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Infrared, Thermal and X-rays Diffraction Analysis of Dysprosium Soaps

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The physico-chemical characteristics of dysprosium soaps (butyrate and valerate) in solid state were investigated by IR, thermal and X-ray diffraction measurement, the IR results reveal that the fatty acids exist in dimeric state through hydrogen bonding and soaps possess partial ionic character. The decomposition reaction was found kinetically of zero order with energy of activation 10.5, 9.8 Kcal mol^{-1} for dysprosium butyrate and valerate, respectively. The X-ray diffraction measurement were used to calculate the long spacing and the result confirm the double layer structure of dysprosium soaps.

Key Words: Dysprosium soaps, Infrared, X-ray, Thermal analysis.

INTRODUCTION

The study of metallic soaps is becoming increasingly important in industrial as well as in academic fields[1-5]. It has been a subject of intense investigation in the recent past on account of its role in such diversified fields as detergents, softeners, hardeners stabilizers, plasticizers, driers, thickeners, greases, lubricants, cosmetics, medicines, germicides and wetting agent, *etc*. Nevertheless the studies on these soaps are limited with the results that only few reference are available in this field[1-5]. The results of infrared, X-ray and thermal studies have been used to obtain structural information in solid state and to determine the order of reaction and energy of activation for the decomposition reaction.

EXPERIMENTAL

All the chemicals used were of BDH/AR grade. The dysprosium soaps (butyrate and valerate) were prepared by direct metathesis of the corresponding potassium soap with the required amount of dysprosium nitrate solution at 50-60ºC under vigorous stirring. The precipitated soaps were recrystallized with a mixture of benzene and methanol and dried under reduced pressure. The infrared spectra of fatty acids and their corresponding dysprosium soaps were recorded with a Perkin-Elmers 'Model 577' grating spectrophotometer in the region 4000-200 cm^{-1} using the KBr disc method.

The X-ray diffraction patterns were obtained with a Rich-Seifert '2002D' Isodebyefle diffractometer using Cu-Kα radiations filtered by a nickel foil over the range of diffraction angle of 2θ = 6-80º. The reading of the diffraction angle were made up to 0.001º and the wavelength of the radiations was taken as 1.54 Å. The thermogravimetric analysis of dysprosium soaps was carried out by a Perkin-Elmer thermogravimetric analyzer (TG-S-2) in nitrogen atmosphere at a constant heating rate of 10º/min maintaining similar conditions throughout the experiments.

RESULTS AND DISCUSSION

The IR spectral data dysprosium soaps (butyrate and valerate) and their corresponding fatty acids are recorded in Table-1. The absence of water of crystallization in the soap is supported by absence of ν(OH) at 3500 cm^{-1} in their IR specta.

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

Assignments	Butyric acid	Dy. Butyrate	Valeric acid	Dy. Valerate
CH$_3$, C-H asym. str.	2960 ms	2960 m	2960 ms	2960 m
CH$_2$, C-H asym. str.	2910 ms	2930 vw	2910 ms	2925 vw
CH$_3$, C-H sym. str.	2860 w	2880 m	2860 w	2880 m
OH, str.	2660 w	–	2660 w	–
C=O, str.	1700 vs	–	1700 vs	–
COO, C-O asym. str.	–	1550 s	–	1550 s
COO, C-O sym. str.	–	1450 m	–	1450 m
C-O, str. OH in plane def.	1430 m	–	1430 m	–
CH$_2$ (adjacent to COOH group) def.	1410 s	–	1410 s	–
CH$_3$, sym. def.	1375 s	1345 w	1375 s	1360 vw
Progressive bonds (CH$_2$) twisting and wagging	1280-1130 s	1315-1215 m	1280-1130 ms	1320-1200 m
CH$_3$, rocking	1100 s	1100 m	1100 s	1100 m
OH, out of plane def.	640 ms	–	940 ms	–
CH$_2$, rocking	720 s	720 w	720 s	720 vw
COOH, bending	680 ms	–	680 ms	–
COOH, wagging	550 ms	–	550 ms	–
(Dy-O)	–	340 m	–	340 m

In the IR spectra of dysprosium soaps the characteristics ν(C=O) (1700 cm^{-1}) ν(OH) stretch (2580-2600 cm^{-1} and ν(OH) out-of-plane deformation (935 cm^{-1}) vibration of free acids which are characteristic bands of dimeric carboxylic acids were found completely absent in their respective regions. The absorptions maxima near 690 and 550 cm^{-1} in the spectra of fatty acids are associated with carboxylic group bending and wagging modes. The IR spectra of the acids in carboxylic region show considerable changes on complex formation. In dysprosium soaps, two absorption bands are observed near 1550 and 1450 cm^{-1} corresponding to asymmetric and symmetric vibration of carboxylate ion. The complete disappearance of the carboxyl frequency near 1700 cm^{-1} in the spectra of dysprosium soaps indicate that there is a complete resonance in the two C-O bonds of carboxylic group of the soap molecules. The metal to oxygen bond in these soaps is of ionic character. The bands observed at 340 cm^{-1} in the spectra of dysprosium soaps corresponding to (Dy-O) bond.

