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The preparation and thermal stability studies of metal soaps of hura creptitans seed oil

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ABSTRACT

Oil extracted from Hura Crepitans seeds was used to prepare metal soaps of Zinc, Lead, manganese and Cobalt by chemical displacement method. The metal soaps obtained were subjected to thermal treatments at 443K, 453K and 463K. Thermal decomposition rate constants, activation energies and other thermodynamic data were obtained for each metal soap. Thermal stabilities of the soaps were found to decrease in the order: Co > Pb > Mn > Zn. The free energy and enthropy values of the soaps indicated that their decomposition processes are non-spontaneous.

KEYWORDS

Hura Crepitans;
Metals;
Soap;
Thermal stability.

INTRODUCTION

Soaps represent the oldest known surfactants. They have been known for at least 2300years. In the period of the Roman Empire, the Celts produced soap from animal fat and plant ashes, which served as alkali. They gave this product the name saipo from which the word soap is derived. The term soap is mainly applied to the water-soluble alkali metal salts of fatty acids, although ammonia or triethanol amine salts are also used as technical soaps.

With sodium, potassium and ammonia, the soaps are soluble in water, produce lather in abundance and have cleansing action. The alkaline-earth and heavy metal soaps of these same acids are insoluble in water and manifest properties and characteristics which differentiate them sharply from water soluble alkalis[1].

Metallic soaps (soaps of alkaline-earth and heavy metals) are understood to refer to the sparingly soluble or insoluble salts of saturated and unsaturated, straight – chain and branched, aliphatic carboxylic acids unsaturated fatty acids with alkaline, alkali earth or transition metals[2]. Metal soaps are also known as fatty acid salts[3]. Metal soaps are composed of a metal and acid portion supplied as solution in solvent or oil. They are represented by the general formula $[RCOO]_x$ M and R is an aliphatic or alicyclic radiation and M is a metal with valence x. In the case of neutral soaps, x equals the valence of the metal M. Acid salts (the ratio of acid equivalents to metal equivalent is greater than 1) contain free acid whereas neutral soaps contain no free acid. Basic salts are characterized by a higher metal to acid equivalent ratio than the normal metallic soap[4].

Metal soaps are prepared by using any one of the following processes: Double decomposition, direct reaction of carboxylic acid with metal oxides, hydroxides carbonates and direct reaction of metals with molten fatty acid. In these processes, the metal soaps are produced in the form of solid, paste and liquids[5]. The properties exhibited by metal soaps are determined by nature of the organic acid, the type of metal and its concentration, presence of solvent, additives, and method of production. On the other hand, the colour of metallic soaps depends on the amount and type of metal present. Organic materials present determine almost entirely the odor of metallic soaps[4].

Some commercially important metal soaps include those of Aluminum, Barium, Cadmium, Calcium, Cobalt, Copper, Iron, Lead, Lithium, Nickel and Zirconium. Significant application areas for metal soaps include lubricants, and heat stabilizers in plastics as well as driers in paints, varnishes, printing ink and the likes. Other uses are as processing aids in rubber, fuel additives, catalysts, gel thickeners, emulsifiers, water repellants and fungicides c

Several workers have reported the use of vegetable oils obtained from different seeds in the preparation of Heavy metal soaps[7-12]. This present work examines the preparation and assessment of the thermal stabilities of metal soaps of Cobalt, Manganese, Lead and Zinc prepared using oil obtained from Hura Crepitans seeds.

EXPERIMENTAL

Materials and methods

Hura crepitan seed oil extracted by mechanical procedure from matured seeds. Lead nitrate [$Pb(N0_3)_2$], Manganese sulphate [$MnS0_4.H_20$], Cobaltous chloride [$Cocl_2.6H_20$] and Zinc [$ZnS0_4.7H_20$] were obtained and used as received.

Preparation of metal soaps of Hura Crepitan seed oil.

The method adopted for preparing the metal soaps was that described by burrows et al[13]. In the procedure, 9.2g of the oil was dissolved in 5oml hot ethanol followed by treatment with 20ml of 20% w/v Hydroxide solution. 100ml of 30% w/v solution of the different metal salts was slowly added while stirring. The solid metal soaps formed were filtered off, washed with hot water and then air-dried.

Thermal assessment of the metal soaps.

For the thermal stability evaluation of the prepared soaps, 0.5g of the separate metal soaps, were separately and accurately weighed into a previously weighed silica glass container before transferring into a furnace set at predetermined temperatures [443, 453 and 463k] for varying periods of time. The residual weight of each sample was measured after withdrawing it from the furnace and allowing it to cool to room temperature in a desiccator. The weight loss was determined in each instance.

RESULTS AND DISCUSSION

The rate of decomposition of metal soaps is generally considered as a first order kinetics thus[14].

$$\frac{dm}{dt} = k\ (mo - mx) \qquad (1)$$

where mo and mx are the initial and residual weight of the metal soap after heating, and k is the rate constant for the decomposition process. By rearranging equation (1), we get:

$$\log\ (m_o - m_x) = \log m_o - kt / 2.303 \qquad (2)$$

by plotting the logarithm of the residual weight of each metal soap against the corresponding time, t of heating, the rate constants shown in TABLE 1 were obtained.

