

Spectroscopic and Thermo-gravimetric Analysis of Terbium Myristate

Kamal Kishore^{1*}, Manpreet Singh¹, Chitra Singh² and S. K. Upadhyaya³

¹Department of Chemistry, Eternal University, Baru Sahib, Sirmour-173101 (H.P.) INDIA

²Department of Education Science & Mathematics, Regional Institute of Education, Shyamla Hills, Bhopal – 462013, INDIA

³P. G. Department of Chemistry, S. S. L. Jain College, Vidisha-464001 (M.P.) INDIA

*Correspondence: E-mail: k_81kishore@yahoo.co.in

(Received 06 Sept, 2017; Accepted 19 Nov, 2017; Published 29 Dec, 2017)

ABSTRACT: The terbium myristate has been investigated by IR, X-ray diffraction and thermogravimetric analysis (TGA). The IR result reveals that fatty acids exist as dimer through hydrogen bonding and terbium myristate possess partial ionic character. The X-ray diffraction suggests that molecular axes are somewhat inclined to the basal plane. The metal cation fit into spaces between oxygen atoms of the ionised carboxyl group without giving a large strain of the bond. The thermal decomposition reaction is found kinetically of zero order and value of energy of activation is in the region of 3.84 to 8.55 K cal mol⁻¹.

Keywords: Terbium myristate; diffraction order and thermogravimetric analysis.

INTRODUCTION: Metallic soaps are simple carboxylates of alkaline-earth and other polyvalent metals. The metal is chemically bound to the anionic headgroup of the fatty acid by both ionic and covalent linkages. The anionic headgroup of a fatty acid molecule consists of a terminal carboxylate group. The physico-chemical properties metal soaps have been investigated by several workers. Mehrotra et al.¹⁻³ studied the ionic nature of rubidium and cesium soaps by infrared techniques. Solanki and Bhandari⁴ characterised uranyl soaps whereas Varma and Jindal⁵ analysed cerium soaps by using infrared and electronic absorption spectra. Kinetic study of high oleic sunflower oil saponification was carried out by Gaëlle Poulenat et al.⁶ by using FTIR spectroscopy. Kambe et al.⁷ studied the thermal transition of cobalt soaps by differential thermal analysis and thermogravimetric analysis. Mehrotra et al.⁸ investigated the thermal behaviour of lanthanum and cerium soaps. The thermogravimetric analysis of aluminium soaps was carried out by Rai and Mehrotra⁹. The thermal stability of potassium soaps was investigated by Ilina et al.¹⁰ Gallot and Skoulios¹¹ used x-ray diffraction to study the polymorphism of the polar groups of sodium, potassium and lithium soaps in ribbon phases. They explained the appearance of the smectic phase in sodium just prior to the melting point as being related to the melting of the polar groups, whereas in lithium stearate no transition from ribbons to lamellae oc-

curred prior to melting. They attributed this difference to relatively weak association of lithium soap headgroups. Marques et al.¹² found liquid crystallinity in cerium (III) soaps with higher alkyl chain and observed the variation on melting point with chain-length. Binnemans et al.¹³ reported the mesophase behaviour of lanthanum (III) tetradecanoate and higher homologues as a smectic A phase. Only a relatively small amount of literature exists concerning the solution properties of terbium myristate^{14 & 15}. A thorough knowledge of their physical properties still appears to be lacking. The reported work deals with studies of infrared, X-ray and thermogravimetric analysis (TGA) of terbium myristate in order to investigate the structure and kinetics of thermal decomposition.

MATERIALS AND METHODS: The chemical synthesis of terbium myristate had already communicated.¹⁴ The infrared absorption spectra were obtained with a Thermo Nicolet 370 spectrophotometer in region of 4000-400 cm⁻¹ 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_α 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⁻¹ under nitrogen atmosphere using thermobalance (Perkin Elmer Diamond TGA/DTA).

RESULTS AND DISCUSSION:

Infrared absorption spectra: The infrared absorption bands for terbium myristate has been assigned and compared with the potassium myristate and myristic acid (Table 1). The absorption maxima, which is characteristic of aliphatic portion of the acid molecule, remain unchanged even when acid is converted into potassium or terbium myristate. The absorption maxima of fatty acids near 2660-2640, 1700, 1400, 950-940, 690-680 and 550 cm^{-1} 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 new absorption bands due to symmetric and antisymmetric stretching vibrations of carboxylate ion near 1440-1390 cm^{-1} and 1560-1540 cm^{-1} , respectively, instead of one band of the carboxyl group at 1700 cm^{-1} 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^{16 & 17}.

