

Infrared, X-Ray and Thermal Studies of Magnesium Soaps

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The IR results indicate that the fatty acids have dimeric structure achieved through hydrogen-bonding between the carboxyl groups of two fatty acid molecules whereas the magnesium soaps possess ionic character; x-ray analysis showed that magnesium soaps have single layer structure with molecular axes slightly inclined to the basal plane. The results of thermogravimetric analysis were explained by using Freeman Carroll and Horowitz-Metzger's equations to calculate the energy of activation and order of decomposition reaction.

INTRODUCTION

A survey of literature reveals that the physico-chemical characteristics of alkali and alkaline earth metal soaps have been investigated by several workers¹⁻⁷ whereas only a few references are available on magnesium soaps. Although these soaps are being widely used in many industries, the technological applications of these soaps in industries are based on empirical know-how and the selection of soaps is dependent largely on economic factors; the physico-chemical characteristics and the structure of metal soaps depends mainly on the method and conditions of preparation. The present manuscript reports the results of infrared, X-ray and thermogravimetric analysis of magnesium caprylate and laurate.

EXPERIMENTAL

AnalaR grade magnesium sulphate, caprylic acid, lauric acid and acetone were used without further purification. Magnesium soaps were prepared by the direct metathesis of corresponding potassium soaps with the required amount of aqueous solution of magnesium sulphate at 50-60°C under vigorous stirring. The precipitated soaps were washed with doubly distilled water and acetone to remove the excess of magnesium ions and unreacted fatty acids. These soaps were dried under reduced pressure and stored over calcium chloride.

The purity of magnesium soaps was checked by elemental analysis and the results were found in agreement with the theoretically calculated values.

The infrared absorption spectra of fatty acids and their magnesium soaps were obtained with a Perkin-Elmer model in the region of 4000-400 cm⁻¹ using potassium bromide disc method.

X-ray diffraction patterns of these soaps were obtained with a North American Philips X-ray diffractometer using Cu-K_α radiations filtered by a nickel foil.

The instrument yields an automatically recorded curve of the 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 λ is 1.54056 Å.

The thermogravimetric analysis of magnesium soaps was carried out at constant rate of heating (20°C/min) under nitrogen atmosphere in a thermobalance, Mettler TG 50.

RESULTS AND DISCUSSION

The infrared spectral bands and their tentative assignments for magnesium soaps (caprylate and laurate) are assigned and recorded in Table-1, and compared with the results of their corresponding fatty acids. The vibrational frequencies characteristic of the aliphatic portion of fatty acids do not vary even when acid is converted into magnesium soaps. The fatty acids (caprylic and lauric) display a very broad intense peak due to OH stretching near 2650 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 magnesium soaps show marked difference 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 magnesium soaps. The complete disappearance of the carbonyl frequency in the vicinity of 1700 cm^{-1} and appearance of two absorption bands of carboxyl group corresponding to the symmetric and asymmetric vibrations⁸ of carboxylate ion near 1456 cm^{-1} respectively in the spectra of magnesium soaps indicate that there is a complete resonance in C—O bonds of carbonyl group of soap molecules and the two bonds become identical with their 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 magnesium soap should have an ionic character.

In the spectra of caprylic and lauric acids, no bands corresponding to asymmetric and symmetric vibrations of carboxylate ions are observed; naturally, the OH stretching bands near $2650\text{--}2640 \text{ cm}^{-1}$ and the OH deformation band near $940\text{--}930 \text{ cm}^{-1}$ observed in the spectra of fatty acids disappeared in the spectra of magnesium soaps. The progressive band with medium and weak intensity observed in the region of $1350\text{--}1110 \text{ cm}^{-1}$ for magnesium soaps are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecules of soaps and fatty acids.

It was also observed that these absorption peaks are weaker in the spectra of magnesium soaps than the spectra of corresponding fatty acids.

The aforesaid results confirm that the fatty acids (caprylic and lauric) in the solid state exist with dimeric structure through hydrogen-bonding whereas the metal to oxygen bonds in magnesium soaps are ionic in nature. It is also proved

that the soap molecules retain the resonance character of carboxyl group. The assigned frequencies are in agreement with the results of other workers⁹.

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

S. No.	Assignments	Caprylic Acid	Magnesium Caprylate	Magnesium Laurate
1.	CH_3 , $\text{C}-\text{H}_{\text{asym}}$, stretching	2950 w	3120 w	2918 s
2.	CH_2 , $\text{C}-\text{H}_{\text{asym}}$, stretching	2920 s	2923 s	2852 s
3.	CH_2 , $\text{C}-\text{H}_{\text{sym}}$, stretching	2850 s	2858 s	2812 m
4.	OH, stretching	2650 w	-	-
5.	$\text{C}=\text{O}$ stretching	1700 vs	-	-
6.	COO^- , $\text{C}-\text{O}_{\text{asym}}$, stretching	-	1577 s	1562 vs
7.	CH_2 , deformation	1460 m	1456 w	1460 s
8.	COO^- , $\text{C}-\text{O}_{\text{sym}}$, stretching	-	1346 m	1405 vw
9.	$\text{C}-\text{O}$ stretching, $\text{O}-\text{H}$ in-plane deformation	1430 w	-	-
10.	CH_2 adjacent to COOH group deformation	1410 vs	-	-
11.	CH_3_{sym} deformation	1350 w	1309 s	1315 vw
12.	Progressive bands (CH_2 twisting and wagging)	1340 1040 m	1330 1114 vw	1350 1110 mw
13.	CH_3 rocking	1100 vs	1114 vw	1110 mw
14.	OH out-of-plane deformation	940 s	-	-
15.	CH_2 rocking	720 ms	720 vw	723 mw
16.	COOH bending mode	690 m	-	-
17.	COOH wagging mode	550 m	-	-

X-Ray Diffraction Studies: The intensities of diffracted X-rays as a function of diffraction angle 2θ for magnesium caprylate and laurate were recorded over the range $10-70^\circ\text{C}$. The interplanar spacing d has 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 spacing 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 up to 16th order for magnesium caprylate confirmed good crystallinity of these soaps.