The result confirm that the fatty acids in solid state exist in a dimeric structure through hydrogen bonding between two molecules of fatty acids whereas metal-to-oxygen bonds in metal soaps are ionic in nature.

X-ray diffraction analysis

Since the metal soaps do not give large crystals sufficient for a detailed single crystal examination, the structure of these soaps was characterized by their X-ray diffraction patterns.

In the diffraction patterns of dysprosium soaps a large number of intense peaks arising from the diffraction of X-rays by planes of dysprosium ions have been observed over the range of 3-65°C of diffraction angle. The interplaner spacing (d) were calculated from the positions of intense peaks using Bragg's relationship, $n\lambda = 2d \sin\theta$, where λ is the wavelength of radiation. The calculated spacing together with the relative intensities with respect to the most intense peaks are given in that Tables 2 and 3.

TABLE-2

X-RAY DIFFRACTION ANALYSIS OF DYSPROSIUM BUTYRATE

2θ	θ	Sin θ	λ/2sin θ	d	n	I/I_0
5.958	2.979	0.0520	14.8350	14.835	1	1.00
12.271	6.136	0.1069	7.2129	14.426	2	0.28
18.739	9.370	0.1628	4.7355	14.207	3	0.22
24.878	12.439	0.2154	3.5790	14.316	4	0.07
32.882	16.441	0.2830	2.9238	14.619	5	0.06

Average value of d = 14.481 Å

The appearance of the diffraction upto 5th and 7th order in the diffraction patterns of dysprosium butyrate and valerate, respectively confirm good crystallinity for these soaps. The average planar distances *i.e.*, long spacing for dysprosium butyrate and valerate 14.480 and 17.079 Å, respectively.

TABLE-3
X-RAY DIFFRACTION ANALYSIS OF DYSPROSIUM VALERATE

2θ	θ	$\sin\theta$	$\lambda/2\sin\theta$	d	n	I/I_0
5.518	2.479	0.0450	17.1335	17.133	1	1.00
10.293	5.147	0.0897	8.4943	17.188	2	0.04
16.160	8.080	0.1406	5.4847	16.454	3	0.06
19.910	9.955	0.1729	4.2661	17.064	4	0.08
25.437	12.719	0.2202	3.5016	17.508	5	0.06
33.919	16.960	0.2917	2.6429	16.291	6	0.04
35.063	17.532	0.3012	2.4493	17.915	7	0.04

Average value of d = 14.481 Å

The difference in the observed values of long spacing of dysprosium butyrate and valerate is 2.0 Å, which corresponds double the length of additional methylene ($-CH_2-$) groups in the fatty acid radical constituent of the soap molecules.

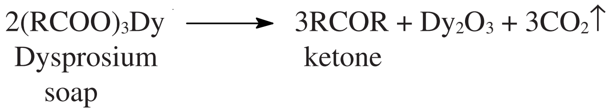
The observed values of the long spacing, however, are smaller than the calculated dimensions of these ions from Pauling's values of atomic radii and bond angles and this suggests that the molecular axes of these soap are some what inclined to the basal planes.

The metal ions Dy^{3+} fit into the spaces between the oxygen atoms of the ionized carboxyl group without a large strain of bonds. Many diffraction peaks in the intermediate range are also observed in the diffraction patterns of dysprosium soaps and are attributed to the diffraction of X-rays by planes of atoms of much smaller separation than the basal planes. The calculated spacing from these peaks correspond to the shorter side spacing *i.e.*, the lateral distance between one soap molecule and the next in a layer.

It is proposed that the metal ions in dysprosium soaps are arranged in a a parallel planes *i.e.*, a basal plane equally spaced in the soap crystal with fully extended zig-zag chains of fatty acid radicals on both sides of each basal plane and the dysprosium soaps have double layer structure as proposed by Vold and Hattiangdii[6].

