

## IR, X-Ray Diffraction and Thermo-gravimetric Analysis of Terbium Laurate

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**ABSTRACT:** The physico-chemical studies on terbium laurate in solid state were carried out by IR, X-ray diffraction and thermogravimetric analysis (TGA) measurements. The IR results revealed that fatty acid exist as dimer through hydrogen bonding and terbium soaps possess partial ionic character. The X-ray diffraction measurements were used to calculate the long spacings. The decomposition reaction was found kinetically of zero order and value of energy of activation for terbium laurate was found to be in the region of 3.41 to 8.20 K cal mol<sup>-1</sup>.

**Keywords:** Terbium laurate; infrared spectroscopy; X-ray diffraction and thermogravimetric analysis.

**INTRODUCTION:** A wide variety of metal soap finds important applications in different industries. The information of the nature and structure of these soaps is of great significance for their uses in various industries. The physico-chemical properties of rare earth metal soaps have been investigated by several workers<sup>1-11</sup> & <sup>25</sup>. Marques et al.<sup>12</sup> found liquid crystallinity in cerium (III) soaps with higher alkyl chain and observed the variation on melting point with chain-length. Binnemans et al.<sup>13</sup> reported the mesophase behaviour of lanthanum (III) teteradecanoate and higher homologues as a smectic A phase. Only a relatively small amount of literature exists concerning the properties of terbium soaps. A thorough knowledge of their physical properties still appears to be lacking. The present work deals with studies of infrared, X-ray and thermogravimetric analysis (TGA) of terbium laurate in order to investigate the structure and kinetics of thermal decomposition.

**MATERIAL AND METHODS:** The chemical synthesis of terbium laurate had already published<sup>14</sup>. The infrared absorption spectra were obtained with a Thermo Nicolet 370 spectrophotometer in region of 4000-400 cm<sup>-1</sup> using KBr disk method. X-ray diffraction patterns of terbium soaps were obtained with a Bruker AXS D 8 Advance X-ray diffractometer using

Cu-K<sub>α</sub> radiations filtered by a nickel foil over the range of 3-80°. The thermogravimetric analysis was carried out at constant heating rate of 15°C min<sup>-1</sup> under nitrogen atmosphere using thermobalance (Perkin Elmer Diamond TGA/DTA).

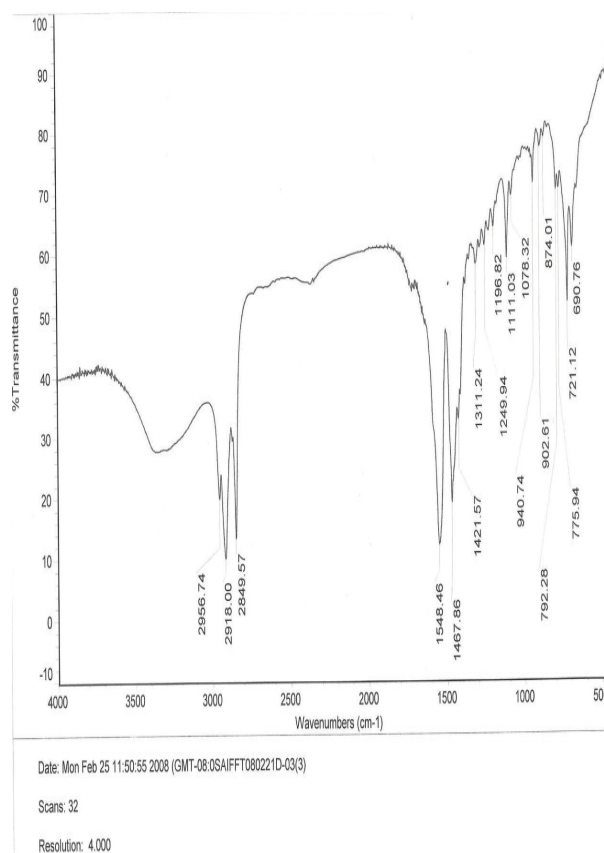
### RESULTS AND DISCUSSION:

**Infrared Absorption Spectra:** The infrared absorption bands for terbium laurate has been assigned and compared with the potassium laurate and lauric acid (Table 1). The absorption maxima, which is characteristic of aliphatic portion of the acid molecule, remain essentially unchanged even when acid is converted into potassium or terbium soap. The absorption maxima in the spectra of fatty acids near 2660-2640, 1700, 1400, 950-940, 690-680 and 550 cm<sup>-1</sup> is associated with the localized carboxyl group of the acid molecule in the dimeric form and confirm the presence of hydrogen bonding between two molecules of fatty acid. The appearance of two absorption bands corresponding to symmetric and antisymmetric stretching vibrations of carboxylate ion near 1440-1390 cm<sup>-1</sup> and 1560-1540 cm<sup>-1</sup>, respectively, in absorption spectra of terbium laurate instead of one band of the carboxyl group at 1700cm<sup>-1</sup> in the spectra of fatty acid confirms the compound formation and indicate that it is ionic in nature (Figure 1). The assigned frequencies are in good agreement with the results of other workers<sup>15-17</sup>.

