



Physico-Chemical and Acoustical Study of Calcium Soap

Gyan Prakash

VSSD College Kanpur-208002, UP, INDIA

Email: gyanprakashvssd1921@gmail.com

Abstract

The Physicochemical characteristics and structure of Calcium Myristate 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 Calcium soap is kinetic of zero order and the value of activation energy is 26.80 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 Calcium Myristate 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 calcium Myristate at different concentrations and temperature 40±0.05°C. The ultrasonic parameters indicate that there are significant interaction between the Calcium Myristate and solvent molecules in dilute solutions. It also implies that solutes do not aggregate appreciably below the critical micelle concentration (13.0 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

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(O₂CR)_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 Calcium Myristate soap [14]. Therefore, the present work is focused on synthesis and characterization of Calcium Myristate 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 Calcium Myristate

Myristic acid ($C_{13}H_{27}COOH$) of AR-Grade, potassium hydroxide (KOH) and calcium nitrate ($Ca(NO_3)_2$) were taken as constituent chemicals for the preparation of the chosen soap. Initially, Myristic acid was purified by distilling under reduced pressure. Potassium soap was prepared by refluxing equivalent amounts of Myristic 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. Calcium soap was prepared by direct metathesis of Potassium soap with a slight excess of the solution of calcium nitrate at 50-55°C under vigorous stirring. Calcium soap was purified by re-crystallization and stored over calcium chloride. The purity of calcium soap was confirmed by the determination of their melting point.

2.2 Preparation of Calcium Myristate 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 Calcium Myristate

X-ray diffraction pattern for calcium Myristate 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° (where θ is Bragg's angle). The thermo-gravimetric analysis of calcium 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 calcium Myristate were obtained with a Perkin-Elmer 577 Model Grating spectrophotometer in the region of 4000 - 200 cm^{-1} using the Potassium bromide disc method.

2.4 Ultrasonic measurements of Calcium Myristate solution

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

3. Result and Discussion

The structural feature of calcium Myristate has been demonstrated on the basis of X-ray diffraction pattern. The X-ray diffraction pattern of calcium Myristate 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 calcium Myristate suggests good crystallinity having long-spacing average planar distances for calcium Myristate is 40.58 \AA . The long spacing of calcium 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 calcium Myristate soap is 42.0 \AA .

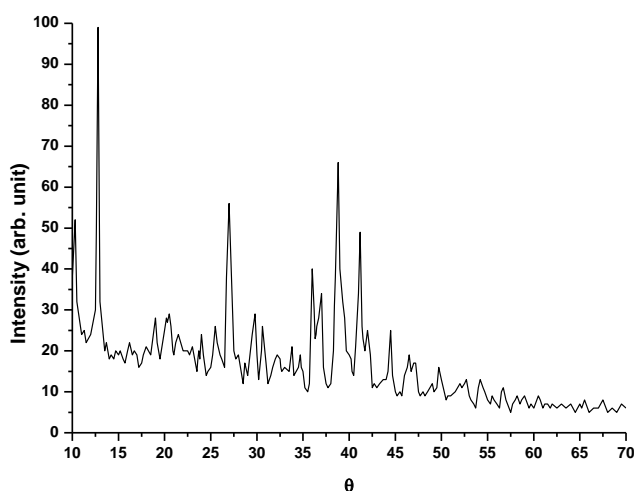


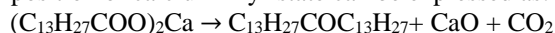
Figure 1: XRD of Calcium Myristate

The Pauling values of atomic radii and bond angles suggest that the molecular axes of calcium Myristate molecules are somewhat inclined to the basal planes. The calcium ions, Ca^{+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 calcium soap is in agreement with the single-layer structure of soap proposed by Vold and Hattiangdi [15]. The value of long spacing for homogeneous soaps of calcium suggests that there are no abrupt changes in the manner of crystallization of these soaps. The results of calcium soap are in agreement with the results of other alkaline earth metal soaps [16-17].