Table 1: IR absorption spectral frequencies (cm^{-1}) with their assignments.

S.No.	Assignments	Myristic Acid	Potassium myristate	Terbium myristate
1	CH_3 , C-H asymmetric-stretching	2960 ν_w	2955 w	2958.00 w
2	CH_2 , C-H asymmetric-stretching	2920 ν_s	2920 ν_s	2916.94 ν_s
3	CH_2 , C-H symmetric-stretching	2840 ν_w	2840 ν_w	2849.22 ν_s
4	OH, stretching	2640 ν_w	2640 ν_w	-
5	C=O, stretching	1700 ν_s	-	-
6	COO^- , C-O asymmetric stretching	-	1550 ν_s	1541.15 ν_s
7	CH_2 , deformation	1465 m_s	1460 m_s	1468.73 s
8	COO^- , C-O symmetric stretching	-	1420 m	1410.20 w
9	C-O stretching, O-H in plane deformation	1430 m_s	1445 m_s	-
10	CH_2 (adjacent to COOH group), deformation	1405 ν_s	-	-
11	CH_3 , symmetric deformation	1370 w	-	-
12	Progressive bands (CH_2 twisting and wagging)	1350-1190 w	1340-1100 w	1355-1180 ν_w
13	CH_3 , rocking	1120 w	1105-1120 w	1110.72 m_s
14	OH, out of plane deformation	940 m	-	940.96 w
15	CH_2 , rocking	735-725 m_s	755-725 m_s	721.02 s
16	COOH bending mode	690 m_s	700 m_s	691.32 m
17	COOH wagging mode	550 m_s	580- 545 s	-

Key to abbreviations: ν_w = very weak ; ν_s = very strong; s = strong; m = Medium; m_s = Medium strong; w = weak.

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

S. No.	2θ	$\sin \theta$	$\lambda / 2 \sin \theta$	d (Å)	Order (n)
1	4.534	0.0395	19.47	38.94	2
2	6.707	0.0585	13.17	39.50	3
3	9.030	0.0787	9.78	39.14	4
4	11.203	0.0976	7.89	39.46	5
5	13.594	0.1183	6.51	39.05	6
6	20.320	0.1764	4.37	39.30	9
7	24.984	0.2163	3.56	39.17	11
8	27.275	0.2358	3.27	39.20	12
9	34.260	0.2945	2.61	39.23	15
10	48.778	0.4129	1.86	39.17	21

Table 3: Weight loss of Terbium myristate with temperature and time.

S. No.	Time t (min.)	Temperature T (K)	Weight of soap decomposed w x 10 ⁵ (gm)	dw/dt x 10 ⁵	W _r x 10 ⁵
1	2	303	00.0	0.0	446.0
2	4	333	13.3	3.3	433.0
3	6	363	28.2	4.7	418.0
4	8	393	29.8	3.7	416.0
5	10	423	33.1	3.3	413.0
6	12	453	35.1	2.9	411.0
7	14	483	37.1	2.6	409.0
8	16	513	41.4	2.6	405.0
9	18	543	46.3	2.6	400.0
10	20	573	60.1	3.0	386.0
11	22	603	156.7	7.1	290.0
12	24	633	293.1	12.2	153.0
13	26	663	381.5	14.7	65.0
14	28	693	393.1	14.0	53.0
15	30	723	402.9	13.4	43.0
16	32	753	416.6	13.0	30.0
17	34	783	419.9	12.3	26.0
18	36	813	426.5	11.8	19.0
19	38	843	433.1	11.4	13.0
20	40	873	439.7	11.0	7.0
21	42	903	441.3	10.5	5.0
22	44	933	443.0	10.1	3.0
23	46	963	445.0	9.7	1.0
24	48	993	446.3	9.3	0.0

X-ray Diffraction Patterns: The intensities of the diffracted X-rays as a function of the diffraction angle, 2θ , has 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 λ 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 $3-80^\circ$ diffraction angles. The interplanar spacing for different order diffractions has mentioned in Table 2. The average planar distance i.e. the long spacing for terbium myristate is $39.22 \text{ \AA}$. The maximum average d -spacing of the bilayer structure was calculated for an all trans conformation of the myristate chain perpendicular to the metal ion base plan by using equation¹².

$$d_{max} = 2d_{C-H} + 2(n-1)d_{C-C} \sin 55^\circ + 2d_{C-O} + 2r_{Tb^{3+}}$$

Where; n is the total number of carbon atoms in the chain, $d_{C-H} = 1.09 \text{ \AA}$, $d_{C-C} = 1.54 \text{ \AA}$, $d_{C-O} = 1.36 \text{ \AA}$ and $r_{Tb^{3+}} = 1.18 \text{ \AA}$. A good agreement is found between the experimental and calculated values.

