

Structural Analysis of Terbium Stearate in Solid State

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Abstract

Infrared red spectra of terbium stearate confirmed that stearic acid has a dimeric structure due to hydrogen bonding between two molecules of stearic acid, whereas metal to oxygen bond in terbium stearate have an ionic character but are not purely ionic. The double layer structure of terbium stearate is verified by X-ray diffraction study, with the molecular axis slightly inclined to the basal plane. In thermal analysis, the decomposition reaction of terbium stearate is found to be kinetically of zero order, with activation energies ranging from 14 to 16 kcal mol⁻¹ on the basis of different equations.

Key Words: terbium stearate, IR spectra, X-ray studies, thermal analysis.

I. Introduction

Despite the fact that there has been a lot of research on alkali, alkaline earth, and transition metal carboxylates, there are only a few references available on rare earth metal carboxylates, which have a lot of applications in industry. The characteristics and structure of metal carboxylates are greatly affected by method and condition adopted for synthesis, so metal carboxylates studies are necessary to understand their behavior in different conditions [1-6]. The objective of this study was to use infrared, X-ray, and thermal measurements to investigate the properties and structure of terbium stearate in the solid state.

II. Experimental Details

The fatty acid was purified by distillation under reduced pressure. Terbium (III) stearate was prepared by metathesis of an aqueous solution of terbium nitrate with a hot solution of the potassium stearate. The precipitated carboxylate was filtered and washed with distilled water, alcohol and finally with acetone. The metal stearate thus obtained was first dried in an air oven and finally under reduced pressure and were further purified by recrystallization [7-9].

The melting point of purified terbium stearate was 122°C. The carboxylate was analyzed for carbon, hydrogen and metal content and the results were found to be in agreement with the theoretically calculated values.

The infrared absorption spectra of stearic acid and the terbium stearate were determined using a Perkin-Elmer model 577 grating Spectro-photometer in the region 4000-400 cm⁻¹ using the potassium bromide disc method. The X-ray diffraction patterns for terbium stearate was obtained with a Philips PW 1730 diffractometer using Fe-K α , radiations filtered by a nickel foil over the range of diffraction angles. $2\theta = 3-60^\circ$, where α 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 stearate was carried out at constant rate of heating in a thermobalance (Mettler TG50, U.S.A.) by maintaining similar conditions throughout the investigations.

III. Results and Discussion

Infrared absorption spectra

The infrared spectral data of terbium stearate is listed in Table-1 and compared with that of stearic acid. The stearic acid display very broad intense peak due to -OH stretching near 2650 cm⁻¹. The appearance of the absorption band near 1700 cm⁻¹ in the spectra of stearic acids indicates that it exists as dimer. One of the characteristic bands of dimeric carboxylic acid results from the out-of-plane bending -OH group appearing near 950 cm⁻¹. The absorption maxima near 680 cm⁻¹ and 550 cm⁻¹ in the spectra of stearic acid are associated with carboxyl group bending and wagging modes [10].

In terbium (III) stearate, 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 spectra of stearic acid. These bands correspond to symmetric and antisymmetric stretching vibrations of the stearate ion as pointed out by Duval, Lecomte and Douville [11]. The complete disappearance of the carboxyl frequency in the spectra of terbium stearate indicates that there is a complete resonance in the two C-O bonds of the carboxyl group of the stearate molecules. The metal-to oxygen bond is not purely ionic but is partially covalent in

character. The band observed at 440 cm^{-1} in the spectra of terbium stearate corresponds to the Tb-O bond. The absorption bands observed near 2650 , 950 , 680 and 550 cm^{-1} , which are associated with the carboxyl group of stearic acids, disappear completely in the spectra of terbium stearate.

The results confirm that the stearic acid in solid state exist with dimeric structure through hydrogen bonding between two molecules of stearic acid whereas metal to oxygen bonds in terbium stearate are ionic in character but bonds are not purely ionic.

