

# Comparative Physico Chemical Studies on Manganese and Iron Soaps in Solid State



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## Abstract

The Physicochemical characteristics of manganese and iron soaps, myristate and stearate, in solid state were investigated by I.R , X rays diffraction and thermogravimetric analysis. The I.R. results confirm that these soaps have partial ionic character and the fatty acids exist as dimer through hydrogen bonding. The X ray diffraction measurement results revealed that soaps have double layer structure with molecular axes slightly inclined towards the basal plane. Thermogravimetric analysis result shows that thermal reaction were found to be kinetically zero order and the energy of activation for the decomposition processes for soaps were found to be 7.67 to 17.84 k.cal /mol.

**Keywords:** Iron, Manganese, X-Ray Diffraction, Thermal Analysis, Infrared, Physicochemical, Metallic Soaps.

## Introduction

The study of metallic soaps is becoming increasingly important in industrial as well as in academic fields. Several workers<sup>1-7</sup> studied on nature and structure of these soaps are of great importance for their use in industries and for explaining their characteristic under different condition. The present work deals with the infrared, X ray and thermal analysis of manganese and iron soaps in solid state and has been initiated with a view to obtain information ionic nature, structure and energy of activation for the decomposition reaction.

## Experimental

All the chemical used were of AR grade. Manganese and iron soaps were prepared by direct metathesis of corresponding potassium soap (myristate and stearate) with slight excess of the solution of manganese chloride and ferric chloride, respectively under stirring. The precipitated soaps were washed several times with distilled water and acetone. The soaps were purified by recrystallization with benzene – methanol mixture. The purity of the soaps were confirmed by determining their melting points. The infrared absorption spectra of myristic and stearic acid and of corresponding potassium, manganese and iron soaps were obtained with a NICOLET 5 DXFT instrument (U.S.A.) in the region of 4000 – 200 cm<sup>-1</sup> using potassium bromide disc technique.

The X-ray diffraction patterns for manganese and iron metal soaps of myristate and stearate were obtained with a RIGAKU (Geigerflex – RB – RU – 200) X-ray diffractometer using Cu – K $\alpha$  radiations filtered by a nickel foil over the range of diffraction angle  $2\theta = 30$  to  $80^\circ$  (where  $\theta$  is Bragg's angle). The XRD curves were recorded under the applied voltage of 35kv using scanning speed of 10 per minute and chart speed of 1 cm per minute. The wavelength of the radiations was taken as 1.54 Å.

The thermogravimetric analysis of manganese and iron soaps was carried out by 780 series-Stanton Redfort (U.K.) in the static air medium at constant heating rate 100 per minute and maintaining similar conditions through the investigations.

## Results and Discussion

### Infrared Spectra

The wave number of some important absorption maxima in infrared absorption spectra of manganese and iron soaps, myristate and stearate, were assigned spectra of manganese and iron as compared with those fatty acid, myristic acid, and spectra of manganese stearic acid, as mentioned in table 1 and 2.

**Table 1**  
**IR Absorption Frequencies (Cm<sup>-1</sup>) Together With Their Assignments**

S. No.	Assignment	Stearic acid	Potassium stearate	Manganese stearate
1.	CH <sub>3</sub> , C – H asymmetric stretching	2950 s	2950 ms	--
2.	CH <sub>2</sub> , C – H asymmetric stretching	2920 vs	2910 vs	2880 s
3.	CH <sub>2</sub> , C – H symmetric stretching	2860 s	2860 s	2860 s
4.	OH, stretching	2650 w	--	--
5.	C=O, stretching	1700 vs	--	--
6.	COO <sup>-</sup> , C – O asymmetric stretching	--	1560 vs	1550 vs
7.	COO <sup>-</sup> , C – O symmetric stretching	--	1440 m	1445 s
8.	CH <sub>2</sub> , deformation	1465 ms	1465 ms	1460 s
9.	C – O, stretching, OH in plane deformation	1430 vs	--	--
10.	CH <sub>2</sub> (adjacent to COOH group) deformation	1410 m	--	--
11.	CH <sub>3</sub> , symmetric deformation	1370 w	1370 m	1340 s
12.	Progressive bands (CH <sub>2</sub> twisting and wagging)	1350 – 1100 m	1320 – 1190 m	--
13.	CH <sub>3</sub> , rocking	1110 w	1110 w	1110 w
14.	OH, out of plane deformation	940 w	--	--
15.	CH <sub>2</sub> rocking	720 s	715 ms	710 s
16.	COOH, bending mode	680 w	--	--
17.	COOH, wagging mode	550 w	--	--
18.	Mn – O bond	--	--	460 vs

