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Infrared Absorption Spectra and X-Rays Diffraction Studies on Yttrium Soaps in Solid State

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Abstract

The infrared absorption spectra and x-rays diffraction analysis were used to determine the structure of yttrium soaps (myristate and palmitate) in solid state. The IR results reveal that the fatty acids exist in dimeric structure through intermolecular hydrogen bonding and yttrium soaps ionic in nature. The x-ray diffraction measurements confirm that yttrium soaps possess double layer structure with long spacings.

Keywords: Metal soaps, IR, X-ray Diffraction.

Introduction

The transition metal soaps are being widely used in industry, technology and allied sciences. The uses of metal soaps largely depend on their physical state, stability, chemical reactivity and solubility in polar and non polar solvents. These metal soaps has been a subject intense investigation in the recent past on account of its role in such diversified field as medicine, cosmetic emulsifier, lubricant, germicides and anti oxidant. The methods of preparation of potassium soaps and metal soaps were described by several workers (1-6). The infrared absorption spectra, x-ray diffraction studies and thermal behavior of cerium and thorium laurate were studied by Gupta et al.(7). The thermal decomposition kinetics of nickel and manganese soaps were studied by Mehrotra et al.(8). The physicochemical studies on erbium soaps of saturated higher fatty acids in solid state studied by Rajesh et al.(9). The viscometric and spectral studies of copper soap in benzene and methanol mixture were studied by Rawat(10). The studies on miceller properties of scandium and yttrium metal soaps was studied by Khirwar (11). The studies of ultrasonic velocity and allied properties of magnese, cobalt and copper soaps in non aqueous medium Rawat (12). In the present work attempts have been made to determine the structure of yttrium soaps (myristate and palmitate) in solid state through the infrared absorption spectra and x-rays diffraction studies.

Aim of the Study

The results of the survey of literature reveals that the physico-chemical properties of yttrium soaps have not been systematically investigated while they have many uses in industries and academic field. The aim of this research work is to study the structure of yttrium soaps in solid state through infrared absorption spectra and x- rays diffraction analysis.

Review of Literature

Present research work reviews the literature relevant with the aim of study. The spectroscopic studies of metallic soaps have been studied by several workers. Some of them are listed below.

1. Rajesh Dwivedi (2014) was studied the Physicochemical Studies on Erbium Soaps of Saturated Higher Fatty Acids in Solid State.
2. Anushri Gupta (2012) was studied the infrared absorption spectra, x-ray diffraction studies and thermal behavior of cerium and thorium laurate.
3. M.S.Khirwar (2011) was studied the studies on miceller properties of scandium and yttrium metal soaps.

Experimental

The yttrium soaps (myristate and palmitate) were synthesized by direct metathesis of corresponding potassium soaps with the required amount of aqueous solution of yttrium nitrate at 50-55^{0}C under vigorous stirring. The precipitated soaps were washed several times with distilled water and then acetone to remove the fatty acid and metal nitrate. The

soaps were purified by recrystallization with the benzene and DMSO mixture, dried in an air oven at 50-60^{0}C and the finally drying of the soaps were carried out under reduced pressure.

The IR absorption spectra of myristic acid, palmitic acid and their corresponding potassium, and yttrium soaps (myristate and palmitate) were recorded with Perkin Elmer: 577 model grating spectrophotometer in the region of 4000-400 cm^{-1} using potassium bromide disc method.

The X-ray diffraction patterns of yttrium soaps (myristate and palmitate) were obtained with a Rich-Seifert 2002D isodebyeflex diffractometer using cu-k_α radiations filtered by a nickel foil over the range of diffraction angle, $2\Theta = 3^0$ to 65^0 (where Θ is Bragg's angle).The XRD curves were recorded under the applied voltage of 35KV using scanning speed of 1^0 per minute and chart speed of 1 cm per minute. The wave length of radiations was taken as 1.543Å.

Result and Discussion

Infrared Absorption Spectra

The IR spectra of yttrium soaps (myristate and palmitate) with their assignments are recorded (Fig. 1-2) compared with the results of corresponding fatty acid and potassium soap(Table.1). The absorption maxima characteristic of the aliphatic portion of the acid molecule remain unchanged on the formation of corresponding potassium and yttrium soaps. The symmetrical vibration of CH_2 at 2840-2850 cm^{-1}, the asymmetrical stretching vibration of CH_2 at 2910-2930 cm^{-1}, the asymmetrical stretching vibration of CH_3 at 2960-2970 cm^{-1} and the deformation of CH_3 at 1310-1380 cm^{-1} are observed in spectra of potassium, yttrium and as well as in corresponding fatty acid.

The absorption bands observed near 2630-2640, 1680-1690, 1400-1450, 920-930, 670-680, 540 cm-1 in spectra of fatty acids have identified the presence of localized COOH group in the form of dimeric structure and the existence of intermolecular hydrogen bonding between two molecules of the acid.

