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Thermogravimetric, X-Ray Diffraction and Infrared Studies on Samarium and Praseodymium Hexadecanoate in Solid State

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Abstract- **The kinetics of thermal decomposition of samarium and praseodymium hexadecanoate (palmitate) was found to be of zero order and the energy of activation for the decomposition reaction for samarium and praseodymium hexadecanoate was in the range of 30-35 KJ mol^{-1}. The X-ray analysis showed that samarium and praseodymium hexadecanoate soaps have double layer structure with molecular axis slightly inclined to the basal plane. The IR results confirmed that the fatty acids exists with dimeric structure through hydrogen bonding between the carboxyl groups of two acid molecules, whereas the metal soaps have an ionic character.**

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I. Introduction

A metallic soap is a chemical combination of a metallic element with a fatty acid organic group. Because of the presence of both lyophillic and lyophobic moieties in the same molecule and their increased solubility in non polar solvents lend to them unique characteristics. Due to their unique characteristics, metal soaps found to be very important class of complexes in technological and academic fields. The alkaline, alkaline earth and transition metal soaps have been thoroughly investigated but the lanthanide and actinide soaps have remained overlooked class of complexes. These compounds have several interesting application based on the metal ion radius, hardness, softness, valency and alkyl chain structure. They find extensive applications in protective coating agents, paints, ink driers, polymer stabilizers, catalysts, waterproofing agents, lubricants, fuel additives and fungicides[1-2]. They are also used in photo thermogravimetry[3] and in manufacturing of pharmaceuticals.

Metal soap with elements of lanthanide series were synthesized for the first time by Mishra et al[4].Mehrotra et al[7-8] investigated acoustical and thermodynamic properties of lanthanide soaps and concluded that these soaps behave as weak electrolyte in dilute solutions. Koga and matuura[9] studied the X-ray diffraction pattern and IR spectra of alkaline earth metal soaps. The present paper deals with the studies of the structure of samarium and praseodymium hexadecanoate in solid state using X-ray, IR and TGA. The results have been used to evaluate various kinetic parameters.

II. Experimental

a) Materials

i. Fatty Acids

The fatty acids used in this studies were supplied from from Indian Rare Earth Limited, Kerala) were used for the present investigation. The purities of fatty acids were confirmed to be over 98.5%.

ii. Metal salts

The inorganic chemicals used in the preparation of metal soaps were analr.grade: samarium nitrate and praseodymium nitrate.

iii. Preparation of metal soap

The samarium and Praseodymium hexadecanoate 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.

iv. Apparatus

Infrared absorption spectra of hexadecanoic acid corresponding to potassium, samarium hexadecanoate and praseodymium hexadecanoate were recorded with Fourier transform infrared spectrometer, Tensor 27, Bruker in the region 4000-400 cm-1 using potassium bromide disc method.

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

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The thermo gravimetric analysis of samarium metal soaps was undertaken at constant rate of heating (20°c/min) under nitrogen atmosphere in a thermo balance. The results of TGA of samarium metal soaps were obtained from Sophisticated Instrumentation Centre (S.I.C), IIT, Indore.

III. Result and Discussion

The infrared spectral bands (Figures 1 & 2) and their tentative assignments for samarium hexadecanoate and praseodymium hexadecanoate are assigned and compared with potassium hexadecanoate, as well as with corresponding fatty acid (hexadecanoic acid) Tables I& II.

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 dimeric12 structure and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acid.

The infrared spectra of potassium, samarium & praseodymium hexadecanoate 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, samarium & praseodymium hexadecanoate. The disappearance of carboxyl frequency (1700cm-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.

