Studies on Spectroscopic and Thermal Behavior of Terbium Decanoate

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Abstract

Metal carboxylate was prepared by metathesis of potassium decanoate with terbium nitrate aqueous solution. Thermal study reveals that metal carboxylate breakdown processes are kinetically of zero order, with activation energies ranging from 11 to 13 kcal mol^{-1}. Infrared red spectra of terbium decanoate and decanoic acid indicated that fatty acids have a dimeric structure due to hydrogen bonding between two molecules of carboxylic acid, whereas metal to oxygen bond in terbium decanoate is ionic in nature. X-ray diffraction confirms the double layer structure of terbium decanoate and zig zag chains of fatty acid radical constituent of carboxylate molecule extend straight forward on both side of each basal plane, with the molecular axis slightly inclined to the basal plane.

Key Words: terbium decanoate, IR spectra, X-ray study, thermal behavior.

Introduction

In recent years metal carboxylates have been used in industries and various other fields like emulsifiers, lubricants, water proofing agents, additives, coolants and also in medical devices. However, technological applications of these are mostly based on empirical know-hows. The method of preparation, properties and industrial applications of alkali, alkaline earth and transition metal carboxylates have been thoroughly investigated but the references on rare earth metal carboxylates are scanty [1-9]. The present work has been initiated to investigate the structure of terbium decanoate by infra-red and x-ray diffraction pattern and thermal behavior from thermogravimetric measurement.

Methodology

The fatty acids were purified by distillation under reduced pressure. Terbium (III) decanoate was prepared by metathesis of an aqueous solution of terbium nitrate with a hot solution of the potassium decanoate. The precipitated carboxylate was filtered and washed with distilled water, alcohol and finally with acetone. The metal carboxylate thus obtained was first dried in an air oven and finally under reduced pressure and was further purified by recrystallization [10-14].

The melting point of purified terbium decanoate was 103°C. The carboxylate was analyzed for carbon, hydrogen and metal contents and the results were found to be in agreement with the theoretically calculated values.
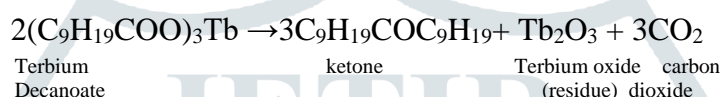
The infrared absorption spectra of decanoic acid and terbium decanoate were determined using a Perkin-Elmer model 842 grating Spectro-photometer in the region 4000-400 cm^{-1} using the potassium bromide disc method. The X-ray diffraction patterns for terbium decanoate was obtained with a Philips PW 1730 diffractometer using Fe-Kα, radiations filtered by a nickel foil over the range of diffraction angles. $2\theta = 3$-$60°$, where θ is the Bragg's angle. The readings of the diffraction angles were made up to $0.001°$ and the wavelength of the radiations was

taken as 1.937 Å. The thermogravimetric analysis of terbium decanoate was carried out at constant rate of heating 10°C/min in nitrogen atmosphere by a thermogravimetric analyzer (Perkin Elmer TG-2), maintaining similar condition throughout the investigation.

Results and Discussion

Thermogravimetric Investigation

The result of thermogravimetric analysis of terbium decanoate show that the final residues is metal oxide and the weight of the residue is in agreement with the theoretically calculated weight of terbium oxide from the molecular formula of the carboxylate. A white substance is found condensed at the cold part of the sample tube surrounding the samples and it is identified as ketone (M.P. 14.6°C). The thermal decomposition of terbium decanoate can be expressed as:

$$2(C_9H_{19}COO)_3Tb \rightarrow 3C_9H_{19}COC_9H_{19} + Tb_2O_3 + 3CO_2$$

| Terbium | ketone | Terbium oxide | carbon |
| Decanoate | | (residue) | dioxide |

The thermogravimetric data were used to calculate the energy of activation and to find the order of reaction for the decomposition of terbium decanoate using equations of Freeman- Carroll [15] and Coats-Redfern [16]. Results of the thermogravimetric analysis shows that the decomposition process takes place in three steps. The first step of decomposition could not be considered for kinetic analysis as it is very fast. The second step represents the major decomposition process. The third step shows 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 rate expression

$$(\Delta[log\,(dw/dt)])/(\Delta[log\,Wr]) \quad v/s \quad (\Delta[1/T])/(\Delta[logWr].$$

The plots of [log (dw/dt) / log Wr] vs [(- 1/T) / log Wr] have been found to be linear with zero intercept and value of activation energy from slope (-E / 2.303R) of the plot is calculated to be 11.0 K Cal mol^{-1}.

TABLE 1: ENERGY OF ACTIVATION ($k\ cal.mol^{-1}$) FOR THE DECOMPOSITION OF TERBIUM DECANOATE BY USING VARIOUS EQUATIONS

EQUATIONS	I STEP
Freeman and Carroll	11.0
Coats and Redfern	13.7

The energy of activation for the decomposition for carboxylate also calculated by using the equations of and of Coats and Redfern [16]. The values of energy of activation calculated from these equations are summarized in Table-1. It is concluded that the decomposition reaction of terbium decanoate is kinetically of zero order and the activation energy for the process lies in the range of 11.0-13.7 kcal mol^{-1}.

