

Thermal Stability and Structural Analysis of Terbium Caprylate

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ABSTRACT: The physico-chemical analysis of terbium caprylate (anionic surfactant) was carried out by FTIR, X-Ray Diffraction (XRD) and thermogravimetric analysis (TGA) measurements. The IR results have shown that caprylic acid exist as dimer through hydrogen bonding and terbium caprylate possess partial ionic character. The X-ray diffraction measurements have been used to calculate the long spacings. Thermogravimetric analysis has shown that this compound is thermally stable up to 480°C. The thermal decomposition reaction found zero ordered kinetic and value of energy of activation was found to be in the region of 3.29 to 7.43k cal mol⁻¹.

Keywords: Terbium caprylate; thermal stability; activation energy and thermogravimetric analysis.

INTRODUCTION: Metallic soaps are the combination of metallic elements with a fatty acids organic group. The applications of metallic soaps depend largely on their physical state, stability and chemical reactivity, together with their volatility and solubility in common organic solvents and their mixtures of different organic solvents. The structures of metallic complexes have been studied by Nokamoto et al.¹ by using infrared spectroscopy. Mehrotra et al.^{2,4} studied the ionic nature of rubidium and cesium soaps by infrared techniques. Solanki and Bhandari⁵ characterised uranyl soaps whereas Varma and Jindal⁶ 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.⁷ by using FTIR spectroscopy. 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. Gallot and Skoulios¹⁰ 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 occurred prior to melting. They attributed this difference to relatively weak association of lithium soap head-

groups. The present work deals with the thermal stability, FTIR and X-ray diffraction of terbium caprylate in order to evaluate kinetics of thermal decomposition, type of bonding and structural information.

MATERIALS AND METHODS: Synthesis of terbium caprylate has already been communicated¹¹. The thermogravimetric analysis has performed at constant heating rate of 15°C min⁻¹ under nitrogen atmosphere by thermobalance (Perkin Elmer Diamond TGA/DTA). The FTIR absorption spectra was taken with a Thermo Nicolet 370 spectrophotometer in region of 4000-400 cm⁻¹ using KBr disk method. X-ray diffraction patterns was 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°.

RESULTS AND DISCUSSION:

Infrared Absorption Spectra: The FTIR absorption maxima of terbium caprylate have been assigned, recorded (Table I) and compared with the results of their corresponding fatty acids and potassium caprylate. The vibrational frequencies characteristic of aliphatic chain of caprylic acid does not vary even when fatty acid is converted into potassium and terbium caprylate. The infrared spectra of caprylic acid indicates that the carboxyl group show the characteristic

frequencies at 2500-2700 cm^{-1} (broad O-H stretching vibrations), 1700 cm^{-1} (C=O stretching vibrations), 1400 cm^{-1} and 1200-1300 cm^{-1} (O-H in plane bending and C-O stretching) and at 930 cm^{-1} (out of plane bending of O-H group). The O-H stretching vibrations (2500-2700 cm^{-1} of carboxyl groups present in dimers) and C=O stretching band at 1700 cm^{-1} are most characteristics one among all absorption bands. Infrared absorption spectra of caprylic acid also exhibit the absorption maxima near 690 cm^{-1} and 550 cm^{-1} due to bending and wagging modes of carboxyl group and are independent of the chain-length of the fatty acid radical. The appearance of the absorption band near 1700 cm^{-1} in IR spectra of caprylic acid reveals that it exists as dimer¹² and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acid.

The infrared spectra of potassium and terbium caprylate indicate marked differences with the absorption spectra of corresponding fatty acids in some spectral region. The characteristic vibrations of free acid are found completely missing in their respective regions

in the IR spectra of potassium and terbium caprylate. The strong spectral band due to C=O stretching of acid molecule at 1700 cm^{-1} had disappeared completely in the spectra of potassium and terbium caprylate (Figure 1). The disappearance of the carboxyl frequency (1700 cm^{-1}) in the spectra of terbium caprylate have shown that there may be a complete resonance the two C-O bonds of the carboxyl group of the terbium caprylate molecule and group has an ionic structure. The C-O bonds on carbonyl group of molecule become identical with their force constants assuming the value intermediate between these of normal double and single bonds.

The appearance of two absorption bands of the carboxylate group due to symmetric and asymmetric vibration of carboxylate ion near 1440-1390 cm^{-1} and 1560-1540 cm^{-1} in absorption spectra of terbium caprylate instead of one band of the carboxyl group at 1700 cm^{-1} in the absorption spectra of caprylic acid confirmed the formation of the terbium caprylate and indicate to have an ionic nature.

