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Spectroscopic Analysis of Praseodymium Soaps

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ABSTRACT: The spectroscopic characteristics of praseodymium soaps (Caprylate& Laurate) in solid state were investigated by Infrared absorption spectra, X-ray diffraction patterns and Thermal analysis. The IR results report that the fatty acids subsist in dimeric state through hydrogen bonding and praseodymium caprylate and praseodymium laurate were ionic in nature. The X-ray diffraction measurements were used to calculate the long spacing and the results assert the double layer structure of praseodymium caprylate and laurate. The TGA technique was used for Praseodymium soaps to determine their thermal degradation inert atmosphere, which was found to be a multi-step decomposition related to the release of the metal soaps.

Keywords: Praseodymium soap; IR; X-ray diffraction and TGA.

INTRODUCTION: The term metallic soap is used to describe alkaline earth and heavy metal salts of fatty acids that are insoluble in water and soluble in fatty acids preferably linoleats, caprylate, laurate, myristate, palmitate, stearate successively. The solubility depends on temperature .Metallic soaps are widely used in stabilizers, plasticizers, lubricants, catalysers, cosmetics, medicines, emulsifier and water-proofing agents.[1-4] The physicochemical properties of metal soaps in solid state have been investigated by several workers.[1-17] S. K. Upadhyaya et al.[5] studied thermal, infrared and x-ray diffraction analysis of manganese and zinc soaps. Lanthanum soap were prepared by Skrylev et al.[6]

MATERIAL AND METHODS: AnalaR grad fatty acids (caprylic, laurate), potassium hydroxide, methanol, benzene, ethanol, and metal salt were used for the present investigation (purity 99.9% received from Indian Rare Earth Limited, Kerala).The inorganic metal salt used for preparation of praseodymium soaps was acetate. The metal soaps were prepared by the direct metathesis of corresponding potassium soaps (potassium caprylate and potassium laurate) by pouring a slight stoichiometric excess of aqueous metal salt solution into the clear soap dispersion at raised temperature with vigorous stirring.

$$(CH_3COOH)_3Pr + 3ROOK \rightarrow 3(RCOO)_3Pr + 3CH_3COOK$$

(Praseodymium soap)

Where R is C_7H_{15}, $C_{11}H_{23}$ for caprylate and laurate respectively. The precipitated soaps were filtered and final washed with alcohol and acetone. After initial drying in an air oven 50^0-60^0 C, final drying was carried out under reduced pressure.

The infrared absorption spectra of caprylic acid, lauric acid and corresponding potassium, praseodymium caprylate, praseodymium laurate were recorded with a” FTIR –Bruker, Tensor 27” spectrophotometer in the region 4000-400 cm^{-1} using potassium bromide disc method.

The X-ray diffraction patterns of praseodymium soaps (praseodymium caprylate and praseodymium laurate) were obtained with “PXRD-Rlgaku, Smartlab “X-ray diffractometer using Cu-Kα radiation filtered by a nickel foil. The instrument yields an automatically recorded curve of intensity of diffracted X-ray versus diffraction angle 2θ.Bragg’s spacing corresponding to interplanar separation of the reciprocal

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

Where the wavelength (λ) of radiation was taken 1.5406 Å.

Thermogravimetric analysis of praseodymium caprylate and praseodymium laurate was undertaken at heating sample from 50^0 C to 930^0 C at constant rate of heating (20^0 C/min) under nitrogen atmosphere in a TGA Mettler Toledo (IIT Indore)

RESULTS AND DISCUSSION:

Infrared Absorption Spectrum: Figures 1and 2 shows the infrared absorption spectra of praseodymium caprylate and praseodymium laurate. The frequencies (cm^{-1}) of the absorption maxima in the Table 1. The vibrational frequencies characteristic of aliphatic chain of fatty acid do not very even when fatty acid is converted into potassium and praseodymium soaps.