Spectroscopic Investigations

IR spectral study

The infrared spectral data of terbium decanoate are listed in Table-2 and compared with that of corresponding fatty acid. The decanoic acid display very broad intense peak due to -OH stretching near 2660 cm^{-1}. The appearance of the absorption band near 1700 cm^{-1} in the spectrum of fatty acid indicates that the fatty acids exist as dimmer. One of the characteristic bands of dimeric carboxylic acid results from the out-of-plane bending -OH group appearing near 930cm^{-1} The absorption maxima near 690 cm^{-1} and 550 cm^{-1} in the spectrum of fatty acid are associated with carboxyl group bending and wagging modes [17].

In terbium decanoate, two absorption bands are observed near 1470 cm^{-1} and 1550 cm^{-1} instead of one strong absorption band corresponding to carboxyl group observed near 1700 cm^{-1} in the spectrum of fatty acid. These bands correspond to symmetric and antisymmetric stretching vibrations of the carboxylate ion [18]. The complete disappearance of the carboxyl frequency in the spectrum of terbium decanoate indicates that there is a complete resonance in the two C-O bonds of the carboxyl group of the decanoate molecule. The metal-to-oxygen bond ionic in character. The absorption hands observed near 2650, 930, 690 and 530 cm^{-1}, which are associated with the carboxyl group of fatty acid, disappear completely in the spectrum of terbium carboxylate.

The results confirm that the decanoic acid exist with dimeric structure through hydrogen bonding between two molecules of fatty acid whereas metal to oxygen bonds in terbium decanoate is ionic in character but bond is not purely ionic.

TABLE 2: INFRARED ABSORPTION SPECTRAL FREQUENCIES (cm^{-1})

| S.NO.	ASSIGNMENT	DECANOIC ACID	TERBIUM DECANOATE
1.	CH$_3$, C-H asymmetrical stretching	2960 W	2960 M
2.	CH$_2$, C-H asymmetrical stretching	2920 M	2920 M
3.	CH$_2$, C-H symmetrical stretching	2850 S	2850 S
4.	OH, stretching	2660 S	-
5.	C=O stretching	1700 S	-
6.	COO$^-$, C-O asymmetrical stretching	-	1550 S
7.	COO$^-$, C-O symmetrical stretching	-	1470 M
8.	C-O, Stretching, OH in-plane deformation	1440 M	-
9.	CH$_2$ (adjacent to COOH group) deformation	1410 S	1420 W
10.	CH$_3$, symmetrical deformation	1350 W	1330 W
11.	Progressive bands (CH$_2$ twisting and wagging)	1270-1220 W	1270-1210 W
12.	CH$_3$ rocking	1110 VS	1110 W
13.	OH, out-of-plane deformation	930 S	-
14.	CH$_2$, rocking	720 S	720 S
15.	COOH, bending mode	690 M	-
16.	COOH, wagging mode	530M	-
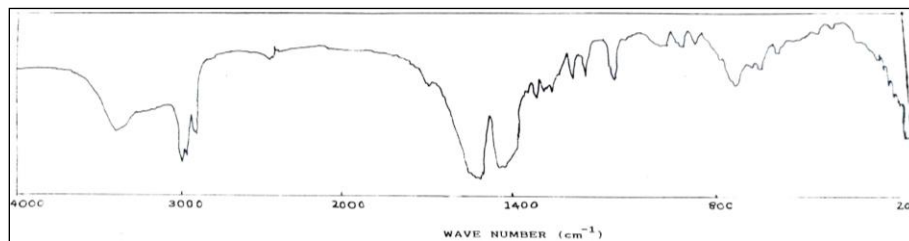
Fig 1. Infrared Spectrum of Terbium Decanoate

X-Ray Diffraction Analysis

Since, the crystals of metal carboxylate do not grow to give large crystals sufficient for a detailed single crystal examination, X-ray diffraction pattern of terbium decanoate was investigated to characterize its structure.

The intensities of diffracted X-rays as a function of diffraction angle, 2θ, for terbium decanoate are recorded with the help of an X-ray spectrophotometer and the recorded curves were reproduced over the range of 3-63°. The interplanar spacings, d, were calculated from the position of the intense peaks using Bragg's relationship, $n\lambda = 2d \sin\theta$, were λ is the wavelength of radiation. The calculated spacings together with the relative intensities with respect to the most intense peak are given in Table-2.

A large number of peaks, arising from the diffraction of X rays by planes of metal ions (known as basal planes), were observed over the range of 3° to 60° of the diffraction angles in the diffraction patterns of terbium decanoate. The appearance of the diffraction up to 12th order confirms good crystallinity for terbium decanoate. The interplanar spacing calculated for 4th, 5th, 6th, 7th and 8th,9th and 12th order diffraction for terbium decanoate are 29.132. 29.175, 28.941, 28.609, 28.280 and 28.035 and 29.580 Å, respectively. The average planar distance i.e., the long spacing for terbium decanoate is 28.02Å(Table-3).

