Infra-Red Absorption Spectra, X-Ray Diffraction Analysis and Thermogravimetric Studies on Neodymium Caprylate, Laurate and Myristate

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ABSTRACT: IR, X-ray diffraction and thermogravimetric studies were used to illustrate the structure of neodymium caprylate, laurate and myristate in solid state. IR results reveals that the fatty acids exists with dimeric structure through intermolecular hydrogen bonding and neodymium caprylate, laurate and myristate were ionic in nature. The X-ray diffraction measurement confirms that these soaps possess double layer structure with a molecular axis slightly inclined to the basal plane. The results of thermogravimetric analysis reveals that the thermal decomposition reaction was kinetically of zero order and energy of activation for the decomposition process lies in the range of 24-32 KJmol^{-1}.

INTRODUCTION: Metal soaps are extensively used in industry as detergents, plasticizers, softeners, greases, lubricants, cosmetics, medicines and stabilizers[1-4]. Other uses of metal soaps are as fungicides and pesticides[5], optical polymer fibers[6 & 7], Coating pigment in Paper industry[8] and in the preparation of nanofilms[9]. The valent thermal behavior of divalent and higher valent metal soaps has been carried out by Akanni et al[10]. The characterization of metal soaps has been done by Robinet et al[11]. Binnemans et al[12] identified the mesophormism formed by La[III] tetradeconate and its higher homologous as a smectic A (smA) phase. In comparison of earlier studies on metal soaps, we report here results of our studies on IR, X-ray and thermal measurements of neodymium caprylate, laurate and myristate with a view to investigate the characteristic and structure of these soaps in solid state.

MATERIALS AND METHODS: AnalaR grade caprylic acid, lauric acid, myristic acid, benzene, ethanol, neodymium acetate (purity 99% Indian Rare-Earth Limited, Kerala) were used for the present investigation. The neodymium caprylate, laurate and myristate were prepared by the direct metathesis of corresponding potassium soaps by pouring a slight stoichiometric excess of aqueous solution of neodymium acetate into the clear dispersion at raised temperature with vigorous stirring. After initial drying in an air oven at 50-60°C, final drying was carried out under reduced pressure. The precipitate was filtered off and washed with hot distilled water and acetone.

Infrared absorption spectra of caprylic acid, lauric acid and myristic acid and their corresponding potassium, neodymium caprylate, laurate and myristate were recorded with a Thermo Nicolet Avtar " 370" spectrophotometer in the region 4000-400cm^{-1} using potassium bromide disc method.

The X-ray diffraction patterns of neodymium caprylate, laurate and myristate were obtained with a "Bruker AXS D8 Advance" x-ray diffractometer using Cu-Kα radiations filtered by a nickel foil. The instrument yields an automatically recorded curve of intensity of diffracted x-rays vs diffraction angle 2θ.

Thermogravimetric analysis of neodymium caprylate, laurate and myristate was undertaken at heating the samples from 35° C to 683° C at constant rate of heating (20°C /min) under nitrogen atmosphere in a Diamond TGDTA temperature scan.

RESULTS AND DISCUSSION: The Infrared spectral bands (Figures 1, 2 and 3) and their tentative assignments for neodymium soaps are assigned and compared with potassium soaps as well as with corresponding fatty acids Table 1.

The characteristic frequencies in the spectra of fatty acid at 2640 (O-H stretching vibrations), 1700 (C=O stretching vibrations), 1450 (O-H in plane bending and C-O stretching) and at 950 cm^{-1} (Out of Plane bending of O-H group) indicates the presence of carboxyl group in the form of dimeric structure and confirms the existence of inter molecular hydrogen bonding between two molecules of fatty acids.

Table 1: Frequencies (cm⁻¹) of Absorption maxima with their assignments of myristic acid, Potassium myristate, Neodymium myristate.

