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Infrared, X-Ray and Thermogravimetric Studies on Cerium and Gadolinium Myristate Soaps

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ABSTRACT

Cerium and gadolinium myristate soaps were prepared by direct metathesis of potassium myristate. The IR results showed that the fatty acid exists in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two acid molecule, whereas cerium and gadolinium myristate have an ionic character. The X-ray analysis indicated that the zig-zag chains of the fatty acid radical constituent of the soap molecules extend straight forward on both sides of eacs basal plane and the molecular excess of the soap molecules are slightly inclined to the basal plane.

1. Introduction

The most striking feature of metallic soaps has been their increasing importance in industries. Although a great deal of work has already been reported on the alkali, alkaline earth and transition metal soaps but the studies on rare earth metal soaps remained scanty, inspite of their large application in various industries as emulsifying agents, mordants, water-proofing agents,lubricants, additives and varnish driers. However, technological applications of these soaps are mostly based on empirical know-how and the selection of a soap is dependent largely on economic factors.

A metal soap is largely present in dilute solutions as metal cations and fatty acid anions. Many physical properties of soap solution exhibit a characteristic transition over a narrow range of concentration. This transition is generally related to the formation of aggregates arising from the intrinsic amphiphilic nature of soap molecules. The transition region has been used to determine the critical micellar concentration, CMC, above which multi-molecular aggregates (micelles) are formed. The forces that hold amphiphilc molecules together in micelles arise from weaker van der walls, hydrophobic, hydrogen-bonding and screened electrostatic interactions. The present work deals with the characteristics of gadolinium and cerium soaps state using infrared, X-ray diffraction patterns and thermogra vimetric measurements.

2. Experimental

All the chemicals were used of AR grade. The lanthanide myristates were prepared by the direct metathesis of potassium myristate with the required amount of gadolinium acetate of cerium chloride at 50-55o^{C} under vigorous stirring. The precipitated soaps were washed with double distilled water and acetone to remove the excess of metal ions and unreacted myristic acid. The purity of the soaps was checked by the elemental analysis and the results were found in agreement with the theoretical values. The reproducibility of the results was checked by preparing two samples of the same soap under similar conditions.

The infrared absorption spectra were obtained with a Perkin-Elmer 577 grating spectrophotometer in the region 400-4000 cm. The TGA was carried out at a constant heating rate of 15^{0} min (in a Mettler TG 50 instrument.) The X-ray diffraction patterns were obtained with Philips PW-1730 X-ray diffractometer using Cu-Ka radiations filtered by a nickel foil over the range of diffraction angle 20=3-40^{o} , where 0 is the Braggs angle. The wavelength of radiations was 1.542 .

3. Results and discussion

Infrared absorption spectra

The infrared spectral bands and their tentative assignments for gadolinium and cerium soaps are assigned and compared with the potassium myristate and myristic acid (Table 1) The vibrational frequencies characteristic of the aliphatic portion of fatty acids do not vary even when acid is converted into potassium or lanthanide soaps. The myristic acid displays a very board intense peak due to OH stretching near 2640 cm. The appearance of the absorption band near 1700 cm in the spectrum of myristic acids reveals that the myristic acid exists as a dimer and confirms the existence of intermolecular hydrogen bonding between two molecules of myristic acid. One of the characteristic bands of dimeric carboxylic acid results from the out-of-plane bending – OH group appearing near 940 cm. The absorption maxima near 690 and 550 cm in the spectrum of myristic acid are associated with carboxyl group bending and wagging modes and are dependent on the chain length of the fatty acid redical.

Table-1
Frequencies (cm^{-1}) of absorption maxima with their assignment of gadolinium and cerium myristates

