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Infrared Absorption Spectra, X-rays Diffraction Studies and Thermal Behavior of Cerium and Thorium Laurate

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ABSTRACT : IR, X-ray diffraction and thermal analysis were used to illustrate the structure of cerium and thorium laurate in solid state. IR results reveal that the fatty acid exists with dimeric structure through intermolecular hydrogen bonding and cerium and thorium laurate were ionic in nature. The X-Ray diffraction measurements confirm that these soaps posses double layer structure with long spacing. Decomposition reaction was found kinetically of zero order with energy of activation for cerium laurate lies in the range 26.92–37.62 KJ mol^{-1} and for thermal decomposition lies in the range 33.34–42.63KJ mol^{-1}.

Keywords : IR, X-ray diffraction, thorium laurat.

I. INTRODUCTION

Metallic soaps are materials of considerable commercial importance. Significant application areas [1-5] for metal soaps include lubricating greases which is intended to improve flow, coating smoothness, finish, printability, antidusting effects, driers in paints, dry cleaning industries, cosmetic gels, heat stabilizers for plastics and in the development of polyvinylchloride as an important commercial polymer. Other uses of metal soaps are as fungicides and pesticides [6], optical polymer fibers [7, 8], coating pigment in paper industry [9] and in the preparation of nanofilms [10]. The studies on the nature and structure of these soaps are of great importance for their use in industries and for explaining their characteristics under different conditions. The physicochemical properties of metal soaps in solid state have been investigated by several workers. Upadhyaya et al. [11] studied thermal, infrared and x-ray diffraction analysis of manganese and zinc soaps. The valent thermal behavior of divalent and higher valent metal soaps have been carried out by Akanni et al, [12]. Folarin et al, [13] determined relative thermal stability of metal soaps of Ximenia americana and Balanites aegyptiaca seed oils. The characterization of metal soaps has been done by Robinet et al, [14].

In comparison of earlier studies on metal soaps, we report here results of our studies on thermal, IR and X-ray measurements of cerium and thorium laurate with a view to investigate the characteristic and structure of these soaps in solid state.

II. MATERIAL AND METHODS

AnalaR grade lauric acid, benzene, methanol, ethanol, cerium nitrate and thorium chloride (purity 99.9% received from Indian Rare Earth Limited, Kerala) were used for the present investigation. The cerium and thorium laurate were prepared by the direct metathesis of corresponding 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°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 lauric acid and corresponding potassium, cerium and thorium laurate were recorded with a Thermo Nicolet Avtar ‘‘370’’ spectrophotometer in the region 4000-400cm^{-1} using potassium bromide disc method.

The X-Ray diffraction patterns of cerium and thorium laurate were obtained with a "Bruker AXS D8 Advance" x-ray diffractometer using Cu-Kα radiations filtered by a nickel foil. The instrument yield an automatically recorded curve of intensity of diffracted x-rays vs. diffraction angle 2θ.

Thermogravimetric analysis of cerium and thorium laurate was undertaken at heating the samples from 50°C to 930°C at constant rate of heating (20°C/min) under nitrogen atmosphere in a Diamond TGDTA temperature Scan.

III. RESULTS AND DISCUSSION

The infrared spectral bands (Fig. 1 & 2) and their tentative assignments for cerium and thorium laurate are assigned and compared with potassium laurate as well as with corresponding fatty acid (lauric acid) Table-1.

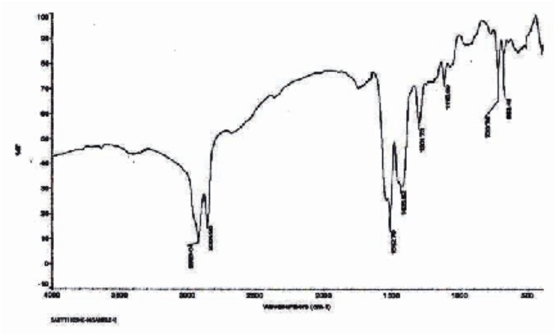

Fig.1. Infrared Absorbation Spectrum of Cerium Laurate.