TABLE 3: X-RAY DIFFRACTION INVESTIGATION OF TERBIUM DECANOATE

S.No.	2 θ	θ	Sin θ	D	d	n
1.	15.261	7.630	0.133	7.283	29.132	4
2.	19.191	9.595	0.166	5.835	29.175	5
3.	23.220	11.610	0.201	4.819	28.914	6
4.	27.340	13.715	0.237	4.087	28.609	7
5.	31.763	15.881	0.274	3.535	28.280	8
6.	36.763	18.128	0.311	3.115	28.035	9
7.	46.291	23.145	0.393	2.465	29.580	12

The result is in agreement with the calculated values of long spacing for decanoate (32.0Å) ion. The value of the long spacing for the carboxylate is approximately equal to double the length of the fatty acid radical of the carboxylate molecule. It is therefore suggested that the zig-zag chains of the fatty acid radicals extend straight forward on both sides of each basal plane.
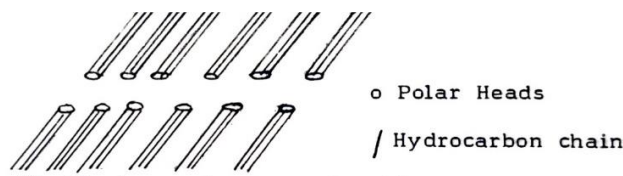
o Polar Heads

/ Hydrocarbon chain

Fig 2. Double Layer Structure of Carboxylate

The observed value of the long spacing for terbium decanoate (28.02Å) is smaller than the calculated dimension of decanoate (32.0Å) ion from Pauling's values of atomic radius and bond angle and this suggests that the molecular axis of terbium decanoate is somewhat inclined to the basal plane. The metal ions fit into spaces between oxygen atoms of the ionized carboxyl group without putting great strain on the bonds.

A number of diffraction peaks in the intermediate range of the diffraction angles were also observed in the diffraction patterns of terbium decanoate, these being attributed to the diffraction of X-rays by planes of atoms of much smaller separation than the basal planes. The calculated spacings from these peaks correspond to the shorter side spacings i.e., the lateral distances between one carboxylate molecule and the next in a layer. It is observed that the long spacing peaks are fairy intense while the short spacing peaks are relatively weak. On the basis of long and short spacings, it is suggested that the metal ion in terbium decanoate are arranged in a parallel plane i.e., a basal plane equally spaced in the carboxylate crystal with fully extended zig-zag chains of fatty acid radicals on both sides of each basal plane and the terbium decanoate have a double layer structure as proposed by Vold and Hattiangdi [19].

References

[1]   Verma R.P. and Jindal R., Tenside Detergents,20(4),193(1983).

[2]   Mehrotra K.N., Gahlaut A.S. and Sharma Meera, J. Colloid Interface Sci.,110,120(1987).

[3]   Skellon J.H. and Spence J.W., J. Appl. Chem., London,3,10 (1953).

[4]   Solanki A.K., and Bhandari A.M., Tenside Detergents,18,34, (1981).

[5]   Gonen M., Ozturk S., Balkose S., Okur S. and Ulku S., Ind. Eng. Chem. Res.,49,4,1732,   (2010).

[6]   Zhao Yue, Grivel Jean Claud,Suarez Guevara M.J. and Watenphul A.,Thermochimica Acta,612(2015).

[7]   Shukla R.K. and Mishra V., Asian J. Cuem.,15,1703(2003).

[8]   Nene P.N., Adv Nat. Appl. Sci., 2(2), 73, (2008).

[9]   Jongen L., Binnemans K., Hinz D. and Meyer G., Liquid Crystals 28,1727(2001).

[10]   Mehrotra R.C., Wiss Z. Friedrich Schiller Univ., Jena Math Naturewiss., 14, 171, (1965).

[11]   Mehrotra K. N. and Sharma N., Polish J. Chem.,70,1236, (1996).

[12]   Sharma G. J. Indian Chem Soc.,84,144, (2007).

[13]   Kishor K. and Upadhyaya S.K., Tenside Surfactants Detergents, 47,184, (2010).

[14]   Sharma V., Sharma M. and Gautam D., Tenside Surfactants Detergents,47(4)254(2010).

[15]   Freeman E. S. and Carroll B., J.Phys. Chem., 62,394 (1958).

[16]   Coats W. and Redfern J.P., Nature 68,201 (1964).

[17]   Silverstein R.M., Bassler G. C. and Morrill T.C., Spectroscopic Identification of Organic Compounds, John Willy & Sons, New York, p.107.

[18]   Duval C., Lecomte J. and Douville F., Ann. Phys.,17,5, (1942).

[19]   Vold R.D. and Hattiangdi G.S., Ind. Eng. Chem.,41,2311(1