

Infrared, X-Ray and Thermogravimetric Studies on Strontium Valerate, Caprylate and Laurate

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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 strontium soaps possess ionic character. The X-ray analysis showed that strontium soaps have single 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 38-63 KJ mol⁻¹.

INTRODUCTION

Carboxylate of metals other than alkali metals are generally insoluble in water and called *metallic soaps*. The most striking feature of metal soaps is their increasing importance in various industries. The proven utility of divalent or trivalent metal soaps as dispersants¹, lubricants²⁻⁴, catalysts^{5,6}, stabilizers⁷ and corrosion inhibiting agents^{8,9} has fascinated research workers¹⁰⁻¹². The data available on strontium soaps are scanty and little effort has been made to correlate them with the behaviour of the soaps in organic solvents. The characterisation of heavy metal soaps by X-ray diffraction method was done by Hattiangdi *et al.*¹³ The thermal behaviour of the stearates and hydroxy stearates of magnesium, calcium, strontium and barium was studied by Buyanova *et al.*¹⁴ by DTA and polarising microscopy.

The present paper deals with the characteristics of strontium valerate, caprylate and laurate in solid state using infrared, X-ray diffraction patterns and thermogravimetric technique.

EXPERIMENTAL

AnalaR-grade SrCO₃, valeric acid, caprylic acid, lauric acid and acetone were used without further purification. Strontium laurate was prepared by the direct metathesis of corresponding potassium soaps with the required amount of aqueous solution of strontium carbonate at 50-60°C under vigorous stirring, while for the preparation of strontium valerate and caprylate, the calculated amount of strontium carbonate and fatty acids was suspended in distilled water and heated to 80°C with constant stirring. After the evolution of CO₂ ceased, the solutions were evaporated to obtain strontium soaps. These soaps were washed with distilled water and acetone to remove the excess of strontium ions and unreacted fatty acid. These soaps were dried under reduced pressure at room temperature, and stored over calcium chloride. The purity of strontium soaps was checked by elemental analysis and the results were found in agreement with the theoretically calculated values. The absence of hydroxyl group was confirmed by IR spectra. The purified soaps

have the following melting points.

Strontium valerate	196.0°C
Strontium caprylate	210.0°C
Strontium laurate	213.0°C

The infrared absorption spectra of fatty acids and of corresponding strontium soaps were obtained with a Perkin Elmer 577 model in the region of 4000–400 cm^{-1} using potassium bromide disc method. The thermogravimetric analysis of strontium soaps was carried out at constant rate of heating (20°/min) under nitrogen atmosphere in a thermobalance, mettler TG 50.

X-ray diffraction patterns of these soaps were obtained with a North American Philips Company X-ray diffractometer using $\text{Cu-K}\alpha$ radiations filtered by a Nickel foil. The instrument yields an automatically recorded curve of intensity of diffracted X-rays vs diffraction angle (2θ). Bragg's spacing corresponding to interplanar separations of the reciprocal crystal lattice were calculated from the peaks using the relationship $n\lambda = 2d \sin \theta$ where $\lambda = 1.5418 \text{ \AA}$

RESULTS AND DISCUSSION

The infrared spectral bands and their tentative assignments for strontium soaps valerate, caprylate and laurate, are assigned and compared with the results of their

TABLE-1

INFRARED ABSORPTION SPECTRAL FREQUENCIES (cm^{-1}) WITH THEIR ASSIGNMENTS OF STRONTIUM SOAPS

Assignments	Caprylic acid	Strontium valerate	Strontium caprylate	Strontium laurate
CH_3 , C—H asym. stretching	2950 w	2960 s	2960 w	2960 w
CH_2 , C—H asym. stretching	2920 s	2910 s	2920 s	2920 s
CH_2 , C—H sym. stretching	2850 s	2860 s	2850 s	2850 s
OH stretching	2650 w	—	—	—
C=O stretching	1700 vs	—	—	—
COO^- , C—O asym. stretching	—	1500 s	1530 s	1530 s
CH_2 deformation	1460 m	1460 m	1470 w	1470 w
COO^- , C—O sym stretching	—	1400 s	1410 m	1410 m
C—O stretching, O—H in-plane deformation	1430 w	—	—	—
CH_2 (adjacent to $-\text{COOH}$) deformation	1410 vs	—	—	—
CH_3 sym. deformation	1350 w	1320 ms	1350 s	1390 vw
Progressive bands (CH_2 twisting and wagging)	1340–1040 m	1280–1130 ms	1360–1100 w	1350–1100 w
CH_3 rocking	1100 vs	1100 s	1110 w	1110 s
OH out-of-plane deformation	940 s	—	—	—
CH_2 rocking	720 m	730 ms	720 vw	710 vw
COOH bending mode	690 m	—	—	—
COOH wagging mode	550 m	—	—	—

