Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2017, 6 (3): 417-422

(International Peer Reviewed Journal)

Thermo Gravimetric Analysis of Calcium Soaps

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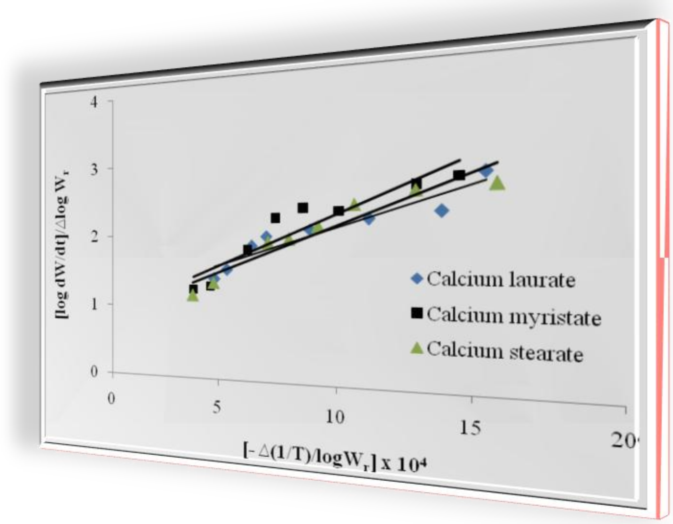
Accepted on 15th May 2017, Published online on 27th May 2017

ABSTRACT

The thermo gravimetric analysis were made on calcium soaps (Laurate, Myristate and Stearate) with a view to determine the rate of reaction, order of reaction and activation energy.The result show that the order of reaction for decomposition of calcium soaps is zero order and the energy of activation lie between 13.40-30.63 K Cal mol^{-1}. These results were discussed in term of some well known equation and the resultsobtained were in agreement with properties.

Graphical Abstract



Freeman Carroll's Type Plots (Calcium soaps)

Highlights

Soaps are widely used in daily lives, industry, technology and allied science.

The uses of metal soaps largely depend on their physical state, stability, chemical reactivity and solubility in polar and non polar solvents.

Calcium soaps (Laurate, Myristate and Stearate) were synthesized by direct metathesis of corresponding potassium soaps.

Thermo gravimetric analysis was used in the prediction of rate of reaction, order of reaction and activation energy.

Rate of decomposition and energy of activation of calcium soaps has been correlated.

Keywords: Metal soaps, order of reaction, activation energy, X-rays.

INTRODUCTION

The alkaline earth metal soaps are being widely used in industry, technology and allied science; the uses of metal soaps largely depend on their physical state, stability, chemical reactivity and solubility in polar and non polar solvents. These metal soaps have been a subject of intense investigation in the recent past on account of its role in such diversified field as medicine, cosmetic, emulsifier, lubricant, germicides and antioxidants. The methods of preparation of potassium soaps and metal soaps were described by several workers [1-7] The IR spectra and X-ray diffraction patterns of calcium soaps were studied by Upadhyay et al [8]. The IR spectra X-Ray and Thermal Analysis of lanthanum soaps were studied by Shukla et al [9]. Mehrotra et al [10]investigated the viscometric and spectral studies of copper soaps in benzene as well as methanol and its spectral studies done by Rawat et al[11].In their further studies Rawat et al [12] evaluated the Ultrasonic velocity and allied properties of transition metal in non- aquous medium. The thermo gravimetric analysis of scandium soap was investigated by Khirwar et al [13].In the present research work the author has been made to determine the various physical properties like activation energy, order of reaction and rate of reaction of calcium soaps by thermogravimetric analysis.

MATERIALS AND METHODS

The calcium soaps (Laurate, Myristate and Stearate) were synthesized by direct metathesis of corresponding potassium soaps with the required amount of the solution of calcium nitrate at 50 to 55^0 C under vigorous stirring. The precipitated soaps thus obtained were filtered and washed several times with hot conductivity water followed by alcohol. The washed samples were dried in an air oven, then the final drying was carried out under reduced pressure. The purity of the soaps were checked by IR Spectra. Thermogravimetric analysis of calcium soaps were carried out by a "Perkin-Elmer (Pyris Diamond)" Thermogravimetric analyser TGS2 at constant heating rate (10^0perminute) in nitrogen atmosphere.