It is observed that values of average planar distance i.e. long spacing for terbium myristate ($39.22 \text{ \AA}$) is smaller than the calculated dimensions of myristate ion ($42.00 \text{ \AA}$) from Pauling's values¹⁸ of atomic radii and bond angles. This suggest that the molecular axes of terbium myristate 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 myristate 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 posses double layer structure as proposed by Vold and Hattiangdi¹⁹.

Thermogravimetric Analysis (TGA): The thermal decomposition of terbium myristate can be expressed as;



Where; R is $\text{C}_{13}\text{H}_{27}$ for myristate. The TGA curves exhibit three stages of decomposition (Figure 2). The 1st stage is rapid and could not be subjected to kinetic

analysis. The 2nd stage represents the major decomposition. Finally, 3rd stage show very small change with further increase in temperature. The weight loss of Terbium myristate with temperature and time is mentioned in table 3. The TGA shows that the final residue left on heating is 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 colder part of the sample tube, which is detected as keton. Thermal stability measurement shows that terbium myristate is stable upto 314.74°C.

TGA data have been used to calculate the energy of activation and order of reaction for the decomposition by using the Freeman-Carroll's²⁰ 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_r = difference between the total loss and loss in weight at time, t i.e. W₀ - W_t 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_r] vs 1/T / log W_r 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 8.55 K Cal mol⁻¹.

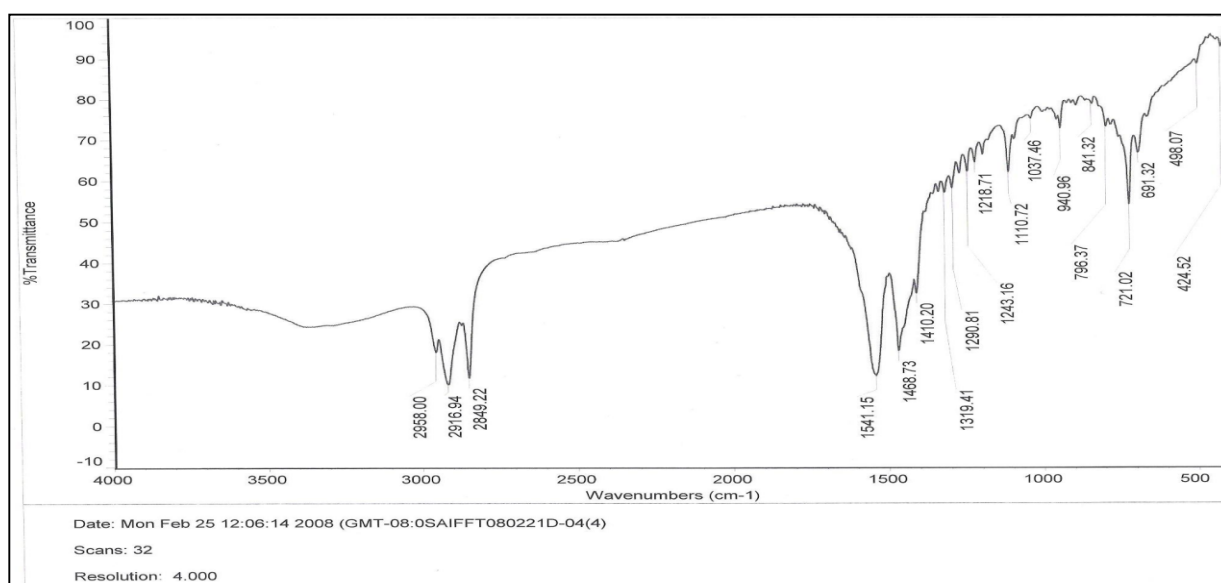


Figure 1: Infrared Absorption Spectrum of Terbium myristate.

