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Comprative Infrared Studies of Cerium and Thorium Soaps

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ABSTRACT

Infrared spectra tests have shown that fatty acids exist with a dimeric structure through hydrogen bonding between two molecules of fatty acids whereas metal-to-oxygen bonds in metal soaps have an ionic character but the bonds are not purely ionic.

Key words: Infrared, Cerium, Thorium, Soaps.

INTRODUCTION

In spite of much work reported on alkali, alkaline earth and transition metal soaps, only few references[1-18] are available on tare earth metal soaps which have found wide application in industry. The present work was carried out with a view to investing the characteristics and structure of cerium and thorium soaps in the solid state by using infrared.

EXPERIMENTAL

The fatty acids were purified by distillation under reduced pressure. Cerium and thorium (vi) soaps (laurate and myristate) were prepared the metathesis of an aqueous solution of cerium nitrate and thorium nitrate with a hot solution of the corresponding sodium soap. The precipitated soaps were filtered and washed with distilled water, alcohol and finally with acetone. The metal soaps thus obtained were first dried in an air oven and finally under reduces pressure and were further purified by recrystallization.

The melting points of purified cerium and thorium soaps were laurate 44°C and myristate 54^0c. The soaps were analysed for carbon, hydrogen and metal contents and the result were found to be in agreement with the theoretically calculated values.

The infrared absorption spectra of lauric and myristic acids and their corresponding cerium and thorium soaps were determined using a Perkin-Elmer model 577 grating spectrophotometer in the region 4000-400 cm^{-1} using the potassium bromide disc method.

RESULTS AND DISCUSSION

Infrared absorption spectra

The infrared spectral data of cerium and thorium soaps are listed in table 1,2,3,4 and compared with that of their corresponding fatty acids. The fatty acids (lauric and myristic acid) display a very broad intense peak due to –OH stretching near 2660-2650 cm^{-1} . The appearance

Table 1: Frequencies (cm^{-1}) of Absorption maxima with their Assignments

S. No.	Assignments	lauric acid	Sodium laurate	Cerium laurate
1.	CH_3 C- H asym, stretch,	2960vw	2940vw	2960w
2.	CH_2 C- H asym, stretch,	2920vs	2910M	2940vs
3.	CH_2 C-H sym stretch,	2855s	2840Ms	2880s
4.	OH stretch,	2660vs	-	-
5.	C = 0 stretch,	1680s	-	-
6.	COO^-, C-O asym, stretch,	-	1550vs	1540vs
7.	CH_2 deform,	1470M	1460w	1470vw
8.	COO^-, C-O sym, stretch	-	1430w	1450vw
9.	C-O stretch, O-H in - plane deform	-	1430Ms	-
10.	CH_2, (Adjacent to COOH group) deform	1405vs	-	-
11.	CH_3, Sym, deform	1350w	1330w	1340Br
12.	Progressive bands (CH_2 twisting and wagging)	1270-1220W	1300-1200W	1310-1200W
13.	CH_3 Rocking	1110W	1100vw	11105
14.	OH, out-of-plane deform	930vs	-	-
15.	CH_2,Rocking	730vs	720vs	730Ms
16.	COOH, bending mode	690M	-	-
17.	COOH, wagging mode	550m	-	-
18.	Ce-O bond	-	-	450s

Key to abbreviation : MS = Medium strong S = strong VS = Very Strong
M = Medium BR = Broad W=Weak VW= Very Weak

Table 2: Frequencies (cm^{-1}) of Absorption maxima with their assignments

S. No	Assignments	Myrestic Acid	Sodium myrestate	Cerium myrestate
1.	CH_3, C-H asym stretch,	2960W	2940W	2920VW
2.	CH_2, C-H asym stretch,	2920VS	2920VS	2900W
3.	CH_2, C-H sym stretch,	2850S	2890S	2840MS
4.	OH, stretch,	2650W	-	-
5.	C = 0 stretch,	1700VS	-	-
6.	COO^-, C-O asym, stretch,	-	1600VS	1650M
7.	CH_2 deform,	1470 1>1	1475MS	1455VW
8.	COO^-, C-O sym, stretch,	-	1430MS	1430VW
9.	C-O stretch, O-H in-plane deform	1440M	-	-
10.	CH_2 (Adjacent to COOH group)	1405 W	-	-
11.	CH_3 sym, deform,	1350W	1330W	1320W
12.	Progressive bands (CH_2 twisting and wagging)	1350 J-1090 W	1375 - 1200W	1300 -1160S
13.	CH_3 Rocking	1110 VW	1 110 VW	1090VS
14.	OH, Out-of- plane deform	9505	-	-
15.	CH2/Rocking	720W	720MS	720VS
16.	COOH, bending mode	690MS		
17.	COOH, Wagging mode,	550ws	-	-
18.	0-0 bond	-	-	440VS

Key to abbreviation :
MS = Medium strong S = strong VS = Very Strong M = Medium
BR = Broad W=Weak VW= Very Weak

Table 3: Frequencies (CM^{-1}) Absorption Maxima with their Assignments.