The peaks at small angles arise from diffraction of X-rays by planes of atoms whose separations are proportional to the length of the soap molecule. In magnesium caprylate and laurate the magnesium 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 basal plane.

The interplanar spacing for magnesium soap are recorded in Table-2 and the average planar distance, *i.e.*, long spacing for magnesium caprylate and the laurate are 24.40 Å and 33.44 Å, respectively. The difference between the long spacing of magnesium caprylate and laurate is 7.04 Å which approximately corresponds to double the length of fatty acids radicals constituent of the soap molecules. It is therefore, suggested that the zig-zag chains of fatty acid radical constituent of the soap molecules extend straight forward on both sides of each basal plane.

The results of X-ray diffraction analysis reveal that the observed values of the long spacing (caprylate 24.40 Å and laurate 33.44 Å) for magnesium soaps are lower than the calculated dimensions of caprylate and laurate ions from Pauling's value of atomic radii and bond angles. This suggests that the molecular axes of magnesium soaps are somewhat inclined to the basal plane and the magnesium ions fit into spaces between oxygen atoms of the ionised carboxyl group without giving large strain on the bonds. Various diffraction angles are also observed in the diffraction patterns of magnesium soaps and these are attributed to the diffraction of X-rays by planes of atoms of much smaller separation than the basal planes.

TABLE-2
X-RAY DIFFRACTION ANALYSIS OF MAGNESIUM SOAPS

S. No.	2θ	θ	sin θ	$\frac{\lambda}{2 \sin \theta}$	d (Å)	η
(AVERAGE VALUE OF d = 24.40 Å)						
Magnesium caprylate						
1.	14.645	7.322	0.127	6.0436	24.174	4
2.	21.525	10.762	0.187	4.1249	24.749	6
3.	29.500	14.750	0.255	3.0254	24.203	8
4.	33.000	16.500	0.284	2.7121	24.408	9
5.	38.340	19.170	0.328	2.3458	25.803	11
6.	40.910	20.455	0.394	2.2041	24.245	11
7.	52.750	26.375	0.444	1.7339	24.274	14
8.	58.745	29.225	0.488	1.5704	25.126	16
(AVERAGE VALUE OF d = 33.44 Å)						
Magnesium laurate						
1.	10.815	5.407	0.094	8.1737	32.694	4
2.	15.780	7.890	0.137	5.6114	33.668	6
3.	16.410	8.205	0.143	5.3973	32.383	6
4.	18.795	9.397	0.163	4.7175	33.022	7
5.	21.235	10.617	0.184	4.1806	33.444	8
6.	23.740	11.870	0.205	3.7448	33.739	9
7.	24.180	12.090	0.209	3.6777	33.099	9
8.	27.555	13.777	0.238	3.2344	32.344	10

The calculated spacings from these 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 spacing, it is proposed that the magnesium 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 magnesium soaps have single layer structure¹⁰.

Thermogravimetric Studies: The thermal decomposition of magnesium 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 magnesium carbonate as the weights of the residues were almost in agreement with the theoretically calculated weights of magnesium soaps and magnesium 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 magnesium soaps may be expressed as



where R is equal to C₇H₁₅ and C₁₁H₂₃ for caprylate and laurate, respectively. The results of thermal decomposition of magnesium soaps were explained in the light of some well known equations. The Freeman-Carroll's rate expressions¹¹ for the thermal decomposition of these soaps, when they disappear with continuously constant increase in temperature and time and when some of the products are gaseous, can be expressed as follows:

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

where T is temperature on absolute scale, R is gas constant, E is energy of activation, n-order of decomposition reaction, W_r is difference between the total loss in weight and the loss in weight at time *t*, *i.e.*, W₀ - W_r, and (dw/dt) is value of rate of weight loss obtained from the loss in weight vs. time curves at appropriate times.

The plot of the loss in weight of the soap, W, against time, *t*, passes from zero and the values of (dw/dt) are obtained from the curves by drawing a tangent at appropriate times. The plots of Δ[log(dw/dt)]/Δ(log W_r) vs. Δ(1/T)/Δ(log W_r) provide a linear relationship. Slope of this enables us to calculate energy of activation for the decomposition process and intercept provides n, the order of decomposition reaction which was found to be zero for magnesium caprylate and laurate, respectively. The values of energy of activation for the decomposition reaction were found in between 20–30 kJ mol⁻¹ for magnesium soaps.

Horowitz and Metzger's equation¹² also provides a method for the calculation of energy of activation for the thermal decomposition of magnesium soaps. Horowitz and Metzger's equation can be represented as:

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

where α is fraction of soap decomposed at time t , E is energy of activation, T_s is 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 in between 15–30 kJ mol⁻¹ for magnesium soaps.

The results of thermogravimetric analysis of magnesium soaps show that the reaction for the thermal decomposition of these soaps is kinetically of zero order and the energy of activation for the decomposition process lies in the range of 15–30 kJ mol⁻¹.

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