

Infrared, X-Ray Diffraction Studies and Thermogravimetric Behaviour of Magnesium Myristate and Magnesium Palmitate

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Magnesium soaps *i.e.*, magnesium myristate and magnesium palmitate were prepared by the metathesis of potassium soaps with an aqueous solution of magnesium sulphate. The infrared results showed that the fatty acid exists in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two acid molecules, whereas magnesium soaps have an ionic character. The X-ray diffraction analysis indicates 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 thermal decomposition of these soaps was found kinetically of zero order and energy of activation for the decomposition process was in the range of 15-32 KJ mol⁻¹.

Key Words: Magnesium myristate, Magnesium palmitate, X-Ray diffraction, Thermogravimetry.

INTRODUCTION

The most striking feature of metallic soaps has been their increasing importance in industries. Although a great deal of work has already been reported on alkali metal soaps, but the studies on alkaline earth metal soaps remained scanty¹⁻⁷, in spite of their large applications in various industries as emulsifying agents, mordants, water proofing agents, lubricants and varnish driers. However, technological applications of these soaps are mostly based on empirical know-how and the selection of a soap is dependent largely on economic factors.

The present paper deals with the characteristics of magnesium soaps *i.e.*, magnesium myristate and magnesium palmitate in solid state using infrared, X-ray diffraction patterns and thermal analysis.

EXPERIMENTAL

The magnesium soaps were prepared by the direct metathesis of potassium soaps with the required amount of aqueous solution of magnesium sulphate at 50-55 °C under vigorous stirring. The precipitated magnesium soaps were washed with double distilled water and acetone to remove the excess of metal ions and unreacted fatty acid. The purity of the soaps was checked by the element analysis and the results were found in agreement with the theoretical values. The reproducibility of the results was checked by preparing two samples of the same soap under similar conditions.

The infrared absorption spectra were obtained with a Perkin-Elmer 577 grating spectrophotometer in the region 4000-400 cm⁻¹ using potassium bromide disc method. The X-ray diffraction patterns of these soaps were obtained with a North American Philips X-ray diffractometer using CuK_α radiations filtered by a nickel foil. The instrument yields an automatically recorded curve of the intensity of diffracted X-ray *versus* diffraction angle (2θ). Bragg's spacing corresponding to interplaner 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

Infrared absorption spectra: The infrared spectral bands and their tentative assignments for magnesium soaps are assigned and compared with their corresponding potassium soaps and fatty acids (Table-1). The vibrational frequencies characteristics of the aliphatic portion of fatty acids do not vary even when acid is converted into potassium or magnesium soaps. The fatty acids display a very broad intense peak due to OH stretching in 2650-2640 cm⁻¹ region. The appearance of the absorption band at *ca.* 1700 cm⁻¹ in the spectrum of fatty acid reveals that the fatty acid exists as dimer and confirms

TABLE-1
INFRARED SPECTRAL BANDS (cm⁻¹) OF MAGNESIUM SOAPS

Assignment	Myristic acid	Magnesium myristate	Magnesium palmitate
CH ₃ , C-H asym. str.	2960vw	2920vs	2920vs
CH ₂ , C-H asym. str.	2920vs	2852s	2852s
CH ₂ , C-H sym. str.	2840w	2820vw	2634vw
OH str.	2640w	–	–
C=O str.	1700vs	–	–
COO ⁻ , C-O asym. str.	–	1542s	1544s
CH ₂ , deformation	1465m	1467s	1467s
COO ⁻ , C-O sym. str.	–	1419w	1421w
C-O, O-H in-Plane deformation	1405vs	–	–
Progressive bands (CH ₂ twisting and wagging)	1350-1190w	1294-1114w	1305-1110w
CH ₃ rocking	1120w	1114w	1110w
OH out-of-plane deformation	940m	–	–
CH ₂ rocking	735w	725w	723w
COOH bending	690w	–	–
COOH wagging	550w	–	–

the existence of intermolecular hydrogen bonding between two molecules of fatty acid. The absorption maxima near 690-550 cm⁻¹ in the spectrum of fatty acids are associated with carboxyl group bending and wagging modes and are dependent on the chain length of the fatty acid radical. The characteristic vibrations of free fatty acid were found absent in their respective regions in the spectra of potassium and magnesium soaps show marked differences in some special spectral regions.

