

## KINETICS OF DECOMPOSITION AND OPTICAL OF RUBIDIUM SOAPS

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**ABSTRACT**

Isothermal decomposition of solid Rubidium soaps, (caprylate and caprate) as a function of temperature was studied. Thermal decomposition can be expressed in quite agreement with Prout-Tompkins equation and used to estimate the constants  $k_1$ ,  $k_2$  and intercept  $c_1$ ,  $c_2$  of this equation. The rubidium soaps in alkanolic solution in presence of thioflavin T was analyzed by colorimetric method. Beer-Lambert's law is in quite agreement for the relation between the optical density and soap concentration over wide range.

**KEYWORDS:** Isothermal, colorimetric, decomposition, information, solution, concentration, equation.**INTRODUCTION**

Thermal decomposition of metallic salts of carboxylate finds importance in industry and pharmaceutical area as it provides valuable data for kinetics, apparent activation and particle Nature. Wide range of technical applications of thermal decomposition of solid involving solid state chemistry in the industrial and academic field are explored time to time. Isothermal decomposition kinetics proved of practical interest and help to determine apparent activation energy, frequency factor and activation entropy of numerous metallic compounds<sup>[1-4]</sup>. The kinetics of decomposition were analyzed using different related equations to establish decomposition kinetics<sup>[5]</sup>. The technique is employed to investigate the behavior of metallic mono and dicarboxylate isothermally and determined thermal stability parameters and kinetics of solids<sup>[6-7]</sup> useful to understand reaction mechanism.

Metallic carboxylates with amphiphilic character acquire remarkable structure and exhibit physico-chemical property useful in industry, agriculture and medicine as catalyst, inhibitor, fungicide, metallurgical process, coating smoothness and thus possess indelible position for human culture. Investigation to collect more information for their utility in research and other field was carried out<sup>[8]</sup>. Research workers have tried to establish that metal ion content can be detected successfully in organic solvents even in traces with colorimetric investigation.<sup>[9-12]</sup>

**MATERIALS AND METHODS****Experiment**

The chemicals of BDH/Analar were used in the

experiment. The soaps were prepared, purified, dried and characterized as in previous article.

**Differential thermal analysis**

Differential thermal analysis of rubidium soaps Caprylate and Caprate was carried out on a Stanton thermo balance using alumina as a reference material. It is a deflection type instrument in which dual recorder and a temperature programmer are provided to obtain the change in weight and furnace temperature simultaneously as a function of time on curvilinear chart paper. A change in weight up to 1g at 1mg sensitivity or 0.1g at 0.1mg sensitivity may be followed and recorded automatically. The simple programmer system gives the rate of heating of about 250°C per hour. The heating rate was 7.5°C/min. The reproducibility of the measurements was checked by repeating the measurements.

**Colorimetry**

The absorption measurements in the region of 300-550 m $\mu$  were carried out with Hilgers' Unispec H700 photoelectric spectrophotometer. A Bausch and Lomb 'Spectronic 20' colorimeter with a red filter and I P-40 photo tube was used for absorption measurements in the longer wavelength region (600-900 m $\mu$ ). The reproducibility of the measurements was checked by repeating the measurements.

The absorption spectra of Thioflavin T with and without rubidium soaps in non-aqueous solution were taken in order to select the wave length to perform the experiment. After determining the maxima, absorption value for soap solutions of different concentration containing the same amount of Thioflavin T at the wavelength, where maxima existed were determined

**RESULT AND DISCUSSION**

**Colorimetry**

The absorption maxima for Thioflavin T in different solvents are observed at the following wave length.

Solvent	Wave mμ
Methanol	412
Butanol	414
Pentanol	415

The absorption maxima are well defined in all solvents and are within the range 412-415 mμ. figure 1. The plots of optical density against the concentration of rubidium soaps (Caprylate, Caprate) in alkanols (methanol, butanol, pentanol) are characterized by an intersection of two straight lines at definite soap concentration (c.m.c), indicating the formation of the micelles Fig. 2 and 3. It is observed that the molecules of alcohol and dye penetrate into the palisade layer of the soap micelle with their polar group contiguous to the polar group of soap molecules and the hydrocarbon portion parallel to the hydrocarbon portion of the soap molecules and a larger micelle is produced.

The colorimetric method can be successfully used for the estimation of metal ion (rubidium) content at λ max in dilute solutions of rubidium soaps containing suitable amount of dye and for the determination of the c.m.c of these soaps.

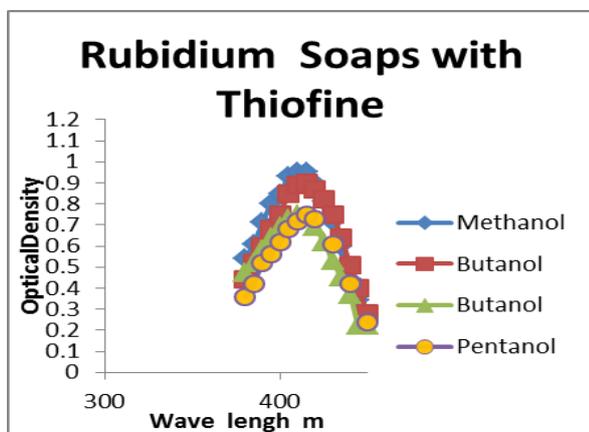


Fig.-1.

