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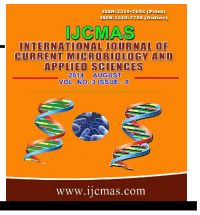

Original Research Article

Physicochemical Studies on Erbium Soaps of Saturated Higher Fatty Acids in Solid State

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Physico-chemical Studies, Erbium Soaps, Fatty Acids

A B S T R A C T

In this study, simultaneous TG/DTG-DTA technique was used for erbium metal soaps to determine their thermal degradation in inert atmosphere, which was found to be a multi-step decomposition related to the release of the metal soaps. Decomposition reaction was found kinetically of zero order with energy of activation for erbium soaps lies in the range 23.54–30.07 KJ mol-1. The kinetics of the decomposition was studied thermo gravimetrically in the temperature range 160 – 200^{o} C. The thermal stability of the soaps was assessed in terms of temperatures at which various extents of decomposition were attained and weight loss at the initial stage of decomposition. The structures of erbium soaps in solid state were determined on the basis of IR spectra and thermal analysis. In erbium soaps of lauric acid, myristic acid, palmitic acid and stearic acid are exists with dimeric structure through intermolecular hydrogen bonding confirmed by IR spectra and erbium soaps were ionic in nature.

Introduction

The study of metallic soaps has various important in technical & academic field. Metal soaps are widely used in industries and allied science[1-10] as an 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 cord and rubber, fungicides and pesticides[11], optical polymer fibers[12], coating pigment in paper industry[13] and in the preparation of nanofilms[14]. Soaps of rare earth metals had been used as thermal stabilizers to elevated temperature for the fabrication of poly(vinyl chloride) into useful products[15.16]. Mehrotra et al[17,18] detemined the thermal stability of metal soaps by differential thermal and thermogravimetric analysis while studied the thermo gravimetric behavior of hydrated rare earth acetates was analysed by Rao et al[19] and was concluded that these acetates decompose in two stages. The valent thermal behavior of divalent and higher valent metal soaps have been carried out by Akanni et al,[20]. Folarin et al,[21] determined relative thermal stability of metal soaps of

Ximenia americana and Balanites aegyptiaca seed oils. The energy of actication for rare earth metal soaps was calculated by Mehrotra et al[22]. The thermal analysis of various lanthanide carboxylates was done by Rilling and Roberts[23] and it was concluded that the final products were the halides in case of halo substituted carboxylic acids.

Recently, IR spectral and thermal decomposition of erbium soap of saturated higher fatty acids were investigated employing several techniques in conjunction with thermal analysis techniques.

Materials and Methods

The TGA of erbium soaps were carried out at a constant heating rate 10^0C/min. in nitrogen atmosphere and maintaining similar conditions by a Perkin – Elmer Thermo gravimetric analyzer TG S-2.The IR spectra of fatty acids and of corresponding sodium and erbium soaps were recorded on Perkin Elimer – 842 spectrophotometer.

All chemical were obtained as reagent grade from Aldrich and used as received. Solvents for preparation and physical measurements of 'extra pure' grade were obtained from Fluka without further purification. The erbium soaps were prepared by the direct metathesis of corresponding sodium soaps (laurate, myristate, palmate and stearate) by pouring a slight stochiometric 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.

Results and Discussion

The thermal decomposition rate of metal soaps is generally considered to follow a zero order kinetics[24,25] and may be expressed as follows:

$$dW/dT = K(W_0 - W_1) \quad (1)$$

where w0 is the initial weight of the metal soap and w1 is the residual weight of the metal soap after heating while k is the rate constant. Rearranging and integrating (1) gave

$$\log (W_0 - W_1) = \log W0 - KT/2.303 \quad (2)$$

The values of the rate constant for the decomposition of the metal soaps were obtained from the plots of logarithm of %weight loss against time.

Slow cooling rates were used in order to obtain the stable solid forms, and slow heating rates were used to facilitate polymorphic transformations; better resolution was gained in those samples capable of being encapsulated in the crystalline state, especially when prepared from ethanol. Proper cooling curves detected only typical supercooling effects. No exothermic events were observed on heating.

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

$(RCOO)_3\,Er \rightarrow Er^{3+} + 3RCOO^-$

$2(RCOO)_3\,Er \rightarrow 3RCOR + Er_2O_3 + 3CO_2$

Where R= $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$, and $C_{17}H_{35}$.

It was found that the order of reaction for the decomposition of erbium soaps is zero

and the values of energy of activation obtained from Freeman- Carroll's[26], Horowitz-metzger's[27] and coats- Redfern's[28] equations and the values are given below-

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 eqations-

$$\Delta S = 2.303R \log (Zh/KTs)$$
$$\Delta G = E - Ts(\Delta S)$$

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

Erbium Laureate : 96 ^{0}C
Erbium Myristate : 101 ^{0}C
Erbium Palmate : 106 ^{0}C
Erbium Stearate : 110 ^{0}C

The IR spectra of erbium soaps of saturated higher fatty acids are reported and compared with the results of the corresponding fatty acids, the absorption bands observed near 2960-2935, 1720-1700, 1450-1430, 930-900, 665 and 535 cm^{-1} have indicated the presence of localized -COOH group 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 2960-2935, 1720-1700 and 930-900cm^{-1} corresponding to the –OH group in the spectra of fatty acids have disappeared in the spectra of corresponding potassium and erbium soaps. The complete disappearance of the carboxylic band near 1700 cm^{-1} in the spectra of erbium soaps, indicates that there is a complete resonance between the two C=O bond of the carboxylic groups erbium soaps.

The spectra of metal soaps show a medium sharp peak in the region 579-518 cm^{-1} for M-O stretching. The IR spectra of erbium soaps show prominent peaks between 3453-3418 cm^{-1} due to –OH stretching indicating the presence of water of crystallisation. However, no such peaks are observed in case of erbium soaps. These results correspond very well with thermodynamic analysis of the stated metal soaps.

Energy of Activation of erbium soaps in Kcal Mol^{-1} from different equations

Soaps	Freeman-Caroll's	Coat-Redfern's	Horowitz-Metzger's
Laureate	12.5	12.7	13.5
Myristate	11.3	15.5	14.6
Palmate	10.2	14.4	11.7
Stearate	9.7	16.4	12.8

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