Thermogravimetric analysis

The results of thermogravimetric analysis of dysprosium soaps (butyrate and valerate) are given in Fig. 1. It is found that the final residue is metal oxide and the weight of the residue are in agreement with the theoretically calculated weight of dysprosium oxide from the molecular formulae of soaps. A white substance is found deposited at the cold part of the sample tube surrounding the sample and it is identified by determination of boiling points as butanone (79.6ºC) and valerone (168.2ºC) and in case of dysprosium butrate and valerate, respectively. The thermal decomposition of dysprosium soaps can be expressed as:



$$\underset{\text{Dysprosium soap}}{2(RCOO)_3Dy} \longrightarrow \underset{\text{ketone}}{3RCOR} + Dy_2O_3 + 3CO_2\uparrow$$

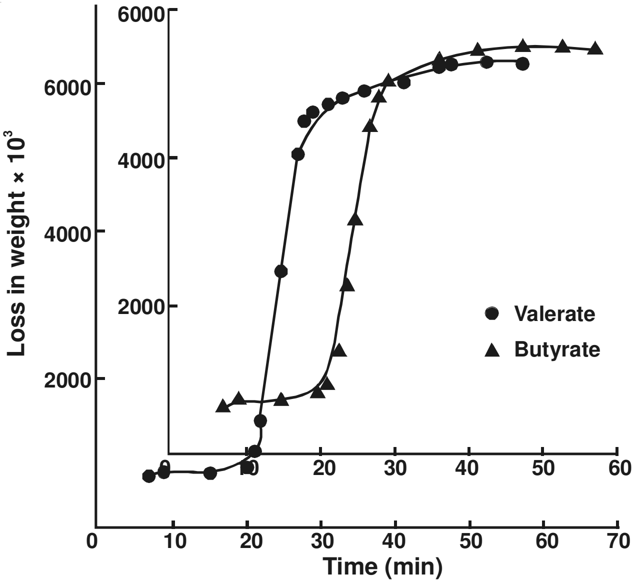


Fig. 1. Thermograms of dysprosium soaps

Thermogravimetric data were used to calculate the energy of activation and to find the order of reaction for the decomposition of dysprosium soaps using the equations of Freeman and Carroll[7] which may be written as:

$$\frac{\Delta\log(dw/dt)}{\Delta(\log Wr)} = \frac{-E_a}{2.303R}\frac{\Delta(1/T)}{\Delta(\log Wr)} + n$$

E_a = energy of activation, R = gas constant, n = order of reaction, T = temperature on absolute scale, Wr = difference between the total loss in weight and the loss in weight at time t, *i.e.* Wo-Wt.

dw/dt = rate of weight loss obtained from the loss in weight *vs.* time curve at appropriate time. The plots of Δlog (dw/dt)/Δ(log Wr) *vs* Δ(1/T)/Δ(log Wr) have been found to be linear with intercept equal to zero (Fig. 2). It is therefore concluded that the order of reaction for the decomposition of dysprosium soaps is zero and the value of energy of activation from the slope ($-E_a/2.303R$) of the plots (Fig. 2) are 10.5 and 9.8 Kcal mol^{-1} for butyrate and valerate, respectively.

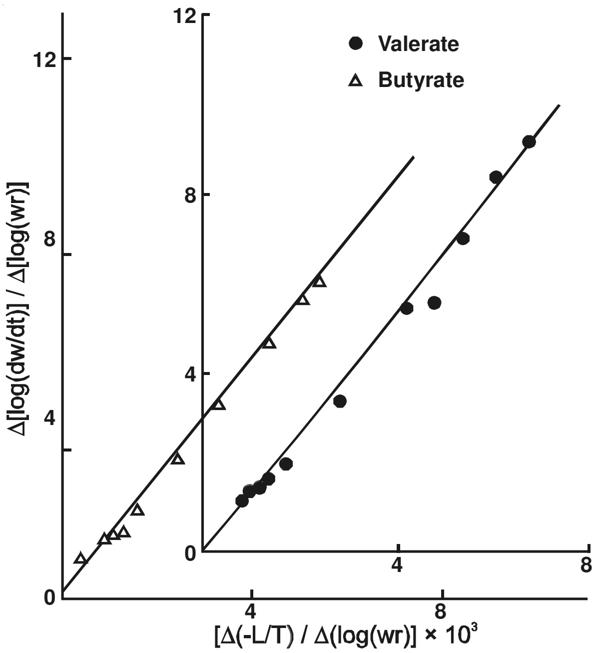


Fig. 2. Freeman Carroll's type plots of dysprosium soaps

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