Assignments	Myristic acid	Potassium myristate	Gadolinium myristate	Cerium myristate
CH_3, C-H asym stretch.	2960 Vm	-	2960 S	2960 S
CH_2, C-H asym stretch.	2920 Vs	2920 Vs	2920 Vs	2920 Vs
CH_2, C-H asym stretch.	2640 Vw	2640 Vw	-	-
OH stretch	2640 Vw	2640 Vw	-	-
C=O stretch	1700 Vs	-	-	-
COO^-, C-O asym. stretch.	-	1550 Vs	1530 S	1530 S
CH_2 deform.	1465 Ms	1460 Ms	1470 S	1470 S
C-O stretch. + O-H in-plane deformation	1430 Ms	1445 Ms	1455 M	1455 M
COO^-, C-O sym. stretch	-	1420 M	1410 M	1410 M
Progressive bands (CH^2 twist and wag)	1350-1190 W	1100 W	1150 S	1150 S
CH_3 rocking	1120-1065 W	1105-1120W	1040 S	1000 M
		-		
OH out-of-plane deform	940 M	923 S	-	-
COO^- deformation	-	755-725Ms	940 M	940 M
CH_2 racking	735 –	700 Ms	720 S	720 M
	725 Ms	580-545 S	680-620 M	675 M
COOH, bending mode	690 Ms	-	600-500 M	550 M
COOH, wagging mode	550 Ms		440 S	440 S
M-O bond	-			

Key to abbrcviations : S= strong, M= medium, W=wcak, Vs- very strong, Ms= medium strong, Vw= very wcak

The infrared spectra of potassium and lanthanide myristates show marked differences with the spectra of corresponding fatty acids in some spectral regions. The characteristic vibrations of free myristic acid were found completely absent in their respective regions in the spectra of potassium and lanthanide myristates. The complete disappearance of the carbonyl frequency at 1700 cm^{-1} and the appearance of two absorption bands of carbonyl group corresponding to the symmetric and asymmetric vibrations of carboxylate ion near 1415 and 1530 cm^{-1}, respectively, in the spectra of potassium and lanthanide soaps indicate that there is a complete resonance in the C-O bonds of carbonyl group of the soap molecule and the two bonds become identical with the force constants assuming the value intermediate between those of normal double and single bonds. It is, therefore, concluded that the resonance character of the ionized carboxyl group is retained in these metal soaps.

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Resonance hybrid structure of carboxylate ion

It may be pointed out that the metal-ro-oxygen bonds in the ionized structure of gadolinium and cerium myristate should have an ionic character. However, the bonds in gadolinium and cerium myristates are not purely ionic but partially covalent in character. The band observed at 440 cm^{-1} corresponds to M-O bond in the specira of lanthanide soaps.

In the spectrum of myristic acid, no band corresponding to asymmetric and symmetric vibrations of carboxylate ion is observed. Naturally, the – OH stretching band near 2640 cm and – OH deformation band at 940 cm observed in the spectrum of myristic acid disappeared in the spectra of potassium, gadolinium and cerium myristates. The progressive bands with medium or weak intensity observed in the region of 1390-1150 cm for gadolinium myristate and 1340-1150 cm for cerium myristate are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecules of the soap or acid. It may be pointed out that these absorption peaks are weaker in the spectra of metal soaps than in the spectra of fatty acids.

The results confirm that the myristic acid in solid state exists in a dimeric structure through hydrogen bonding whereas the metal-to-oxygen bands in gadolinium and cerium myristate are not purely ionic but somewhat covalent in character. It is also proved that soap molecules retain the resonance character of the carboxyl group. The IR spectra of these metal soaps do not show any absorption maxima in the region of 3500-3300 cm which indicates the absence of any coordinated water molecules in soaps.

X-Ray diffraction analysis

Since a large crystal of metal soaps sufficient for detailed crystal examination can not be prepared, the X-ray diffraction patterns of gadolinium and cerium myristates have been investigated to characterize the structure of these soaps in solid state. The intensities of diffracted X-ray as a function of diffraction angle, 20, for gadolinium and cerium myristate were recorded with the help of X-ray diffractometer and the recorded curves were reproduced over the range of 3-60^{0}C. the interplanar spacing, d, were calculated from the position of intense peaks using Bragg's relationship, nx=2d sin0, where __ os the wavelength of the radiation. The calculated spacings together with the relative intensities with respect to the most intense peaks are recorded in Table-2

Table-2
X-ray diffraction analysis of gadolinium myristates

No.	2	Ø	$\sin\theta$	$\frac{\lambda}{2\sin\theta}$	D(	N
1	6.73	3.36	0.0586	13.15	39.45	3
2	8.93	4.47	0.0779	9.89	39.58	4
3	11.17	5.59	0.0974	7.92	39.59	5
4	13.41	6.71	0.1168	6.60	39.61	6
5	15.65	7.82	0.1361	5.66	39.64	7
6	17.39	8.96	0.1558	4.96	39.58	8
7	20.17	10.09	0.1751	4.40	39.62	9
8	22.30	11.15	0.1934	3.99	39.86	10
9	24.84	12.82	0.2150	3.59	34.44	11
10	34.21	17.10	0.2941	2.62	39.32	15
11	43.65	21.82	0.3717	2.07	39.40	19

