



Physico-Chemical and Acoustical Study of Magnesium Laurate

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Abstract The Physicochemical characteristics and structure of Magnesium Laurate were studied by X-ray, TGA and IR measurements. The X-ray diffraction patterns show that the metal ions in Soap Crystals are arranged in parallel planes equally spaced with fully extended zig-zag chains of fatty acid radicals on both sides of each basal plane and the soap possesses a single-layer structure. The TGA indicates that the decomposition reaction of Magnesium soap is kinetic of zero order and the value of activation energy is 28.72 kcal mol⁻¹. The Infrared spectral results confirmed that the fatty acids exist with dimeric structure through intermolecular hydrogen bonding between the carboxyl group of two acid molecules whereas Magnesium laurate has an ionic character. The ultrasonic velocities and associated parameters (adiabatic compressibility, acoustic impedance and inter-molecular free length) were measured in the non-aqueous mixture (70% chloroform and 30% propylene glycol) of Magnesium laurate at different concentrations and temperature 40±0.05°C. The ultrasonic parameters indicate that there are significant interaction between the Magnesium laurate and solvent molecules in dilute solutions. It also implies that solutes do not aggregate appreciably below the critical micelle concentration (14.00 x10⁻³ mole dm⁻³). The properties of the studied material are found to resemble the characteristics of metallic soaps.

Keywords X-ray, TGA, IR, Ultrasonic Parameters, Magnesium Laurate

1. Introduction

The organic derivative of metals or alkali metal or alkaline earth metals is termed as metallic soap. Generally, the carboxylate of metal is known as metallic soap whose general formula is M(RCOO)_n, here 'M' is metal in oxidation state, 'n' and 'R' are organic radical containing 6 to 7 carbon atoms. Now a day, an enormous work on synthesis and characterization of the metallic soaps has been reported in literature [1-5]. The soaps have been found to have wide range application as waterproofing agent, emulsifier, drier, hardener, softener, lubricant, stabilizer, plasticizer, antioxidant, catalyst, preservative, fungicide, germicide, antiseptic, additive and detergent in cement, paper, wood, textile, leather, rubber, petroleum, varnish, grease, oil, cosmetic and pharmaceutical, industries [6-13]. The physicochemical and acoustical characteristics of metal soaps can be controlled up to an extent by the method and conditions of their preparation, hence the studies of metal soaps are of significance for their uses in various industries. Very few work has been found reported regarding structural, physico-chemical, thermal characterization of the Magnesium laurate soap [14-15]. Therefore, the present work is focused on synthesis and characterization of Magnesium laurate soap. The structural, thermal, optical and physico-chemical properties of the chosen soap have been established by studying and analysing the XRD, TGA, IR and ultrasonic measurements.



2. Experimental

2.1 Chemical and Synthesis of Magnesium Laurate

Lauric acid ($C_{11}H_{23}COOH$) of AR-Grade, potassium hydroxide (KOH) and Magnesium nitrate ($Ca(NO_3)_2$) were taken as constituent chemicals for the preparation of the chosen soap. Initially, Lauric acid was purified by distilling under reduced pressure. Potassium soap was prepared by refluxing equivalent amounts of lauric acid and potassium hydroxide solution in a water bath for 10-14 hours. The soap was purified by re-crystallization with methanol and then dried under reduced pressure. Magnesium soap was prepared by direct metathesis of Potassium soap with a slight excess of the solution of Magnesium nitrate at 50-55°C under vigorous stirring. Magnesium soap was purified by re-crystallization and stored over Magnesium chloride. The purity of Magnesium soap was confirmed by the determination of their melting point.

2.2 Preparation of Magnesium Laurate solution

The solvent liquid was prepared mixing 70% Chloroform and 30% propylene glycol in volume by volume ratio. The soap solution of different concentration was prepared by adding the calculated amount of soap in the solvent mixture.

