Spectral and Thermal Studies on Dysprosium Carboxylates

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ABSTRACT

In the present manuscript, Dysprosium carboxylates of Carboxylic Acids (Lauric, Myristic and Palmitic) have been prepared and characterized by IR, X-ray diffraction and Thermogravimetric analysis (TGA) measurements.

The IR spectra result shows that the fatty acid exist in dimeric state through hydrogen bonding and carboxylates possess partial ionic character. The X-ray diffraction measurements have been used to calculate the long spacing and the results confirmed the single layer structure of Dysprosium carboxylates. The decomposition reaction was found kinetically of zero order and the values of energy of activation for the decomposition process have been found in the range of 15.00 – 28.11 k.cal mol^{-1}.

INTRODUCTION

Dysprosium Carboxylates are material which serve a wide range of industrial applications as water proofing agent, emulsifier, hardner, lubricant stabilizer, plasticizer, antioxidant, fungicide and germicide, antiseptic; Textile, Paper and Pharmaceutical industries.

The studies on the nature and structure of dysprosium carboxylates are of great importance for their uses in industries and for explaining their characterization under different conditions. Many metal carboxylates have been prepared by fusion and metathesis methods and their, X-ray, Thermal spectroscopic and acoustic behaviour were investigated by several workers(1-13).

In this manuscript, we report on the structural and Thermal behaviour of dysprosium carboxylates. The structure of the compound have been studied by IR and X-ray diffraction analysis and their thermal behaviour have also been investigated by Thermogravimetric analysis.

EXPERIMENTAL

Preparation of carboxylates :- The chemical used for present research were of AR/GR grade. Dysprosium carboxylates (Laurate, Myristate and Palmitate) have been prepared by direct metathesis of the Corresponding Potassium carboxylate with slight excess of solutions of Dysprosium Nitrate at 50 – 55ºC under vigorous stirring. The Precipitated carboxylates were filtered and washed with distilled water and acetone to remove the excess of metal ions and unreacted potassium carboxylates.

The carboxylates were purified by recrystallisation with a mixture of benzene and methanol and dried under reduced pressure. The purity of these carboxylates were confirmed by determination of their melting point.

Measurements :- The IR spectra were obtained with Perkin Elmer "577 Model" Grating spectrophotometer in the region of 4000 – 200 cm^{-1} using potassium bromide disc method.

The XRD powder patterns of Dysprosium carboxylates were measured with rich siemens "2002 D" Iso debyeflex Diffractometer using Cu-Lα radiations filtered by a nickel foil over the range of diffraction angle $2\theta = 4^o$ to 40^o (where θ is Bragg's angle).

The X-Ray Diffraction curved were recorded under the applied voltage of 45 KV using scanning speed 1° per minute and chart speed of 1 cm per minute. The wave length of the radiation has been taken as 1.542A°.

The Thermogravimetric analysis of Dysprosium carboxylates have been carried out by perkin-Elmer Thermogravimetric analyzer 'TG-S-2' at constant heating rate (10° Per minute) in nitrogen atmosphere and maintaining similar conditions through out the investigations .

RESULTS AND DISCUSSION

The spectra of Dysprosium carboxylates (Laurate, Myristate and Palmitate) have been recorded and compared with the results of the corresponding fatty acids (Table-1)

The absorption bands observed near 2660, 1680 – 1700, 1404-1413, 930-950, 690 and 550 cm^{-1} in the spectra of fatty acids were associated with the localised COOH (carboxyl group) of the acid molecules in the dimeric state and confirmed the existance of hydrogen bonding between two molecule of carboxylic acids.

The absorption bands observed near 2640-2660, 1680 – 1700 and 930-350 cm^{-1} corresponding to the –OH group in the spectra of carboxylic acids have disappeared in the spectra of corresponding potassium and Dysprosium carboxylates. The obsorption maxima corresponding to 690 and 550 cm^{-1} in the spectra of carboxylic acids have been assigned to the bending and wagging modes of the vibrations of carbonyl group of the carboxylic molecule, respectively. These frequencies are not observed in the spectra of potassium and Dysprosium carboxylates. The complete disappearance of the carbonyl frequency in the region of 1680-1700, cm^{-1} and appearance of absorption bands of carboxyl group corresponding to the symmetrical and asymmetrical vibrations of carboxyl ion near 1410-1450 and 1550-1600 respectively in the spectra of potassium and dysprosium carboxylates indicate that there in a complete resonance in the two C–O bands of carboxyl group of the carboxylate molecules and the two bonds become identical with their force constants assuming an intermediate values between those of normal, double and single bonds.