The absorption bands observed near 2630-2640, 1680-1690 and 920-930 cm^{-1} corresponding to the -OH group in the spectra of fatty acids have disappeared in the spectra of corresponding potassium and yttrium soaps. The absorption maxima corresponding to 670-680 and 540 cm^{-1} in the spectra of fatty acids have been assigned to the bending and wagging modes of the vibrations of the carbonyl group of the acid molecules, respectively.

The IR spectra of potassium soaps and yttrium soaps show marked difference with the spectra of corresponding fatty acids in some spectral regions. The characteristic vibrations of free acids were found completely absent in the spectra of corresponding potassium and yttrium soaps. The complete disappearance of the carbonyl frequency in the region of 1680-1690 cm^{-1} and appearance of two absorption bands of carboxyl group corresponding to the symmetrical and asymmetrical vibrations carboxylate ion near 1460-1470 cm^{-1} and 1540-1550 cm^{-1} respectively in the spectra of yttrium soaps indicate that there is a complete resonance in the C-O bonds of carboxyl groups of the soap molecules and the two bonds become identical with their force constants assuming an intermediate value between those of normal double and single bonds.

It is therefore, concluded that the resonance character of the ionized carboxyl group is retained in yttrium soaps. The fatty acids exist with dimeric structure through intermolecular hydrogen bonding between carboxyl groups of two acid molecules whereas metal-to-oxygen bonds in yttrium soaps are ionic in nature. The IR spectra of yttrium soaps do not show any absorption maxima in the region of 3500-3000 cm^{-1} which confirms that the absence of any co-ordinated water molecule in yttrium soaps molecule.

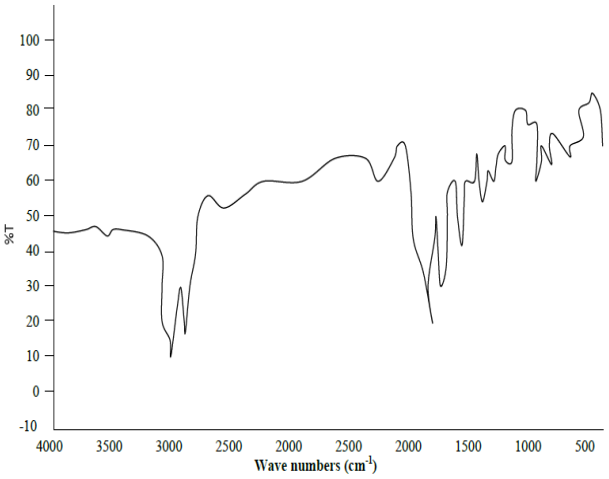

Fig. 1
Infrared Absorption Spectra of Yttrium Myristate

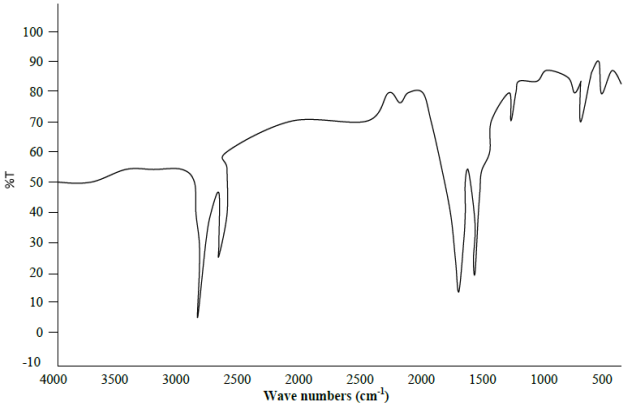

Table 1
Frequencies (cm^{-1}) of Absorption Maxima with their Assignments of Acids and their Soaps

Sr. No.	Assignments	Myristic Acid	Potassium Myristate	Yttrium Myristate	Palmitic Acid	Potassium palmitate	Yttrium Palmitate
1	CH_3, C-H Asym. Stretch.	2960VW	2940W	2960M	2960VS	2950W	2960MS
2	CH_2, C-H Asym. Stretch.	2910VS	2910VS	2910W	2900S	2920S	2920S
3	CH_2, C-H Sym. Stretch.	2840S	2840VS	2840M	2840S	2850S	2840S
4	O-H, Stretch.	2630W	-	-	2640W	-	-
5	C = O, Stretch.	1690VS	-	-	1690VS	-	-
6	COO, C-O Asym. Stretch.	-	1590W	1540S	-	1560VS	1545S
7	COO, C-O Sym. Stretch.	-	1450W	1460M	-	-	1460S
8	C-O Strech. + O-H in plane deformation	1400W	1410S	-	1450W	1430MS	-
9	CH_2 (adjacent to COOH group) deformation	1365VW	-	-	1400W	-	-
10	CH_3,Sym. deformation	1330W	1330W	1330M	1345W	1360W	1310S
11	Progressive bands (CH_2, twisting and wagging)	1340 - 1180W	1330 - 1180W	1310 - 1160WB	1340 - 1090VW	1370W	1290 - 1180WB
12	CH_3, rocking	1110W	1090W	1100M	1100W	1190M	1100W
13	OH, out-of-plane deformation	930M	-	-	920W	1110W	-
14	CH_2, rocking	715MS	710S	710M	710M	-	710M
15	COOH, bending mode	680MS	-	-	670W	720MS	-
16	COOH, wagging mode	540M	-	-	540W	-	-
17	Y-O, bond	-	-	410W	-	-	440M

