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Infra-Red Absorption Spectra, X-Ray Diffraction Studies and Thermal Behavior of Samarium Laurate and Myristate

Darshana Rodric[1*], S. K. Upadhyaya[2] and Kamal Kishore[3]

[1&2] P.G. Department of Chemistry, S. S. L. Jain P. G. College, Vidisha (M.P.) INDIA*
[3] Department of Chemistry, Career Point University, Hamirpur (H.P.) INDIA
[*] Correspondence: E-mail: darshana.rodric@gmail.com

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ABSTRACT: Rare earth elements Samarium salts of dodecanoic acid (Lauric acid) and tetradecanoic acid (Myristic acid) have been prepare and characterized. The compounds have the stoichiometry $Ln(C_{11}H_{23}COO)_3$, where Ln= Sm. IR, X-ray diffraction and thermogravimetry were used to illustrate the structure of Sm laurate and myristate in solid state. IR results reveal that the fatty acid exists with dimeric structure through intermolecular hydrogen bonding and Sm laurate & myristate were ionic in nature. The X-ray diffraction measurements confirm that these soaps possess double layer structure. The results of thermogravimetric analysis reveals that the decomposition process of these soaps is of zero order and the energy of activation for the decomposition process lies in the range of 30-35 KJ mol^{-1}.

Keywords: IR Spectra; X-ray diffraction; Samarium laurate and Samarium myristate.

INTRODUCTION: Metal soaps are water insoluble compounds containing alkaline earth and rare earth metals combined with monobasic carboxylic acid of 7-22 carbon atoms. The most important groups of metal soaps consist of driers that promote or accelerate the drying, curing of hardening of oxidizable coating vehicles such as paints. Metal soaps can also be used as water proofing agents on subtracts such as fabric paper, masonry and metals, a grease and lubricant thickeners[1-2].Other uses of metal soaps are as fungicides, pesticides[3], cosmetic gels, optical polymer fibers[4-5] and in the preparation of nanofilms[6]. Although rare earth containing metal soaps has long been studied [7-10], their mesomorphism was discovered only recently. By high temperature X-ray diffraction analysis, Binnemans et al[11] identified the mesomorphism formed by La^{III} tetradeconate and its higher homologous as a smectic A (smA) phase. In comparison of earlier studies on metal soaps, we report of our studies on IR and X-Ray measurements of Samarium laurate and myristate with a view to investigate the characteristic and structure of these soaps in solid state.

MATERIAL AND METHODS: AnalaR grade lauric acid, myristic acid, benzene, methanol, ethanol, samarium nitrate (purity 99.9% received from Indian Rare Earth Limited, Kerala) were used for the present investigation. The samarium laurate and myristate were prepared by the direct metathesis of corresponding potassium soaps by pouring a slight stoichiometric 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 myristic acid corresponding potassium, samarium laurate and myristate 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 laurate and myristate 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.

RESULTS AND DISCUSSION: The infrared spectral bands (Figures 1 & 2) and their tentative assignments for samarium laurate and myristate are assigned and compared with potassium laurate, potassium myristate as well as with corresponding fatty acid (lauric acid and myristic acid) Tables 1 & 2.

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[12] structure and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acid.

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

S. No.	Assignment	Lauric Acid	Potassium laurate	Samarium laurate
1	CH_2, C-H asym stretch	2920vs	2920vs	2921vs
2	CH_2, C-H sym stretch	2850s	2890s	2851vs
3	O-H stretch	2640vw	-	-
4	C=O stretch	1700vs	-	-
5	COO-, C-O asym stretch	-	1600vs	1524s
6	CH_2 deform	1465ms	1475ms	1466ms
7	C-O stretch + O-H in plane deform	1450ms	-	-
8	COO-, C-O sym stretch	-	1440s	1438vs
9	CH_2 (adjacent to COOH group)	1405m	-	-
10	CH_3 sym deform	-	1380ms	-
11	Progressive bands(CH_2,Twist and wag)	1350-1090w	1375-1200w	1314vs
12	CH_3 rocking	1120vw	1110vw	1110w
13	OH out of plane deform	950s	-	-
14	CH_2 rocking	725w	720ms	721s
15	COOH bending mode	690ms	-	-
16	COOH wagging mode	550ms	-	-

Abbreviations: vs = very strong; ms = medium strong; w =weak; s =strong; m = medium; vw =very weak.