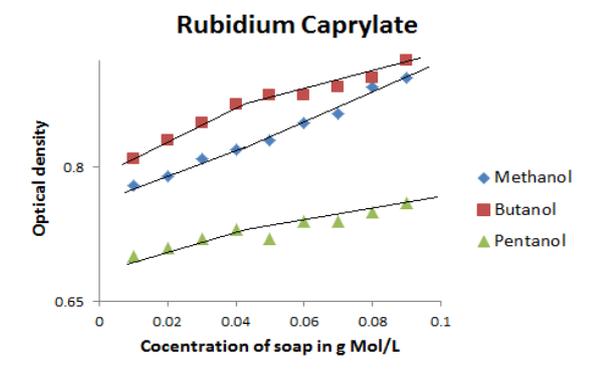


Fig.-2.

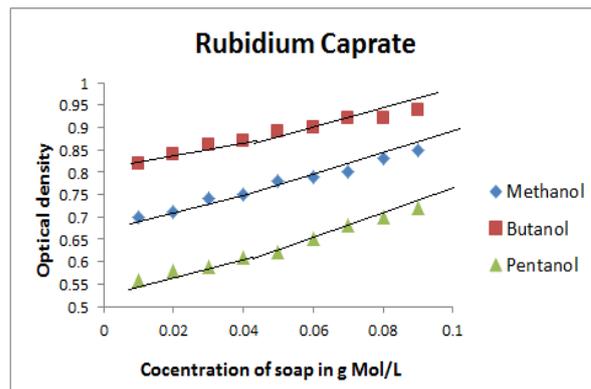


Fig.-3.

**Isothermal Decomposition**

The behavioral change in isothermal decomposition of rubidium caprylate at 260<sup>0</sup>, 400<sup>0</sup> and 560<sup>0</sup> C are studied and tabulated in fig. 4. This reveals that the fraction of the soap decomposed, α, increases with time, t, similar is the case with caprate. This increase trend relation is non-linearly with time in a small region of initial and final stage of the decomposition. Further the non-linear character decreases with the increase of temperature and almost vanishes at 560<sup>0</sup> C.

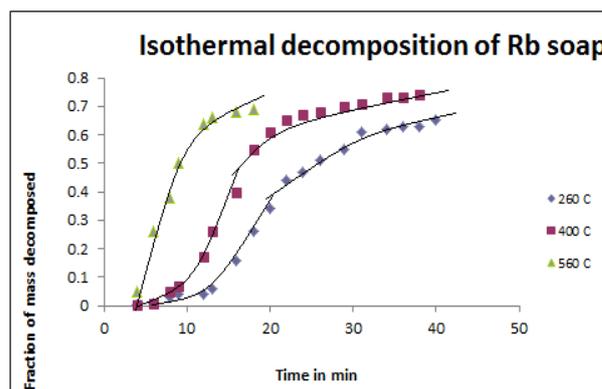


Fig. 4: Plot of fraction of mass decomposed α vs time, t in min.

The decomposition of soap initially is of slow reaction stage preceding the acceleratory stage and causes nonlinearity. The intermediate isothermal decomposition at 400<sup>0</sup> C is most adequately expressed by an equation: α = kt + c

Where α, k, t are the fraction of the soap decomposed, rate constant, time and a constant for the isothermal decomposition of rubidium soaps respectively.

In fig.4 the middle portion of the plot of the fraction of soap decomposed α vs time t, at 260<sup>0</sup> and 400<sup>0</sup> C are characterized by an intersection of two straight lines, indicating that the acceleratory and decay stage of isothermal decomposition may have different rate constant at these temperatures. Evidently, two different rate constants k<sub>1</sub> and k<sub>2</sub> are necessary in the above equation to discuss the isothermal decomposition of

rubidium soaps at 260<sup>0</sup> and 400<sup>0</sup> C. The slopes of the plots of the fraction of soap decomposed  $\alpha$  vs time,  $t$  are used to get the value of rate constants,  $k_1$  and  $k_2$  recorded in Table 1.

**Table 1:**  $k_1$  and  $k_2$  rate constants for isothermal decomposition of rubidium soaps at different temperatures.

Name of the soap	Temperature for decomposition				
	260 <sup>0</sup> C		400 <sup>0</sup> C		560 <sup>0</sup> C
	$k_1$	$k_2$	$k_1$	$k_2$	$k$
Caprylate	0.04	0.02	0.06	0.03	0.08
Caprate	0.04	0.02	0.05	0.02	0.07

The values of  $k_1$  are higher than those of  $k_2$ , explaining the rapid mode of acceleratory decomposition stage in comparison to decay stage of decomposition of these soaps. The value of rate constant increases for both the stage as the temperature rises. The increase in chain length of acid in the soap does not make any noticeable difference in the value of rate constant  $k_1$  and  $k_2$  for the decomposition of soaps.

