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Thermal, Infrared and X-Ray Diffraction Studies on Manganese and Zinc Soaps

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The IR results showed that manganese and zinc laurates and palmitates have an ionic character. The X-ray diffraction patterns indicated that the zig-zag chains of fatty acid radical constituent of the soap molecules extend straight forward on both sides of each basal plane and the molecular axes of the soap molecules are somewhat inclined to the basal plane and these soaps possessed single layer structure. The thermal decomposition of manganese and zinc soaps has been studied both as a function of temperature and of time. The thermogravimetric analysis has shown that the order of decomposition reaction is kinetically of zero order and the energy of activation for the process lies in the range of 27–36 kJ mol^{-1}.

INTRODUCTION

The importance of metal soaps has already been realised owing to their proven utility in different industries as dispersants,[1] lubricants,[2–4] catalysts,[5,6] stabilizers[7] and corrosion inhibiting agents.[8,9] Although a great deal of work has already been reported on the alkali and alkaline earth metal soaps but the studies on transition metal soaps remained scanty, in spite of their large applications in various industries. These soaps are useful for specific purposes on account of their various fundamental physico-chemical properties.

The present paper deals with the studies of infrared, X-ray and thermal analysis of manganese and zinc laurates and palmitates in order to elucidate the structure of these soaps in solid state.

EXPERIMENTAL

All chemicals were of BDH/AR grade. Manganese and zinc soaps were prepared by the direct metathesis of corresponding potassium soaps with the required amounts of solutions of metal acetates in alcohol-water mixture at 50–60°C with vigorous stirring. These soaps were purified by recrystallization and the purity was checked by elemental analysis, infrared absorption spectra and by the determination of melting points.

Potassium bromide disc method was used for infrared absorption analysis. The IR spectra of fatty acids and of corresponding transition and potassium soaps were

obtained using Perkin-Elmer "577 model" grating spectrophotometer in the region of 4000–400 cm^{-1}.

X-ray diffraction patterns of transition metal soaps were obtained with a North American Philips Company X-ray Diffractometer using Cu-K_α radiations filtered by a nickel foil. The instrument yields an automatically recorded curves- for intensity of diffracted X-rays *vs.* diffraction angle (2θ). Bragg's spacings corresponding to interplanar separation of the reciprocal crystal lattice were calculated from the peaks using the relationship $n\lambda = 2d \sin \theta$, where $\lambda = 1.5418$ Å.

The thermogravimetric analysis of transition metal soaps was carried out at constant rate of heating (20°C min^{-1}) under the atmosphere of nitrogen using a Stanton Redcroft Model TGA apparatus.

RESULTS AND DISCUSSION

Infrared Absorption Spectra

The infrared spectral bands and their tentative assignments for manganese, zinc and nickel soaps are compared wih the corresponding potassium soaps and fatty acids. The vibrational frequencies characteristic of the aliphatic portion of fatty acids do not vary even when fatty acid is converted into potassium or transition metal soaps. The fatty acids display a very broad intense peak due to OH stretching near 2640 cm^{-1}. The appearance of the absorption band near 1700 cm^{-1} in the spectra of fatty acids reveals that the fatty acid exists as dimer and confirms the existence of intermolecular hydrogen bonding between two molecules of fatty acids. One of the characteristic bands of the dimeric caboxylic acids results from the out-of-plane bending of OH^- group appearing near 920 cm^{-1}. The absorption maxima near 690 and 550 cm^{-1} in the spectra of fatty acids are associated with carboxyl group bending and wagging modes and are independent of the chain-length of the fatty acid radical.

The complete disappearance of the absorption bands near 1700 cm^{-1} in the spectra of manganese and zinc soaps indicates that there is a complete resonance in the two COO^- bands of carboxylic group of the soap molecules and the group has an ionic structure. The appearance of two absorption bands of the carboxyl group corresponding to the symmetric and asymmetric vibrations of the carboxylate ion at 1410 and 1520 cm^{-1} in the spectra of manganese and zinc soaps instead of one band of the carboxyl group at 1700 cm^{-1} in the spectra of fatty acids confirms the formation of soaps. The progressive bands with medium or weak intensity observed in the region 1390–1150 cm^{-1} for these metal soaps are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecules of the soaps or fatty acids. It may be pointed out that these absorption peaks are weaker in the spectra of metal soaps than in the spectra of fatty acids. These soaps show no peak between 3650–3590 cm^{-1} due to the absence of water of crystallisation.