The infrared spectra of fatty acids indicate that the carboxyl group shows the characteristics frequencies at 2500-2700 cm^{-1}. (Broad O-H stretching vibrations), The appearance of the absorption band near 1700 cm^{-1} in IR spectra of fatty acid reveal that fatty acid exist as dimer[6] and confirms the existence of Intramolecular hydrogen bonding between two molecule of fatty acid. 1430 cm^{-1} (C-O stretching, O-H in plane deformation) and 940 cm^{-1} (O-H out of plane deformation).

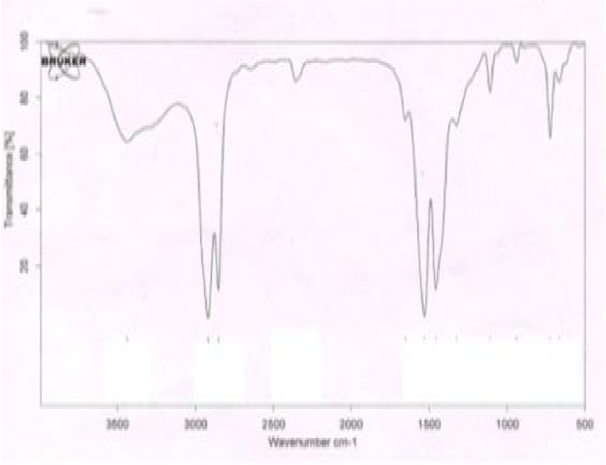

Figure 1: Infrared spectrum of praseodymium caprylate.

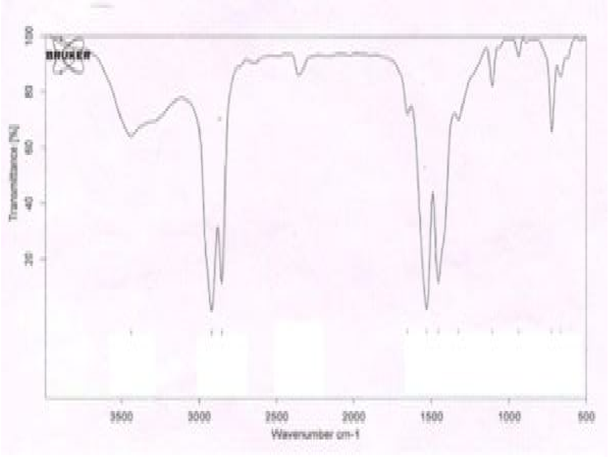

Figure 2: Infrared spectrum of praseodymium laurate.

The IR absorption bands at 2640-2650, 930-950 690 and 550 cm $^{-1}$which are completely or partly associated with the OH group in the infrared absorption of fatty acids, either disappeared or changed rarely in intensity in the spectra of corresponding potassium and praseodymium soaps. The presence of water of crystallization give rise to weak bend at 3400-3100 cm $^{-1}$ which is usually narrow and in such case a weak bend at 1640-1615 cm^{-1} due to H-O-H bending is also observed [7].The IR spectra of these soaps show o broad peak at near about 3300 cm^{-1} and other peaks at 1640-1615 cm $^{-1}$ which supports the water of crystallization is not observed in the spectra of praseodymium soaps, which confirm the absence of water of crystallization [8].The progression bands occurring in the 1400-1050 cm $^{-1}$ are assigned to the twisting and wagging vibrations of the chain of successive methylene group of soap molecule. It is noticed that these absorption are somewhat weaker in potassium and praseodymium soaps than in corresponding fatty acids. The absorption maxima with strong intensity observed in the region 750-710 cm^{-1} in the spectra of praseodymium soaps. These absorption bands are associated with the fundamental mode of CH_2 rocking vibration of a chain of successive methylene group $(CH_2)_n$ and are sensitive to the crystallization of soap.

Table: 1 Infrared absorption spectral frequencies (cm^{-1}) with their assignments.