The result confirms that the fatty acid exist with dimeric structure through intermolecular hydrogen bonding between carboxyl groups of two acid molecules, whereas potassium, dysprosium carboxylates are ionic in nature and the metal – to –oxygen bond the carboxylate has an ionic character.

The IR spectra of dysprosium carboxylates donot show any absorption maxima in the region of 3500-3300 cm^{-1} which confirms the absence of any co-ordinated water molecule in these carboxylates.

X-RAY DIFFRACTION ANALYSIS

The X-ray diffraction pattern of Dysprosium carboxylates (Laurate, Myristate and Palmitate) have been investigated in order to characterize their structure and the intensities of diffracted X-ray as a function of diffraction angle, 2θ are measured in the range of 4° to 40° with the help of X-ray spectrophotometer and the calculated interplanar spacing together with the relative intermediate are recorded (table 2 – 4). Bragg's equation has been used to calculate the interplaner spacing, d from position of intense peaks.

$$n\lambda = 2\ d\ \mathrm{sins}\theta$$

Where λ = wave length of radiation

The appearance of diffraction for laurate, myristate and palmitate upto 14th, 15th and 18th for Dysprosium suggested good crystallinity for these carboxylates.

The average planer distance i.e. long spacing for dysprosium laurate, myristate and palmitate are 36.685, 41.599 and 46.138 A° respectively. It has been observed that the difference in long spacing of Dysprosium carboxylates (laurate and myristate : 4.919, myristate and palmitate : 4.539 A°). A correspond to double the length of methylene (-CH_2) groups in the fatty acid radical constituent of these carboxylate molecules. It is, therefore, concluded that zig-zag chain of fatty acid radical constituent of the molecules extend straight forward on both sides of each basal plane. The values of long spacings for Dysprosium carboxylates are some what smaller than the calculated diamensions of anions (laurate : 37.0, myristate : 42.0 and Palmitate : 47.0) from the Pauling's values of atomic radii and bond angles. It is, therefore, concluded that the molecular axes of these carboxylate molecules are some what inclined to the basal p lanes. The metal ions Dy^{+3} fit into spaces between oxygen atoms of the ionised carboxyl groups without a large strain of the bond.

A number of diffraction peaks in the intermediate range are also observed in the diffraction patterns of Dysprosium carboxylates and are attributed to the diffraction of X-ray by planes of atoms much smaller separation than the basal planes. The calculated spacing for these peaks corresponds to the smaller size spacing, i.e., the lateral distances between one molecule and the next in a layer. It is observed that long spacing are fairly intense while the short spacing peaks are relatively weak.

On the basis of long and short spacing, it is suggested that the metal ions in metal carboxylates are arranged in parallel plane, i.e., a basal plane equally spaced in the crystal of carboxylates with fully extended zig-zag chains of the fatty acid radical on both sides of each basal plane and the carboxylates possess single layer structure with molecular axes somewhat inclined to the basal planes.

THERMOGRAVIMETRIC ANALYSIS

The results of thermogravimetric analysis of Dysprosium carboxylates (Laurate, Myristate and Palmitate) are recorded in (Table 5-7).

On thermal decomposition the final residue of Dysprosium oxide. This conclusion is in harmony with theoretically calculated weight of Dysprosium Oxide from the molecular formula of the corresponding carboxylates. Some white crystalline powder condensed at the cold part of the sample tube and it is identified as laurone (69.3°C) and Myristone (78°C) and palmitone (82.2°C) for (Laurate, Myristate and palmitate) respectively.

The thermal decomposition of Dysprosium carboxylates can be expressed as–

$2(RCOO)_3M$	→	3R.CO.R.	+	M_2O_3	+	$3CO_2$
Metal Carboxylate		Ketone		Metal Oxide		Carbon Dioxide

Where M is Dysprosium, R is $C_{11}H_{23}$, $C_{13}H_{27}$ and $C_{15}H_{31}$ for Laurate, Myristate and Palmitate respectively.