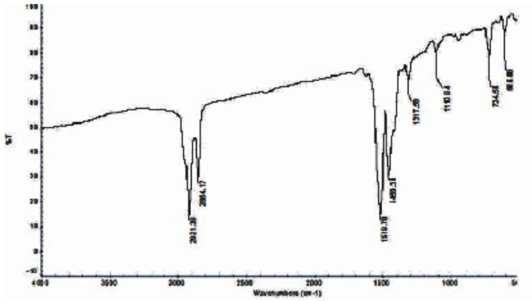

Fig. 2. Infrared Absorbation Spectrum of Thorium Laurate.

Table 1: Frequencies (cm^{-1}) of Absorption maxima with their Assignments of Lauric acid, Potassium Laurate, Cerium Laurate and Thorium Laurate.

S.No	Assignment	Lauric Acid	Potassium Laurate	Cerium Laurate	Thorium Laurate
1.	CH_2, C-H asym stretch	2920vs	2920vs	2923s	2921vs
2.	CH_2, C-H sym stretch	2850s	2890s	2854 s	2854vs
3.	O-H stretch	2640vw			
4.	C = O stretch	1700vs			
5.	COO-, C-O asym stretch	—	1600vs	1512 s	1519vs
6..	CH_2 deform	1465ms	1475ms	1435v	1420v
7.	C-O strech + O-H in plane deform	1450ms			
8.	COO-, C-O sym stretch		1440 s	1436 s	1459vs
9.	CH2 (adjacent to COOH group)	1405 m			
10.	CH3 sym deform		1380ms		
11.	Progressive bands (CH_2, twist and wag)	1350-1090 w	1375-1200w	1301 m	1317v
12.	CH_3 rocking	1120vw	1110vw	1115 w	1110w
13.	OH out-of-plane deform	950 s			
14.	CH_2 rocking	725w	720ms	723m	724 m
15.	COOH bending mode	690ms			
16.	COOH wagging mode	550ms			

Key to abbreviations

vs =very strong, ms = medium strong, w = weak, s = strong, m = medium, vw = very weak.

The characteristic frequencies in the spectra of fatty acid at 2640 (O-H stretching vibrations), 1700 (C=O stretching vibrations), 1450 (O–H in plane bending and C – O stretching) and at 950 cm^{-1} (out of plane bending of O–H group) indicates the presence of carboxyl group in the form of dimeric [15] structure and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acid.

The infrared spectra of potassium, cerium and thorium laurate illustrate marked difference with the spectra of corresponding fatty acids in some spectral region. Some characteristic vibrations of free fatty acids were found completely absent in their respective regions in the spectra of potassium, cerium and thorium laurate. The disappearance of carboxyl frequency (1700 cm^{-1}) in the spectra of these 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 lies in the vicinity of 1420–1475 cm^{-1} and 1512–1600 cm^{-1}, respectively in the spectra of potassium, cerium and thorium laurate 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. The infrared spectra of cerium and thorium laurate do not show any absorption maxima in the region 3600–3590 cm^{-1} which confirms the absence of water of crystallization in these soaps.

A perusal of data collected in Table 1 indicates that the lauric acid exist with dimeric structure through intermolecular hydrogen bonding between carboxylic groups of two fatty acid molecules whereas potassium, cerium and thorium laurate were ionic in nature.

IV. X-RAY DIFFRACTION ANALYSIS

The x-ray diffraction patterns of cerium and thorium laurate have been investigated to characterize the structure in solid state. The intensities of diffracted X-ray as a function of diffraction angle, 2 (twice the Bragg angle) for cerium and thorium laurate were recorded with the help of x-ray diffrectrometer and the recorded curves are reproduced over the range of 2-80° corresponding to successive order of single long spacing. The abscissa is, however, is marked angstrom (Å) units for ready reference. Bragg's spacing corresponding to interplanar separation of the reciprocal crystal lattice, were calculated from the peaks in the curves using the relationship

$$n\lambda = 2d \sin \theta$$

where λ = 1.5418Å. The calculated spacing together with relative intensities with respect to the most intense peaks are recorded in (Table 2) for cerium and thorium laurate.