2.3 XRD, TGA and IR measurements of Magnesium Laurate

X-ray diffraction pattern for Magnesium laurate was obtained with a Rich-Seifert 2002 D Isodebyeflex Diffractometer using $Cu-K\alpha$ (1.54\AA) radiations filtered by a nickel foil over the range of diffraction angle $2\theta = 10^\circ - 70^\circ$ (where θ is Bragg's angle). The thermo-gravimetric analysis of Magnesium soap was carried out by 'Perkin-Elmer (Pyris Dimond)'. Thermo-gravimetric Analyzer TG S2 at a constant heating rate (10° per minute) in a nitrogen atmosphere and maintaining similar conditions throughout the Investigation. The infrared absorption spectra of Magnesium laurate were obtained with a Perkin-Elmer 577 Model Grating spectrophotometer in the region of $4000-200\text{ cm}^{-1}$ using the Potassium bromide disc method.

2.4 Ultrasonic measurements of Magnesium Laurate solution

The ultrasonic measurements of the solutions of Magnesium laurate were carried out with a multi-frequency Ultrasonic Interferometer (Mittal Enterprises, New Delhi) at a frequency of 2 MHz at a constant temperature ($313 \pm 0.05^\circ\text{K}$). The Uncertainty of velocity measurements was 0.2%.

3. Result and Discussion

The structural feature of Magnesium laurate has been demonstrated on the basis of X-ray diffraction pattern. The X-ray diffraction pattern of Magnesium laurate has shown in Fig 1. The intensities of diffracted X-rays as a function of diffraction angle is depicted in Fig 1. The appearance of diffractions for Magnesium laurate suggests good crystallinity having long-spacing average planar distances for Magnesium laurate is 32.46\AA . The long spacing of Magnesium soaps correspond to double the length of methylene ($-CH_2$) groups in the 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 straight forward on both sides of each basal plane. The calculated dimensions of anions for Magnesium laurate soap is 37.0\AA . The Pauling values of atomic radii and bond angles suggest that the molecular axes of Magnesium laurate molecules are somewhat inclined to the basal planes. The Magnesium ions, Mg^{+2} fit into space between oxygen atoms of the ionized carboxyl group without a large strain of the bond. The value of the long spacing of Magnesium soap is in agreement with the single-layer structure of soap proposed by Vold and Hattiangdi [16]. The value of long spacing for homogeneous soaps of Magnesium suggests that there are no abrupt changes in the manner of crystallization of these soaps. The results of Magnesium soap are in agreement with the results of other alkaline earth metal soaps [17-18].



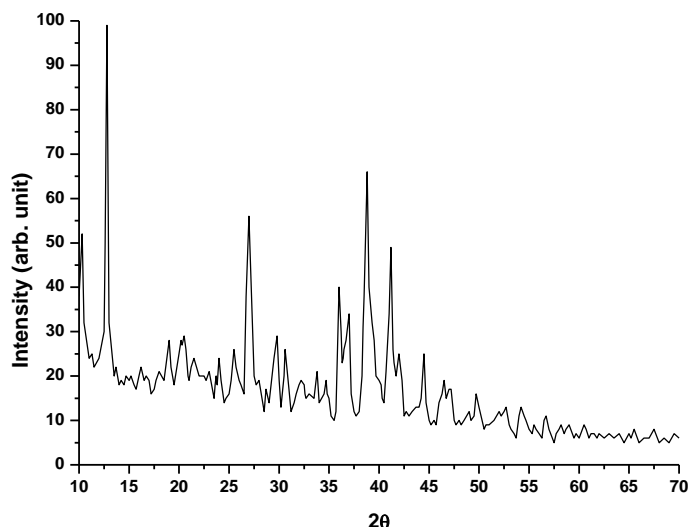
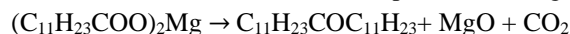


Figure 1: XRD of Magnesium Laurate

As the temperature enhances, the decomposition of Magnesium laurate occurs with production of Magnesium oxide as final residue. The thermal decomposition of Magnesium laurate can be expressed as:



Magnesium oxide is a white crystalline powder, which can be identified by the determination of melting point. For the present case, the observed melting point of residue (laurane) was 69.3°C, which confirm the formation of MgO. The order of above reaction and activation energy can be theoretically determined using TGA data (weight of final residue and decomposition rate) and the following Freeman and Carroll's expression [16,17].

$$\frac{\Delta \log \left(\frac{dW}{dt} \right)}{\Delta \log W_r} = - \frac{E}{2.303R} \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log W_r} + n \quad (1)$$

Where, dW/dt =Rate of weight loss obtained from the loss in weight vs time curves at appropriate times; W_r = Difference between the total loss in weight and the loss in weight at time t ($W_0 - W_t$); E =Energy of activation, n =Order of reaction, T =Temperature in K.