S. No.	**Assignment**	**Caprylic Acid**	**Potassium Caprylate**	**praseodymium caprylate**
1	CH_3,C-H asymmetric-streching	2950 w	2960 w	2958.3(m)
2	CH_2,C-H asymmetric-streching	2920 s	2920 vs	2923.22 (s)
3	CH_2,C-H symmetric-streching	2850 s	2860 m	2856.77
4	OH,streching	2650w	-	-
5	C=O,streching	1700 vs	-	-
6	COO^-,C-O asymmetric stretching	-	1550 m	1538.44
7	CH_2, deformation	1460	1460 w	1455.23 (m)
8	COO^-,C-O symmetric stretching	-	1430 m	1420
9	C-O streching,O-H in plane deformation	1430 w	-	-
10	CH_2 (adjacent to COOH group),deformation	1410 vs	-	-
11	CH_3,symmetric deformation	1350 w	1350 w	1370.5
12	Prograsive bands (CH_2 twisting and wagging)	1340-1040 m	1340-1100 w	1350-1112.28 (w)
13	CH_3,rocking	1100 vs	1050 w	1115.95
14	OH ,out of plane deformation	940 s	-	940.61 (m)
15	CH_2 ,rocking	720 ms	730 ms	722.40 (m)
16	COOH,bending mode	690 m	-	674.19 (m)
17	COOH, wagging mode	550 ms	-	520 (w)

Key to abbreviation's = weak; s = strong;V_s *= very strong;m = medium;* M_s *= medium strong;*V_w *= very weak.*

The result show that the fatty acids in the solid state state exist with dimeric structure through hydrogen bonding between carbonyl group of the two acid molecule whereas potassium, praseodymium caprylate and laurate ionic in nature.

X-ray diffraction analysis: X-ray diffraction patterns cover an important position as one of fundamental data in the investigation of metal soaps. X-ray diffraction could be successfully employed for obtaining, the complete information about the intermolecular interaction in the molecule, a detail picture of thermal vibration of each atom in the crystal.

By using the X-ray diffractometer, automatically recorded curves of the intensity of the diffracted X-ray v.s. the diffraction angle 2θ have been obtained Bragg's interplanar spacing, *d*, where calculated from the position of the peaks in each curve using the relation.

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

where λ is the wave length of the radiation in figure 2 the diffraction patterns of the two praseodymium soap thus obtained are reproduced over the range of diffraction angle 3^o-80^o. These are attributing to the diffraction of X-ray by planes of soaps in much smaller separation than the based. The calculated spacing together with relative intensities with respect to the most intense peaks is recorded in table 2 for praseodymium caprylate and praseodymium laurate.

Table 2: X-ray analysis and determination of long spacing, d of pr-caprylate and pr-laurate.

S. No.	2 θ	θ	Sin θ	λ/2 Sin θ	d (Å)	n
1	3.522	1.761	0.0307	25.0912	25.1	1.00
2	7.261	3.6305	0.0633	12.169	25.79	2.12
3	10.731	5.3655	0.0935	8.2385	25.5	3.10
4	14.339	7.1695	0.1248	6.1722	25.72	4.17
5	17.975	8.9875	0.1562	4.931	25.06	5.08
6	21.357	10.6785	0.1852	4.1592	25.85	6.22
7	25.3	12.65	0.2189	3.5189	25.96	7.38
8	28.996	14.498	0.2503	3.0775	25.69	8.35
9	32.749	16.3745	0.2819	2.7325	25.83	9.45
10	36.511	18.2555	0.3132	2.4594	25.95	10.55
11	40.334	20.167	0.3447	2.2346	25.87	11.58
12	44.19	22.095	0.3761	2.0481	25.73	12.56
13	48.125	24.0625	0.4077	1.8893	25.91	13.71
Average value of *d* = *25.689Å*						
S. No.	**2 θ**	**θ**	**Sin θ**	**λ/2 Sin θ**	**d (Å)**	**n**
1	3.238	1.619	0.0282	28.216	34.61	1.27
2	5.118	2.559	0.0446	17.271	34.79	2.01
3	9.685	4.8425	0.0844	9.1267	34.33	3.76
4	10.213	5.1065	0.089	8.655	34.12	3.94
5	12.79	6.395	0.1113	6.759	34.89	5.04
6	14.831	7.4155	0.129	5.971	34.23	5.73
7	16.235	8.1175	0.1412	5.4553	34.96	6.41
8	17.951	8.9755	0.156	4.9378	34.29	6.94
9	19.95	9.975	0.1733	4.4448	34.05	7.66
10	22.104	11.052	0.1916	4.0203	34.59	8.60
11	23.87	11.935	0.2068	3.7248	34.22	9.19
12	28.35	14.175	0.2448	3.1466	34.16	10.86
13	40.49	20.245	0.346	2.2263	34.63	15.55
Average value of d = 34.451 Å						