Table 2: Frequencies (cm^{-1}) of Absorption maxima with their Assignments of Myristic acid, Potassium Myristate, Samarium Myristate.

S.No.	Assignment	Myristic Acid	Potassium Myristate	Samarium Myristate
1	CH3, C-H asym. Stretch	2960vw	-	2956vs
2	CH_2, C-H asym stretch	2920vs	2920vs	2920vs
3	CH_2, C-H sym stretch	2855s	2640vw	2856s
4	O-H stretch	2640vw	2640vw	-
5	C=O stretch	1700vs	-	-
6	COO-, C-O asym stretch	-	1550vs	1530s
7	CH_2 deform	1465ms	1460ms	1466s
8	C-O stretch + O-H in plane deform	1450ms	1445ms	1450w
9	COO-, C-O sym stretch	-	1420m	1410w
10	CH_2 (adjacent to COOH group)	-	-	-
11	CH_3 sym deform	-	-	-
12	Progressive bands(CH_2,Twist and wag)	1350-1090w	1340-1100w	1345w
13	CH_3 rocking	1120w	1110w	1110s
14	OH out of plane deform	940m	-	
15	CH_2 rocking	725w	720ms	723s
16	COOH bending mode	690ms	700ms	-
17	COOH wagging mode	550ms	545s	-

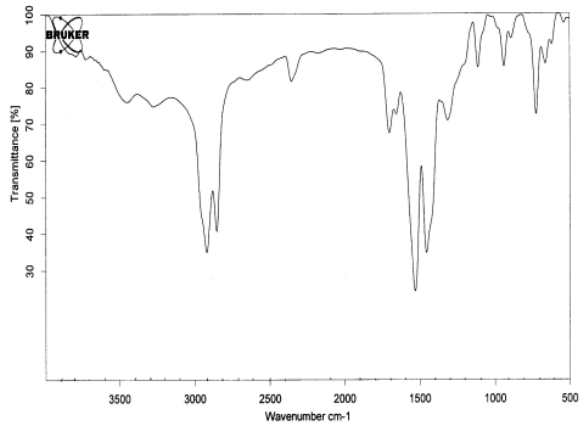

Figure 1: IR of samarium laurate

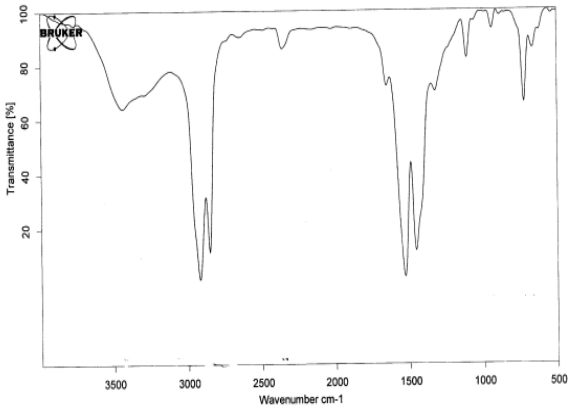

Figure 2: IR of samarium myristate

The infrared spectra of potassium, samarium laurate and myristate 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 laurate and myristate. 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.

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 laurate and samarium myristate confirms the formation of soaps and indicates that these soaps have an ionic character.

In the spectra of lauric and myristic 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 soaps. The progressive bands of the medium and weak intensity observed in the region of 1360-$1110cm^{-1}$ for samarium 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.

These results confirm that the fatty acid (lauric and myristic acids) in the solid state exists with dimeric structure through hydrogen bonding whereas metal to oxygen bond in samarium 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[12-13].

X-Ray Diffraction Analysis: The x-ray diffraction studies of samarium laurate and samarium myristate 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 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[21-22].