Table-1: Thermal decomposition of Magnesium Laurate

S. No.	Time, t (minutes)	Temp. T(K)	Weight of soap decomposed W×10 ³ (gms)	dw/dt×10 ⁶	W _r ×10 ³
1	0	298	0.000	0.00	9.933
2	2	309	0.000	0.00	9.933
3	3	318	0.008	2.66	9.925
4	6	338	0.153	25.50	9.970
5	8	358	0.396	49.50	9.537
6	10	378	0.576	57.60	9.357
7	12	398	0.689	57.40	9.244
8	14	418	0.724	51.70	9.209
9	16	438	0.771	48.10	9.162
10	18	418	0.888	49.30	9.045
11	20	478	1.080	54.00	8.853
12	22	498	1.310	59.00	8.623
13	24	518	1.536	64.00	8.397
14	26	538	1.712	65.80	8.221
15	28	558	1.825	65.10	8.108



16	30	578	2.018	62.20	7.915
17	32	598	3.258	101.80	6.675
18	34	618	6.305	185.00	3.628
19	36	638	7.572	210.30	2.361
20	37	658	8.016	216.60	1.917
21	39	678	8.466	217.00	1.467
22	41	698	8.797	214.50	1.136
23	43	718	9.054	210.55	0.879
24	45	738	9.203	204.50	0.733
25	47	758	9.287	197.50	0.646
26	49	778	9.294	189.60	0.639
27	51	798	9.299	182.30	0.634
28	53	818	9.304	175.50	9.628
29	55	838	9.311	169.20	0.622
30	57	858	9.318	163.40	0.615

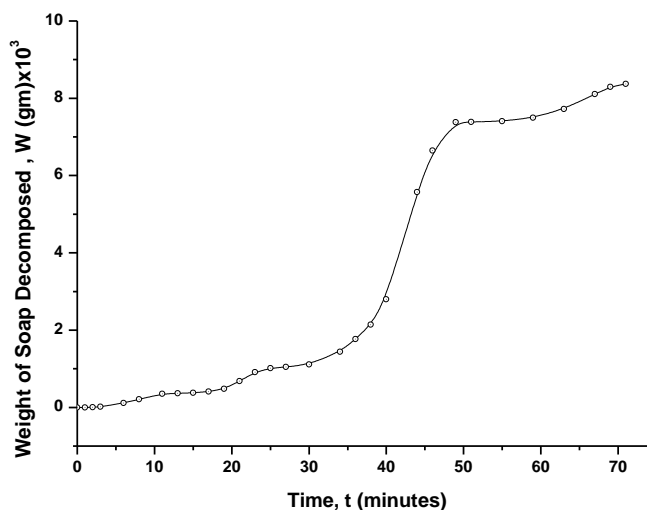


Figure 2: Weight of Magnesium Laurate Decomposed vs Time

The plot of decomposed weight of Magnesium laurate against time t is shown in Fig 2. The rate of weight loss, (dW/dt) are determined with the help of Fig.2 while W_r are evaluated from the total loss in weight of the soap and the loss at a pre-determined time (Table-1). Further, a graph between $\Delta \log(dw/dt)/\Delta(\log W_r)$ against $\Delta(1/T)/\Delta \log W_r$ is plotted and straight line obtained. The straight line plot confirms that the order of reaction for the decomposition of Magnesium laurate is of zero order. Activation energy is obtained with the slope of curve and is found 28.72 kCal/mole. It is suggested that the surface of the molecules remains completely covered all the time by the molecules of the gaseous product as the decomposition is fast and so the rate of decomposition becomes constant and the process is kinetically of zero order.