A fatty acid contains a long paraffin chain of linked –CH_2 group with a carbonyl group –COOH situated at one end point of the chain. It is known from the study of other organic compounds that distance between two carbon neighboring atoms is 1.54.

The calculated values of interplanar spacing for praseodymium caprylate and praseodymium laurate are *25.689Å* and 34.451 Å. The difference in long spacing's of these soaps approximately corresponds to the double the length of methylene (-CH_2) group in the fatty acid radical constituent of the soap molecules. It is there for suggested that the zigzag chains of fatty acid radicals extend in both direction with their axes inclined somewhat to the planes containing the metal ions.

Thermogravimetric Analysis: The thermogravimetric analysis has shown that the final residues are metal oxide and the weight of the residues is almost equal to the theoretically calculated weight of metal oxide from the molecular formula of corresponding metal soap.

The thermal decomposition of praseodymium soaps can be expressed as:

$$2\ Pr(RCOO\ )_3 \rightarrow 3\ RCOR\ +Pr_2O_3 + 3CO_2$$

Where R = C_7H_{15}, $C_{11}H_{23}$ for caprylate and laurate respectively.

The thermal stability of the soaps was assessed in terms of temperature at which various extents of decomposition were attained and weight loss at the initial stage of decomposition. I may be pointed out that some white crystalline powder was condensed at cold part of the sample surrounded the soap is detected as ketone. Thermogravimetric analysis shows that praseodymium soaps decompose insignificantly up to 110^0, slowly between 110^0 C and 310 ^{0}C then very rapidly up to 470^0C and finally show very small change with further increase in temperature.

Freeman and Carroll's expression*used for the thermal decomposition of metal soaps, were soaps disappeared continuously with the constant rate of increase in temperature and with passage of time period. In thermal decomposition of metal soaps one of the product being gaseous and Freeman- Carroll's expression can be expressed as:

$\Delta\{\log(dw/dt)\}/\Delta(\log w_r) = - E/2.303R^*\Delta(1/T)/\Delta(\log w_r) + n$

Where; E = Energy of activation, n = Order of reaction, T = Temperature absolute scale, W_r = Difference between the total loss in weight and loss in weight at time t i. e., $w_o – w_t$ and dw/dt = Rate of weight loss obtained from the loss in weight versus time curves at appropriate times.

The activation energy for thermal decomposition process of praseodymium soaps has been calculated from the slope of the plot of $\Delta\{\log(dw/dt)\}/\Delta(\log w_r)$ versus $\Delta(1/T)/\Delta(\log w_r)$. The order of reaction for the thermal decomposition of praseodymium soaps has found almost zero and the value of energy of activation for thermal decomposition of these soaps are in range 30-35 kj mol^{-1}.

CONCLUSION: The IR results showed that fatty acid exist in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two fatty acid molecules, where praseodymium caprylate and laurate possess ionic character. The X-ray analysis showed that praseodymium caprylate and laurate have double layer structure with molecule axes slightly inclined to the basal plane. The thermal decomposition of these soaps found zero order.

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