Table 3: X-Ray analysis of samarium laurate

S. No.	2θ	θ	sin θ	λ/2 sinθ	dÅ	n
1	2.566	1.283	0.02239	0.04478	34.41	1
2	5.117	2.5585	0.04463	0.08926	34.256	2
3	7.663	3.8315	0.0668	0.1336	34.75	3
4	10.248	5.124	0.0893	0.1786	34.802	4
5	13.617	6.8085	0.1185	0.237	34.613	5
6	14.76	7.38	0.1284	0.2568	34.925	6
7	17.99	8.995	0.1563	0.3126	34.562	7
8	22.166	11.083	0.1922	0.3844	34.106	9
9	23.15	11.575	0.2006	0.4012	34.152	9
10	25.29	12.645	0.2189	0.4378	34.855	10
Average Value of d					34.5431	

Table 4: X-Ray analysis of samarium myristate

S.No.	2θ	θ	sin θ	λ/2 sinθ	dÅ	n
1	2.287	1.1435	0.01995	0.0399	38.601	1
2	4.513	2.2565	0.03936	0.07872	38.225	2
3	6.753	3.3765	0.05888	0.11776	38.562	3
4	8.998	4.499	0.07844	0.15688	38.721	4
5	11.209	5.6045	0.09765	0.1953	38.862	5
6	12.868	6.434	0.1120	0.224	38.443	6
7	15.67	7.835	0.1363	0.2726	38.921	7
8	21.62	10.81	0.1875	0.375	38.841	9
9	22.22	11.11	0.1926	0.3852	38.891	10
10	24.13	12.065	0.2090	0.418	38.945	11
Average Value of d					38.7012	

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[14]. The molecular axes of transition metal soaps were found to be more inclined to the basal plane than rare earth metal soaps[17-20].

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

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

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

Where R = $C_{11}H_{23}$ and $C_{13}H_{27}$

The results of thermal decomposition of samarium soaps were explained in the light of some well known equations, the Freeman-Carroll's[15] and Coats Redfern's[16] 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 $\Delta(1/T)/\Delta(\log w_r)$ 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}.

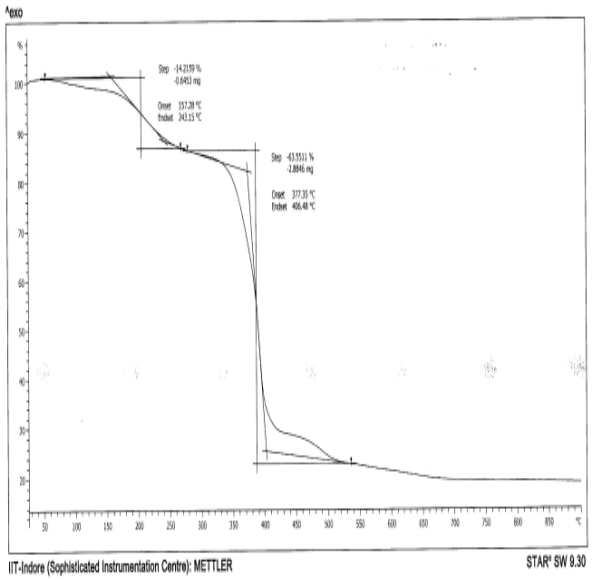

Figure 3: Thermal decomposition of samarium laurate

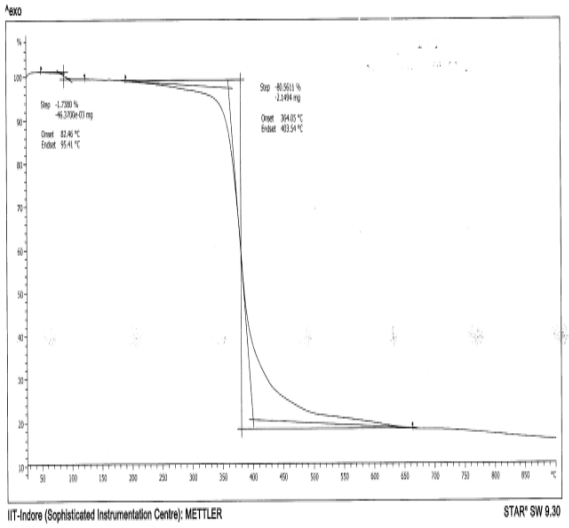

Figure 4: Thermal decomposition of samarium myristate

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 soaps possess ionic character. The X-ray analysis showed that samarium 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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