Key to Abbreviations

VS = very strong, MS = medium strong, W = weak, S = strong, M = medium, VW = very weak.

X-Rays Diffraction Analysis

The x-ray diffraction patterns of yttrium soaps (myristate and palmitate) have been investigated with a view to characterize in solid state. The intensities of diffracted x-ray as a function of diffraction angle, 2θ for yttrium soaps are recorded over the range of $3\text{-}70^0$. The interplaner spacings, d, have been calculated from the position of the intense peaks using Braggs relation-ship.

$$n\lambda = 2d\sin\theta$$

where λ is the wave length of radiation.

The calculated spacings and relative intensities with respect to the most intense peaks are recorded (Table1-2). A large number of peaks arising from the diffraction of x-ray by planes of metal ion (known as basal planes) are observed in the diffraction patterns of yttrium soaps. The appearance of diffraction for yttrium myristate upto the 11^{th} order and yttrium palmitate upto the 10^{th} order confirms good crystallinity for yttrium soaps.

The long spacings average planer distance for yttrium myristate and yttrium palmitate are 37.84, 40.47 Å, respectively. The difference in long spacings of yttrium soaps (myristate and palmitate: 2.63 Å) correspond almost to the length of methylene (CH_2) group in the fatty acid radical constituent of the soap molecules. It is therefore suggested that the Zig-Zag chains of the fatty acid radical constituent of the soap molecules extend straight forward on the both sides of each basal plane. The values of long spacings for metal soaps are very smaller then calculated dimensions of anions (myristate: 42.0 Å and palmitate: 47.0 Å) from the Paulings values of atomic radii and bond angles. It is therefore, concluded that the molecular axes of yttrium soap molecules are somewhat inclined to the basal planes. The metal ions, Y^{3+} fit into spaces between oxygen atoms of the ionized carboxyl group without a large strain of the bond.

A number of diffraction peaks in the intermediate range are also observed in the diffraction patterns of yttrium soaps and are attributed to the diffraction of x-ray by plans of atoms of much smaller separation than the basal planes. The calculated spacings i,e the lateral distances between one soap 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.

The values of the long spacings for yttrium soaps are agreement with the double layer structure of the soaps proposed by Vold and Hattiangdi[13]. On the basis of long and short spacings, it is suggested that the metal ions are arranged in parallel planes equally spaced in the soap crystal with fully extended Zig-Zig chains of fatty acid radicals on both sided of each basal plane.

The results suggest that yttrium soaps possess double layer structure with molecular axes somewhat inclined to the basal planes.

Table 2
X-rays Diffraction Analysis of Yttrium Myristate

Sr. No.	2θ	θ	$\sin\theta$	D	d(Å)	n
1	3.275	1.637	0.0285	18.851	37.702	2
2	5.674	2.837	0.0494	12.351	37.053	3
3	8.271	4.135	0.0721	9.213	36.852	4
4	10.235	5.117	0.0891	7.519	37.596	5
5	10.268	5.134	0.0894	6.321	37.931	6
6	19.961	9.980	0.1733	4.126	41.263	10
7	21.286	10.643	0.1846	3.321	36.536	11

Average value of d = 37.84 Å

Table 3
X-rays Diffraction Analysis of Yttrium Palmitate

Sr. No.	2θ	θ	sin θ	D	d(Å)	n
1	3.256	1.628	0.0284	20.273	40.546	2
2	5.125	2.562	0.0447	13.254	39.762	3
3	7.532	3.766	0.0656	10.203	40.814	4
4	0.327	0.163	0.0028	8.035	40.176	5
5	0.219	0.109	0.0019	6.925	41.551	6
6	0.201	0.100	0.0017	5.831	40.819	7
7	0.188	0.094	0.0016	3.962	39.625	10

Average value of d = 40.47 Å

Conclusion

It is concluded that the structure of yttrium soaps in solid state studied by the Infrared Absorption Spectra exist in dimeric state through intermolecular hydrogen bonding and ionic in nature. X-Rays Diffraction results confirm that these metal soaps possess double layer structure with long spacing.

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