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

S. No.	Assignments	Caprylic Acid	Potassium caprylate	Terbium caprylate
1	CH ₃ , C-H asymmetric-stretching	2950 w	2960 w	2956.31 m
2	CH ₂ , C-H asymmetric-stretching	2920 s	2920 v _s	2923.27 s
3	CH ₂ , C-H symmetric-stretching	2850 s	2860 m	2852.12 m _s
4	OH, stretching	2650 w	-	-
5	C=O, stretching	1700 v _s	-	-
6	COO ⁻ , C-O asymmetric stretching	-	1550 m	1548.23 v _s
7	CH ₂ , deformation	1460 m	1460 w	1466.82 s
8	COO ⁻ , C-O symmetric stretching	-	1430 m	1423.63 m
9	C-O stretching, O-H in plane deformation	1430 w	-	-
10	CH ₂ (adjacent to COOH group), deformation	1410 v _s	-	-
11	CH ₃ , symmetric deformation	1350 w	1350 w	1376.90 v _w
12	Progressive bands (CH ₂ twisting and wagging)	1340-1040 m	1340-1100 w	1345-1176.39 w
13	CH ₃ , rocking	1100 v _s	1050 w	1109.92 s
14	OH, out of plane deformation	940 s	-	940.30 m _s
15	CH ₂ , rocking	720 m _s	730 m _s	723.42 m
16	COOH bending mode	690 m	-	689.63 m
17	COOH wagging mode	550 m _s	-	-

Key to abbreviations: v_w = very weak; v_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.	2 θ	Sin θ	$\lambda / 2 \text{ Sin } \theta$	d (Å)	n
1	7.280	0.0635	12.13	24.27	2
2	10.730	0.0935	8.24	24.71	3
3	14.536	0.1265	6.09	24.35	4
4	17.911	0.1557	4.95	24.74	5
5	21.490	0.1864	4.13	24.79	6
6	25.491	0.2206	3.49	24.44	7
7	29.072	0.2510	3.07	24.56	8
8	36.748	0.3152	2.44	24.44	10
9	47.816	0.4053	1.90	24.70	13
10	56.332	0.4720	1.63	24.48	15

Table: 3 Weight loss of Terbium caprylate in TGA.

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	689.7
2	4	333	14.7	3.7	675.0
3	6	363	47.2	7.9	642.5
4	8	393	54.7	6.8	635.0
5	10	423	64.7	6.5	625.0
6	12	453	82.2	6.8	607.5
7	14	483	89.7	6.4	600.0
8	16	513	104.7	6.5	585.0
9	18	543	109.7	6.1	580.0
10	20	573	112.2	5.6	577.5
11	22	603	227.2	10.3	462.5
12	24	633	564.7	23.5	125.0
13	26	663	604.7	23.2	85.0
14	28	693	617.2	22.0	72.5
15	30	723	629.7	21.0	60.0
16	32	753	644.7	20.1	45.0
17	34	783	652.2	19.2	37.5
18	36	813	654.7	18.2	35.0
19	38	843	657.2	17.3	32.5
20	40	873	664.7	16.6	25.0
21	42	903	669.7	15.9	20.0
22	44	933	672.2	15.3	17.5
23	46	963	674.7	14.7	15.0
24	48	993	677.2	14.1	12.5
25	50	1023	679.7	13.6	10.0
26	52	1053	682.2	13.1	7.5
27	54	1083	684.7	12.7	5.0
28	56	1113	687.2	12.3	2.5
29	58	1143	689.7	11.9	0.0