The plots of the loss in weight, w of the carboxylates vs time, t (fig.2) for Dy. carboxylate have been explained in terms of equations proposed by Freeman- Carroll's[14] and Coats – Redfern's[15].

Freeman and Carroll's rate expression for the thermal decomposition of carboxylates where the carboxylates disappears continuously with time and temperature and one product is gaseous may be expressed as –

$$\frac{\Delta\left[\log\left(dw/dt\right)\right]}{\Delta\left(\log Wr\right)} = \frac{-E}{2.303R} \quad \frac{\Delta\left(1/T\right)}{\Delta\left(\log Wr\right)} + n$$

Where E = Energy of activation, n = Order of decomposition reaction, T = Temperature on absolute scale. R = Gas constant, W = Difference between the total loss in weight and the loss in weight at time, t i.e. $w_0 - w_t$ and (dw/dt) = value of rate of weight loss obtained from the loss in weight vs time curves at appropriate times.

The plots of $\Delta\log$ [(dw/dt)] / ($\Delta\log w_r$) against Δ(1/T/Δlog Wr) (Fig. 3) have been found to the linear with an intercept equal to Zero. It is, therefore, concluded that the reaction of thermal decomposition of Dysprosium carboxylates zero order and the values of energy of activation lie between 15.00 + 24.00 k. cal. mol^{-1} (Table 8)

The values of energy of activation for the thermal decomposition of Dysprosium carboxylate have also been calculated by using Coats and Redfern's equation, which may be written as –

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

Where α = Fraction of the Carboxylate decomposed, T = Temperature on absolute scale, R = Gas constant. A = Frequency factor, a = Rate of heating in ºC per minutes, E= Energy of activation, and n = Order of the reaction,

The equation for zero order reaction can be written as :

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

The Plot of log (α /T^2) against 1/T should be a straight line with its slope equal to [-E/2.303R]. The values of the energy of activation obtained from the plots (fig. 4) lie, between 18.75 – 28.11 kcal mol^{-1} and are in agreement with the values obtained from Freeman-Carroll's equation.

It is concluded that the decomposition reaction of Dysprosium carboxylates is kinetically of zero order and the energy of activation for the process lie in the range of 15.00 to 28.11 k.cal.mol^{-1}.

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Table 1

Infrared Absorption frequencies (cm^{-1}) together with their assignments

S.No.	Absorption	Dysprosium		
		Laurate	Myristate	Palmitate
1.	CH_3, C-H asymmetrical stretching	2954	2950	2956
2.	CH_2, C–H asymmetrical stretching	2918	2919	2916
3.	CH_2, C–H symmetrical stretching	2848	2850	2856
4.	OH, stretching	—	—	—
5.	C=O stretching	—	—	—
6.	COO^-, C–O asymmetrical stretching	1560	1547	1541
7.	CH_2 deformation	1463	1465	1466
8.	COO^-, C–O symmetrical stretching	1420	1412	1418
9.	CH_2, (adjacent to COOH group) deformation	—	—	—
10.	CH_3, asymmetrical deformation	1330	1339	1351
11.	Progressive bonds (CH_2 twisting and wagging)	1310-1193	1315-1192	1316-1198
12.	CH_3, rocking	1111	1114	1108
13.	OH, out of plane deformation	—	—	—
14.	CH_2, rocking	723	720	722
15.	COOH bending Mode	—	—	—
16.	COOH wagging Mode	—	—	—
17.	M—O bond	428	431	440

Table 2

X-ray diffraction Analysis of Dysprosium Laurate

S.No.	2θ	D	d(A°)	n	I/I_0(%)
1.	5.301	16.673	33.346	2	86.66
2.	7.956	11.113	33.339	3	100.00
3.	13.282	6.666	39.996	6	9.69
4	19.433	4.578	36.624	8	18.45
5.	21.959	4.048	36.432	9	18.91
6.	24.029	3.704	37.040	10	6.27
7.	26.821	3.324	36.564	11	7.91
8.	29.024	3.077	36.924	12	2.52
9.	32.074	2.906	37.778	13	6.48
10.	32.274	2.772	38.808	14	5.38