S.No.	Assignment	Myristic acid	Potassium myristate	Neodymium myristate
1	CH_2,C-H asym stretch	2920vs	2920vs	2919s
2	CH_2,C-H sym stretch	2850s	2890s	2851s
3	O-H stretch	2650vw	2640vw	-
4	C=O stretch	1700vs	-	-
5	COO-,C-O asym stretch	-	1550vs	1528s
6	CH_2 deform	1465ms	1460ms	1464s
7	C-O stretch + O-H in plane deform	1449m	1445ms	-
8	COO-,C-O sym stretch	-	1449s	1410w
9	CH_2 (adjacent to COOH group)	-	-	-
10	CH_3 Sym deform	-	-	1319vw
11	Progressive bands(CH_2, Twist and wag)	1350-1090w	1375-1200w	1244-1111w
12	CH_3 rocking	1120-1065w	1105-1120w	1111m
13	OH out of plane deform	940ms	-	940m
14	CH_2 rocking	720w	720ms	722ms
15	COOH bending mode	690ms	-	658m
16	COOH wagging mode	550ms	-	-

Key to abbreviations: vs = very strong; ms = medium strong; w= weak; s= strong; m= medium; vw = very weak.
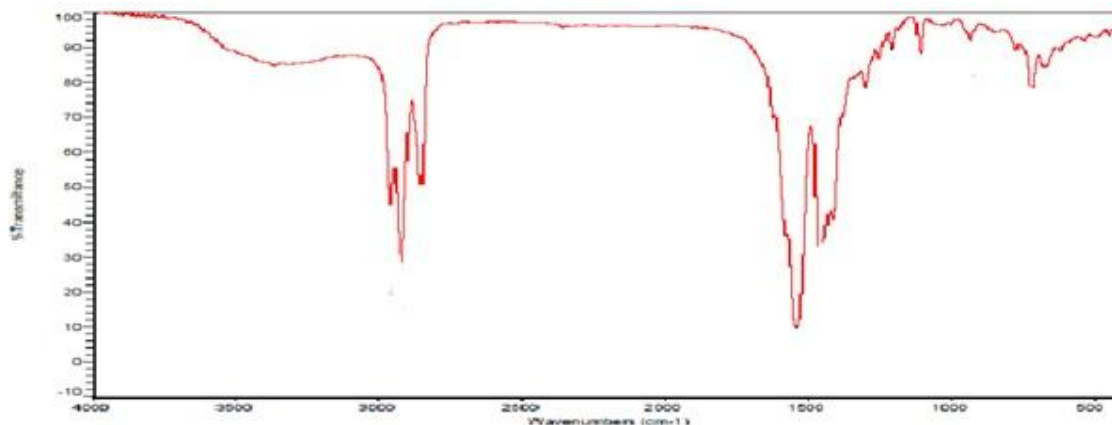

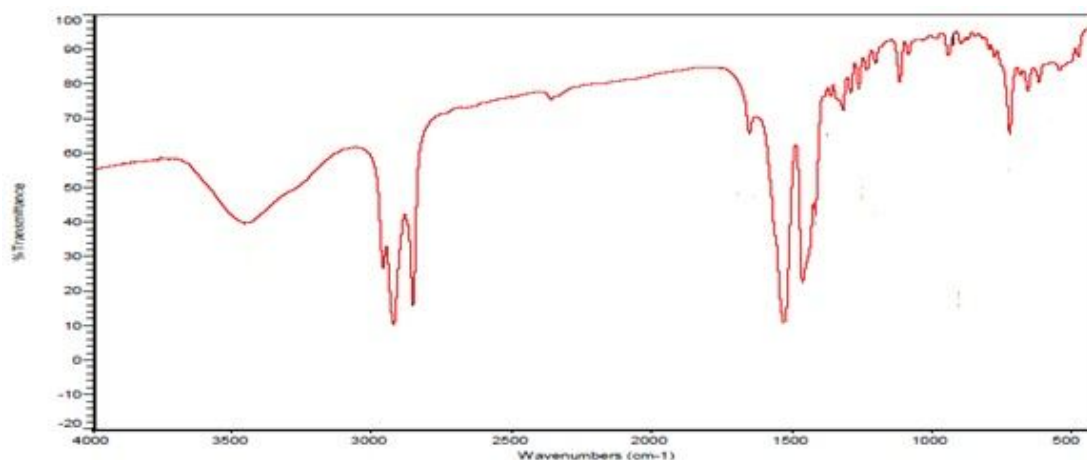**Figure 1: IR of Neodymium Caprylate.**
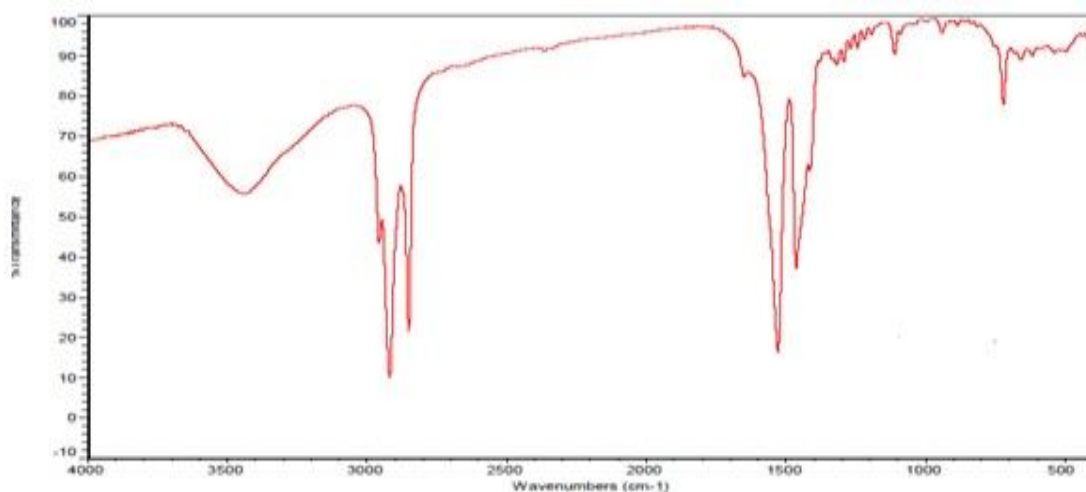