**Table 2**  
**IR Absorption Frequencies (Cm<sup>-1</sup>) Together With Their Assignments**

S. No.	Assignment	Stearic acid	Potassium stearate	Iron (III) stearate
1.	CH <sub>3</sub> , C – H asymmetric stretching	2960 s	2955 ms	--
2.	CH <sub>2</sub> , C – H asymmetric stretching	2910 vs	2915 vs	2885 s
3.	CH <sub>2</sub> , C – H symmetric stretching	2840 s	2855 s	2850 s
4.	OH, stretching	2640 w	--	--
5.	C=O, stretching	1700 vs	--	--
6.	COO <sup>-</sup> , C – O asymmetric stretching	--	1550 vs	1555 vs
7.	COO <sup>-</sup> , C – O symmetric stretching	--	1445 m	1440 s
8.	CH <sub>2</sub> , deformation	1460 ms	1460 m	1455 s
9.	C – O, stretching, OH in plane deformation	1420 vs	--	--
10.	CH <sub>2</sub> (adjacent to COOH group) deformation	1410 m	--	--
11.	CH <sub>3</sub> , symmetric deformation	1380 w	1380 w	1345 s
12.	Progressive bands (CH <sub>2</sub> twisting and wagging)	1350 – 1110 m	1325 – 1180 m	--
13.	CH <sub>3</sub> , rocking	1100 w	1100 w	1100 w
14.	OH, out of plane deformation	945 w	--	--
15.	CH <sub>2</sub> rocking	730 s	710 ms	705 s
16.	COOH, bending mode	685 w	--	--
17.	COOH, wagging mode	550 w	--	--
18.	Fe – O bond	--	--	430 vs

The absorption maxima of aliphatic portion of both fatty acids remain unchanged on the formation of potassium manganese and iron soaps. The absorption band observed near 2640,1700,1370-1410-940,690,cm<sup>-1</sup> in myristic acid and 2650,1700,1410-1430,940,680 cm<sup>-1</sup> in stearic acid are associated with the localized group as explain by K.Nakanishi<sup>8</sup> and C.Duval<sup>9</sup> of acid molecule in dimeric state and which confirm the existence of intermolecular hydrogen bonding.

The absorption maxima near 1700,1410,690,550, in myristic acid and 1700,1430,680,550cm<sup>-1</sup> in stearic acid are characteristic frequencies of carboxyl group

were not observed in the spectra of potassium, manganese and iron soaps. The complete disappearance of carbonyl frequency in the vicinity of 1700 cm<sup>-1</sup> and the appearance of absorption bands of carboxyl group corresponding to the symmetric vibrations of carboxylate ion near 1415 – 1445, 1430 – 1415, 1350 - 1440 cm<sup>-1</sup> and for asymmetric vibrations 1540 – 1560, 1550 – 1560 and 1540 - 1560 cm<sup>-1</sup> in potassium, manganese and iron soaps, respectively, indicate that there is a complete resonance in the C – O bonds of carbonyl group of the soap molecules 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 ionized carboxyl group is retained in these metal soaps.

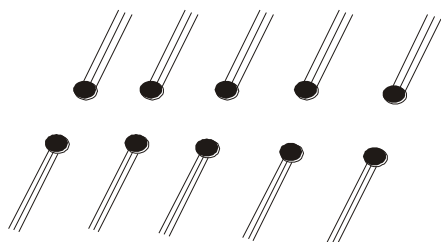
The band observed near  $440 - 460 \text{ cm}^{-1}$  assigned to Mn – O bond in the spectrum of manganese soaps of myristic and stearic acid and bond near  $420 - 430 \text{ cm}^{-1}$  assigned to Fe – O bond i.e metal to oxygen bond, respectively. The IR spectra of these metal soaps do not show any absorption maxima in the region of  $3500-3300 \text{ /cm}$  which confirms absence of water of crystallization.

The result shows that the fatty acids exist with dimeric structure through hydrogen bonding between two carboxyl group of two acid molecule and manganese and iron soap ionic in nature and the metal to oxygen bond in these soaps have ionic character. The assigned frequencies are in agreement with the result of other workers.

#### X-Ray Diffraction Analysis

The metal soaps do not form large crystal sufficient for a detailed single crystal examination and so the X-ray diffraction patterns of manganese and iron soaps of different fatty acids have been analysed to characterize the structure of these soaps in solid state.

In X-ray diffraction patterns of manganese and iron soaps (myristate and stearate), numerous peaks are observed over the range of the diffraction angle  $5-80^\circ$ . The interplanar spacings,  $d$ , have been calculated from the position of intense peaks using Bragg's relationship,  $n\lambda = 2d \sin\theta$ , together with the relative intensities with respect to most intense peak. The appearance of diffractions upto  $26^{\text{th}}$  and  $38^{\text{th}}$  order for myristate and stearate of manganese and  $14^{\text{th}}$  and  $38^{\text{th}}$  for myristate and stearate of iron confirms good crystallinity for these soaps.