X-Ray Diffraction Patterns

A fatty acid consists of a paraffin chain of linked —CH_2 group with a carboxyl —COOH group situated at one extremity of the chain. We know that the stearic

acid molecule consists of a chain lying flat in one plane in which the —CH_2 groups forms a zig-zag line. The zig-zag pattern is ascertained by comparing the lengths of the strearic acid and palmitic acid molecules and noting that the difference between the two is 2.52 Å. Since stearic acid has 17 —CH_2 groups in each molecule and palmitic acid has only 15, the observed difference in length amounts to 1.26 Å per —CH_2 group. However, it is known by the study of other types of organic compounds that the distance between two neighbouring carbon atoms is 1.54 and not 1.26 Å}. Therefore, this discrepancy can only be explained by assuming that in fatty acids the —CH_2 groups are not linked in a straight chain, but in a zig-zig structure in which the lines connecting the centres of the groups form an angle of 109°33′. The chain-length without the carboxyl group amounts to 20.2 Å, while the carboxyl group adds another 4.2 Å to the longitudinal axis; the total length of stearic acid molecule thus becomes 24.4 Å.

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 manganese laurate, zinc laurate, manganese palmitate and zinc palmitate the metal 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 manganese and zinc ions. A large number of intense peaks arising from the diffraction of X-rays by planes of metal ions (known as basal plane) were observed over the range 5–65° of the diffraction angle in the diffraction patterns of manganese and zinc laurates and palmitates. The appearance of diffractions upto 40th order for manganese palmitate suggests good crystallinity for manganese soaps. The calculated values of interplanar spacings for manganese and zinc soaps are recorded in Tables 1 and 2. The average planar distance *i.e.* long spacings for manganese laurate, zinc laurate, manganese palmitate and zinc palmitate are 34.25, 34.72, 43.98 and 44.20 Å, respectively. The difference in the long spacings of manganese and zinc soaps 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 constituents of the soap molecules extend straight-forward on both sides of each basal plane.

The comparison of the long spacings of manganese laurate (34.25 Å), zinc laurate (34.72 Å), manganese palmitate (43.98 Å) and zinc palmitate (44.20 Å) shows that the long spacings increase with the increase in the ionic radii of metal ion constituents of the soap molecules. It is, therefore, concluded that the angle of inclination of the molecular axis of soap molecules to the basal plane is somewhat affected by the metal ions.

The results of X-ray diffraction analysis reveal that the observed values of long spacings of manganese laurate and palmitate are lower than the calculated dimensions of laurate 37 Å and palmitate 47 Å ions from Pauling's values of atomic radii and bond angles. This suggests that the molecular axes of manganese and zinc soaps are inclined to the basal plane and the metal ions fit into spaces between oxygen atoms of the ionised carboxyl group without giving large strain on the bonds.

TABLE-1
X-RAY ANALYSIS OF MANGANESE LAURATE

S. No.	2θ	sin θ	$\frac{\lambda}{2 \sin \theta}$	d (Å)	*n*
1.	10.392	0.0906	8.5129	34.0516	4
2.	12.961	0.1129	6.8305	34.1525	5
3.	18.619	0.1618	4.7657	33.3599	7
4.	21.431	0.1859	4.1463	33.1704	8
5.	22.701	0.1968	3.9171	35.2539	9
6.	30.211	0.2606	2.9583	35.4996	12

Average value of d = 34.25 Å

X-RAY ANALYSIS OF ZINC LAURATE

1.	15.059	0.1310	5.8832	35.299	6
2.	20.446	0.1775	4.3437	34.750	8
3.	23.369	0.2025	3.8066	34.259	9
4.	25.596	0.2215	3.4802	34.802	10
5.	28.853	0.2421	3.0944	34.038	11
6.	31.004	0.2673	2.8844	34.613	12
7.	33.352	0.2870	2.6865	34.925	13
8.	39.094	0.3346	2.3041	34.562	15
9.	40.963	0.3499	2.2032	35.252	16
10.	50.867	0.4295	1.7951	34.106	19
11.	54.533	0.4581	1.6828	35.338	21

Average value of d = 34.72 Å

Various diffraction peaks in the intermediate range of the diffraction angle are also observed in the X-ray diffraction patterns of manganese and zinc soaps and are attributed to the diffraction of X-rays by planes of atoms of much smaller separation than the basal plane. 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 suggested that the manganese and zinc 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 these soaps have single layer[10] structure.