TABLE 1: INFRARED ABSORPTION SPECTRAL FREQUENCIES (cm^{-1}) WITH THEIR ASSIGNMENTS

S.NO.	ASSIGNMENT	STEARIC ACID	TERBIUM STEARATE
1.	CH_3 , C-H asymmetrical stretching	2960 W	2960 W
2.	CH_2 , C-H asymmetrical stretching	2920VS	2920 VS
3.	CH_2 , C-H symmetrical stretching	2850 S	2860 S
4.	OH, stretching	2650 W	-
5.	C=O stretching	1700 VS	-
6.	COO^- , C-O asymmetrical stretching	-	1550 S
7.	COO^- , C-O symmetrical stretching	-	1470 S
8.	C-O, Stretching, OH in-plane deformation	1420 S	-
9.	CH_2 (adjacent to COOH group) deformation	1375 M	1400M
10.	CH_3 , symmetrical deformation	1350 W	1340 W
11.	Progressive bands (CH_2 twisting and wagging)	1230-1170 W	1310-1200 W
12.	CH_3 rocking	1110 W	1120 W
13.	OH, out-of-plane deformation	950 W	-
14.	CH_2 , rocking	730 S	720 S
15.	COOH , bending mode	680 MS	-
16.	COOH , wagging mode	550 MS	-
17.	Tb-O, bond	-	440W

X-Ray Analysis

Generally, the crystals of terbium stearate do not grow to give large crystals sufficient for a detailed single crystal examination so that X-ray diffraction patterns of terbium stearate was investigated to characterize its structure.

The intensities of diffracted X-rays as a function of diffraction angle, 2θ , for terbium stearate is 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, $n\lambda = 2d \sin\theta$, where λ is the wavelength of radiation. The calculated spacings together with the relative intensities with respect to the most intense peak is given in Table-2 for terbium stearate.

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 stearate. The appearance of the diffraction up to 23rd in case of terbium stearate confirms good crystallinity.

The interplanar spacings calculated for 2nd, 4th, 6th, 11th, 12th, 14th, 18th and 23rd order of diffractions for terbium stearate are 49.049 , 49.048 , 48.840 , 49.555 , 49.356 , 49.490 , 48.762 , and 48.645Å , respectively and the average planar distance is 49.10Å (Table-3). The results are in agreement with the calculated values of long spacings for stearate (52.0Å) ions. The values of the long spacings for terbium stearate are approximately equal to double the length of the stearic acid radical of the stearate molecule. It is therefore suggested that the zig-zag chains of the stearic acid radicals extend straight forward on both sides of each basal plane.

The observed values of the long spacings for terbium stearate (49.10Å) is smaller than the calculated dimensions of stearate (52.0Å) from Pauling's values of atomic radii and bond angle and this suggests that the molecular axis of terbium stearate are 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.

TABLE 2: X-RAY DIFFRACTION ANALYSIS OF STEARATE

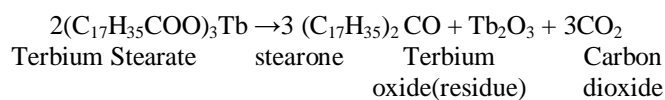
S.NO.	2 θ	θ	Sin θ	D	d	n
1.	4.527	2.263	0.039	24.503	49.049	2
2.	9.078	4.539	0.079	12.262	49.048	4
3.	13.678	6.839	0.119	8.140	48.840	6
4.	24.857	12.428	0.215	4.505	49.555	11
5.	27.229	13.614	0.235	4.113	49.356	12
6.	31.828	15.914	0.274	3.353	49.490	14
7.	41.920	20.960	0.385	2.709	48.762	18
8.	54.491	27.245	0.485	2.115	48.645	23

Average value of $d = 49.10 \text{ \AA}$

A number of diffraction peaks in the intermediate range of the diffraction angles were also observed in the diffraction patterns of terbium stearate, 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 fairly intense while the short spacing peaks are relatively weak. On the basis of long and short spacings, it is suggested that the metal ions in terbium stearate 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 stearate have a double layer structure as proposed by Vold and Hattiangdi [12] for other metal carboxylates.