The average planar distance i.e long spacing for manganese myristate and stearate are  $39 \text{ \AA}$  and  $47.6 \text{ \AA}$  and this difference is  $8.6 \text{ \AA}$ , for iron myristate and stearate are  $39.45 \text{ \AA}$  and  $47.05 \text{ \AA}$  and the difference is  $7.6 \text{ \AA}$  corresponds to double the length of additional methylene in the fatty acid radical constituents of the soap molecules. The observed values of long spacings were smaller than the calculated dimensions of these anions from Pauling's values of atomic radii and bond angles which suggests that the molecular axis of these soap molecules are somewhat inclined to the basal planes. The metal ions  $\text{Mn}^{++}$  and  $\text{Fe}^{+++}$  fit into spaces between oxygen atom of the ionized carboxyl group without a large strain of the bond.

A large number of peaks in the intermediate range are also observed in the diffraction patterns of manganese and iron soaps and are attributed to the diffraction of the X-rays by planes of atom of much smaller separation than the basal planes. The calculated spacings from their peaks correspond to the shorter side spacings i.e. the lateral distance 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 on the basis of long and short spacings. The values of long spacings for manganese and iron soaps are in agreement with the double layer structure of the soaps proposed by Vold and Hattiangdi<sup>10</sup> in which the metal ions arranged in parallel planes equally spaced in the soap crystal with fully extended zig-zag chain of fatty acid radicals on both sides of each basal planes.

● Polar head

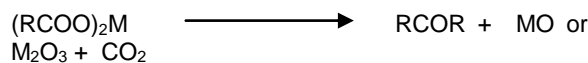
/ Hydrocarbon chain

The result suggests that manganese and iron soaps of different acids possess single layer structure with molecular axes somewhat inclined to the basal plane.

#### Thermogravimetric Analysis

The results of thermal analysis of manganese and iron soaps show that the final residue is metal oxide and the weights of the residue are in agreement with the theoretically calculated weights of manganese oxide and iron oxide from molecular formula of the corresponding soaps. It is found that some white powder condenses at the cold part of the sample tube surrounding the soap and it is identified as myristone and stearone for myristate and stearate of manganese and iron, respectively.

The thermal decomposition of these soaps may be expressed as :



Where R is  $-\text{C}_{13}\text{H}_{27}$ , and  $-\text{C}_{17}\text{H}_{35}$  for myristate and stearate, respectively and M is manganese and iron metal. The results of thermal decomposition of manganese and iron soaps have been explained in terms of various equations, these are Freeman–Carroll, Coats–Redfern and Horowitz–Metzger's equations.

Freeman–Carroll<sup>11</sup> rate expression for the thermal decomposition of various soaps may be expressed as :

$$\frac{\Delta[\log(d\omega/dt)]}{\Delta \log \omega_r} = -\frac{E}{2.303R} \times \frac{\Delta[1/T]}{\Delta(\log \omega_r)} + n$$

Where,

T = Temperature on absolute scale;

n = order of decomposition reaction

E = Energy of activation;

$\omega_r$  = Difference between the total loss in weight and the loss in weight at time, t i.e.  $\omega_0 - \omega_t$ ; and

( $d\omega/dt$ ) = Value of rate of weight loss obtained from the loss in weight vs time curves at appropriate time.

The plots of  $\frac{\Delta[\log d\omega/dt]}{\Delta[\log \omega_r]}$  vs.  $\frac{\Delta(1/T)}{\Delta(\log \omega_r)}$  have been

found to be linear with an intercept equal to zero. Therefore it is concluded that the order of reaction for the decomposition of manganese and iron soaps is zero. The energy of activation calculated from the plots lies in the range 15.17-10.05 k.cal/ mol.

**Coats and Redfern's**<sup>12</sup> equation can be expressed as :

$$\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n)} \right] = \log \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT}$$

Where,

$\alpha$  = Fraction of the soap decomposed;

T = Temperature on absolute scale;

R = Gas constant;

A = Frequency factor;

a = Rate of heating in °C per minute;

E = Energy of activation; and

n = Order of reaction

It may be pointed out that the plots of  $\log(\alpha/T^2)$  against (1/T) should be a straight line with its slope equal to  $(-E/2.303R)$ .

The values of the energy of activation for manganese and iron soaps is found in the range of 17.84 – 7.67 K. cal. Mol<sup>-1</sup>

#### Conclusion

It is, therefore, concluded that the thermal decomposition of metal soaps are kinetically of zero order and the activation energy for the process lies in the range of 38.18 – 7.67 K. cal. Mol<sup>-1</sup> for manganese and iron soaps.

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