Table 1 : Frequencies (cm^{-1}) of Absorption maxima with their Assignments of hexadecanoic acid, Potassium decanoate, Samarium hexadecanoate.

s.no	Assignment	Palmitic Acid	Potassium palmitate	Samarium palmitate
1	CH3, C-H asym. Stretching	2960ms	2960ms	2956.59vs
2	CH$_2$, C-H asym stretching	2920vs	2910vs	2918.80vs
3	CH$_2$, C-H sym stretching	2850s	2850s	2850.61s
4	O-H stretching	2654w	2650w	_
5	C=O stretching	1700vs	_	_
6	COO-, C-O asym stretching	1550vs	_	1529s
7	CH$_2$ deformation	1460ms	1460m	1466s
8	C-O stretch + O-H in plane deformation	1450ms	_	_
9	COO-, C-O sym stretching	1430ms	_	1423w
10	CH$_2$ (adjacent to COOH group),deformation	_	1410ms	_
11	CH$_3$ sym deformation	1380ms	1350w	1302w
12	Progressive bands(CH$_2$,Twist and wag)	1325-1190m	1340-1100vw	1191m
13	CH$_3$ rocking	1100w	1110vw	1110s
14	OH out of plane deformation	_	930vw	_
15	CH$_2$ rocking	720ms	720w	721s
16	COOH bending mode	690w	680w	686m
17	COOH wagging mode	550s	550ms	_

The appearance of the two absorption bands of the carboxyl group corresponding to the symmetric and asymmetric vibrations of two carboxylate ions lies in the vicinity of 1410-1438cm-1 and 1524-1600 cm-1, respectively in the spectra of potassium, samarium & praseodymium hexadecanoate confirms the formation of soaps and indicates that these soaps have an ionic character.

Table 2 : Frequencies (cm^{-1}) of Absorption maxima with their Assignments of hexadecanoic acid, Potassium decanoate, Praseodymium hexadecanoate

S.N	ASSIGNMENT	Palmitic acid	potassium palmitate	praseodymium Palmitate
1	CH_3,C-H asymmetric-streching	2960 ms	2960 ms	2959 (m)
2	CH_2,C-H asymmetric-streching	2920 vs	2910 vs	2919.69 (Vs)
3	CH_2,C-H symmetric-streching	2850 s	2850 s	2850.55 (s)
4	OH,streching	2654 w	2650 w	-
5	C=O,streching	1700 vs	-	1713.07 (w)
6	COO^-,C-O asymmetric stretching	1550 vs	-	1536.79 (Vs)
7	CH_2, deformation	1460 ms	1460 m	1458.62 (
8	COO^-,C-O symmetric stretching	1430 ms	-	
9	C-O streching,O-H in plane deformation	1450 ms	-	
10	CH_2 (adjacent to COOH group),deformation	-	1410 ms	
11	CH_3,symmetric deformation	1380 ms	1350 w	
12	Prograsive bands (CH_2 twisting and wagging)	1325-1190 m	1300-1100 vw	
13	CH_3,rocking	1100 w	1110 vw	
14	OH ,out of plane deformation	-	930 vw	
15	CH_2 ,rocking	720 ms	720 w	
16	COOH,bending mode	690 w	680 w	
17	COOH, wagging mode	550 s	550 ms	

In the spectra of hexadecanoic acids, no bands corresponding to symmetric and asymmetric of carboxylate ions are observed. Naturally the OH stretching band near 2650-2550 cm-1 and OH deformation band at 940cm-1 observed in the spectra of fatty acids disappeared in the spectra of samarium & praseodymium soaps. The progressive bands of the medium and weak intensity observed in the region of 1360-1110cm-1 for samarium & praseodymium soaps are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecule of the soap and fatty acids.