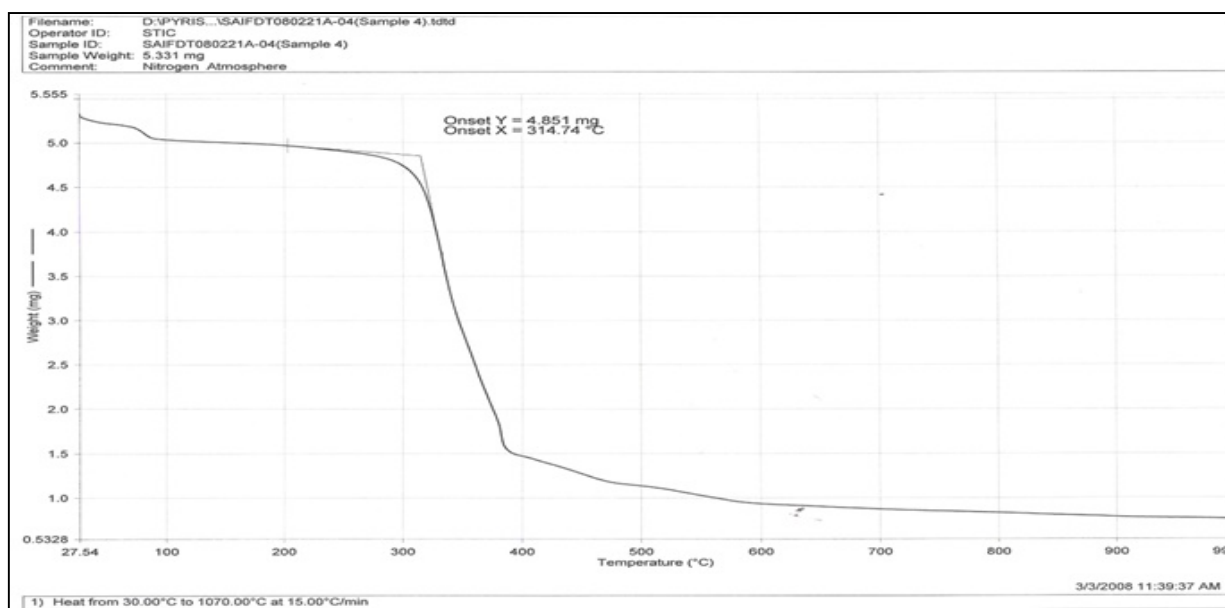


Figure 2: Thermogram of Terbium myristate.

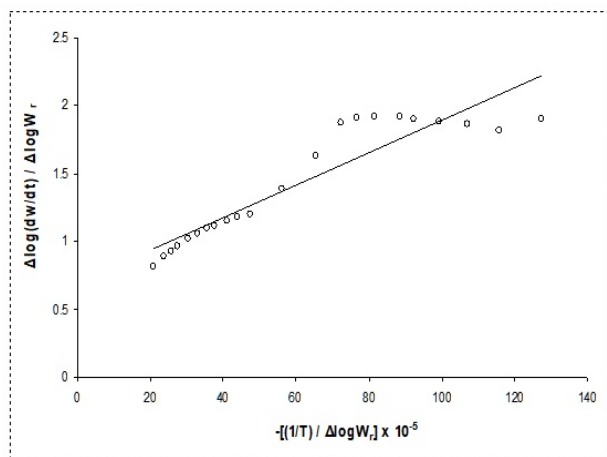


Figure 3: Freeman-Carroll's plot.

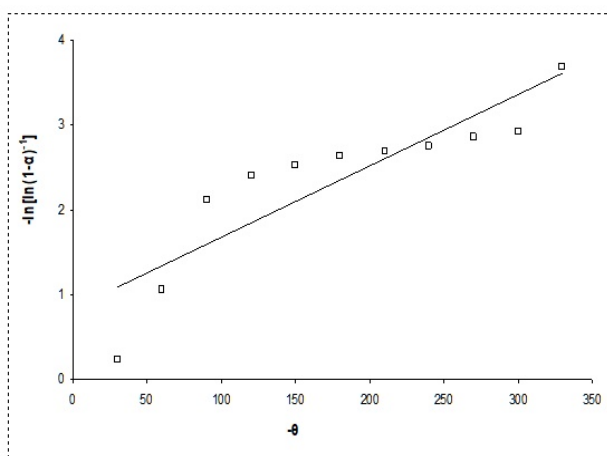


Figure 4: Horowitz-Metzger's plot.

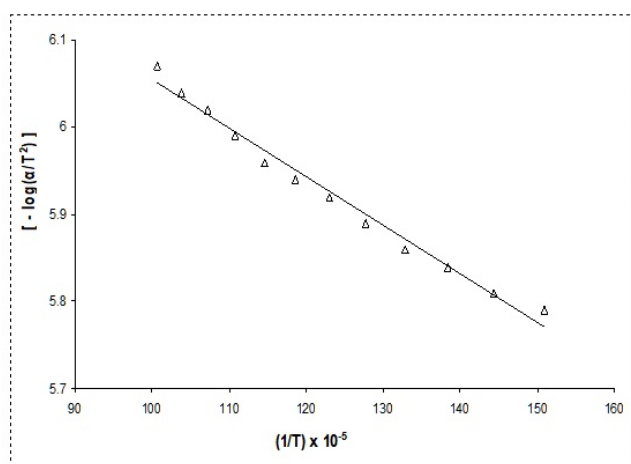


Figure 5: Coats-Redfern's plot.