Average value of d = 36.685 A°

Table 3

X-ray diffraction Analysis of Dysprosium myristate

S.No.	2θ	D	d(A°)	n	I/I_0(%)
1.	6.568	13.992	41.976	3	10.63
2.	8.619	10.305	41.220	4	4.33
3.	11.692	8.138	40.690	5	6.80
4	12.982	6.995	41.970	6	10.52
5.	14.423	5.982	41.874	7	9.62
6.	20.023	4.732	42.588	9	2.75
7.	23.013	4.302	43.020	10	5.95
8.	26.022	3.391	40.692	12	6.38
9.	27.813	3.148	40.924	13	2.64
10.	31.024	2.983	41.762	14	1.90
11.	32.184	2.725	40.875	15	0.96

Average value of d = 41.599 (A°)

Table-4

X-ray diffraction Analysis of Dysprosium Palmitate

S.No.	2 θ	D	d(A°)	n	I/I$_0$(%)
1.	4.642	22.584	46.168	2	6.84
2.	10.972	9.263	46.315	5	18.83
3.	21.942	6.178	49.424	8	9.98
4	22.342	4.268	46.480	11	7.92
5.	23.606	4.132	46.584	12	16.32
6.	25.982	3.541	46.033	13	19.12
7.	27.642	3.092	43.288	14	10.13
8.	29.982	3.022	45.330	15	4.50
9.	32.040	2.860	45.760	16	2.65
10.	33.680	2.684	45.628	17	1.73
11.	36.022	2.584	46.512	18	0.84

Average value of d = 46.138 (A°)

Table-5

Thermogravimetric Data of Dysprosium laurate

S.No.	Temperature T (K)	Time (t) (Minute)	Weight of Carboxylate decomposed $w \times 10^3$ (gms)	$dw/dt \times 10^6$	$Wr \times 10^3$	$\frac{\Delta[\log(dw/dt)]}{\Delta(\log Wr)}$	α	$-\log(\alpha/T^2)$
1.	279	3.2	—	—	1.1860	—	—	—
2.	328	9.0	0.0103	1.1444	1.1757	2.0279	0.010	7.0274
3.	371	17.0	0.0223	1.3117	1.1637	2.0047	0.022	6.8002
4.	425	22.0	0.0252	1.1455	1.1608	2.0240	0.025	6.866
5.	464	26.0	0.0568	2.1846	1.129	1.9206	0.056	6.589
6.	495	30.0	0.0838	2.7933	1.1020	1.8776	0.082	6.476
7.	521	36.0	0.1132	3.1444	1.0728	1.8531	0.111	6.389
8.	545	41.0	0.1427	3.4805	1.0433	1.8306	0.139	6.329
9.	569	50.0	0.2957	5.9140	0.8903	1.7138	0.289	6.049
10.	574	54.0	0.3215	5.9537	0.8645	1.7059	0.314	6.0210
11.	589	59.0	0.3328	5.6406	0.8532	1.7110	0.325	6.0279
12.	619	70.0	0.4032	5.7600	0.7828	1.6868	0.394	5.9878
13.	643	74.0	0.5628	7.6054	0.6232	1.5968	0.550	5.8761
14.	656	76.0	0.7203	9.4776	0.4657	1.5098	0.704	5.7864
15.	698	77.0	0.8625	11.2012	0.3235	1.4188	0.843	5.7627
16.	733	79.0	1.0030	12.6962	0.1830	1.3100	0.980	5.7382
17.	747	83.0	1.1241	13.5443	0.0619	1.1568	1.099	5.7058
18.	793	88.0	1.1632	13.2187	0.0228	1.0510	1.137	5.7432
19.	830	94.0	1.1738	12.4872	0.0122	0.9979	1.147	5.7783
20.	874	99.0	1.1860	11.9798	—	—	1.159	5.8194