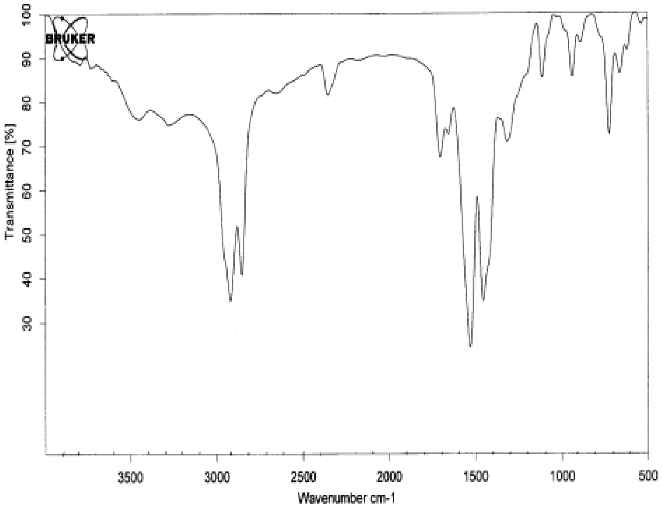

Fig. 1: IR of Samarium hexadecanoate

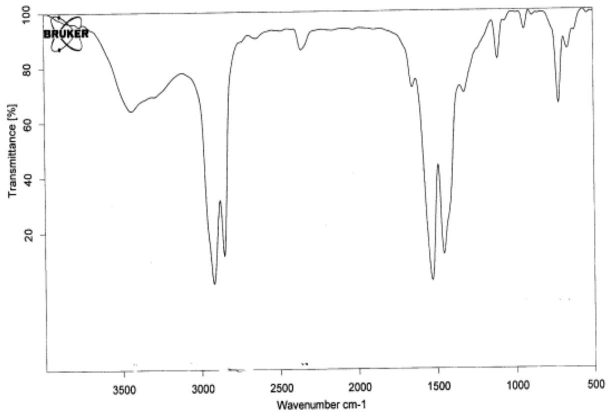

Fig. 2 : IR of Praseodymium hexadecanoate

These results confirm that the fatty acid (hexadecanoic acids) in the solid state exists with dimeric structure through hydrogen bonding whereas metal to oxygen bond in samarium & praseodymium soaps are ionic in nature. It is also proved that the soap molecules retain the resonance character of the carboxylic group. The infrared spectra of samarium soaps do not indicate any maxima in the region of 3500-3300 cm-1 which confirms the absence of any coordinated water molecules in the soaps. The assigned frequencies are in agreement with the results of other worker[5-6].

a) X-Ray Diffraction Analysis

The x-ray diffraction studies of samarium & praseodymium hexadecanoate has been done to characterize the structure in the solid state (table 3& 4). The intensities of diffracted x-ray as a function of diffraction angle,2(twice the Bragg angle) for samarium & praseodymium soaps were recorded with the help of x ray diffractometer and the recorded curves are reproduced over the range of 2-80°C corresponding to successive order of single long spacing [9-10].

Table 3 : X-Ray analysis of samarium hexadecanoate

S.no	2θ	θ	sin θ	λ/2 Sin θ	d (Å)	n
1	2.127	1.0635	0.0185	0.037	41.512	1
2	4.12	2.06	0.0359	0.0718	41.654	2
3	6.10	3.05	0.0532	0.1064	41.225	3
4	8.073	4.0365	0.0703	0.1406	41.385	4
5	10.085	5.0425	0.0878	0.1756	41.474	5
6	12.08	6.04	0.1052	0.2104	41.579	6
7	12.73	6.365	0.1108	0.2216	41.734	7
8	14.054	7.027	0.1223	0.2446	41.856	8
9	15.08	7.54	0.1312	0.2624	41.942	10
10	22.29	11.145	0.1932	0.3864	41.88	11
11	25.54	12.77	0.221	0.442	41.982	12

Average value of d = 41.656

Table 4 : X-Ray analysis of praseodymium hexadecanoate

S.no	2 θ	θ	Sin θ	λ/2 Sin θ	d (Å)	n
1	2.381	1.19	0.0207	37.212	46.92	1
2	3.887	1.943	0.0339	22.7227	47.43	2
3	7.11	3.555	0.062	12.4241	47.67	4
4	7.814	3.907	0.0681	11.3113	47.79	4
5	9.804	4.902	0.0854	9.0199	47.85	5

6	12.677	6.338	0.1103	6.9836	47.39	7
7	13.76	6.88	0.1197	6.435	47.54	7
8	15.77	7.885	0.1371	5.6185	47.82	9
9	17.78	8.89	0.1545	4.9857	47.71	10
10	19.779	9.889	0.1717	4.4863	47.65	11
11	21.81	10.905	0.1891	4.0735	47.69	12

Average value of d = 47.580

On the basis of long and short spacing, it is proposed that the metal ions in transition and rare earth metal soaps 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 possesses double layer structure. The double layer structure of some heavy metal soaps was also suggested by Vold et al[11]. The molecular axes of transition metal soaps were found to be more inclined to the basal plane than rare earth metal soaps [12-13].