Figure 2: IR of Neodymium Laurate.

Figure 3: IR of Neodymium Myristate.

The infrared spectra of potassium, neodymium caprylate, laurate and myristate illustrate marked difference with the spectra of corresponding fatty acids in some spectral region. Some characteristic vibrations of free fatty acids were found completely absent in their respective regions in the spectra of potassium, neodymium caprylate, laurate and myristate. The disappearance of carboxyl frequency (1700cm^{-1})in the spectra of these soaps indicate that there may be a complete resonance in the two C-O bonds of the carboxyl groups of the soap molecule. The two C-O bonds become identical with their force constants assuming an intermediate value between those of normal double and single bonds.

The appearance of the two absorption bands of the carboxyl group corresponding to the symmetric and asymmetric vibrations of two carboxylate ions lies in the vicinity of 1410-1435 cm^{-1} and 1510-1600 cm^{-1} respectively in the spectra of potassium, neodymium caprylate, neodymium laurate and neodymium myristate instead of one band near 1700cm^{-1} confirms the formation of soaps and indicates that these soaps have an ionic character.

In the spectra of caprylic, lauric and myristic acids, no bands corresponding to symmetric and asymmetric of carboxylate ions are observed. Naturally the OH stretching band near 2650-2550 cm^{-1} and OH deformation band at 940 cm^{-1} observed in the spectra of neodymium soaps. The progressive bands of the medium and weak intensity observed in the region of 1360-1109 cm^{-1} for neodymium soaps are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecule of the soap and fatty acids.

These results confirm that the fatty acid (caprylic, lauric and myristic acids) in the solid state exists with

dimeric structure through hydrogen bonding whereas metal to oxygen bond in neodymium soaps are ionic in nature. It is also proved that the soap molecules retain the resonance character of the carboxylic group. The infrared spectra of neodymium soaps do not indicate any absorption maxima in the region of 3600-3590cm^{-1} which confirms the absence of any coordinated water molecules in the soaps.

A perusal of data collected in Table 1 indicates that the myristic acid exist with dimeric structure through intermolecular hydrogen bonding between carboxylic groups of two fatty acid molecules whereas potassium, neodymium myristate were ionic in nature.

X-Ray Diffraction Analysis: The x-ray diffraction studies of neodymium caprylate, laurate and myristate has been carried out to characterize the structure of these soaps in the solid state. The intensities of diffracted x-ray as a function of diffraction angle, 2θ (twice the Bragg angle) for neodymium soaps were recorded with the help of x-ray diffractometer and the recorded curves are reproduced over the range of 2-80°corresponding to successive order of single long spacing[13 & 14].