The infrared spectral bands for Magnesium laurate with their assignments are recorded in Fig-3. The spectrum is compared with the results of lauric acid and potassium soap (Table-2). There are marked differences in the spectra of lauric acid and Magnesium laurate in certain regions of spectra. However, the absorption maxima, which are Characteristics of the aliphatic portion of lauric acid molecules, remain unchanged when acid is converted to Magnesium laurate.



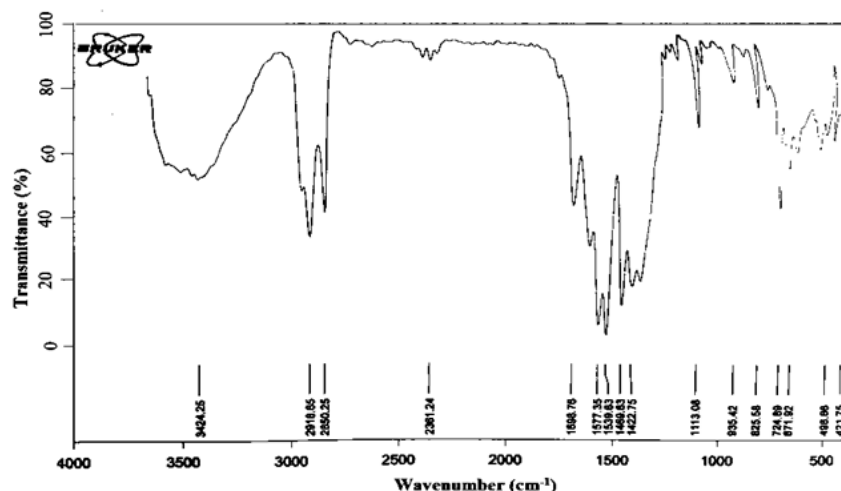


Figure 3: IR absorption spectrum of Magnesium Laurate

The absorption maxima observed at 2650, 1700, 690, 550 cm^{-1} in the spectrum of lauric acid are associated with the localised carboxyl group of the acid molecule in the dimeric form involving hydrogen bonding. In the spectra of corresponding potassium and Magnesium soaps, the characteristic vibrations of free acids were found completely absent. The complete disappearance of the carbonyl frequency in the region of 1700 cm^{-1} and the appearance of two absorption bands of the carboxyl group corresponding to the symmetrical and asymmetrical –vibrations of carboxylate ion near 1412-1430 cm^{-1} and 1540-1600 cm^{-1} respectively in the spectra of potassium, Magnesium laurate indicate that there is a complete resonance in the C-O bonds of the carboxyl group of the soap molecules and the two bonds become identical with their force constants assuming an intermediate value between those of normal double and single bonds. The results confirmed that the fatty acids exist with dimeric structure through intermolecular hydrogen-bonding between carboxyl groups of two acid molecules whereas potassium and Magnesium soap are ionic and the Magnesium-to-oxygen bond of the soap has an ionic character.

Table 2: Infrared-absorption frequencies (cm^{-1}) together with their assignments

S. No.	Absorption	Lauric acid	Potassium Laurate	Magnesium Laurate
1	CH ₃ , C-H asymmetric Stretching	2960 W	2940 W	2960 VW
2	CH ₂ , C-H asymmetric Stretching	2920 VS	2920 VS	2920 S
3	CH ₂ , C-H symmetric Stretching	2850 S	2890 VS	2851 VS
4	OH, Stretching	2650 S	-	-
5	C=O Stretching	1700 VS	-	-
6	COO ⁻ , C-O asymmetrical Stretching	-	1600 V	1540 W
7	CH ₂ , deformation	1470 M	1475 MS	1468 S
8	COO ⁻ , C-O symmetrical Stretching	-	1430 MS	1412 VS
9	CH ₂ , (adjacent to COOH group) deformation	1405W	-	-
10	CH ₃ , symmetric deformation	1350W	1330 W	1357 VW
11	Progressive bands (CH ₂ twisting and Wagging)	1350-1090 W	1375-1200W	1307-1082 S
12	CH ₃ rocking	1110 VS	1110 W	1114 S
13	OH, out of plane deformation	950 S	-	-
14	CH ₂ rocking	720W	720 MS	722 VS
15	COOH bending mode	690 MS	-	-
16	COOH Wagging mode	550MS	-	-
17	Mg –O bond	-	-	443VS