**Table 1: IR absorption spectral frequencies (cm<sup>-1</sup>) with their assignments.**

S.No.	Assignments	Lauric Acid	Potassium laurate	Terbium laurate
1	CH <sub>3</sub> , C-H asymmetric-stretching	2960 v <sub>w</sub>	2940 w	2956.74 w
2	CH <sub>2</sub> , C-H asymmetric-stretching	2920 v <sub>s</sub>	2920 vs	2918.00 s
3	CH <sub>2</sub> , C-H symmetric-stretching	2850 s	2890 s	2849.47 s
4	OH, stretching	2650 v <sub>w</sub>	2640 v <sub>w</sub>	-
5	C=O, stretching	1700 v <sub>s</sub>	-	-
6	COO <sup>-</sup> , C-O asymmetric stretching	-	1550 v <sub>s</sub>	1548.46 s
7	CH <sub>2</sub> , deformation	1465 m <sub>s</sub>	1460 m <sub>s</sub>	1467.86 m <sub>s</sub>
8	COO <sup>-</sup> , C-O symmetric stretching	-	1449 s	1421.57 w
9	C-O stretching, O-H in plane deformation	1449 m	1445 m <sub>s</sub>	-
10	CH <sub>2</sub> (adjacent to COOH group), deformation	-	-	-
11	CH <sub>3</sub> , symmetric deformation	-	-	1370.00 v <sub>w</sub>
12	Progressive bands (CH <sub>2</sub> twisting and wagging)	1350-1090 w	1375-1200 w	1340-1180 v <sub>w</sub>
13	CH <sub>3</sub> , rocking	1120-1065 w	1105-1120 w	1111.03 m
14	OH, out of plane deformation	940 m <sub>s</sub>	-	940.74 m
15	CH <sub>2</sub> , rocking	720 w	720 m <sub>s</sub>	721.12 m <sub>s</sub>
16	COOH bending mode	690 m <sub>s</sub>	-	690.75 m
17	COOH wagging mode	550 m <sub>s</sub>	-	-

Key to abbreviations: v<sub>w</sub> = very weak; v<sub>s</sub> = very strong; s = strong; m = Medium; m<sub>s</sub> = Medium strong; w = weak

**Figure 1: Infrared Absorption Spectrum of Terbium laurate.**

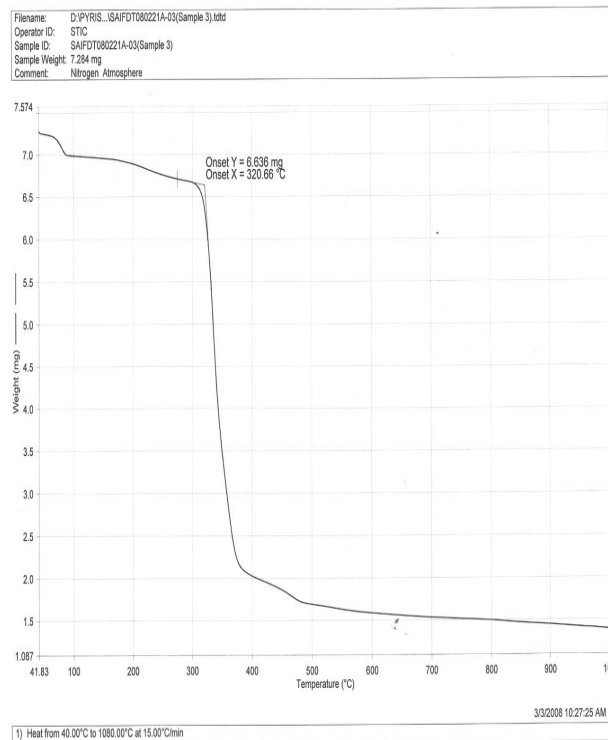
**X-ray Diffraction Patterns:** X-ray diffraction patterns of terbium laurate have been investigated to characterize the structure of these soaps. The intensities of the diffracted X-rays as a function of the diffraction angle,  $2\theta$ , for terbium soaps is recorded and the interplanar spacing,  $d$ , has been calculated from the position of the intense peak using Bragg's relationship  $n\lambda = 2d \sin \theta$ , where  $\lambda$  is wavelength of the radiation. A number of peaks arising from the diffraction of X-ray by planes of metal ion (basal planes) have been observed over the range of 3-80° diffraction angles. The interplanar spacing,  $d$ , for 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup>, 8<sup>th</sup>, 9<sup>th</sup>, 10<sup>th</sup>, 15<sup>th</sup>, 17<sup>th</sup> and 20<sup>th</sup> order diffractions for terbium laurate is 33.28, 33.38, 33.74, 33.23, 33.61, 33.80, 33.09, 33.19, 33.43 and 33.58 Å, respectively (Table 2). The average planar distance i.e. the long spacing for terbium laurate is 33.43 Å.