The complete disappearance of the carbonyl frequency at 1700 cm⁻¹ and the appearance of two absorption bands of carboxyl group corresponding to the symmetric and asymmetric vibrations of carboxylate ion near 1405 and 1560 cm⁻¹, respectively in the spectra of magnesium soap indicate that there is a complete resonance in the C-O bonds of carbonyl group of the soap molecule 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 the ionized carboxyl group is retained in these metal soaps. It may also be pointed out that the metal to oxygen bonds in the ionized structure of magnesium soaps should have an ionic character.

In the spectrum of fatty acid, no band corresponding to asymmetric and symmetric vibrations of carboxylate ion is observed. Naturally, the -OH stretching band near 2640 cm⁻¹ and -OH deformation band at 940 cm⁻¹ observed in the spectrum of fatty acid disappeared in the spectra of potassium soaps. The progressive bands with medium or weak intensity observed in the region of 1294-1114 cm⁻¹ for magnesium myristate and 1305-1110 cm⁻¹ for magnesium palmitate are assigned to the wagging and twisting vibrations of the chains of successive methylene groups of the molecules of the soap or fatty acid. It may be pointed out that these absorption peaks are weaker in the spectra of metal soaps than in the spectra of fatty acids.

The results confirm that the myristic and palmitic acid in solid state exist in a dimeric structure through hydrogen bonding whereas the metal to oxygen bonds in magnesium myristate and palmitate are ionic in nature. It is also proved that the soap molecules retain the resonance character of the carboxyl group. The assigned frequencies are in good agreement with the results of other workers^{8,9}.

X-Ray diffraction patterns: The X-ray diffraction patterns of magnesium soaps have been investigated to characterize the structure of these soaps in solid state. The intensities of diffracted X-rays as a function of diffraction angle, for magnesium soaps were recorded with the help of X-ray diffractometer and the recorded curves were reproduced over the range of 10-70 °C. The interplanar spacing *d*, were calculated from the position of intense peaks using Bragg's relationship, $n\lambda = 2d \sin \theta$ where λ is the wavelength of the radiations. The calculated spacing together with the relative intensities with respect to the most intense peaks are recorded in Table-2. A large number of intense peaks arising from the diffraction of X-rays by planes of magnesium ions (known as basal planes) were observed over the range of 10-70 °C of diffraction angle in the diffraction patterns of magnesium soaps. The appearance of the diffractions up to 14th order for these soaps suggests good crystallinity for the soaps. The order of diffraction decreases with the decrease in chain length of the soap molecules. The interplanar spacing *d*, calculated for 5th, 6th, 7th, 8th, 9th, 10th and 13th order diffraction for magnesium myristate and magnesium palmitate are 35.23, 35.66, 35.80, 35.03, 35.17 [Å], respectively. The average planar distance, *i.e.*, the long spacing for magnesium myristate is 35.66 Å.

TABLE-2
X-RAY DIFFRACTION ANALYSIS OF MAGNESIUM SOAPS

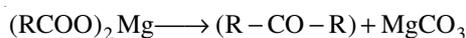
Magnesium myristate					Magnesium palmitate				
θ	$\sin \theta$	$\frac{\lambda}{2 \sin \theta}$	<i>d</i> (Å)	<i>n</i>	θ	$\sin \theta$	$\frac{\lambda}{2 \sin \theta}$	<i>d</i> (Å)	<i>n</i>
6.25	0.108	7.04	35.23	5	6.21	0.108	7.11	42.67	6
7.00	0.122	6.31	37.90	6	7.51	0.139	5.88	41.21	7
7.44	0.129	5.94	35.66	6	8.46	0.147	5.23	41.87	8
8.40	0.146	5.26	36.88	7	9.41	0.163	4.70	42.36	9
8.61	0.149	5.14	35.80	7	10.34	0.179	4.28	42.88	10
8.83	0.153	5.01	35.11	7	10.79	0.187	4.11	41.14	10
9.42	0.163	4.70	37.64	8	11.31	0.196	3.92	43.19	11
10.98	0.196	4.04	36.37	9	12.63	0.218	3.52	42.24	12
11.41	0.197	3.89	35.03	9	15.02	0.259	2.97	41.69	14
11.78	0.204	3.77	37.71	10	–	–	–	–	–
16.53	0.284	2.70	35.17	13	–	–	–	–	–
Average value of <i>d</i> (Å) = 35.66 Å					Average value of <i>d</i> (Å) = 42.36 Å				

The interplanar spacing for magnesium palmitate for 6th, 7th, 8th, 9th, 10th, 12th and 14th order diffraction are 42.67, 41.21, 41.87, 42.36, 41.14, 42.24 and 41.69, respectively. The average planar distance is 42.36 Å. The difference in the observed values of long spacing of magnesium myristate (35.66 Å) and palmitate (42.36 Å) is 6.70 Å which approximately corresponds to double the length of additional methylene (-CH₂) group in the fatty acid radical constituent of the soap molecules. The value of the long spacing for these soaps are almost equal to double the length of fatty acid radical of the soap molecule. It is therefore, suggested that the zig-zag chains of the fatty acid radical extend straight forward on both sides of each basal plane.