Table-6
Thermogarvimetric Data of Dysprosium Myristate

S.No.	Temperature T (K)	Time (t) (Minute)	Weight of Carboxylate decomposed w ×10^3 (gms)	dw/dt × 10^6	Wr × 10^3	$\frac{\Delta[\log(dw/dt)]}{\Delta(\log Wr)}$	α	– log (α/T^2)
1.	283	5.3	0.0158	2.9811	1.4690	1.9505	0.012	6.8244
2.	337	10.0	0.0251	2.5100	1.4597	1.9749	0.019	6.7542
3.	374	19.0	0.0485	2.5526	1.4363	1.9675	0.038	6.5569
4.	429	24.0	0.0633	2.6375	1.4215	1.9594	0.049	6.5747
5.	475	28.0	0.1321	4.7178	1.3527	1.8566	0.103	6.3405
6.	502	33.0	0.1623	4.9181	1.3225	1.844	0.126	6.3010
7.	535	39.0	0.2224	5.7026	1.2624	1.8089	0.173	6.2187
8.	562	44.0	0.3011	6.8432	1.1837	1.7647	0.235	6.1284
9.	578	51.0	0.4003	7.8490	1.0845	1.7219	0.312	6.0297
10.	589	57.0	0.5632	9.8807	0.9216	1.6989	0.438	5.8988
11.	621	61.0	0.6614	10.8426	0.8234	1.6097	0.515	5.8743
12.	545	65.0	0.8432	12.9723	0.6416	1.5307	0.656	5.8022
13.	657	67.0	0.9603	14.3328	0.5241	1.4766	0.747	5.7618
14.	684	68.0	1.0834	15.9323	0.4014	1.4126	0.843	5.7443
15.	717	72.0	1.1104	15.4222	0.3744	1.4042	0.864	5.7769
16.	742	73.0	1.2157	16.6534	0.2691	1.3385	0.946	5.7649
17.	753	77.0	1.3631	17.7025	0.1217	1.2139	1.062	5.7275
18.	799	81.0	1.4238	17.5778	0.0610	1.1282	1.109	5.7601
19.	838	88.0	1.4620	16.6136	0.002	1.0296	1.271	5.7423
20.	884	94.0	1.4848	15.7957	—	—	1.436	5.7358

Table-7
Thermogravimetric Data of Dysprosium Palmitate

S.No.	Temperature T (K)	Time (t) (Minute)	Weight of Carboxylate decomposed $w \times 10^3$ (gms)	$dw/dt \times 10^6$	$Wr \times 10^3$	$\frac{\Delta[\log(dw/dt)]}{\Delta(\log Wr)}$	α	$-\log(\alpha/T^2)$
1.	286	7.0	—	—	2.0864	—	—	—
2.	342	11.2	0.0234	2.0892	2.0630	2.1151	0.024	6.6878
3.	381	17.0	0.0428	2.5176	2.0436	2.0817	0.023	6.8001
4.	433	23.0	0.1012	4.4000	1.9852	1.9823	0.053	6.5486
5.	481	29.0	0.1983	6.8379	1.8881	1.8962	0.103	6.3515
6.	513	35.0	0.3213	9.1800	1.7633	1.8292	0.168	6.1949
7.	543	38.0	0.4624	12.1657	1.6240	1.7619	0.241	6.0875
8.	564	41.0	0.6213	15.1536	1.4651	1.7005	0.324	5.9920
9.	583	43.0	0.7832	18.2139	1.3032	1.6428	0.408	5.9207
10.	594	47.0	1.1428	24.3149	0.9436	1.5252	0.596	5.7723
11.	625	49.0	1.5257	31.1367	0.5607	1.3861	0.796	5.6908
12.	648	53.0	1.7828	33.6378	0.3036	1.2716	0.929	5.6551
13.	664	54.0	1.8835	34.8796	0.2029	1.2071	0.982	5.6522
14.	693	60.0	1.9436	32.9333	0.1428	1.1656	1.013	5.6758
15.	728	64.0	2.0049	31.3265	0.0815	1.1056	1.045	5.7051
16.	748	70.0	2.0463	29.2328	0.0401	1.0312	1.066	5.7200
17.	761	77.0	2.0648	26.8623	0.0180	0.9634	1.077	5.7306
18.	803	80.0	2.0731	25.9137	0.0133	0.9406	1.081	5.7756
19.	844	81.0	2.0765	23.5965	0.0009	0.6567	1.083	5.8180
20.	892	98.0	2.0864	21.2898	—	—	1.088	5.8641

Table-8

Energy of activation (KCal Mol^{-1}) for the decomposition of Dysprosium carboxylates by using various equations -