RESULTS AND DISCUSSION

The results of thermogravimetric analysis of calcium soaps (Laurate, Myristate and Stearate) and the treatment of the data are tabulated in table (1-3) The calcium oxides left as final residue in thermal decomposition of calcium soaps. The weight of residue is in accordance with theoretically calculated weight of calcium oxide from the molecular formula of the corresponding soap. It is important to note that some white crystalline powder is found condensed at the cold part of the sample tube surrounding the soap and it is identified by the determination of M.P. as Laurone (69.3^0C), Myristone (78.0^0C) and Strearone (88.4^0C) in case of laurate, Myristate and stearate of calcium respectively.
The thermal decomposition of calcium soaps can be expressed as

$$\underset{\text{metal soap}}{(RCOO)_2M} \rightarrow \underset{\text{ketone}}{R_2C{=}O} + \underset{\text{metal oxide}}{MO} + \underset{\text{carbon dioxide}}{CO_2}$$

Where M is calcium metal, R is $C_{11}H_{23}$, $C_{13}H_{27}$ and $C_{17}H_{35}$ for Laurate, Myristate and Stearate respectively.
Freeman and Carroll's [14] expression for the thermal decomposition of calcium soaps, where the soap disappears continuously with time and temperature and one product is gaseous can be expressed as

$$\frac{\Delta \log\left(\frac{dw}{dt}\right)}{\Delta\,(\log w_r)} = -\frac{E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta\,(\log w_r)} + n$$

Where E, n, T, W_r are energy of activation, order of reaction temperature on absolute scale and difference between the total loss in weight and the loss in weight at time t and rate of weight loss obtained from the loss in weight Vs time curves at appropriate times respectively.

The plots of the loss in weight of the soap W against time t are shown in fig. 1 , 2 by drawing tangents at appropriate times. The values of w_r have been calculated from the total loss in weight of the soap and loss at predetermined time (table-1) and the obtained results were plotted as Δlog dw/dt $/ \Delta log\, W_r$ against $\frac{\Delta(1/T)}{\Delta \log w_r}$ in (fig1-2). The treatment of the thermo gravimetric data according to FreemanCarroll's equation is given in (Table-2)

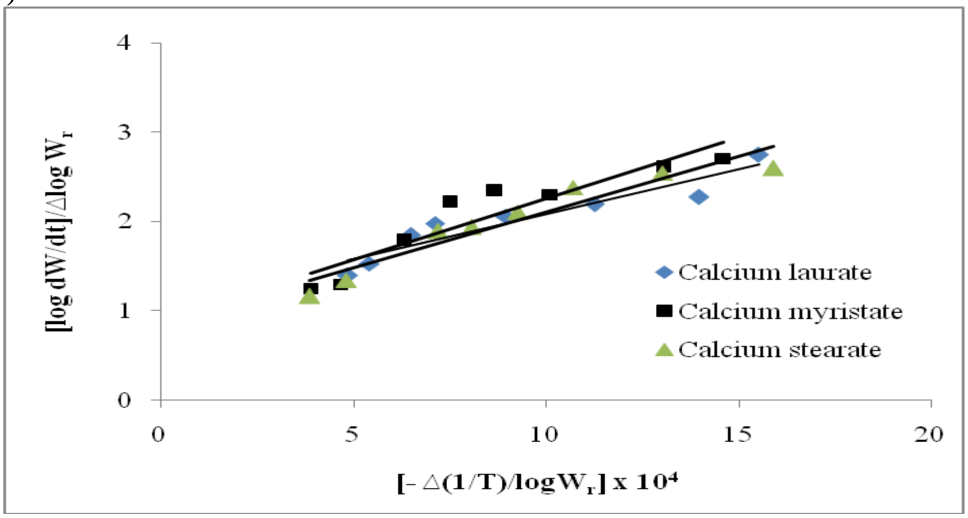


Figure: 1 Freeman-Carroll's Type Plots (Calcium soaps)