Average Value of d=39.55 | |

Cerium myristate						
No.	2	Ø	$\sin\theta$	$\frac{\lambda}{2\sin\theta}$	D(	N
1	6.73	3.37	0.0587	13.13	39.40	3
2	8.95	4.48	0.0781	9.88	39.50	4
3	11.18	5.59	0.0974	7.91	39.56	5
4	13.43	6.72	0.1169	6.59	39.56	6
5	15.68	7.84	0.1364	5.65	39.56	7
6	17.93	8.96	0.1558	4.95	39.58	8
7	20.18	10.09	0.1752	4.40	39.60	9
8	22.45	11.23	0.1947	3.96	39.60	10
9	24.72	12.36	0.2141	3.60	39.62	11
10	26.98	13.49	0.2333	3.30	39.65	12
11	29.31	14.65	0.2530	3.05	39.92	13
12	31.62	15.81	0.2724	2.83	39.62	14
13	33.94	16.97	0.2919	2.64	39.62	15
14	38.83	19.42	0.3324	2.32	39.42	17
15	40.81	20.40	0.3486	2.21	39.80	18
16	43.37	21.69	0.3695	2.09	39.64	19

Average Value of d=39.60 | |

A large number of intense peaks arising from the diffraction of X-rays by plans of gadolinium and cerium ions (know as basal planes) were observed over the range of $3\text{-}50^0$ of the diffraction angle in the diffraction patterns of gadolinium and cerium myristates. The appearance of the diffraction patterns of gadolinium and cerium myristates. The appearance of the diffractions upto 19th order for these soaps suggests good crystallinity for the soaps. The order of diffraction decreases with the decrease in chain length of the soap molecules. The interplanar spacings calculated for 3rd, 4th, 5th, 6th, 7th, 8th, 9th, 10th, 11th, 15th and 19th order diffraction for gadolinium myristate are 39.45, 39.58, 39.59, 39.61, 39.64, 39.58, 39.62, 39.86, 39.44, 39.32 and 39.40/A/, respectively. The average planar distance, i.e. the long spacing for gadolinium myristate is 39.55 A.

The interplanar spacings for cerium myristate for 3rd, 4th, 5th, 6th, 7th, 8th , 9th, 10th, 11th, 12th, 13th, 14th, 15th, 16th, 17th, 18th and 19th order diffiractions are 39.40, 39.50, 39.56, 39.56, 39.58, 39.60, 39.60, 39.62, 39.65, 39.92, 39.62, 39.62, 39.42, 39, 80 and 39.64 A, respectively. The average planar distance is 39.60 A. The difference in the observed values of long spacings of gadolinium myristate (39.55A) and palmitate (44.51A) is 4.96 A which corresponds to double the length of additional methylene ($-CH_2$) group in the fatty acid radical constituent of the soap molecules. The values of the long spacings for these soaps are almost equal to double the length of fatty acid radical of the soap molecule. It is, therefore, suggested that the zig-zag chains of the fatty acid radical extend straight forward on both sides of each basal plane.

The results of X-ray diffraction of lanthanide myristates show that the observed value of the long spacings for these soaps (gadolinium myristate : 39.55 A and cerium myristate : 39.60 A) are smaller than the calculated dimensions of myristate ion (42 A) from pauling's values of atomic radii and bond angles. This suggests that the molecular axes of gadolinium and cerium myristates are somewhat inclined to the basal plane and the metal ions fit into spaces between oxygen atoms of the ionzined carboxyl groups without a large strain of the bonds.

Numerous diffraction peaks in the intermediate range of the diffraction angles are also observed in the diffraction patterns of gadolinium and cerium myristates and these are attribute to the diffraction of X-ray by planes of atoms of much smalier separation than the basal planes. The calculated spacings from these peaks correspond to the shorter side 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 spacing peaks are relatively weak.

On the basis of long and short spacings, it is proposed that the metal ions in gadolinium and cerium myristates are arranged in a parallel plane 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 these soaps have double layer structure as proposed by void and Hattiangdi.

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