The results obtained shows that the rate constants

TABLE 1: Rate constants for the decomposition of metal soaps of Hura Crepitans seed oil at different temperatures.

Metal soap	Temp. (k)	Rate constant (min^{-1})
Co	443	0.053
	453	0.071
	463	0.083
Pb	433	0.060
	453	0.071
	463	0.079
Mn	443	0.065
	453	0.073
	463	0.084
Zn	443	0.070
	453	0.077
	463	0.099

for the thermal decomposition of the metal soaps are temperature dependent, increasing as the decomposition temperature increases. Within the temperature range studied, the rate constant increased by 56.5%, 31.7% 29.2% and 41.4% respectively for Co, Pb, Mn and Zn soaps. For the four metals studied, the rate constants for their thermal decomposition were observed to increase in the order: Zn > Mn >Pb> Co. This was the case for all the decomposition temperatures chosen for this study. Based on these results, the relative thermal stabilities of the metal soaps follows the order: Zn < Mn < Pb < Co.

The activation energy of the metal soaps decomposition can be obtained from the rate constants at different temperature using Arrhenius equation[15].

$$K = k_o e^{-E/RT} \quad (3)$$

$$\ln K = \ln K_o - E/RT \quad (4)$$

Figure 2 provides the plot of In K vs (1/T) for the four metal soaps studied.

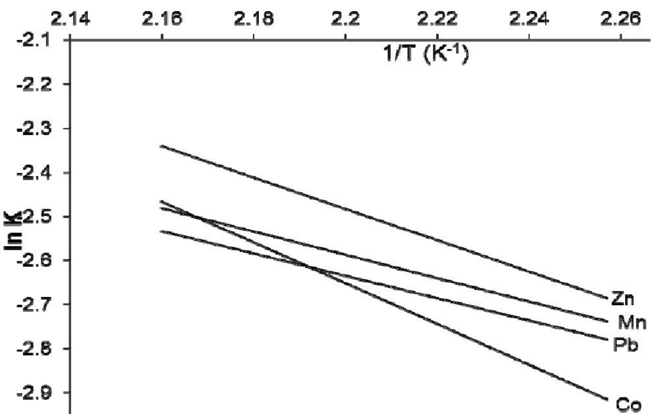

Figure 2 : Graph of Ink vs 1/T for the thermal decomposition of the four metal soaps.

The graphical plots of Ink vs 1/T for the metal soaps is presented in TABLE 2 above. The activation energies for the decomposition of the metals soaps were calculated and are presented in TABLE 2. The activation energy values of the metal soaps lie between 21.02 and 38.44 J/mol. Considering that the activation energy represents the minimum amount of energy required for a chemical reaction to take place (in this case, thermal decomposition of metal soaps), it follows that Cobalt soap with the highest activation energy is most stable and Manganese soap the least thermally stable. This assertion is however, not in consonance with the ranking of the metal soaps thermal stabilities, based on the rate constants for their thermal decomposition. This can be explained by the fact that for unimolecular reaction such as these, not every molecule possessing the activation energy necessarily transform into a product. In the activated complex stage, the molecule may have to assume a certain orientation in order to transform into a product[16].

TABLE 2 : Activation energies and thermodynamic parameters of the metal soaps.

Metal Soap	Ea (kJ/mol.)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol)
Co	38.44	35.96	10.82	0.084
Pb	21.01	18.53	10.13	0.028
Mn	21.93	19.45	10.02	0.032
Zn	29.70	27.22	9.79	0.058

Thermodynamic properties of the metal soaps

The enthalpy of activation can be calculated using the equation[17].

$$\Delta H = Ea - RT \quad (5)$$

Where Ea = Activation Energy J/mol, T = Temperature, K, R = Universal Gas constant J/mol.

The entropy of activation (Δs) and free energy of activation (ΔG) were also calculated using the relationship[18].

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

Where K = rate constant, ΔS = Entropy of activation, J/(mol.k), ΔG = free energy of activation, J/mole.

The enthalpy values for the metal soaps decomposition are positive, indicating the decomposition is endothermic. The free energy and enthropy values obtained indicates that the decomposition process are nonspontaneous for all the metal soaps. Based on the free energy values, Cobalt soap is the most stable and Zinc soap least stable thermally. This result confirms the metal soaps stability as obtained using the rate constant of their thermal decomposition. The results of this study shows values similar to those obtained from previous studies and and further suggest their potential application as thermal stabilizers for polyvinyl chloride[7-12].

CONCLUSION

The results of this study shows that oil from Hura Crepitans seed is suitable for preparing metals soaps having good thermal stabilities. This study also suggests the potential of the metal soaps to function as thermal stabilizers for Polyvinylchloride.

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