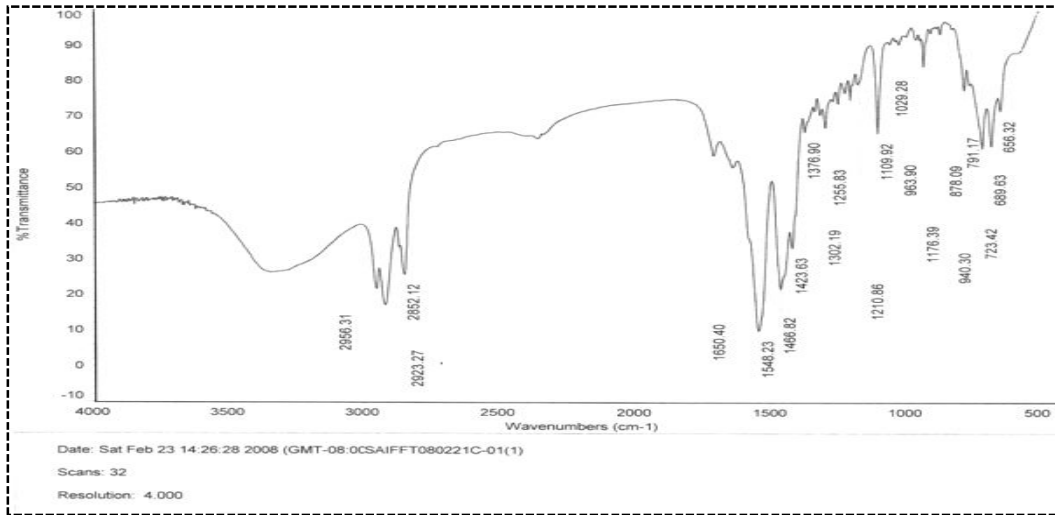


Figure 1: Infrared Absorption Spectrum of Terbium Caprylate.

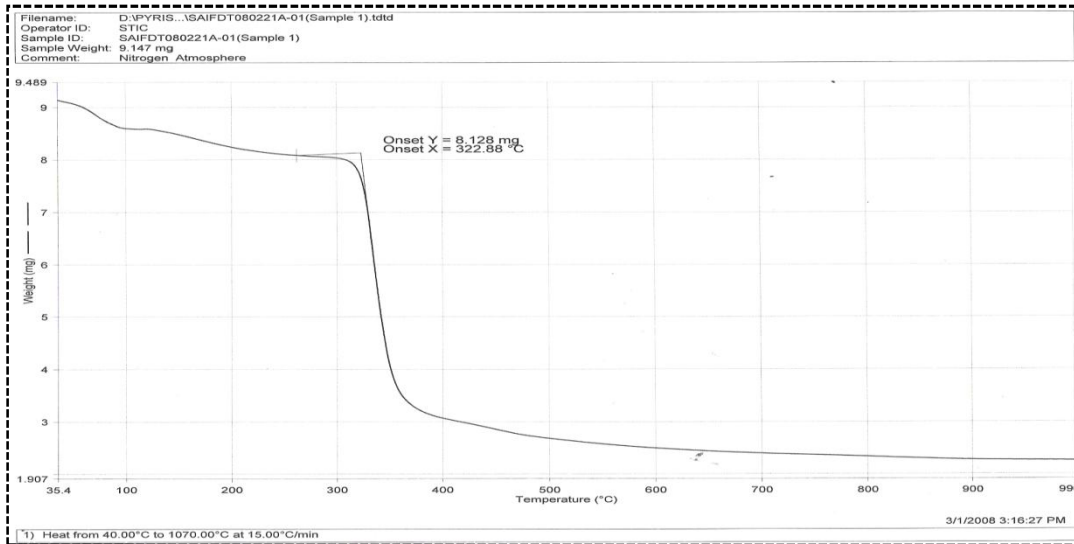


Figure 2: Thermogram of Terbium caprylate.

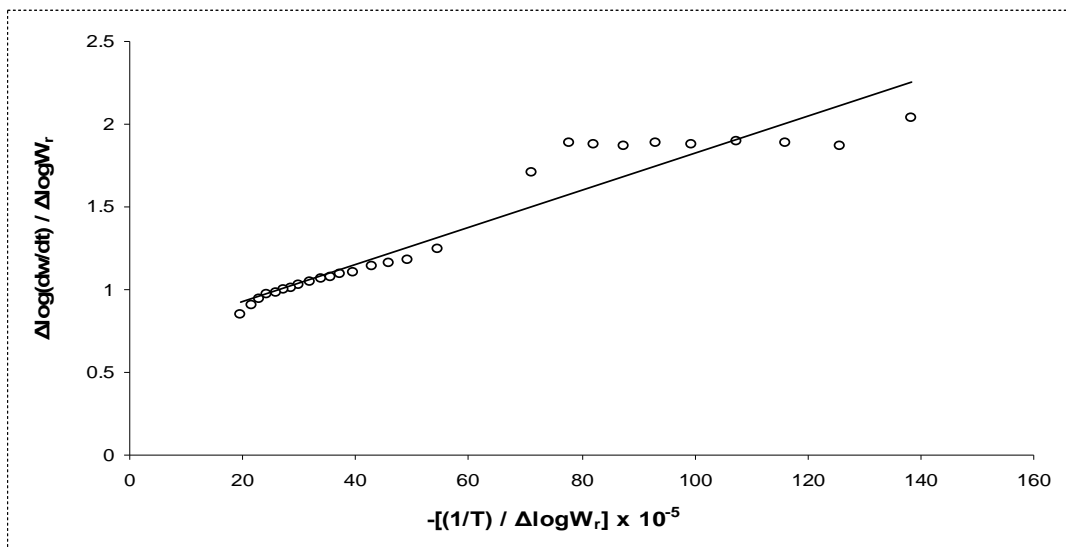


Figure 3: Freeman-Carroll's type plot of Terbium caprylate.