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



Calcium 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 (Myristone) was 78.0°C, which confirm the formation of CaO. 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 calcium Myristate

S. No.	Time, t (minutes)	Temp. T(K)	Weight of soap decomposed $W \times 10^3$ (gms)	$dw/dt \times 10^6$	$W_r \times 10^3$
1	0	298	0	0	9.475
2	3	318	0.005	1.666	9.470
3	5	338	0.017	3.400	9.58
4	8	358	0.020	2.500	9.437
5	10	378	0.039	18.83	9.436
6	13	403	0.183	3.900	9.292
7	15	423	0.400	14.076	9.075
8	17	443	0.408	26.666	9.067
9	19	463	0.417	23.764	9.058
10	21	483	0.429	21.473	9.046
11	23	503	0.439	19.857	9.036
12	24	523	0.448	18.652	9.027
13	26	543	0.456	18.291	9.019
14	28	563	0.466	17.230	9.009
15	30	583	0.498	16.285	8.977
16	32	603	0.625	15.533	8.850
17	34	623	0.953	15.562	8.577
18	36	643	1.216	18.382	8.259
19	38	663	1.899	26.472	7.576
20	40	683	3.923	32.000	5.552
21	42	703	6.722	47.475	2.753
22	44	723	8.170	93.404	1.305
23	45	743	8.519	152.772	0.956
24	47	763	8.536	181.555	0.939
25	49	783	8.541	181.255	0.934
26	51	803	8.551	174.204	0.924
27	53	823	8.568	167.470	0.907
28	57	843	8.593	161.339	0.882
29	59	863	8.636	155.780	0.839



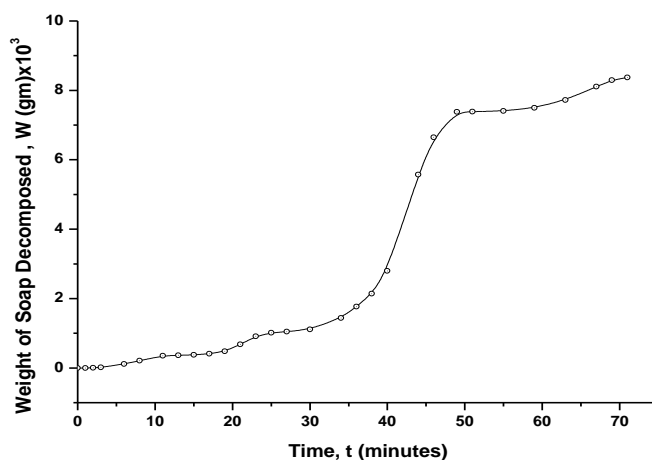


Figure 2: Weight of Calcium Myristate Decomposed vs Time

The plot of decomposed weight of calcium Myristate 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 calcium Myristate is of zero order. Activation energy is obtained with the slope of curve and is found 26.80kJ/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 calcium Myristate with their assignments are recorded in Fig-3. The spectrum is compared with the results of Myristic acid and potassium soap (Table-2). There are marked differences in the spectra of Myristic acid and calcium Myristate in certain regions of spectra. However, the absorption maxima, which are Characteristics of the aliphatic portion of Myristic acid molecules, remain unchanged when acid is converted to Calcium Myristate.