corresponding fatty acids (Table 1). The vibrational frequencies characteristic of the aliphatic portion of fatty acids do not vary even when acid is converted into strontium soaps. The fatty acids (valeric, caprylic and lauric) display a very broad intense peak due to OH stretching near $2650\text{--}2550\text{ cm}^{-1}$. The appearance of the absorption band near 1700 cm^{-1} in the spectra of fatty acids reveals that fatty acids exist as dimer and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acid.

The infrared spectra of strontium soaps show marked differences with the spectra of corresponding fatty acids in some spectral regions. The characteristic vibrations of free fatty acid were found completely absent in their respective regions in the spectra of strontium soaps. The complete disappearance of the carbonyl frequency in the vicinity of $1700\text{--}1680\text{ cm}^{-1}$ and appearance of two absorption bands of carboxyl group corresponding to the symmetric and asymmetric vibrations of carboxylate ion near 1430 cm^{-1} and 1530 cm^{-1} , respectively in the spectra of strontium soaps indicate that there is a complete resonance in the C—O bonds of carbonyl group of soap molecules and the two bonds become identical with force constants assuming the value intermediate between those of normal double and single bonds. It is, therefore, concluded that the resonance character of the ionised carboxyl group is retained in these metal soaps and metal-to-oxygen bonds in the ionised structure of strontium soaps should have an ionic character.

In the spectra of valeric, caprylic and lauric acids, no bands corresponding to asymmetric and symmetric vibrations of carboxylate ions are observed. Naturally, the —OH stretching band near $2650\text{--}2550\text{ cm}^{-1}$ and —OH deformation band at 940 cm^{-1} observed in the spectra of fatty acids disappeared in the spectra of strontium soaps. The progressive bands with medium and weak intensity observed in the region of $1360\text{--}1100\text{ cm}^{-1}$ for strontium soaps are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecule of the soap or fatty acid. It was also observed that these absorption peaks are weaker in the spectra of strontium soaps than in the spectra of corresponding fatty acids.

These results confirm that the fatty acids (valeric, caprylic and lauric) in solid state exist with dimeric structure through hydrogen bonding whereas the metal-to-oxygen bond in strontium 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 strontium soaps do not indicate any maxima in the region of $3500\text{--}3300\text{ cm}^{-1}$ which confirms the absence of any coordinated water molecules in the soap. The assigned frequencies are in agreement with the results of other workers^{15, 16}

X-ray diffraction studies

The intensities of diffracted X-rays as a function of diffraction angle 2θ for strontium valerate, caprylate and laurate were recorded over the range $10\text{--}80^\circ$. The interplanar spacings, d , have been calculated from the position of intense peaks using Bragg's relationship $n\lambda = 2d \sin \theta$ where λ is the wavelength of the radiation. The calculated spacings together with the relative intensities with

respect to the most intense peak are given in Table 2. These peaks are attributed to the diffraction of X-rays by planes of metal ions and are known as basal planes. The appearance of diffraction upto 9th, 18th and 18th order for strontium valerate, caprylate and laurate confirmed that the crystallinity of these soaps increases with increasing chain length.

