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Physicochemical Studies on Cesium Soaps. I. Thermogravimetry and Infrared Absorption Spectra

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ABSTRACT

The infrared absorption spectra of cesium stearate was compared with that of stearic acid, sodium stearate, and rubidium stearate. It is concluded that the fatty acids in the solid state exist with a dimeric structure through hydrogen bonding whereas the alkali metal soaps are ionic in nature. Thermogravimetric analysis shows that the decomposition reaction of the alkali metal soaps is kinetically of zero order and the activation energy for the process lies in the range of 2 to 6 kcal/mol.

INTRODUCTION

The alkali metal soaps have found wide application in industry and play significant roles in the area of pure colloids. The physicochemical characteristics of sodium and potassium soaps have been thoroughly investigated but the soaps of lithium [1-9], rubidium [6, 7, 10-14], and cesium [6, 7, 11, 12, 14] have not been studied systematically. Exact information on the nature and structure of alkali soaps is of great importance for their use in different industries, and a study of the properties of cesium soaps in the solid state as well as in solution was undertaken. The present paper deals with

the study of the infrared absorption spectra and the thermogravimetric analysis of cesium stearate.

EXPERIMENTAL

Preparation of Soap

The required amount of stearic acid was melted and added to a warm solution of cesium carbonate with constant stirring. The soap was digested on a water bath until the evolution of carbon dioxide ceased. The excess acid was removed by washing with benzene and the soap was purified by recrystallization with methanol. After initially drying in an air oven at 100-105°C, the final drying was carried out under reduced pressure. The purity of the soap was checked by the determination of its melting point, 135.4°C. The samples were also analyzed for their carbon and hydrogen content, and the results were found to be in agreement with the theoretical calculated values:

	Carbon %	Hydrogen %
Found	51.98	8.35
Calculated	51.87	8.40

The reproducibility of the results was checked by preparing two samples of the soap under similar conditions.

Measurements

The infrared spectra were measured with a Perkin-Elmer Model 577 grating spectrophotometer using the potassium bromide disk method. The thermogravimetric analysis was carried out at constant rate of heating (10°C/min) in a thermobalance manufactured by Fertilizer Corporation of India, Sindri.

RESULTS AND DISCUSSION

Infrared Absorption Spectra

The wave numbers of the absorption maxima in the spectra of stearic acid, sodium stearate, rubidium stearate, and cesium stearate are assigned and tabulated in Table 1.

TABLE 1. Frequencies (cm^{-1}) of Absorption Maxima with Their Assignments^a

Assignment	Stearic acid	Sodium stearate	Rubidium stearate	Cesium stearate
CH_3 , C-H antisymmetric stretching	2960 s	2960 sh	2940 w	2960 sh
CH_2 , C-H antisymmetric stretching	2920 vs	2920 vs	2900 vs	2920 vs
CH_2 , C-H symmetric stretching	2850 s	2850 s	2830 s	2860 ms
OH, stretching	2650 vs	-	-	2640 vw
C=O, stretching	1700 vs	-	-	-
COO^- , C-O antisymmetric stretching	-	1560 vs	1550 vs	1560 vs
CH_2 , deformation	1468 m	1475 m	1460 ms	1470 ms
COO^- , C-O symmetric stretching	-	1424 m	1400 s	1420 ms, 1430 sh
C-O stretch. + O-H in-plane deformation	1432 m	-	-	-
CH_2 (adjacent to COOH group) deformation	1412 m	-	-	-
CH_3 symmetric deformation	-	1380 sh	1370 w	1385 sh

(continued)

TABLE 1 (continued)