VW= Very weak, VS=Very Sharp, S=Sharp, M=Medium, W=Weak



The density and ultrasonic velocity of prepared solution of soap with different concentration was measured with help of dilatometer and ultrasonic interferometer respectively. The adiabatic compressibility (β), intermolecular free length (L_f) and acoustic impedance (Z) are evaluated with the help of measured density (ρ) and velocity (V) data and following expressions.

$$\left. \begin{aligned} \beta &= V^{-2} \rho^{-1} \\ L_f &= (\beta / K)^{1/2} \\ Z &= V\rho \end{aligned} \right\} \quad (2)$$

Here, K is temperature dependent Jacobson's constant. The measured and evaluated values of density, ultrasonic velocity, adiabatic compressibility, intermolecular free length and acoustic impedance for the prepared solution of Magnesium laurate are given in Table 3 while their variation is shown in Figs. 4-5.

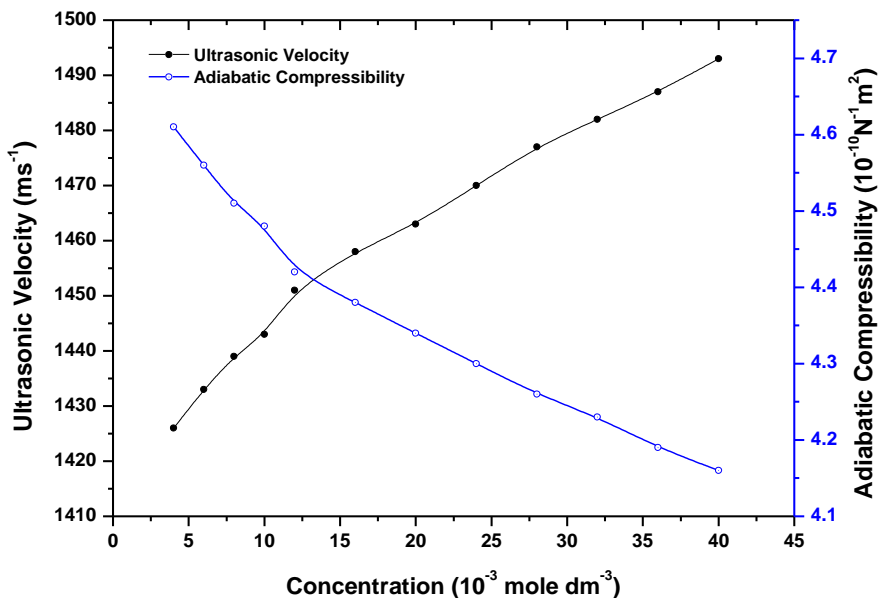


Figure 4: Ultrasonic velocity and Compressibility vs Concentration of Magnesium Laurate

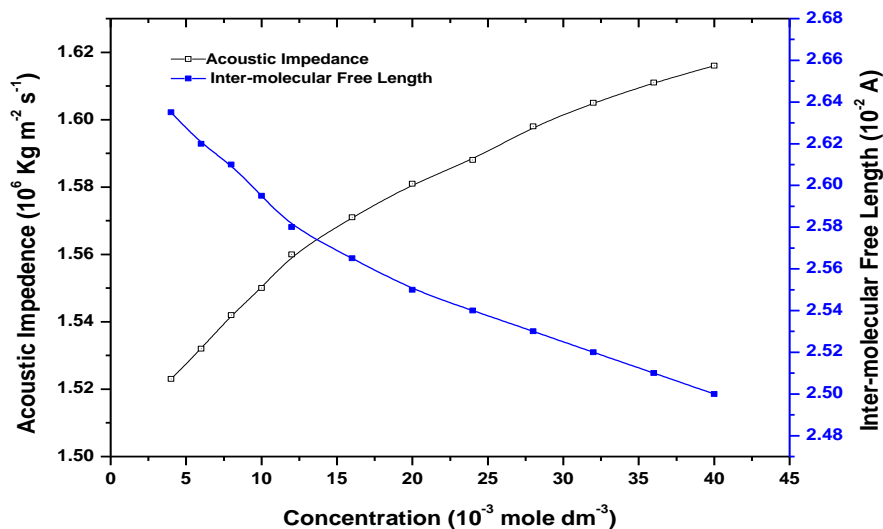


Figure 5: Acoustic Impedance and Inter-molecular free length vs Concentration of Magnesium Laurate