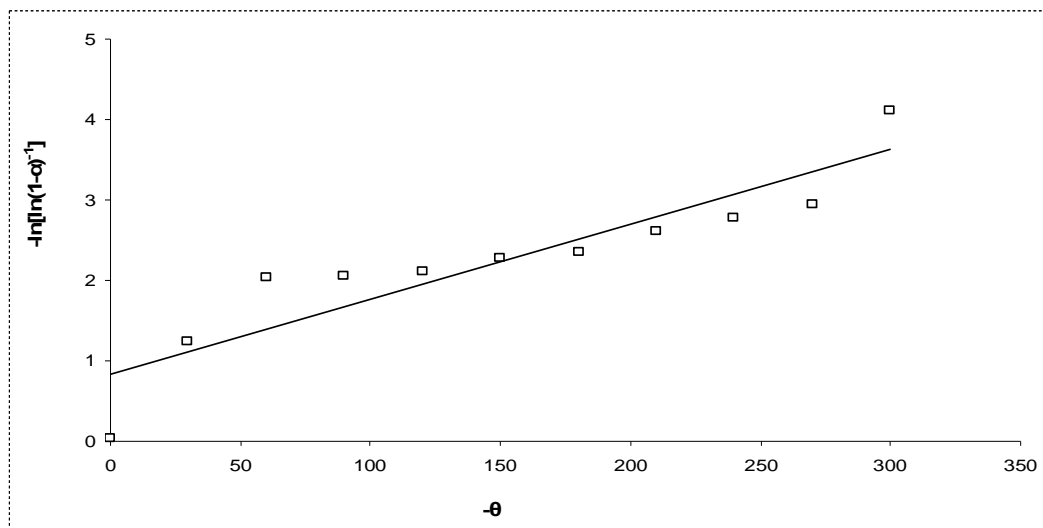


Figure 4: Horowitz-Metzger's plot of Terbium caprylate.

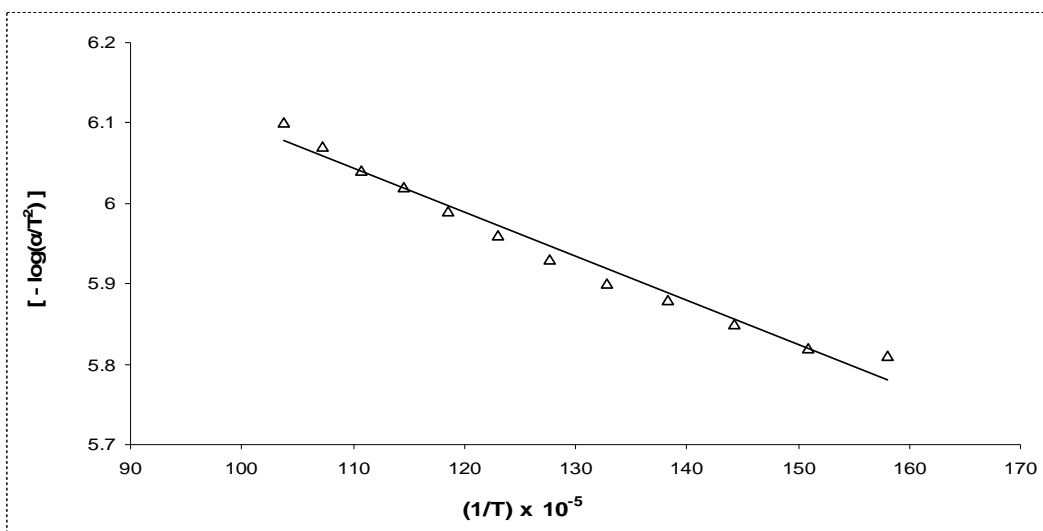


Figure 5: Coats-Redfern's plot of Terbium caprylate.

A broad peak at 3300 cm^{-1} in the spectra of these soaps may have appeared due to the traces of moisture contamination which can be mistaken for hydroxyl bond. In fact the presence of water of crystallization gives rise to a weak bend at $3400\text{-}3100\text{ cm}^{-1}$ which is usually narrow and in such case a weak bend at $1640\text{-}1615\text{ cm}^{-1}$ due to H-O-H bending is also observed¹³.

It is, therefore, concluded that the resonance character of the ionised carboxyl group is retained in these metal soaps and metal to oxygen (M-O) bond is ionic in character.