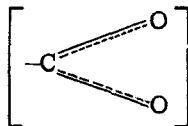
Assignment	Stearic acid	Sodium stearate	Rubidium stearate	Cesium stearate
Progressive bands (CH ₂ twisting and wagging)	1350, 1330, 1313, 1278, 1240, 1221, 1202	1325, 1310, 1280, 1260, 1230, 1210, 1190	1325, 1310, 1285, 1265, 1255, 1220, 1195	1347, 1325, 1305, 1280, 1260, 1235, 1210, 1190
CH ₃ rocking	1110 w	1110 vw	1085 w	1110 vw
OH out-of-plane deformation	940 n	-	-	-
COO ⁻ deformation	-	-	-	920 ms
CH ₂ rocking	730 m 720 m	720 ms	718 s	720 vs
COOH, bending mode	689 s	-	-	-
COOH, wagging mode	550 s	-	-	-
COO ⁻ , rocking vibration	-	530 m	530 m	530 m

^a vw = very weak, w = weak, m = medium, ms = medium strong, s = strong, vs = very strong, dm = diffuse medium, sh = shoulder.

It is observed that the absorption maxima which are characteristic of the aliphatic portion of the acid molecule remain unchanged on going from the acid to the soaps. The absorption maxima at 2650, 1705, 1433, and 937 cm^{-1} in the spectrum of stearic acid are associated with the carboxyl group of the acid molecule in the dimeric state and confirm the presence of hydrogen bonds between two molecules of stearic acid:



The complete disappearance of the strong absorption maximum near 1700 cm^{-1} (characteristic of C=O of the carboxyl group of the acid molecule in the dimeric state) in the spectra of stearates of Na, Rb, and Cs indicates the fact that there is complete resonance in the two C-O bonds of the carboxyl group of the soap molecule and that the group has the following structure:



The appearance of two absorption bands of the carboxyl group corresponding to the symmetric and antisymmetric vibrations of the carboxylate ion at 1400-1430 and 1550-1565 cm^{-1} in the spectra of stearates of Na, Rb, and Cs instead of one band observed at 1705 cm^{-1} in the spectrum of stearic acid confirms that these soaps are ionic in nature and the metal-to-oxygen bonds in these soaps have an ionic character.

It may be pointed out that the absorption maximum corresponding to the antisymmetric vibration of the carboxylate ion at 1550-1565 cm^{-1} was not observed in the spectrum of stearic acid but the C=O stretching band appeared at 1705 cm^{-1} . The absorptions observed at 2650, 1433, and 937 cm^{-1} , corresponding to the OH group in the spectrum of stearic acid, either disappear or change markedly in intensity in the spectra of these soaps. The absorption maxima at 920 cm^{-1} in the spectra of stearates are assigned to the wagging vibration of the ionized carboxyl group of these soaps. Lecomte et al. [15] studied the infrared absorption spectra of metal salts of organic acids and pointed out that the frequencies for the symmetrical stretching vibration, antisymmetrical stretching vibration, and deformation bending vibration lie in the region 1400-1300, 1610-1550, and

950-800 cm^{-1} , respectively. The assigned frequencies for stearates of Na, Rb, and Cs are in agreement with the results of other workers [15, 16].

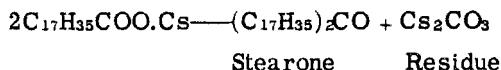
The absorption maxima at 689 and 550 cm^{-1} in the spectrum of stearic acid are assigned to the bending mode and to the wagging mode of the vibrations of carboxyl group of the acid molecule, respectively. These maxima are absent in the spectra of stearates of Na, Rb, and Cs. The absorption maximum of the bending mode of the ionized carboxyl group of the stearate soap molecule is observed at 920 cm^{-1} and the frequencies of the wagging and the rocking modes of the ionized carboxyl group of stearate ion are observed at 610 and 535 cm^{-1} , respectively.

The results confirm that the fatty acids in the solid state exist with a dimeric structure through hydrogen bonding between the carboxyl groups of two acid molecules, whereas the alkali metal soaps are ionic in nature and the metal-to-oxygen bonds of these soaps have an ionic character.

Thermal Analysis

The results of our thermogravimetric analysis of cesium stearate are given in Table 2.