Thermal Analysis

The result of thermogravimetric analysis of terbium stearate show that the final residue 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 stearone (M.P. 88.4°C). The thermal decomposition of terbium stearate can be expressed as:



The thermogravimetric data was used to calculate the energy of activation and to find the order of reaction for the decomposition of terbium stearate using equations of Freeman and Carroll, Horowitz and Metzger and Coats and Redfern. It is concluded that the decomposition of terbium stearate takes place in two steps. The second step of decomposition of terbium stearate is a zero-order reaction and the values of energy of activation obtained from Freeman Carroll's equation [13] for stearate is 14.8 kcal mol, respectively. The values were obtained from the slope of the plot

$$\frac{\Delta[\log(dw/dt)]}{\Delta[\log Wr]} \text{ against } \frac{\Delta[1/T]}{\Delta[\log Wr]}$$

TABLE 3: ENERGY OF ACTIVATION (k cal.mol^{-1}) FOR THE DECOMPOSITION OF TERBIUM STEARATE BY USING VARIOUS EQUATIONS

EQUATIONS	I STEP	II STEP
Freeman and Carroll	14.8	6.2
Horowitz and Metzger	-	3.0
Coats and Redfern	16.8	3.6

The energy of activation for the decomposition also calculated by using the equations of Horowitz and Metzger [14] and of Coats and Redfern [15]. The values of energy of activation calculated from these equations are summarized in Table-3. It is concluded that the decomposition reaction of terbium stearate is kinetically of zero order and the activation energy for the process lies in the range of 14 to 16 kcal mol⁻¹ for first step and 3 to 6.2 kcal mol⁻¹ for second step.

References

- [1]. Chatfield H.W., Paint Manuf., 6,112, (1936).
- [2]. Skellon J.H. and Spence J.W., J. Appl. Chem. London,3,10, (1953).
- [3]. Skellon J.H. and Andrews K.E., J. Appl. Chem., London,5,245, (1955).
- [4]. Solanki A.K., and Bhandari A.M., Tenside Detergents,18,34, (1984).
- [5]. Gonen M., Ozturk S., Balkose S., Okur S. and Ulku S., Ind. Eng. Chem. Res.,49,4,1732, (2010).
- [6]. Nene P.N., Adv Nat. Appl. Sci., 2(2), 73, (2008).

- [7]. Mehrotra R.C., *Wiss Z. Friedrich Schiller Univ., Jena Math Naturewiss.*, 14, 171, (1965).
- [8]. Mehrotra K. N. and Sharma N., *Polish J. Chem.*,70,1236, (1996).
- [9]. Sharma G. J. *Indian Chem Soc.*,84,144, (2007).
- [10]. Kishor K. and Upadhyaya S.K., *Tenside Surfactants Detergents*, 47,184, (2010).
- [11]. Mehrotra K. N., Chauhan M. and Shukla R. K., *Tenside Surf. Det.*, 34(2), 124 (1997).
- [12]. Silverstein R.M., Bassler G. C. and Morrill T.C., *Spectroscopic Identification of Organic Compounds*, John Willy & Sons, New York, p.107.
- [13]. Duval C., Lecomte J. and Douville F., *Ann. Phys.*,17,5, (1942).
- [14]. Vold R.D. and Hattiangdi G.S., *Ind. Eng. Chem.*,41,2311(1949).
- [15]. Freeman E. S. and Carroll B., *J.Phys. Chem.*, 62,394 (1958).
- [16]. Horowitz H.H. and Metzger M., *Anal. Chem.*,35, 1464 (1963).
- [17]. Coats W. and Redfern J.P., *Nature* 68,201 (1964).