The values of intercepts are recorded in table 2, the intercept value decreases with the rise in temperature.

**Table 2:** Value of intercepts  $c_1$  and  $c_2$  for isothermal decomposition of rubidium soaps at different temperatures.

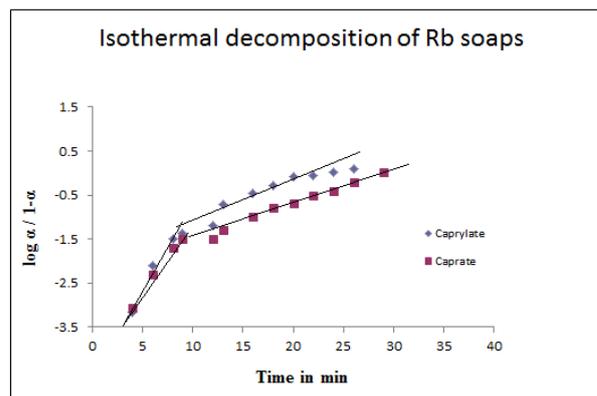
Name of the soap	Temperature for decomposition				
	260 <sup>0</sup> C		400 <sup>0</sup> C		560 <sup>0</sup> C
	$c_1$	$c_2$	$c_1$	$c_2$	$c$
Caprylate	-0.25	+0.05	-0.28	+0.01	-0.3
Caprate	-0.21	+0.03	-0.18	+0.01	-0.22

It may be pointed out that the equations derived from the branching and simple interface theories do not apply to the decomposition of rubidium soaps unites entirely.

Prout- Tompkins, PT equation has been applied to the results of the tga of the soaps to describe the decomposition. The PT equation is as follow:

$$\text{Log} [\alpha / 1 - \alpha] = K t + C$$

Where  $\alpha$ , is the fraction of the soap decomposed,  $t$ , is the time of decomposition,  $K$  is rate constant and  $C$  is a constant.  $\text{Log} [\alpha / 1 - \alpha]$  is plotted against time  $t$  Fig. 5. The plots are characterized by intersection of two straight lines, which implies two stages of decomposition. Evidently, two equations with two different rate constant  $K_1$  and  $K_2$  to understand the decomposition of rubidium soaps is must. The slopes of the plots  $\text{Log} [\alpha / 1 - \alpha]$  vs time  $t$  enables to calculate the rate constants  $K_1$  and  $K_2$  for acceleratory and decay stages for the decomposition of rubidium soaps at different temperatures and recorded in table 3.



**Fig. 5:**  $\log \alpha / 1 - \alpha$  vs time,  $t$ , in min.

**Table 3:** Rate constants  $K_1$  and  $K_2$  for the isothermal decomposition of rubidium soaps at different temperatures in PT equation.

Name of the soap	Temperature for decomposition					
	260 <sup>0</sup> C		400 <sup>0</sup> C		560 <sup>0</sup> C	
	$K_1$	$K_2$	$K_1$	$K_2$	$K_1$	$K_2$
Caprylate	0.33	0.08	0.35	0.09	0.85	0.20
Caprate	0.30	0.06	0.34	0.09	0.87	0.21

The acceleratory stage has higher rate constant than decay stage.

The rate constants show increase trend with increase in temperature for both the stages but are independent with the increase in chain length of acid in soap.

The values of intercept for both acceleratory and decay stages are not effected with the variation of temperature in the PT equation. Remains constant

The value of intercept for acceleratory and decay stage of decomposition of soaps vary from each other table 4, it remains constant for acceleratory stage and show independence nature with the number of carbon atoms in soaps. In case of the decay stage, it varies with the increase in chain length of soap.

**Table 4:** Values of intercept  $C_1$  and  $C_2$  for isothermal decomposition of rubidium soaps at different temperature in PT equation.

Name of the soap	Temperature for decomposition					
	260 <sup>0</sup> C		400 <sup>0</sup> C		560 <sup>0</sup> C	
	$C_1$	$C_2$	$C_1$	$C_2$	$C_1$	$C_2$
Caprylate	-3.0	-1.9	-3.0	-1.8	-3.1	-1.6
Caprate	-3.1	-2.2	-2.9	-2.33	-3.1	-2.6

The course of complete decomposition of soap is explained successfully by Prout – Tompkin’s theory applying two equations with different rate constants.

It may be assumed that during isothermal decomposition of soap, the branching occurs as a result of lateral strains set up in the crystal according to Prout –Tompkin

s' theory. In turn, the lateral strains are relieved by the formation of cracks along which decomposition is favoured. Further, decomposition causes more strains which led to cracking.

The rate controlling factor in the decay stage of decomposition of soap is the number of the decomposed molecules and the decomposition is favoured in those molecules which are adjacent to the products.

## CONCLUSION

The colorimetry analysis is established to detect metal ion rubidium in rubidium soaps solution of alkanols even present in traces. The linear relation between optical density and soaps concentration below and above c.m.c proves the validity of Beer and Lamberts' law. Isothermal and non-isothermal decomposition of solids rubidium soaps can be used as a tool to explore information for decomposition kinetics and mechanism useful for industrial and pharmaceutical region.

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