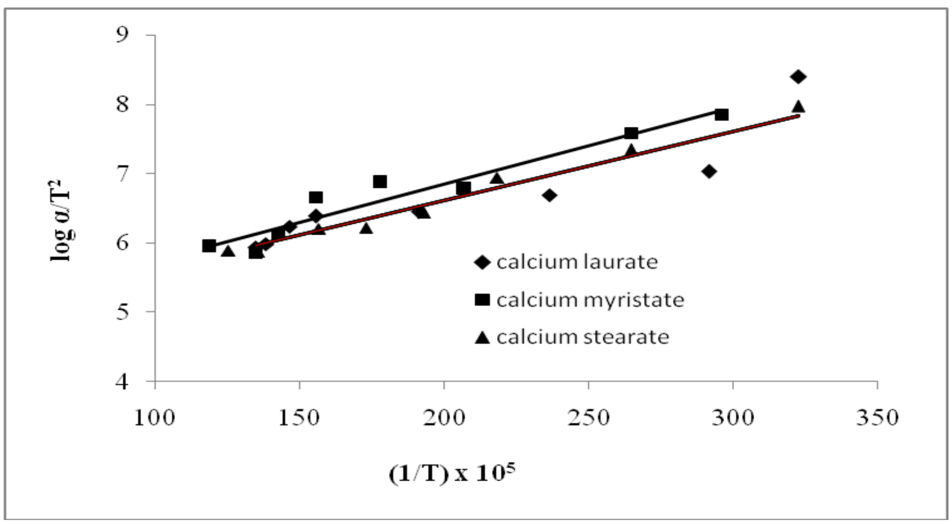


Figure: 2 Coats and Redfern's Type Plots (Calcium soaps)

The results indicate that the order of reaction for decomposition of calcium soaps is of zero order and the values of activation energy lie between 20.29 to 30.63 k cal mol^{-1} (Table-4).

It is suggested that the surface of the soap molecules remains completely covered all the time. By the molecules of the gaseous product as the decomposition is fast and thus the rate of the decomposition becomes constant and the process is of zero order.

By using Coats and Redfern's equation the value of the activation energies for thermal decomposition of calcium soaps have also been calculated and can be expressed as.

$$\text{Log}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303\ RT}$$

Where α ,T,R,A, a, E and n are Fraction of soap, decomposed temperature on absolute scales, Gas constant, frequency factor, Rate of heating in ^{0}C per minute, Energy of activation and order of reaction respectively. The equation for zero order reaction can be written as.

$$\log\left[\frac{\alpha}{T^2}\right] = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303\ RT}$$

The Plot of log α/T^2 against (1/T) should be a straight line with its slope equal to (-E/2.303 RT). The values of the energy of activation obtained from these plots (fig 2) lie between 14.09-22.97 k Cal mols^{-1} and are in agreement with values obtained from freeman Carroll's equation (table-4)
It is therefore confirmed that the rate of decomposition of calcium soaps is kinetically zero order and the energy of activation for the process lies in the range of 14.09- 30.63 k Cal mol^{-1}

Table-1 Thermal Decomposition Data of Calcium Soaps

S. No.	Time t minutes	Temp. T^0C	weight of soap decomposed w $x10^3$g.	dw/dt $x10^6$	$W_r x10^3$
			Calcium Laurate		
1	2	310	0.004	2.00	8.366
2	6	343	0.113	18.83	8.257
3	15	423	0.377	25.13	7.993
4	25	523	1.016	40.64	7.354
5	36	643	1.769	49.13	6.601
6	40	683	2.795	69.87	5.575
7	44	723	5.571	126.66	2.799
8	46	743	6.644	144.43	1.726
			Calcium Myristate		
1	5	338	0.017	3.400	9.458
2	10	378	0.039	3.900	9.436
3	21	483	0.417	19.857	9.058
4	28	563	0.456	16.285	9.019
5	36	643	0.953	26.472	8.577
6	42	703	3.923	93.404	5.552
7	45	743	8.170	181.555	1.305
8	55	843	8.568	155.780	0.907
			Calcium Stearate		
1	2	310	0.001	5.50	9.379
2	10	378	0.069	6.90	9.321
3	18	458	0.253	14.05	9.140
4	24	518	1.030	42.91	8.360
5	30	578	2.170	72.33	7.223
6	35	638	2.688	76.80	6.702
7	45	738	7.824	173.86	1.566
8	51	798	8.803	172.60	0.587

