a dimeric structure on account of hydrogen bonding between the carboxyl groups of two fatty acid molecules, whereas cerium soaps acquire ionic character. The thermal decomposition of these soaps was found to be zero order and posses energy of activation in the range 30-35 KJ mol-1 for the decomposition process.

Fig. 1. Infrared Absorbation Spectrum of Cerium Myristate

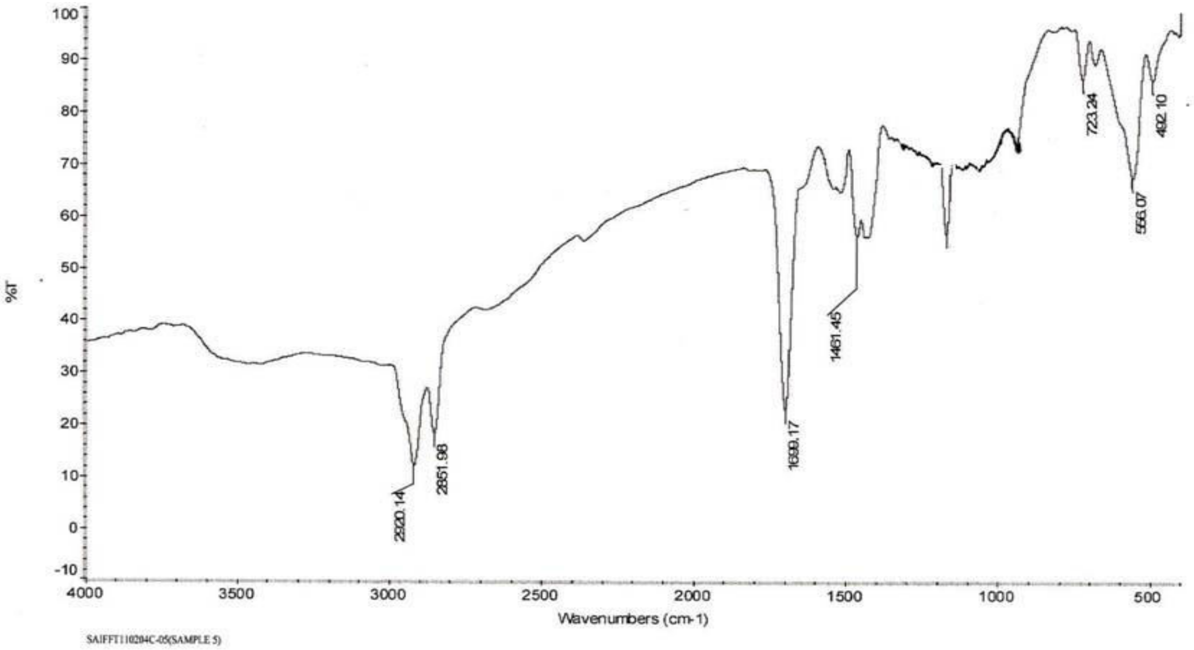


Fig 2 Infrared Absorbation Spectrum of Cerium Palmitate

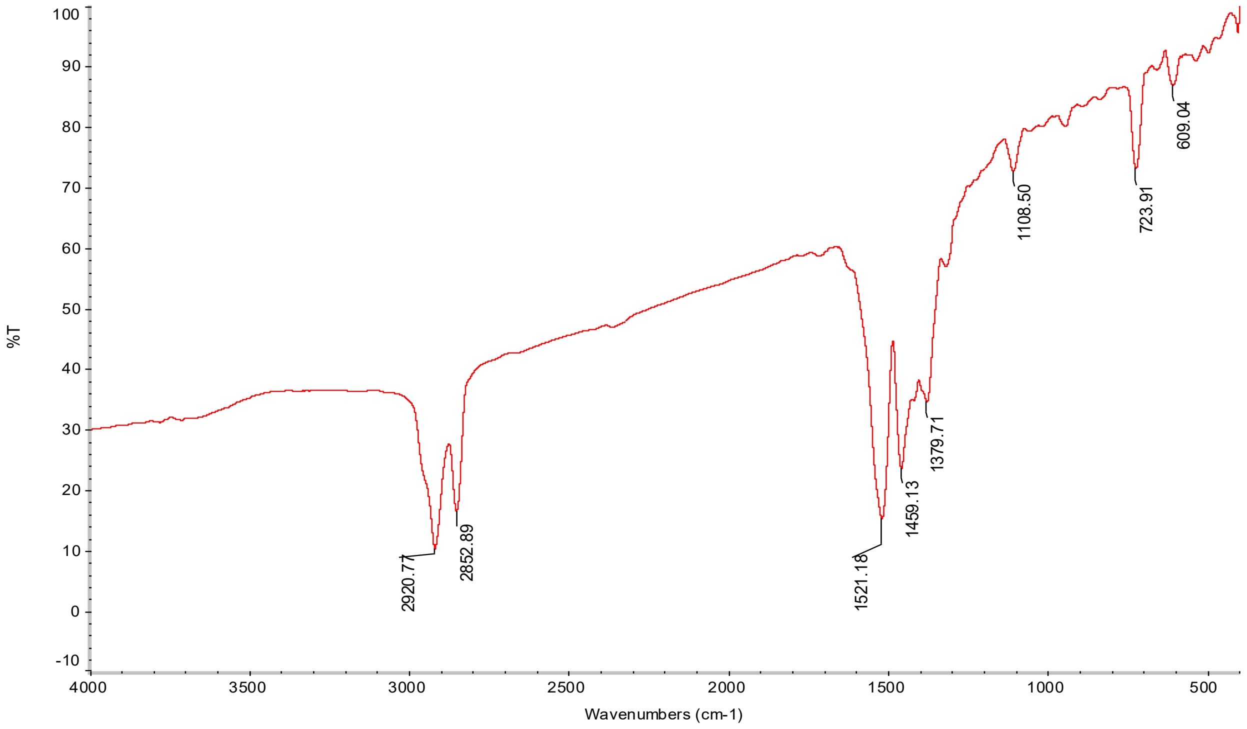


Fig. 3. Thremogram of Cerium Myristate

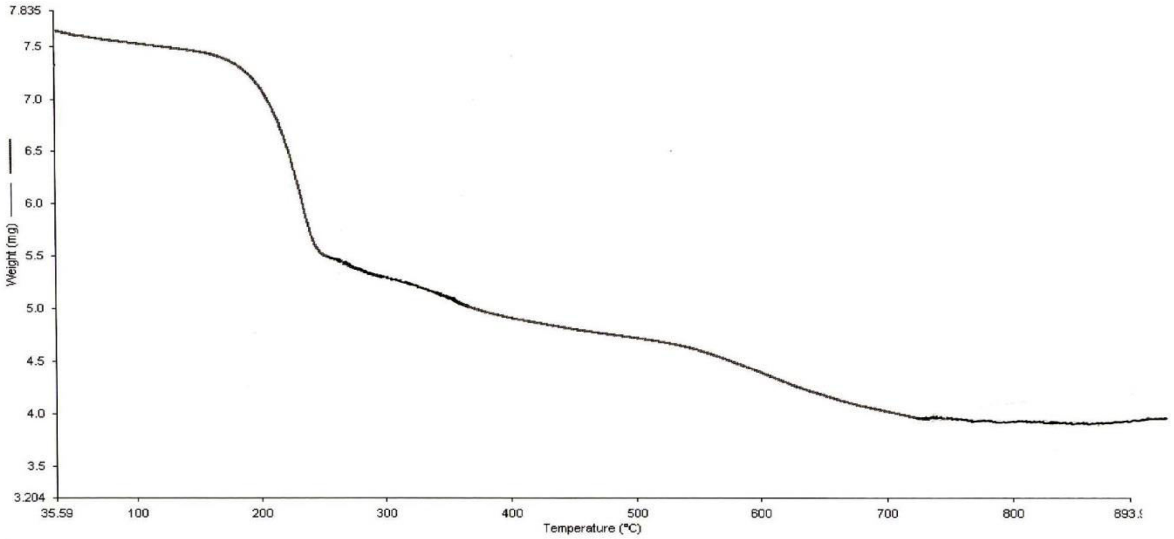
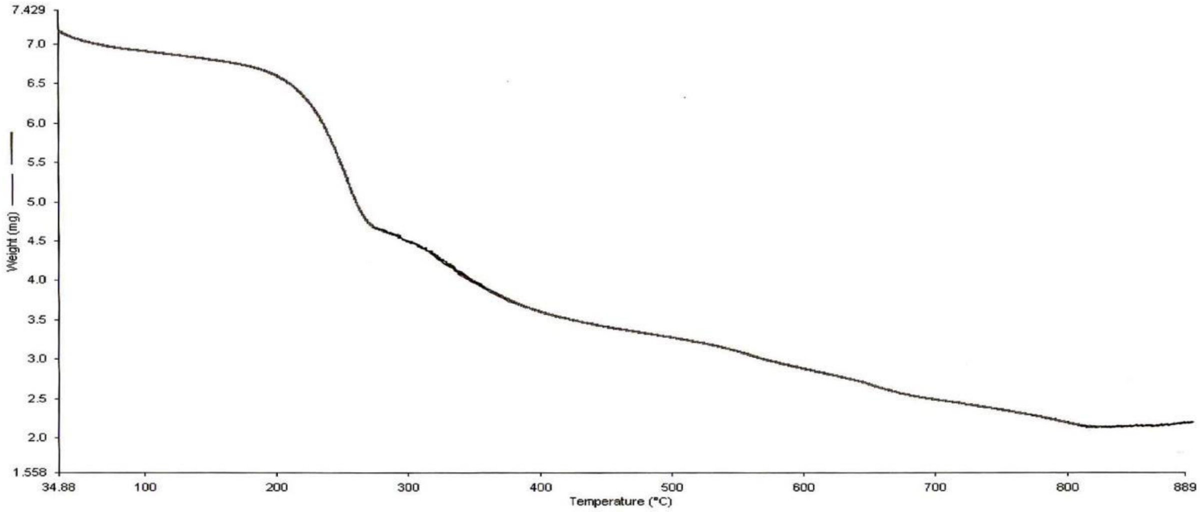


Fig. 4 Thremogram of Cerium Palmitate



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