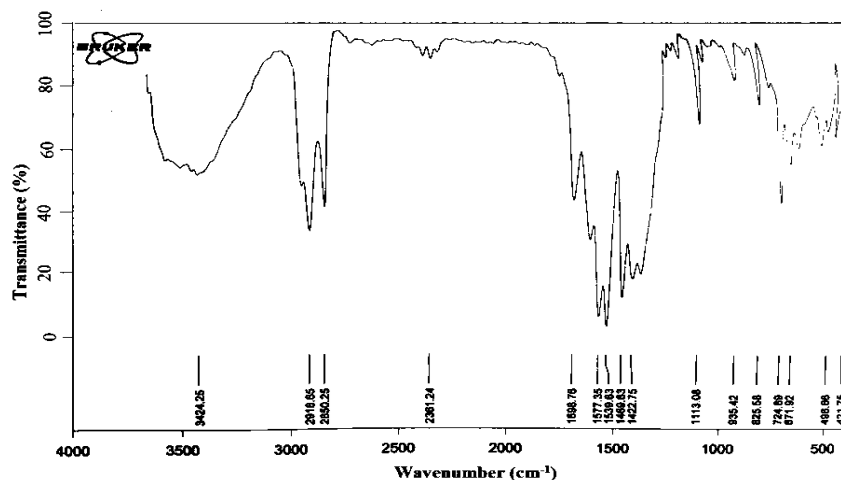


Figure 3: IR absorption spectrum of Calcium Myristate

The absorption maxima observed at 2640, 1700, 690, 550 cm^{-1} in the spectrum of Myristic 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 calcium 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 ν -vibrations of carboxylate ion near 1417-1440 cm^{-1} and 1600-1543 cm^{-1} respectively in the spectra of potassium, calcium Myristate 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 calcium soap are ionic and the calcium-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 Myristate	Calcium Myristate
1	CH ₃ , C-H asymmetric Stretching	2960VW	2940 VW	2937VW
2	CH ₂ , C-H asymmetric Stretching	2920 VS	2920 VS	2917 S
3	CH ₂ , C-H symmetric Stretching	2855 S	2850 VS	2852V S
4	OH, Stretching	2640 VW	-	-
5	C=O Stretching	1700 VS	-	-
6	COO ⁻ , C-O asymmetrical Stretching	-	1600 W	1543S
7	CH ₂ , deformation	1465 MS	1460 MS	1467VS
8	COO ⁻ , C-O symmetrical Stretching	-	1440MS	1417MS
9	CH ₂ , (adjacent to COOH group) deformation	1410W	-	-
10	CH ₃ , symmetric deformation	1375VW	1340 W	1390 S
11	Progressive bands (CH ₂ twisting and Wagging)	1350-1090 W	1360-1080W	1367-1062VW
12	CH ₃ rocking	1110 S	1110 W	1112WS
13	OH, out of plane deformation	950 S	-	-
14	CH ₂ rocking	720W	720 W	724 S
15	COOH bending mode	690 MS	-	-
16	COOH Wagging mode	550MS	-	-
17	Ca -O bond	-	-	436

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 calcium Myristate are given in Table 3 while their variation is shown in Figs. 4-5.