Table 2: Freeman-Carroll's treatment of thermogravimetric data of calcium soaps

Sr. No.	$\frac{1}{T}\times 10^5$	-log Wr	$-log\left(\frac{dw}{dt}\right)$	$\frac{-\Delta\frac{1}{t}}{log\ W_r}\times 10^4$	$\frac{log\frac{dw}{dt}}{\Delta log\ Wr}$
1	322.58	2.077	5.698	15.531	2.743
2	291.54	2.083	4.725	13.996	2.268

3	236.40	2.097	4.599	11.273	2.193
4	191.20	2.133	4.391	8.963	2.058
5	155.52	2.180	4.308	7.133	1.976
6	146.41	2.253	4.155	6.498	1.844
7	138.31	2.552	3.897	5.419	1.527
8	134.58	2.762	3.840	4.872	1.390

Calcium Myristate

1	295.85	2.024	5.468	14.617	2.701
2	264.55	2.025	5.408	13.064	2.607
3	207.03	2.0429	4.702	10.734	2.301
4	177.61	2.0448	4.788	8.685	2.341
5	155.52	2.0666	4.577	7.525	2.214
6	142.42	2.2555	4.029	6.314	1.786
7	134.58	2.8843	3.741	4.666	1.297
8	118.62	3.0423	3.807	3.899	1.251

Calcium Stearate

1	322.58	2.027	5.259	15.914	2.594
2	264.55	2.030	5.161	13.032	2.542
3	218.34	2.039	4.852	10.708	2.379
4	193.05	2.077	4.367	9.294	2.102
5	173.01	2.141	4.140	8.080	1.933
6	156.73	2.173	4.114	7.212	1.893
7	135.50	2.805	3.759	4.830	1.340
8	125.31	3.231	3.762	3.878	1.164

Table-3 Coats Red- Fern's Treatment of Thermo gravimetric data of calcium soaps

Sr. No.	**Temperature** T (K)	$\frac{1}{T} \times 10^5$	α	$\frac{\alpha}{T^2} \times 10^7$	$-log\ \frac{\alpha}{T^2}$
			Calcium Laurate		
1	310	322.58	0.0003	0.04	8.397
2	343	291.54	0.0109	0.93	7.030
3	423	236.40	0.0366	2.04	6.689
4	523	191.20	0.0986	3.60	6.442
5	643	155.52	0.1717	4.15	6.381
6	683	146.41	0.2713	5.81	6.235
7	723	138.31	0.5408	10.34	5.985
8	743	134.58	0.6450	11.68	5.932

Calcium Myristate

1	338	295.85	0.00160	0.14	7.851
2	378	264.55	0.00368	6.25	7.588
3	483	207.03	0.03941	1.68	6.772
4	563	177.61	0.04310	1.35	6.866
5	643	155.52	0.09007	2.17	6.661
6	703	142.42	0.37070	7.50	6.124
7	743	134.58	0.77220	13.98	5.854
8	843	118.62	0.80980	11.39	5.943

Calcium Stearate

1	310	322.58	0.0010	0.10	7.967
2	378	264.55	0.0065	0.45	7.341
3	458	218.34	0.0238	1.13	6.944
4	518	193.05	0.0970	3.61	6.441

5	578	173.01	0.2045	6.12	6.213
6	638	156.73	0.2533	6.22	6.205
7	738	135.50	0.7374	13.53	5.868
8	798	125.31	0.8296	13.02	5.885

Table-4 Energy of activation K cal mol^{-1} for the decomposition of metal soaps by various equations

Sr. No.	**Name of Soaps**	**Freeman-carroll's equation**	**Coats and redferns eqution**
1	Calcium Lautate	20.29	14.09
2	Calcium Myristate	26.80	22.97
3	Calcium Strearate	30.63	20.67

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