It is observed that values of average planar distance i.e. long spacing for terbium laurate (33.43 Å) is smaller than the calculated dimensions of laurate ion (37.00 Å) from Pauling's values<sup>18</sup> of atomic radii and bond angles. This suggest that the molecular axes of terbium laurate are somewhat inclined to the basal

plane and the metal ions fit into spaces between oxygen atoms of the ionized carboxyl group without a large strain of the bonds. It is observed that the long spacing peaks are fairly intense while the short spacing peaks are relatively weak. It is, therefore, concluded on the basis of long and short spacings that metal ions in terbium laurate are arranged in a parallel plane, i.e. a basal plane equally spaced in the soap crystal with fully extended zig-zag chain of fatty acid radicals on both directions of each basal plane and these soaps possess double layer structure as proposed by Vold and Hattiangdi<sup>19</sup>.

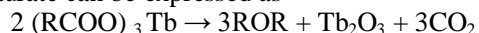
**Table 2: X-ray analysis and determination of long spacings, d of Terbium laurate.**

S. N.	2θ	Sin θ	λ / 2 Sin θ	d (Å)	n
1	7.964	0.0694	11.09	33.28	3
2	10.594	0.0923	8.34	33.38	4
3	13.110	0.1142	6.75	33.74	5
4	15.990	0.1391	5.54	33.23	6
5	21.130	0.1833	4.20	33.61	8
6	23.673	0.2051	3.75	33.80	9
7	26.928	0.2328	3.31	33.09	10
8	40.743	0.3481	2.21	33.19	15
9	46.125	0.3917	1.97	33.43	17
10	54.610	0.4587	1.68	33.58	20



**Figure 2: Thermogram of Terbium laurate.**

**Thermogravimetric Analysis (TGA):** The thermogravimetric analysis has shown that the final residues left on heating terbium laurate, are the metal oxides as the weight of the residue is in agreement with the theoretically calculated weight of terbium oxide. A white substance is found condensed at the cold part of the sample tube and it is detected as corresponding keton. The thermal decomposition of terbium laurate can be expressed as

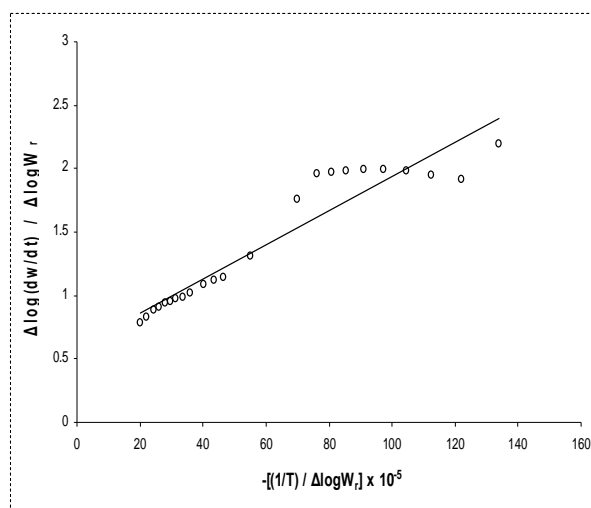


Where R is C<sub>11</sub>H<sub>23</sub> for laurate. The curve of thermogravimetric analysis exhibit three stages of decomposition patterns (Figure 2). The 1<sup>st</sup> stage of decomposition was rapid and could not be subjected to kinetic analysis. The 2<sup>nd</sup> stage represents the major decomposition. Finally, 3<sup>rd</sup> stage show very small change with further increase in temperature.