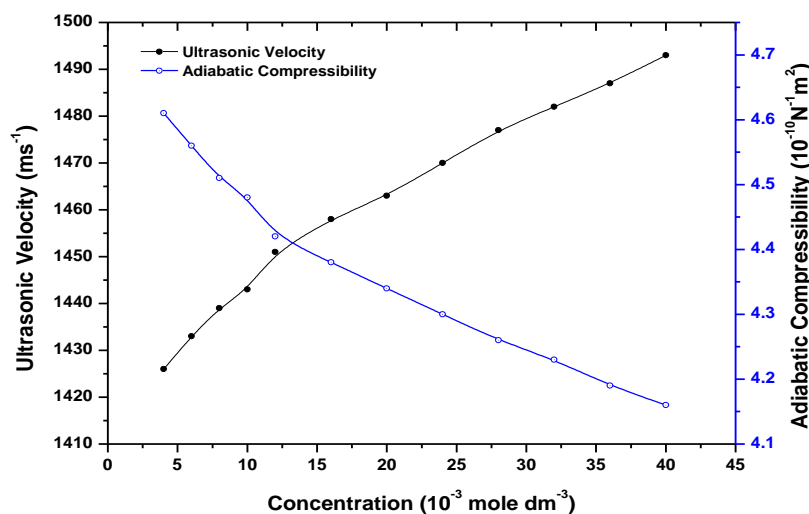


Figure 4: Ultrasonic velocity and Compressibility vs Concentration



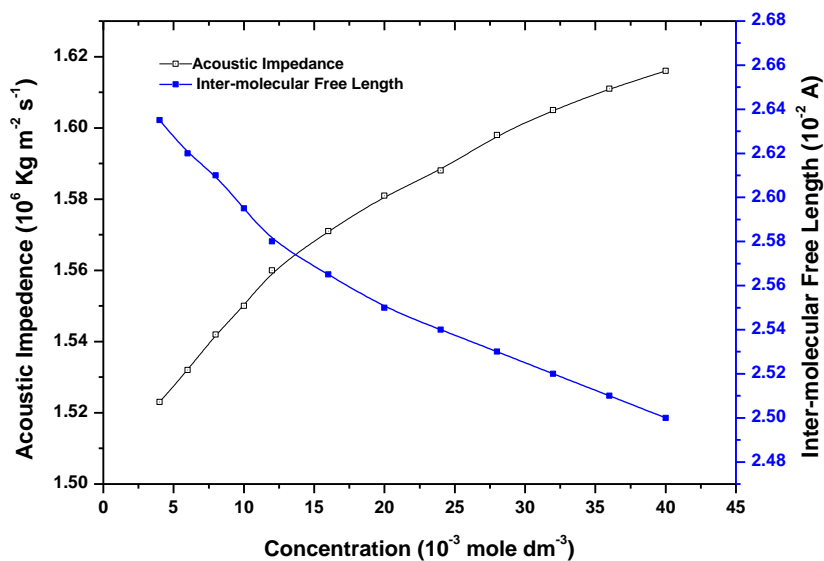


Figure 5: Acoustic Impedance and Inter-molecular free length vs Concentration

Table 3: Ultrasonic Velocity and other acoustic Parameters of calcium Myristate 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 ms^{-1}	Adiabatic Compressibility $\beta \times 10^{10} \text{ m}^2 \text{ N}^{-1}$	Intermolecular free length $L_f \times 10^2 \text{ A}^0$	Acoustic Impedance $Z \times 10^{-6} \text{ Kg m}^{-2} \text{ s}^{-1}$
1	4	1.0676	1430	4.58	2.63	1.527
2	6	1.0696	1437	4.52	2.61	1.537
3	8	1.0716	1444	4.47	2.60	1.547
4	10	1.0736	1451	4.42	2.58	1.558
5	12	1.0760	1456	4.38	2.57	1.567
6	16	1.0772	1464	4.33	2.56	1.578
7	20	1.0780	1470	4.29	2.54	1.584
8	24	1.0788	1476	4.25	2.53	1.592
9	28	1.0796	1486	4.19	2.51	1.604
10	32	1.0800	1491	4.16	2.51	1.610
11	36	1.0808	1495	4.13	2.50	1.615
12	40	1.0812	1501	4.10	2.49	1.622

It is clear from the Table 3 and Figs. 4-5 that density, ultrasonic velocity and acoustic impedance increase with the concentration of calcium Myristate solution while adiabatic compressibility and intermolecular free length decrease with the concentration of calcium Myristate 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 (calcium Myristate) 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 $0.0130 \text{ mole dm}^{-3}$ (Figs 4-5) which establish that calcium Myristate behaves simple electrolyte in the solution and soap molecules do not aggregate appreciably below critical micelle concentration (CMC: $0.0130 \text{ mole dm}^{-3}$). Below CMC, the rate of change in ultrasonic and associate parameters is high and is slow after it. This justifies that at CMC, calcium Myristate molecules are considerably ionized into Ca^{++} ions and anions $\text{C}_{13}\text{H}_{27}\text{COO}^-$ 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 calcium Myristate solution is found to similar that of other metallic soap solutions [18-19]. Hence, solution of calcium Myristate 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 calcium Myristate have good crystallinity having long-spacing average planar distances 40.58Å. The thermal decomposition of Calcium Myristate is of zero order whose activation energy is found 26.80k Cal/mole. IR Characteristics of the aliphatic portion of Myristic acid molecules remain unchanged when acid is converted to calcium Myristate. Study of ultrasonic and associated parameters establish that Calcium Myristate in chloroform and propylene glycol shall form a pure electrolytic, stable, strengthen and durable mixture at critical micelle concentration 0.0130 mole dm⁻³. All the features of Calcium Myristate 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 Calcium Myristate in oil, paint and textile industries.

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