S. No.	Assignments	lauric acid	Sodium laurate	Cerium laurate
1.	CH_3, C-H asym, stretch,	2960VW	2940VW	2960VW
2.	CH_2, C-H asym, stretch,	292NS	29101M	2920VS
3.	CH_2C- H sym, stretch,	2855S	2840MS	2850VW
4.	OH, stretch	2660VS	-	-
5.	C = 0 stretch	1680S	-	-
6.	COO^-, C-O asym, stretch,	-	1550VS	1530VW
7.	CH_2 deform	1470M	1460W	1455VW
8.	COO, C-O sym stretch	-	1430W	1400S
9.	C-O stretch, O-H in-plane deform	1430 MS	-	-
10.	CH_2, (Adjacent to COOH group) deform	1405 VS	-	-
11.	CH3 ,sym- deform	1350W	1330W	1330VW
12.	Progressive bands (CH_2 twisting and Wagging)	1270-1220W	1300 -1200W	1315-1235VW
13.	CH3 Rocking	1110W	1100VW	1110VW
14.	OH, out-of-plane deform	930VS	-	-
15.	CH_2 Rocking	730VS	720VS	720MS
16.	COOH bending mode	690M	-	-
17.	COOH Wagging mode	550M	-	-
18.	Th-O bond	-	-	450W

Key to abbreviation :

MS = Medium strong S = strong VS = Very Strong M = Medium

BR = Broad W=Weak VW= Very Weak

Table 4: Frequencies (cm^{-1}) of Absorption maxima with their assignments

S. No	Assignments	Myrestic Acid	Sodium myrestate	Cerium myrestate
l.	CH_3,C-H asym stretch	2960W	2940W	2940VW
2.	CH_2,C-H asym stretch	2920VS	2920 VS	2910S
3.	CH_2, C- H asym stretch	2850S	2890S	2840VS
4.	OH, stretch	2650W	-	-
5.	C = 0 stretch	700VS	-	-
6.	COO^-, C-O asym deform	-	1600VS	1550VW
7.	CH_2 deform	1470M	1475 MS	1460VW
8.	COO^-, C-O sym stretch	-	1430MS	1415Br
9.	C-O stretch O-H in-plone deform,	1440M		-
10.	CH_2 (Adjacent to COOH group) deform	1405W	-	-
11.	CH_3,sym deform	1350W	1330W	1360VW
12.	Progressive bands (CH_2 twisting and Wagging)	13501090 W	13751200W	13601060VW
13.	CH_3 Rocking	1110VW	1110 VW	1 11 OMS
14.	OH out-of-plane deform	950S	-	-
15.	CH_2 Rocking	720W	720MS	720S
16.	COOH bending mode	690MS	-	-
17.	COOH Wagging mode	550MS	-	-
18.	Th-O bond	-	-	440VS

Key to abbreviation : MS = Medium strong S = strong VS = Very Strong

M = Medium BR = Broad W=Weak VW= Very Weak

of the absorption band near 1700-1680 cm^{-1} in the spectra of fatty acids indicates that the fatty acids exist as dimmers[17] .One of the characteristic bands of dimeric carboxylic acids from the out-of- Plane Bending –OH group appearing near 950-930 cm^{-1}. The absorption maxima near 690 cm^{-1} and 550 cm^{-1}in the spectra of fatty acids are associated with carboxyl group bending and wagging modes.

In cerium and thorium (iv) Soaps, two absorption bands are observed near 1440-1410 $cm^{-1}$and 1610-1540 cm^{-1} instead of one strong absorption band corresponding to carboxyl group observed near 1700 cm^{-1} in the spectra of fatty acids. These bands correspond to symmetric and antisymmetric stretching vibrations of the carboxylate ion as pointed out by Duval, Lecomte and Douville[17]. The complete disappearance of the carboxyl frequency in the spectra of cerium and thorium soaps indicates that there is a complete resonance in the tow C-O bonds of the carboxyl group of the soap molecules. The metal –to- oxygen bond in cerium and thorium soaps in not purely ionic but is partially covalent in character. The bond observed at 440 cm^{-1} in the spectra of cerium and thorium soaps corresponds to the Ce-0,Th-O bond. The absorption bands observed near 2650,940,690 and 550 cm^{-1} which are associated with the carboxyl group of fatty acids, disappear completely in the spectra of cerium and thorium soaps.

The result confirm that the fatty acids in solid state exist with dimeric structure through hydrogen bonding between two molecules of fatty acids whereas metal-to-oxygen bonds in metal soaps are ionic in character but the bonds are not purely ionic.

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