The absorption maxima observed in the IR spectrum of potassium and terbium caprylate are in good agreement with the results obtained by other workers¹⁴⁻¹⁶.

X-Ray Diffraction Analysis: X-ray diffraction pattern of terbium caprylate has shown numerous peaks over the range of $3\text{-}80^\circ$ diffraction angle. The calculated values of interplanar spacings have been recorded in Table 2. The values of average planar distance i.e. the long spacing for terbium caprylate is 24.55 \AA which is somewhat smaller than the calculated dimensions of anions i.e. caprylate (27.00 \AA), from Pauling's values of atomic radii and bond angles. Therefore, it is concluded that the molecular axes of terbium caprylate is somewhat inclined to the basal planes. The numbers of peaks corresponding to shorter side spacings in the intermediate range of diffraction angles are also observed in the diffraction patterns of terbium soaps. It is, therefore, concluded on the basis of long

and short spacings that metal ions in terbium caprylate is arranged in a parallel plane, i.e. a basal plane equally spaced in the 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 Hattiangdi¹⁷.

Thermogravimetric Analysis: The thermal decomposition of terbium caprylate has been studied both as a function of temperature and time (Table 3). The results of thermogravimetric analysis of terbium caprylate have been well explained by some well known equations. The thermal decomposition results in the formation of ketone, metal oxide, the other products being carbon dioxide and hydrocarbons. The thermogravimetric analysis has shown that the final residues are metal oxides and the weights of the residues are almost equal to the theoretically calculated weights of metal oxide from the molecular formula. Therefore, the decomposition of can be expressed by the equation.



Where; R is C₇H₁₅, The curves of thermogravimetric analysis exhibit three stages for decomposition patterns. The first stage of decomposition was rapid and could not be subjected to kinetic analysis. The second stage represents the major decomposition. Finally, show very small change with further increase in temperature (Figure 2). The thermogravimetric analysis shows that terbium soaps decompose insignificantly up to 110°C, slowly between 110°C and 320°C then very rapidly up to 480°C and finally show very small change with further increase in temperature. For thermal decomposition, Freeman-Carroll's¹⁸ expression can be expressed as,

$$\frac{\log dw/dt}{\log W_r} = \frac{-E}{2.303R} \frac{1}{T} + n \quad (2)$$

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_o - w_t
 dw/dt = rate of weight loss obtained from the loss in weight versus time curves at appropriate times.

The activation energy for thermal decomposition process of terbium soaps has been calculated from the

slope of the plots of Δ {log (dw/dt) / Δ (log w_r)} versus Δ (1/t) / Δ (log W_r) shown in Figures 3. The order of reaction for the thermal decomposition has found almost zero and the values of energy of activation for thermal decomposition was found 7.43 k cal mole⁻¹. Horowitz-Metzger¹⁹ and Coats-Redfern²⁰ equations also provided a method for the evaluation of energy of activation for the thermal decomposition. Horowitz and Metzger equation can be represented as,

$$\ln [\ln(1 - \alpha)^{-1}] = \frac{E}{RT^2} \theta \quad (3)$$

Where; α = Fraction of soap decomposed at time, t,
 E = Energy of activation,
 T_s = Temperature on absolute scale at which the rate of decomposition is maximum, and

$$\theta = T - T_s$$

The plots of ln [ln (1-α)⁻¹] versus θ have been shown in Figure 4 and the value of the activation energy was obtained 6.68 k cal mole⁻¹.

The activation energies for the thermal decomposition have been also evaluated by Coats and Redfern equation (Figure 5). The Coats and Redfern equation for zero order reaction can be expressed as,

$$\log \alpha / T^2 = \frac{\log AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad (4)$$

Where; α = fraction of soap decomposed,
 T = Temperature on absolute scale,
 A = frequency factor,
 a = Rate of heating in °C per minute,
 E = Energy of activation,
 R = Gas constant.

It may be reported²¹ that the plots of -log (α/T²) against (1/T) are straight lines with the slope (-E/2.303R). The values of the energy of activation for the decomposition process calculated from Coats-Redfern equation, 3.29 k cal mole⁻¹ is somewhat lower than the values obtained from Freeman-Carroll's and Horowitz-Metzger's equations.

CONCLUSION: The results obtained leads to the conclusion that the thermal decomposition of terbium caprylate is kinetically of zero order and the value of energy of activation for the decomposition process lies in the range 3.29 -7.43 k cal mole⁻¹ and compound is thermally stable up to 480°C. The IR results confirm that caprylic acid exist in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two acid molecules, whereas terbium caprylate has

ionic in nature. The X-ray analysis revealed that the molecular axes are slightly inclined to the basal plane.

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