Table 2: X-Ray Diffraction Analysis of Cerium and Thorium Laurate.

Sl. No.	2θ	λ/2Sin θ	dÅ	n
1.	5.028	17.57	35.14	2
2.	7.395	11.95	35.84	3
3.	9.873	8.95	35.79	4
4.	12.577	7.04	35.19	5
5.	15.060	5.88	35.30	6
6.	17.609	5.04	35.25	7
7.	20.155	4.38	35.06	8
8.	22.700	3.92	35.25	9
9.	25.122	3.54	35.44	10
10.	27.831	3.21	35.26	11
11.	30.219	2.96	35.48	12
12.	37.760	2.38	35.73	15

Average value of *d* = 35.40 Å

Thorium Laurate

S No	2θ	λ/2Sin	dÅ	N
1.	4.687	18.85	37.70	2
2.	7.361	12.00	36.00	3
3.	9.769	9.04	36.17	4
4.	14.577	6.07	36.45	6
5.	17.07	5.18	36.23	7
6.	19.359	4.59	36.69	8
7.	21.944	4.05	36.46	9
8.	29.127	3.07	36.78	12
9.	32.292	2.77	36.04	13
10.	36.758	2.44	36.67	15
11.	39.211	2.30	36.76	16
12.	43.02	2.10	37.84	18

Average value of *d* = 36.65 Å.

The intensity and sharpness (half-width; i.e., angular width of the peak at half its maximum intensity) of the peaks are a measure of degree of crystallinity of the sample. The appearance of diffrections upto the 15th order in cerium laurate and upo the 18th order in thorium laurate confirms good crystallinity for these soaps.

The calculated values of interplaner spacing for cerium and thorium laurate are 35.40Å and 36.65Å. The difference in the long spacing's of these soaps approximately corresponds to double the length of methylene (–CH$_2$) groups in the fatty acid radical constituent of the soap molecules. It is, therefore, suggested that the zig -zag chains of fatty acid radicals extend in both directions with their axes inclined somewhat to the planes containing the metal ions. The observed values of long spacing for cerium and thorium laurate are somewhat smaller than the calculated dimensions of laurate ion: 37.0 Å, from Pauling's value of atomic radii and bond angles and this suggests that the molecular axes of these soaps are somewhat inclined to the basal plane. The result indicates that average value of long spacing for cerium laurate is smaller than the thorium laurate.

In these soaps the metal ions appears to be arranged in planes in which the fatty acid radicals extend in both directions with their axes inclined somewhat to the plane containing the metal ions. The distance between the planes is equal approximately to twice the length of the fatty acid radical, times the sine of the angle of inclination, since the soap molecule either have double layers of cations with acid radicals extending out on either sides therefore, seems that the cations affect the angle of inclination of the molecular axes to the planes containing the cations. These values for long spacing increases with increasing size of the cation.

It is therefore concluded that the cations affect the angle of inclination of the molecular axes to the planes containing the cations. The metal cations fit into spaces between oxygen atoms of the ionized carboxyl group without giving a large strain of the bond.

Numerous diffraction peaks in the intermediate range of the diffraction angles are also observed in the diffraction patterns of the cerium and thorium laurate and these are attributed to the diffraction of x-rays by plane of atoms separated by much smaller distances than those of basal planes and are thus referred to as short spacing. The numerical values gives distance between planes in the reciprocal crystal lattice and can be directly related to real distances between the molecules only by making assumptions about the crystal types. It is observed from the x-ray pattern of the cerium and thorium laurate that long spacing peaks are fairly intense while short spacing peaks are relatively weak.

It is, therefore, concluded on the basis of long and short spacing that metal ions in cerium and thorium laurate are arranged in a parallel plane, i.e. a basal plane equally spaced in the soap crystal with fully extended zig-zag chains of fatty acid radicals on both directions of each basal plane and these soaps possess double layer structure as proposed by Vold and Hattiangdi [16].