b) Thermogravimetric studies

The thermal decomposition of samarium and praseodymium hexadecanoate was studied by thermogravimetric analysis. The heating rate 20°c/min and nitrogen atmosphere were used. The final decomposition product or residues left on heating these soaps were the samarium & praseodymium oxide as the weights of the residues were almost in agreement with the theoretically and calculated weights of samarium & praseodymium soaps and samarium & praseodymium oxide from the molecular formula of the corresponding soap. The thermal decomposition of samarium& praseodymium soaps may be expressed as:-

$$(RCOO)_3Sm \rightarrow Sm^{3+} + 3RCOO^-$$

$$2(RCOO)_3Sm \rightarrow 3RCOR + Sm_2O_3 + 3CO_2$$

$$(RCOO)_3Pr \rightarrow Pr^{3+} + 3RCOO^-$$

$$2(RCOO)_3Pr \rightarrow 3RCOR + Pr_2O_3 + 3CO_2$$

Where R = C11H23 and C13H27

The results of thermal decomposition of samarium & praseodymium soaps were explained in the light of some well known equations, the Freeman-Carroll's[14]and Coats Redfern's [15] equations expressed as follows

$$\frac{\Delta[\log(dw/dt)]}{\Delta(\log W_r)} = -\frac{E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta\log(W_r)} + n$$

The plots of the loss in weight of the soaps, w, against time, t are shown in fig 3 & 4 and values of (dw/dt) are obtained from the curves by drawing tangents at appropriate times. The plots of Δ [log(dw/dt)] / Δ(log w_r) versus Δ(1/T)/Δ(log w_r) provide linear relationship. Slope of this enables us to calculate activation energy for the decomposition process and intercept provides n. The order of the reaction which was found zero and the values of the activation energy for the decomposition were found to be lie between 30-35 KJ mol-1.

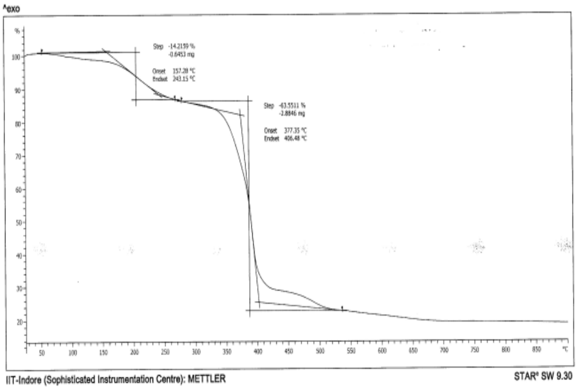

Fig. 3 : Thermal decomposition of samarium hexadecanoate

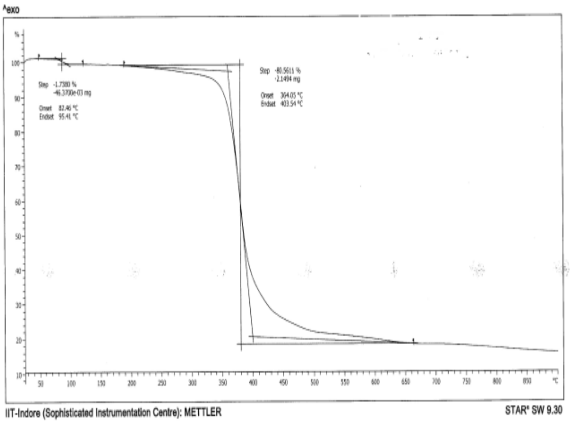

Fig. 4 : Thermal decomposition of praseodymium hexadecanoate

IV. CONCLUSION

The IR results showed that fatty acid exists in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two fatty acid molecules, whereas samarium& praseodymium soaps possess ionic character. The X-ray analysis showed that samarium & praseodymium soaps have double layer structure with molecular axes slightly inclined to the basal plane. The thermal decomposition of these soaps was found to be zero order and the energy of activation for the decomposition process was in the range 30-35 KJ mol-1.

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