



Physicochemical Studies on Gadolinium Soaps in Solid State

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Abstract: Decomposition reaction was found kinetically of zero order with energy of activation for gadolinium soaps lies in the range 26.92–37.62 KJ mol⁻¹ and for thermal decomposition lies in the range 33.34–42.63KJ mol⁻¹. IR spectra and thermal analysis were used to illustrate the structure of gadolinium soaps in solid state. IR results reveal that the fatty acid exists with dimeric structure through intermolecular hydrogen bonding and gadolinium soaps were ionic in nature.

Key words: Gadolinium soaps, TGA, IR and lower carboxylic acids.

I. Introduction

Metal soaps are potentially very useful for applications in various fields¹⁻⁴, such as lubricating greases, intended to improve flow, coating smoothness, finish, printability, antidusting effects, driers in paints, dry cleaning industries, cosmetic gels, heat stabilizers for plastics and in the development of polyvinylchloride as an important commercial polymer. Other uses of metal soaps are as fungicides and pesticides⁵, optical polymer fibers⁶, coating pigment in paper industry⁷ and in the preparation of nanofilms⁸. S K Upadhyaya⁹ studied the conductometric and acoustical properties of gadolinium soaps in nonaqueous medium. The energy of activation of rare earth metal soaps calculated by Mehrotra et al.¹⁰⁻¹³. The valent thermal behavior of divalent and higher valent metal soaps have been carried out by Akanni et al.¹⁴. Folarin et al.¹⁵ determined relative thermal stability of metal soaps of Ximenia americana and Balanites aegyptiaca seed oils. The characterization of metal soaps has been done by Robinet et al.¹⁶.

In comparison of earlier studies on metal soaps, we report here results of our studies on thermal and IR spectra of Gadolinium soaps with a view to investigate the characteristic and structure of these soaps in solid state.

II. Experimental

All acids were purified by distilling under reduced pressure. The Gadolinium soaps were prepared by the direct metathesis of corresponding sodium soaps (Butyrate, Valerate, Caproate and Caprylate) by pouring a slight stoichiometric excess of aqueous metal salt solution into the clear dispersion at raised temperature with vigorous stirring. After initial drying in an air oven 50-60°C, final drying was carried out under reduced pressure. The precipitates was filtered off and washed with hot distilled water and acetone.

The IR spectra of fatty acids and of corresponding sodium and gadolinium soaps were recorded on Perkin Elmer – 842 spectrophotometer. The TGA of gadolinium soaps were carried out at a constant heating rate 10°C/min. in nitrogen atmosphere and maintaining similar conditions by a Perkin – Elmer Thermogravimetric analyzer TG S-2.

III. Result and Discussion

The purity of soaps was confirmed by the determination of melting points. The MP of the purified gadolinium soaps were:

Gadolinium Butyrate : 85.5°C

Gadolinium Valerate : 91.0°C

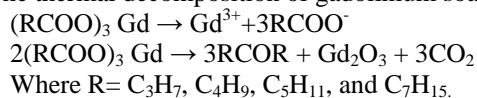
Gadolinium Caproate : 94.5°C

Gadolinium Caprylate : 96.5°C

The IR spectra of gadolinium soaps are reported and compared with the results of the corresponding fatty acids, the absorption bands observed near 2650-2640, 1705-1675, 1425-1400, 960-935, 680 and 560 cm⁻¹ have indicated the presence of localized-COOH group¹⁷ in the form of dimeric structure and the existence of intermolecular hydrogen bonding between two molecules of the fatty acids. The absorption bands observed near 2650-2640, 1705-1675 and 960-935 cm⁻¹ corresponding to the –OH group in the spectra of fatty acids have disappeared in the spectra of corresponding potassium and gadolinium soaps. The complete disappearance of the

carboxylic band near 1700 cm^{-1} in the spectra of gadolinium soaps, indicates that there is a complete resonance between the two C=O bond of the carboxylic groups gadolinium soaps. The bands observed near about 425 cm^{-1} indicate to Gd-O bonds in spectra of gadolinium soaps.

The results of thermogravimetric analysis of gadolinium soaps indicated that the final residue was metal oxide and weight of residue was in agreement with the theoretically calculated weight of gadolinium oxide. The thermal decomposition of gadolinium soaps can be expressed as:



Where R = C_3H_7 , C_4H_9 , C_5H_{11} , and C_7H_{15} .

It was found that the order of reaction for the decomposition of gadolinium soaps is zero and the values of energy of activation obtained from Freeman-Carroll's¹⁸, Horowitz-metzger's¹⁹ and coats-Redfern's²⁰ equations and the values are given below-

Energy of Activation of gadolinium soaps in Kcal Mol⁻¹ from different equations

Soaps	Freeman-Caroll's	Coat-Redfern's	Horowitz-Metzger's
Butyrate	10.2	10.4	11.2
Valerate	9.6	13.9	12.5
Caproate	9.7	13.6	10.0
Caprylate	8.9	14.8	11.8

The values of activation energy E are obtained from the slope $(-E/2.303R)$ of the plots of $\log(dw/dt)$ vs (T^{-1}) , the values of entropy of activation ΔS , and free energy of activation ΔG are calculated by following equations-

$$\begin{aligned}\Delta S &= 2.303R \log(Zh/KTs) \\ \Delta G &= E - Ts(\Delta S)\end{aligned}$$

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