TABLE-2
X-RAY DIFFRACTION ANALYSIS OF STRONTIUM SOAPS

S. No.	2θ	$\sin \theta$	$\frac{\lambda}{2 \sin \theta}$	d (Å)	n
Strontium valerate					
1.	5.672	0.0495	15.5812	15.5812	1
2.	18.110	0.1547	4.8985	14.6955	3
3.	22.457	0.1947	3.9591	15.8364	4
4.	29.410	0.2538	3.0370	15.1850	5
5.	33.843	0.2911	2.6486	15.8916	6
6.	44.668	0.3800	2.0287	14.2009	7
7.	47.924	0.4061	1.8982	15.1856	8
8.	57.810	0.4833	1.5949	14.3541	9
Average value of $d = 15.12 \text{ \AA}$					
Strontium caprylate					
1.	27.310	0.2360	3.2656	26.1248	8
2.	31.755	0.2736	2.8179	25.3611	9
3.	38.890	0.3329	2.3157	25.4730	11
4.	45.472	0.3865	1.9947	25.9310	13
5.	56.105	0.4703	1.6393	24.9895	15
6.	56.510	0.4733	1.6285	24.4275	15
7.	66.283	0.5467	1.4101	25.3818	18
Average value of $d = 25.38 \text{ \AA}$					
Strontium laurate					
1.	15.883	0.1382	5.5798	33.4788	6
2.	20.511	0.1780	4.3301	34.6408	8
3.	23.032	0.1996	3.8615	34.7535	9
4.	29.342	0.2553	3.0439	33.4829	11
5.	31.527	0.2717	2.8377	34.0524	12
6.	35.127	0.3018	2.5547	33.2111	13
7.	37.409	0.3207	2.4040	33.6560	14
8.	39.851	0.3408	2.2621	33.9315	15
9.	41.294	0.3526	2.1863	34.9810	16
10.	45.030	0.3829	2.0132	34.2244	17
11.	47.668	0.4041	1.9078	34.3404	18
Average value of $d = 34.03 \text{ \AA}$					

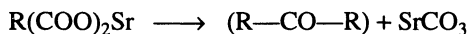
The peaks at small angles arise from diffraction of X-rays by planes of atoms, whose separation is proportional to the length of the soap molecule. In strontium valerate, caprylate and laurate the strontium ions appear to be arranged in planes between which the fatty acid radical constituents extend in both directions with their axes inclined somewhat to the plane containing the strontium ions. The interplanar spacings for strontium soaps are recorded in Table 2 and the average planar distance *i.e.* long spacings for strontium valerate, caprylate and laurate are 15.12, 25.38 and 34.03 Å respectively. The difference between the long spacings of strontium caprylate and laurate is 8.65 Å which approximately corresponds to double the length of fatty acid radical constituent of the soap molecules. It is, therefore, suggested that the zig-zag chains of fatty acid radical constituent of the soap molecules extend straightforward on both sides of each basal plane.

The results of X-ray diffraction analysis reveal that the observed values of the long spacings (valerate = 15.12 Å, caprylate 25.83 Å, laurate = 34.03 Å) for strontium soaps are lower than the calculated dimensions of valerate 17 Å, caprylate 27 Å and laurate 37 Å ions from Pauling's values of atomic radii and bond angles. This suggests that the molecular axes of strontium soaps are somewhat inclined to the basal plane and the strontium ions fit into spaces between oxygen atoms of the ionised carboxylic group without giving large strain of the bonds. Various diffraction peaks in the intermediate range of the diffraction angles are also observed in the diffraction patterns of strontium soaps and these are attributed to the diffraction of X-rays by planes of atoms of much smaller 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 peaks are relatively weak.

On the basis of long and short spacings, it is proposed that the strontium ions in these 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 sides of each basal plane and strontium soap have single layer structure¹³.

Thermogravimetric studies

The thermal decomposition (Fig. 1) of strontium valerate, caprylate and laurate was studied by thermogravimetric analysis. The heating rate 20°C/min and nitrogen atmosphere were used. The final decomposition product or residues left on heating these soaps were the strontium carbonate as the weights of the residues were almost in agreement with the theoretically and calculated weights of strontium soaps and strontium carbonate from the molecular formula of the corresponding soap. The organic moiety on decomposition gives the corresponding ketone and carbon dioxide. The thermal decomposition of strontium soaps may be expressed as:



where R is equal to C₄H₉, C₇H₁₅ and C₁₁H₂₃ for valerate, caprylate and laurate respectively. The results of thermal decomposition of strontium soaps were explained in the light of some well known equations. The Freeman Carroll's¹⁷

rate expressions for the thermal decomposition of these soaps, when they disappear continuously with constant increase in temperature and time and when some of the products are gaseous, can be expressed as follows:

$$\frac{\Delta[\log(dw/dt)]}{\Delta(\log W_r)} = -\frac{E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \log(W_r)} + n$$

where T = temperature on absolute scale, R = gas constant, E = energy of activation, n = order of decomposition reaction, W_r = difference between the total loss in weight and the loss in weight at time t *i.e.* $(W_0 - W_r)$ and dw/dt = value of rate of weight loss obtained from the loss in weight vs time curves at appropriate times.