Table-3: Ultrasonic Velocity and other acoustic Parameters of Magnesium laurate in 70% Chloroform and 30%propylene glycol Mixture at $40 \pm 0.05^\circ\text{C}$

S. No.	Concentration $\text{C} \times 10^3 \text{ mol dm}^{-3}$	Density $\rho \times 10^{-3} \text{ kg ml}^{-3}$	Velocity $V \text{ ms}^{-1}$	Adiabatic Compressibility $\beta \times 10^{10} \text{ m}^2 \text{ N}^{-1}$	Intermolecular free length $L_f \times 10^2 \text{ \AA}$	Acoustic Impedance $Z \times 10^{-6} \text{ Kg m}^{-2} \text{ s}^{-1}$
1	4	1.0651	1426	4.61	2.64	1.518
2	6	1.0678	1433	4.56	2.62	1.530
3	8	1.0686	1439	4.51	2.61	1.538
4	10	1.0705	1443	4.48	2.60	1.544
5	12	1.0725	1451	4.42	2.58	1.557
6	16	1.0735	1458	4.38	2.57	1.565
7	20	1.0745	1463	4.34	2.56	1.571
8	24	1.0754	1470	4.30	2.55	1.580
9	28	1.0748	1477	4.26	2.54	1.587
10	32	1.0761	1482	4.23	2.53	1.594
11	36	1.0769	1487	4.19	2.52	1.601
12	40	1.0773	1493	4.16	2.51	1.608

It is clear from the Table 3 and Figs. 4-5 that density, ultrasonic velocity and acoustic impedance increase with the concentration of Magnesium laurate solution while adiabatic compressibility and intermolecular free length decrease with the concentration of Magnesium laurate solution. The decay in adiabatic compressibility and intermolecular free length and enhancement in velocity and acoustic impedance with concentration confirm the formation of strong bonding at higher concentration evinced by ionic bonding between solute (Magnesium laurate) and solvent (70% Chloroform and 30% propylene glycol). The variations in all parameters are found to show a deviation from the linear nature at concentration $0.0014 \text{ mole dm}^{-3}$ (Figs 4-5) which establish that Magnesium laurate behaves simple electrolyte in the solution and soap molecules do not aggregate appreciably below critical micelle concentration (CMC: $0.0014 \text{ mole dm}^{-3}$). Below CMC, the rate of change in ultrasonic and associate parameters is high and is slow after it. This justifies that at CMC, Magnesium laurate molecules are considerably ionized into Mg^{++} ions and anions $\text{C}_{11}\text{H}_{23}\text{COO}^-$ and these ions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The influence of electrostatic field of the ions is responsible for the orientation of solvent molecules around the ions, which causes critical enhancement in internal pressure and critical decay in compressibility. The ultrasonic features of Magnesium laurate solution is found to similar that of other metallic soap solutions [19-21]. Hence, solution of Magnesium laurate in chloroform and propylene glycol at CMC shall form a stable, strengthen and durable mixture useful for the oil, paint and textile industries.

4. Conclusion

The above discussion reveals that Magnesium laurate have good crystallinity having long-spacing average planar distances 32.46 \AA . The thermal decomposition of Magnesium laurate is of zero order whose activation energy is found 28.72 kCal/mole . IR Characteristics of the aliphatic portion of lauric acid molecules remain unchanged when acid is converted to Magnesium laurate. Study of ultrasonic and associated parameters establish that Magnesium laurate in chloroform and propylene glycol shall form a pure electrolytic, stable, strengthen and durable mixture at critical micelle concentration $0.0014 \text{ mole dm}^{-3}$. All the features of Magnesium laurate is found to resemble the features of metallic soaps. The present findings are not only quite beneficial in the field of further investigation of metallic soaps but also synthesis and application of Magnesium laurate in oil, paint and textile industries.



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