S.No.	Name of the Carboxylates	Freeman and Carroll's equation	Coats and Redfern's Equation
1.	Dysprosium laurates	15.00	18.75
2.	Dysprosium Myristate	17.00	25.76
3.	Dysprosium Plamitate	24.00	28.11

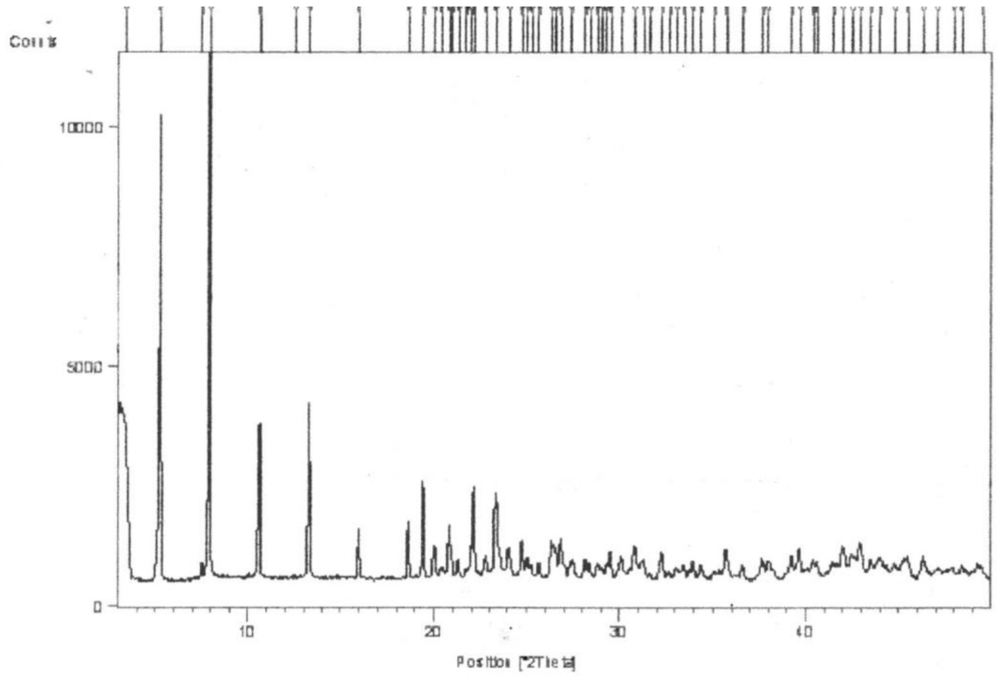

Fig. 1 : X-ray Diffraction analysis of Dysprosium laurate

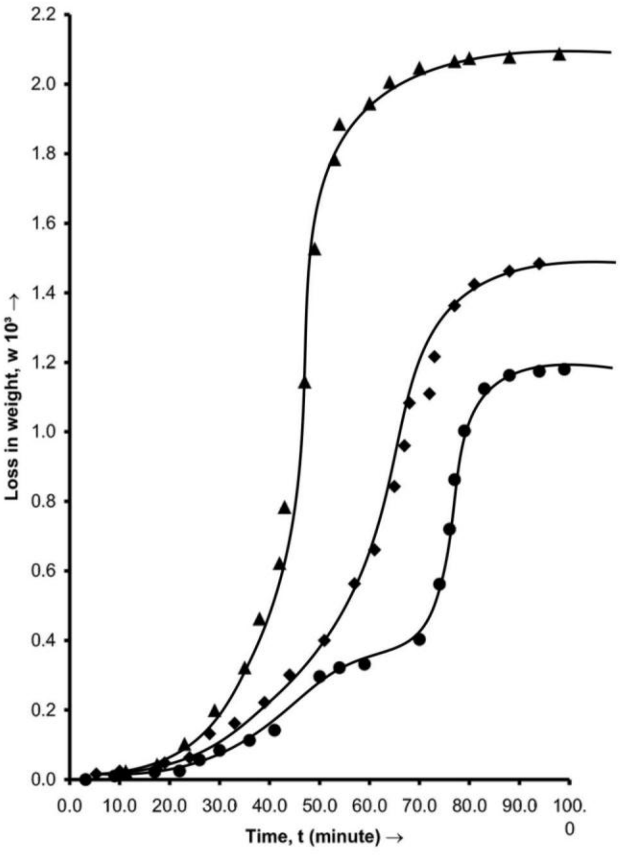

Fig.-2 Thermograms of Dysprosium Carboxylates, Loss in weight (w) vs. time (t) ● Laurate ◆ Myristate ▲ Palmitate