TGA data have been used to calculate the energy of activation and to find the order of reaction for the decomposition using the Freeman-Carroll's<sup>20</sup> rate expression

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

Where, E = energy of activation, R = gas constant, n = order of decomposition reaction, T = temperature on absolute scale, W<sub>r</sub> = difference between the total loss and loss in weight at time, t i.e. W<sub>0</sub> - W<sub>t</sub> and dw/dt = value of rate of weight loss obtained from the in weight vs. time curve at appropriate times. The plots of [log (dw/dt) / log W<sub>r</sub>] vs 1/T / log W<sub>r</sub> have been found to be linear with zero intercept and value of activation energy from slope (-E / 2.303R) of the plot (Figure 3) is calculated to be 8.20 K Cal mol<sup>-1</sup>.



**Figure 3: Freeman-Carroll's plot.**

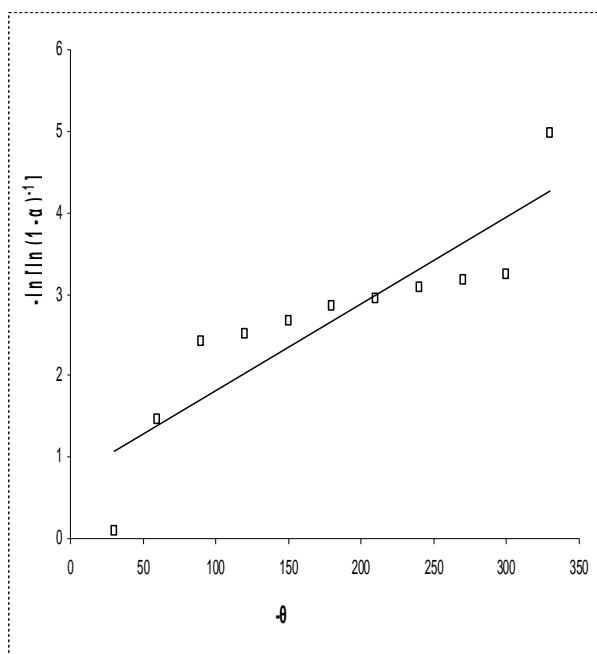


Figure 4: Horowitz-Metzger's plot.

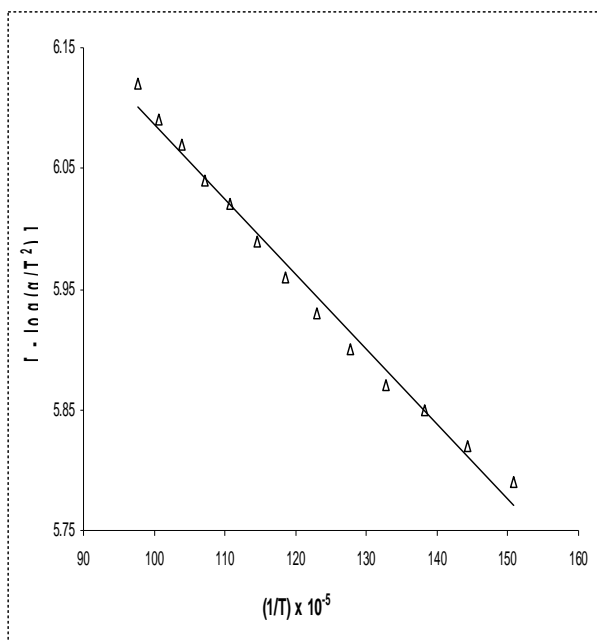


Figure 5: Coats-Redfern's plot.

The energy of activation for the thermal decomposition is also calculated by using the Horowitz-Metzger's<sup>21</sup> and Coats-Redfern's<sup>22</sup> equations. The values of activation energy are calculated from the slopes of plots by using these equations are found in the range of 7.58 -3.41 K Cal mol<sup>-1</sup> (Figures 4 and 5). It can, therefore, be concluded that the decomposition reaction of terbium laurate is kinetically zero order<sup>23,24</sup>

and the activation energy for the decomposition process existed in the range of 3.41 – 8.20 K Cal mol<sup>-1</sup>.

**CONCLUSION:** The IR results confirm that lauric acid exist in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two acid molecules, whereas terbium laurate is ionic in nature. The X-ray analysis revealed that the molecular axes are slightly inclined to the basal plane. The thermal decomposition found to be kinetically of zero order and the energy of activation for the decomposition is in the range of 3.41 – 8.20 K Cal mol<sup>-1</sup>.

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