Bragg's spacing corresponding to interplanar separation of the reciprocal crystal lattice, were calculated from the peaks in the curves using the relationship
nλ =2d sin θ

Where; λ is wavelength which is equal to 1.5418 Å. The calculated spacing together with relative intensities with respect to the most intense peaks. The intensity and sharpness (half-width; i.e., angular width of the peak at half its maximum intensity) of the peaks are a measure of degree of crystallinity of the sample. The difference in the long spacing's of these soaps approximately corresponds to double the length of methylene (-CH$_2$) groups in the fatty acid radical con-

stituent of the neodymium soap molecules. It is, therefore, suggested that the zig-zag chains of fatty acid radicals extend in both directions with axes inclined somewhat to the planes containing the metal ions.

In these neodymium soaps the metal ions appears to be arranged in planes in which the fatty acid radicals extend in both directions with their axes inclined somewhat to the plane containing the metal ions. The distance between the planes is equal approximately to twice the length of the fatty acid radical, times the sine of the angle of inclination, since the soap molecule either have double layers of cations with acid radicals extending out on either sides therefore, seems that the cations affect the angle of inclination of the molecular axes to the planes containing the neodymium ions. These values for long spacing increases with increasing chain length of the neodymium soap molecule.

It is therefore concluded that the cations affect the angle of inclination of the molecular axes to the planes containing the cations. The metal cations fit into spaces between oxygen atoms of the ionized carboxyl group without giving a large strain of the bond. Numerous diffraction peaks in the intermediate range of the diffraction angles are also observed in the diffraction patterns of neodymium soaps and these are attributed to the diffraction of x-rays by plane of atoms separated by much smaller distances than those of basal planes and are thus referred to as short spacing. The numerical values gives distance between planes in the reciprocal crystal lattice and can be directly related to real distances between the molecules only by making assumptions about the crystal types. It is observed from the x-ray pattern of neodymium soaps that long spacing peaks are fairly intense whereas short spacing peaks are relatively weaker.

On the basis of long and short spacing , it may be concluded that metal ions in rare-earth soaps 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 directions of each basal plane and these neodymium soaps possess double layer structure. The double layer structure of some heavy metal soaps was also suggested by Vold et al[15]. The molecular axes of transition metal soaps were found to be more inclined to the basal plane than rare-earth metal soaps[16-19].

The thermal decomposition of neodymium caprylate, laurate and myristate was studied by thermogravimetric analysis. The heating rate 20°C/min and nitrogen atmosphere were used. The final decomposition product or residue left on heating these soaps were the neodymium oxide as the weights of the resi-

dues were almost in agreement with the theoretically calculated weights of neodymium soaps and neodymium oxide from molecular formula of the corresponding soap. The thermal decomposition of neodymium soaps may be expressed as:

$$2(RCOO)_3Nd \rightarrow 3RCOR + Nd_2O_3 + 3CO_2$$

Where; $R = C_7H_{15}$, $C_{11}H_{23}$ and $C_{13}H_{27}$ for caprylate, laurate and myristate respectively.

The results of thermal decomposition of neodymium soaps were explained in the light of Freeman-Carroll's[20] equations expressed as follows

$$\frac{\left(log\left(\frac{dw}{dt}\right)\right)}{\left(\Delta(logW_r)\right)} = \frac{E}{2.303R} - \frac{\Delta\left(\frac{1}{T}\right)}{\Delta(logW_r)} + n$$

The plots of the loss in weight of the neodymium soaps , w, against time, t are shown in figures 4 , 5 & 6 and values of (dw/dt) are obtained from the curves by drawing tangents at appropriate times. The plots of $\Delta(log (dw/dt))/\Delta(log W_r)$ versus $\Delta(1/T) \Delta(log W_r)$ provide linear relationship. Slope of this enables us to calculate activation energy for the decomposition process and intercept provides n. The order of the decomposition reaction which was found to be zero and the values of the activation energy for the decomposition were in the range 24-32 KJ mol^{-1}.