V. THERMOGRAVIMETRIC ANALYSIS

The results of Thermogravimetric analysis of cerium and thorium laurate are given in Figs. 3& 4. It is found that the final residues are the metal oxides and the weights of the residues are almost equal to the theoretically calculated weights of metal oxides from the molecular formula of corresponding metal soap. Therefore the decomposition of cerium and thorium laurate can be expressed by the equations (1) and (2).

$$2Ce(C_{11}H_{23}COO)_3 \rightarrow 3C_{11}H_{23}COC_{11}H_{23} + Ce_2O_3 + 3CO_2 \ldots(1)$$

$$Th(C_{11}H_{23}COO)_4 \rightarrow 2C_{11}H_{23}COC_{11}H_{23} + ThO_2 + 2CO_2 \ldots(2)$$

It may be pointed out that some white crystalline powder was condensed at cold part of the sample surrounding the soap is detected as ketone. Thermogravimetric analysis shows that these soaps decompose significantly up to 110°C slowly between 110 and 320°C then very rapidly up to 480°C and finally show very small change with further increase in temperature.

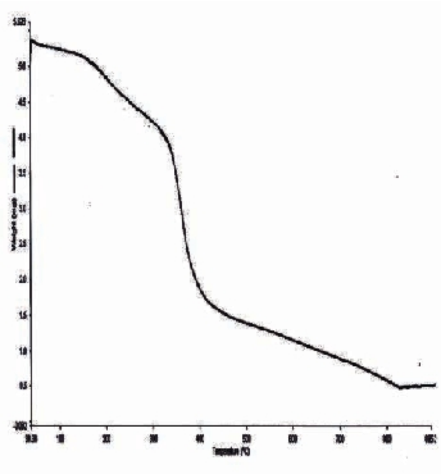

Fig. 3. Thermogram of Cerium Laurate.

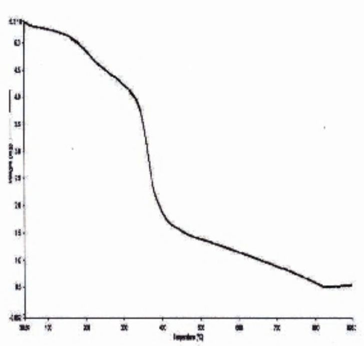

Fig. 4. Thremogram of Thorium Laurate.

Thermogravimetric data were used to calculate the energy of activation and to find the order of reaction for the decomposition of soaps using Freeman and Carroll's [17] rate expression 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:-

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

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. $W_0 - W_t$, 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 and thorium laurate has been calculated from the slope of the plots

$$\Delta\frac{\left(\log\left(\frac{dw}{dt}\right)\right)}{\left(\Delta(\log W_r)\right)} \text{ Verses } \frac{\Delta\left(\frac{1}{T}\right)}{\Delta(\log W_r)}$$ of verses. The order of reaction for the thermal decomposition of cerium and thorium laurate has found almost zero and the values of energy of activation for thermal decomposition for cerium and thorium laurate are 37.62 and 42.63 KJ mol^{-1} respectively. Another equation, the Mac-Callum Tanner equation [18] was also used to calculate, energy of activation E, as follows:

$$\log g(a) = \log\frac{ZE}{OR} - 0.48E^{0.44} - \left(\frac{0.499 + .217E}{T}\right)\times 10^{3}\ldots(4)$$

Where ϕ is the heating rate. The energy of activation calculated from the log $g(\alpha)$ *Vs* T^{-1} curves and the slopes of the curves is equated to $(0.449 + 0.217E) \times 10^3$ The value of $g(\alpha)$ is equal to $-\ln(1-\alpha)$. The values of the energy of activation for the decomposition process of cerium and thorium laurate calculated from Mac-Callum Tanner equation are 26.92 and 33.34 KJ mol^{-1}.

These results indicate that the activation energy increases with increasing size of the cation. The values of activation energy calculated from Freeman-Carroll's and Mac-Callum Tanner equations were in good agreement. The above discussion leads to the conclusion that the surface of cerium and thorium laurate molecule was fully covered by the product, the rate of decomposition becomes constant and the process is kinetically of zero order and the activation energy for the process for cerium laurate lies in the range 26.92 – 37.62 KJ mol^{-1}.and for thorium laurate lies in the range 33.34 – 42.63 KJ mol^{-1}.

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