The plots of the loss in weight of the soaps, W , against time, t , are shown in Fig. 1 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

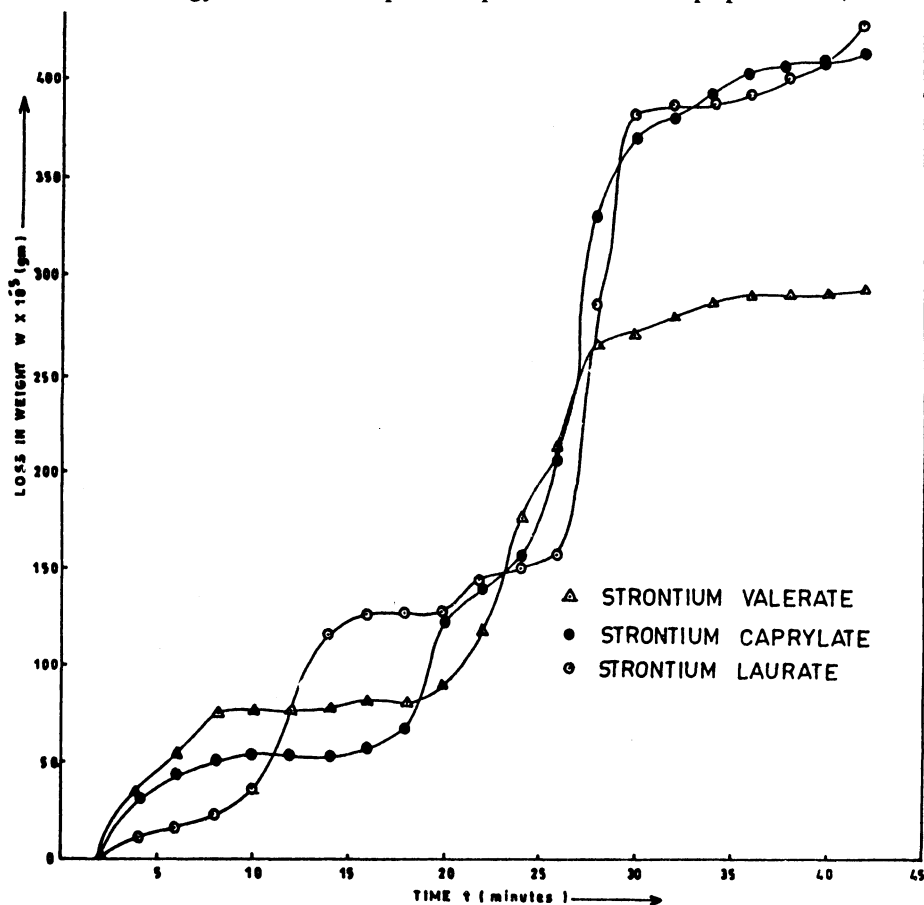


Fig. 1. Thermal decomposition of strontium soaps loss in weight (W) vs time (t).

order of reaction which was found to be 0.37, 0.40 and 0.57 for strontium valerate, caprylate and laurate, respectively. The values of energy of activation for the decomposition were found to be 44.09 KJ mol⁻¹, 47.95 KJ mol⁻¹ and 44.73 KJ mol⁻¹ for strontium valerate, caprylate and laurate respectively.

Horowitz and Metzgers¹⁸ equation also provides a method for the evaluation of energy of activation for the thermal decomposition of strontium soaps Horowitz and Metzger's equation can be represented as:

$$\ln [\ln (1 - \alpha)^{-1}] = \frac{E}{RT_s^2} \cdot \theta$$

where α = fraction of soap decomposed at time t, E = energy of activation, T_s = temperature on absolute scale at which the rate of decomposition is maximum and $\theta = (T - T_s)$.

The values of energy of activation calculated from the plots of $\ln [\ln (1 - \alpha)^{-1}]$ against θ were found to be 39.86 KJ mol⁻¹, 49.50 KJ mol⁻¹ and 63.46 KJ mol⁻¹ for strontium valerate, caprylate and laurate respectively. The results of thermogravimetric analysis of strontium soaps show that the reaction for the thermal decomposition of these soaps is kinetically of zero order and the energies of activation lie in the range 38–63 KJ mol⁻¹.

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