The results of X-ray diffraction of magnesium myristate show that the observed values of the long spacing for these soaps (magnesium myristate 35.66 Å and magnesium palmitate: 42.36 Å) are smaller than the calculated dimensions of myristate and palmitate ions (42 Å) from Pauling's values of atomic radii and bond angles. It is, therefore, suggested that the molecular axes of magnesium myristate and magnesium palmitate are somewhat inclined to the basal plane and the metal ions fit into spaces between oxygen atoms of the ionized carboxyl group without a large strains of the bonds. The calculated spacing from these peaks correspond to the shorter side spacing *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 metal ions in magnesium myristate and magnesium palmitate 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 a single layer structure as proposed by Vold and Hattiangdi¹⁰.

Thermogravimetric analysis: The final residues left on heating these soaps were the metal carbonate as the weight of the residue was in agreement with the theoretically calculated weights of magnesium carbonate from the molecular formula of the corresponding soap. A white substance was found condensed at the cold part of the sample tube surrounding with the sample and it was identified as myristone (m.p. 34 °C). The decomposition of these soaps can be expressed as:



where R is equal to C₁₃H₂₇ and C₁₅H₃₁ for myristate and palmitate, respectively. The results of thermal decomposition of magnesium soaps were explained in the light of various well known equations. The Freeman Carroll's¹¹ rate expressions for the thermal decomposition of these soaps, when they disappeared continuously with the constant rate of increase in temperature and with the passage of time and when some of the products are gaseous, can be expressed as follows:

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

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.* W₀-W_r and (dw/dt) - value of rate 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 was calculated from the slope of the plots of -[log (dw/dt)]/ (log W_r) against Δ(1/T)/Δ(log W_r). It was found that the order of reaction for the thermal decomposition of magnesium myristate and palmitate was zero and the values of energy of activation were found in the range of 22-32 KJ mol⁻¹.

The energy of activation for the thermal decomposition of magnesium myristate and palmitate was also calculated by using the Horowitz-Metzger's¹² and Coats-Redfern's equation¹³. The values of energy of activation for the thermal decomposition by using these equations were found in the range of 15-30 KJ mol⁻¹. It can, therefore be concluded that the decomposition reaction of magnesium myristate and magnesium palmitate was kinetically of zero order and the activation energy for the decomposition process existed in the range of 15-30 KJ mol⁻¹. The results were in good agreement with the values of activation energy obtained for metal soaps by other workers^{14,15}.

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REFERENCES

1. R.C. Mehrotra and W.Z. Friedrich-Schiller, *Univ. Jena Math. Naturwiss. Reihe*, **14**, 171 (1965).
2. L.W. Rayan and W.W. Plechnar, *Ind. Eng. Chem.*, **26**, 909 (1934).
3. H.W. Chatfield, *Paint Manuf.*, **6**, 112 (1936).
4. L.D. Skrylev, V.F. Sazonna, M.E. Kornelli and N.A. Shumitina, *Khim. Khim. Tekhnol.*, **21**, 491 (1978).
5. J.H. Skellon and K.E. Andrews, *J. Appl. Chem. (London)*, **5**, 245 (1955).
6. S.N. Misra, J.N. Misra and R.C. Mehrotra, *J. Inorg. Nucl. Chem.*, **25**, 195 (1963).
7. J.H. Skellon and J.W. Spence, *J. Appl. Chem. (London)*, **3**, 10 (1953).
8. C. Duval, J. Leconte and F. Douville, *Ann. Phys.*, **17**, 5 (1942).
9. R.E. Kagarise, *J. Phys. Chem.*, **59**, 271 (1955).
10. R.D. Vold and G.S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).
11. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
12. H.H. Horowitz and G. Metzger's, *Anal. Chem.*, **35**, 1464 (1963).
13. A.W. Coats and J.P. Redfern, *Nature*, **201**, 68 (1964).
14. A. Rashid and R.A. Bhohe, *J. Indian. Chem. Soc.*, **53**, 442 (1976).
15. K.N. Mehrotra, S.P.S. Saroha and R. Kachhawaha, *Tenside Detergents*, **18**, 28 (1981).