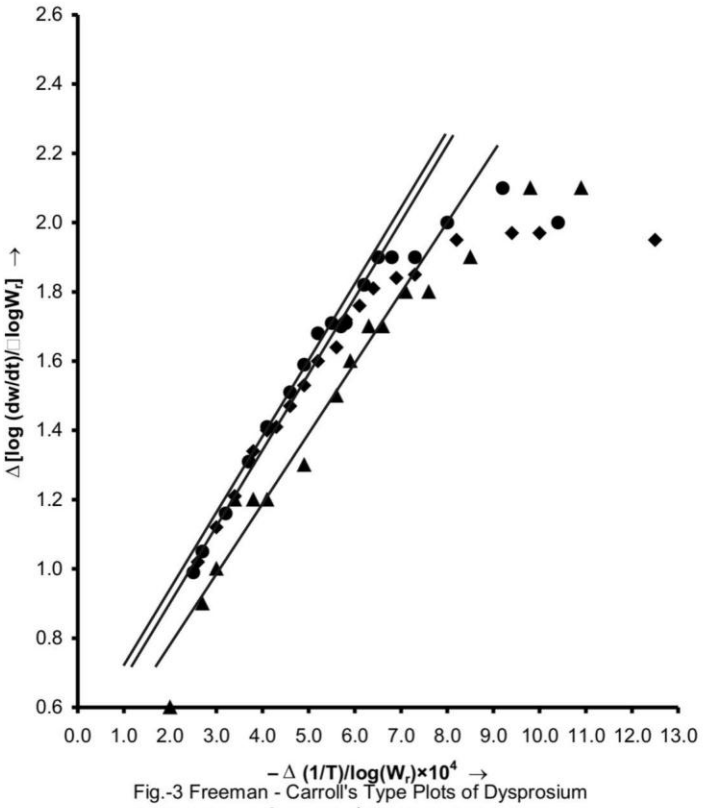

Fig.-3 Freeman - Carroll's Type Plots of Dysprosium Carboxylates ● Laurate ◆ Myristate ▲ Palmitate

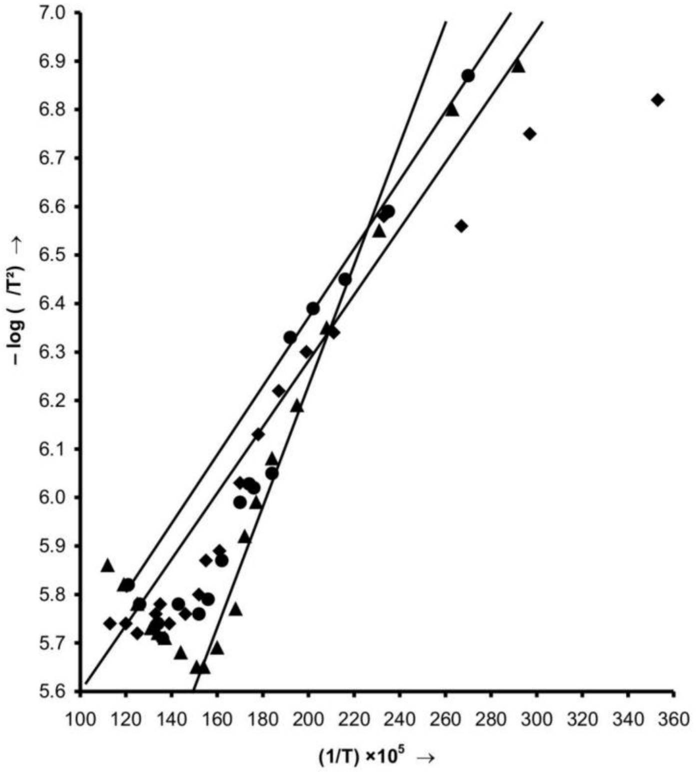

Fig.-4 Coats and Redfern's Type Plots of Dysprosium Carboxylates ● Laurate ◆ Myristate ▲ Palmitate