TABLE-2
X-RAY ANALYSIS OF MANGANESE PALMITATE

S. No.	2θ	sin θ	$\frac{\lambda}{2 \sin \theta}$	d (Å)	n
1.	11.805	0.1028	7.4966	44.9796	6
2.	15.762	0.1371	5.6225	44.9800	8
3.	22.400	0.1942	3.9689	43.6579	11
4.	28.101	0.2428	3.1754	44.4556	14
5.	39.057	0.3343	2.3063	43.8197	19
6.	44.630	0.3797	2.0304	42.6384	21
7.	98.175	0.6305	1.2227	42.7945	35
8.	87.603	0.6922	1.1138	44.5520	40
Average value of d = 43.98 Å					
	X-RAY ANALYSIS OF ZINC LAURATE				
1.	13.904	0.1210	6.3692	44.5844	7
2.	16.221	0.1411	5.4642	43.7136	8
3.	19.952	0.1732	4.4501	44.5010	10
4.	22.103	0.1917	4.0216	44.2376	11
5.	24.088	0.2087	3.6946	44.3352	12
6.	26.155	0.2263	3.4071	44.2923	13
7.	35.102	0.3016	2.5565	43.4608	17
8.	38.477	0.3295	2.3397	44.4543	19

Average value of d = 44.20 Å

Thermogravimetric Analysis

The decomposition results primarily in the formation of the corresponding ketone and metal oxide, the other products being carbon dioxide and hydrocarbons. The thermogravimetric analysis has shown that the final residues are metal oxides and the weights of the residues were almost equal to the theoretically calculated weights of metal oxides from the molecular formula of the corresponding metal soaps. The decomposition of manganese and zinc soaps can be expressed as:

$$\underset{\text{Soap}}{M(RCOO)_2} \xrightarrow{\text{heat}} \underset{\text{Ketone}}{RCOR} + \underset{\text{Residue}}{MO} + CO_2 \qquad (1)$$

where R is $C_{11}H_{23}$ and $C_{15}H_{31}$ for laurate and palmitate and M stands for metals manganese and zinc.

It may be pointed out that some white powder was condensed at the cold part of the sample tube surrounding the soap and it was identified as ketone.

The TG curves of manganese and zinc soaps exhibit a three stage decomposition pattern. The first stage of decomposition was rapid and could not be subjected to kinetic analysis. The second stage represents the major decomposi-

tion of metal soaps. The theromogravimetric studies show that manganese and zinc palmitates decompose insignificantly up to 120°C slowly between 120° to 215°C and then very rapidly upto 530°C and finally show very small change with further increase in temperature.

It is suggested that the decomposition occurs with the evolution of ketone followed by acceleratory and decay stages respectively. The evolution of ketone increases rapidly between 215°C and 530°C and the overall reaction can be expressed by equation (1).

The results of thermal decomposition of manganese and zinc soaps have been explained in the light of various well known equations. The Freeman-Carroll's[11] rate expression for the thermal decomposition of these soaps, where they disappeared continuously with the constant rate of increase in temperature and with the passage of time and when one of the products being gaseous, can be expressed as:

$$\frac{\Delta[\log (dw/dt)]}{\Delta(\log W_r)} = -\frac{E}{2.303R}\frac{\Delta(1/T)}{\Delta(\log W_r)} + n \qquad (2)$$

where E, n, T, W_r and (dw/dt) are respectively energy of activation, order of reaction, order of reaction, temperature on absolute scale, difference between the total loss in weight and the loss in weight at time t, *i.e.* $(W_0 - W_t)$, and rates of weight loss obtained from the loss in weight *vs.* time curves at appropriate times. The values of energy of activation for the decomposition process were calculated from the slope of the plots of $-\Delta[\log (dw/dt)]/\Delta[(\log W_r)]$ against $\Delta(1/T)/\Delta(\log W_r)$. The order of reaction for the thermal decomposition of manganese and zinc soaps was found almost zero and the values of energy of activation (Table-3) were in the range 27–36 KJ mol^{-1}. These results indicate that the values of energy of activation increase with increasing size of the cations and chain-length of the soap.

TABLE-3
VALUES OF ENERGY OF ACTIVATION FOR MANGANESE AND ZINC SOAPS

S. No.	Name of the soap	Energy of activation E (kJ mol^{-1})		
		Freeman Carroll's equation	Horowitz-Metzger's equation	Coats-Redfern's equation
1.	Manganese laurate	27.60	27.50	27.40
2.	Zinc laurate	29.11	29.57	29.50
3.	Manganese palmitate	32.60	32.52	31.96
4.	Zinc palmitate	35.57	34.57	35.51

The aforesaid fact that the process of decomposition of manganese and zinc soaps is kinetically of zero order is in harmony with the fact that the surface of the soap molecules remains completely covered all the time by the molecules of the gaseous product and so the decomposition is fast and the rate of decomposition becomes constant.

Horowitz and Metzger[12] and Coats and Redfern[13] also provided a method for

the evaluation of energy of activation for the thermal decomposition of manganese and zinc laurates and palmitates. The values of energy of activation calculated using these equations (Table-3) are in good agreement with the values obtained by Freeman and Carroll's equation.

The above discussion leads to the conclusion that the surface of manganese and zinc laurates and palmitate molecules was fully covered by the product, the rate of decomposition becomes constant and the process is kinetically of zero order and the activation energy for the decomposition process lies in the range 27–36 KJ mol^{-1}.

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