The energy of activation for the thermal decomposition of neodymium soaps were also calculated by the equations proposed by Horowitz-Metzgers[21] and Coats-Redfern[22]. The values of energy of activation derived from these equations were in fair agreement with the values calculated from Freeman-Carroll's equation.
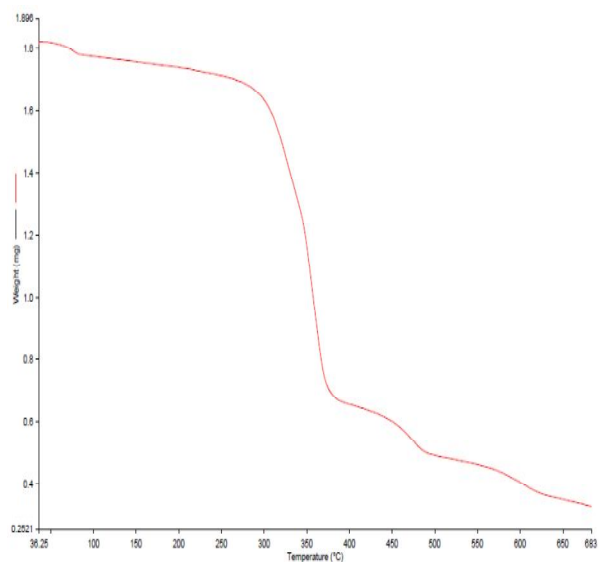

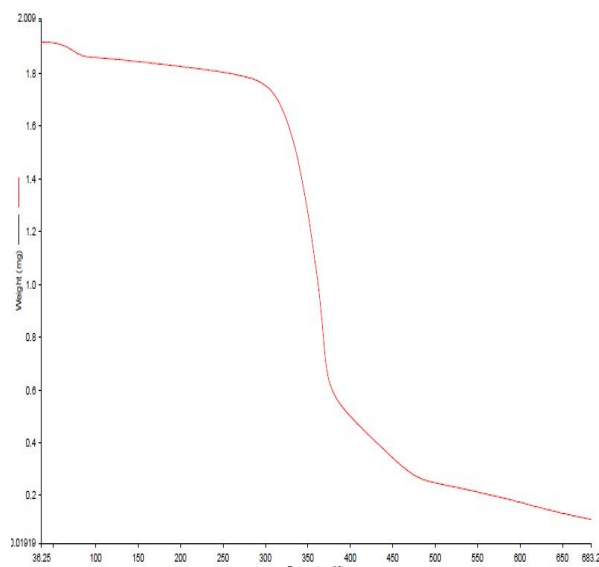**Figure 4:   Thermogram of Neodymium Caprylate.**

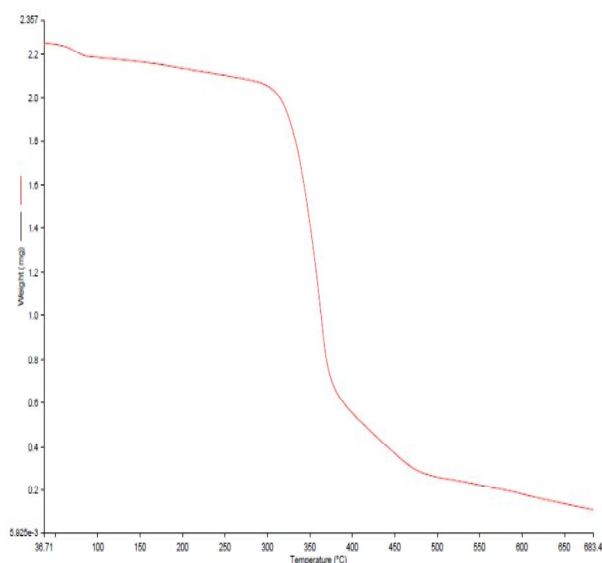**Figure 5: Thermogram of Neodymium Laurate.**

Figure 6: Thermogram of Neodymium Myristate.

CONCLUSION: The IR results showed that fatty acid exists in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two fatty acid molecules, whereas neodymium soaps possess ionic character. The X-ray analysis showed that neodymium soaps possess double layer structure with molecular axes slightly inclined to the basal plane. The thermal decomposition of these soaps was found to be kinetically of zero order and the energy of activation for the decomposition process was in the range 24-32 KJ mol^{-1} .

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