The energy of activation for the thermal decomposition has also calculated by using the Horowitz-Metzger's²¹ and Coats-Redfern's²² equations. The values of activation energy calculated from the slopes of plots by using these equations is found in the range of 8.14 - 8.55 K Cal mol⁻¹ (Figure 4 and 5). It is concluded that the decomposition reaction of terbium

myristate is kinetically zero order and the activation energy for the decomposition process existed in the range of 3.84 to 8.55 K cal mol⁻¹. The results are found in good agreement with other literature data²³.

CONCLUSION: The IR results confirm that myristic acid exists as dimeric structure due to hydrogen bonding between the carboxyl groups of two acid molecules, whereas terbium myristate 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 3.84 to 8.55 K cal mol⁻¹.

ACKNOWLEDGEMENT: We wish to express our sincere thanks to S.T.I.C. Cochin, India for their valuable assistance to make present study possible by physico-chemical technique. One of authors (K.K.) is grateful to Hon'ble Vice Chancellor, Prof. H.S. Dhaliwal and Dean (PG) Prof. B.S. Sohal, Eternal University, Baru Sahib (Himachal Pradesh) India for their constant encouragement and logistic supports.

REFERENCES:

1. Mehrotra, K. N. and Saroha, S. P. S. (1979) *J. Indian Chem. Soc.*, 56(5), 466-469.
2. Mehrotra, K. N. and Godara, V. K. (1982) *Tenside Detergents*, 19(5), 290-294.
3. Mehrotra, K. N. and Rajpurohit, M. S. and Godara, V. K. (1983) *J. Macromol. Sci. Chem.*, 19(2), 181-191.
4. Solanki, A. K. and Bhandari, A. M. (1981) *Tenside Detergents*, 18(1), 34-36.
5. Varma, R. P. and Jindal, R. (1983) *Tenside Detergents*, 20(4), 193-195.
6. Poulenat, G., Sentenac, S., and Mouloungui, Z. (2003) *Journal of Surfactants and Detergents*, 6(4), 305-310.
7. Kambe, H., Ozawa, T., Onone, M. and Igarashi, S. (1962) *Bull. Chem. Soc. Japan*, 35, 81.
8. Mehrotra, R. C., Mishra, S. N. and Mishra, T. N. (1963) *J. Inorg. Nucl. Chem.*, 25, 195-199; 201-203.
9. Rai, A.K. and Mehrotra, R.C. (1963) *J. Indian Chem. Soc.*, 40, 359.
10. Ilina, A. I. and Nedavnyaya, V. G. (1966) *Moslozhir Prom.*, 32(8), 20.
11. Gallot, B. and Skoulios, A. E. (1962) *Acta Crystallographica*, 15, 826-831.
12. Marques E. F., Burrows H. D. and Miguel da Graça M. (1998) *J. Chem. Soc. Faraday Trans.* 94, 1729-1736.

13. Binnemans K., Heinrich B., Guillon D. and Bruce D.W. (1999) *Liq. Cryst.* 26, 1717.
 14. Kishore K. and Upadhyaya S. K. (2010) *Tenside surfactants detergents*, 47, 184-189.
 15. Kishore K. and Upadhyaya S. K. (2011) *Journal of pure & Applied Ultrasonics*, 33(2), 39-42.
 16. Dual C., Leocomte J. and Douville F. (1942) *Ann. Phys.*, 17, 5.
 17. Kagarise R. K. (1955) *J. Phys. Chem*, 59, 271.
 18. Pauling L. (1960) "The Nature of Chemical Bond," Cornell University Press.
 19. Vold R. D. and Hattiangdi G. S. (1949) *Ind. Eng. Chem.*, 41, 2311.
 20. Freeman E. S. and Carroll B. (1958) *J. Phys. Chem.*, 62, 394.
 21. Horowitz H. H., Metzger G. (1963) *Anal. Chem.*, 35, 1464.
 22. Coats A. W. and Redfern J. P. (1964) *Nature*, 21, 68.
 23. Kishore K., Thakur N. and Upadhyaya S. K. (2016) *J. Biol. Chem. Chorn.*, 2(2), 27-31.
- .