The results show that the final residue is cesium carbonate and the weight of the residue is almost equal to the theoretically calculated weight of cesium carbonate from the molecular formula of the soap. It was observed that a white crystalline substance condensed at the cold part of the tube surrounding the sample (cesium stearate), and it is identified as stearone (mp: 88.4°C). The thermal decomposition of the soap can be expressed as



The results of the thermal decomposition of cesium stearate, where the soap disappears continuously with time and temperature and one product is gaseous, can be explained in terms of Freeman and Carroll's rate expression [17]:

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

where E = energy of activation; n = order of reaction; w_r = difference

TABLE 2. Thermogravimetric Analysis

Temperature (°K)	Time (min)	Weight loss (g × 10 ⁴)	Temperature (°K)	Time (min)	Weight loss (g × 10 ⁴)
333	4	10	593	30	430
353	6	20	613	32	430
373	8	25	633	34	430
393	10	40	653	36	490
413	12	45	673	38	520
433	14	65	693	40	550
453	16	110	713	42	590
473	18	140	733	44	640
493	20	230	753	46	890
513	22	340	773	48	1300
533	24	360	793	50	1720
553	26	385	813	52	1730
573	28	430	833	54	1730

between the total loss in weight and loss in weight at time, *t*, i.e., *w*₀ - *w*; and (dw/dt) = values of rate of weight loss obtained from the loss vs time curves.

It may be pointed out that the slope and intercept of the plot of

$$\frac{\Delta \log (dw/dt)}{\Delta \log w_r} \text{ vs } \frac{\Delta \left(\frac{1}{T}\right)}{\Delta \log w_r}$$

are equal to $-E/2.303R$ and *n*, respectively.

The values of (dw/dt) were obtained from the plot of the weight loss of the soap, *w*, against time, *t* (Fig. 1). The values of *w*_{*r*} were calculated from the total loss and the loss at the predetermined time and then the plot of

$$\frac{\Delta \log (dw/dt)}{\Delta \log w_r} \text{ against } \frac{\Delta \left(\frac{1}{T}\right)}{\Delta \log w_r}$$

was obtained (Fig. 2).

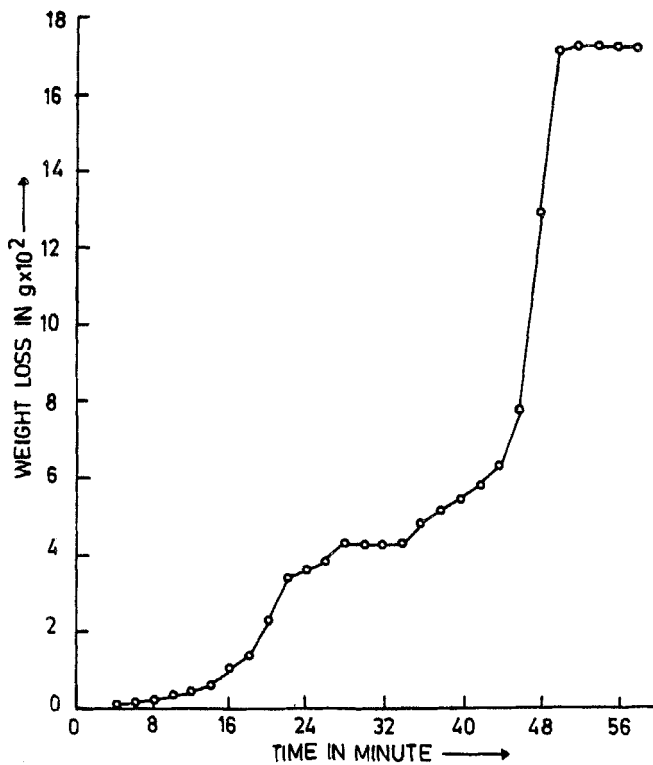


FIG. 1. Plot of weight loss vs time.

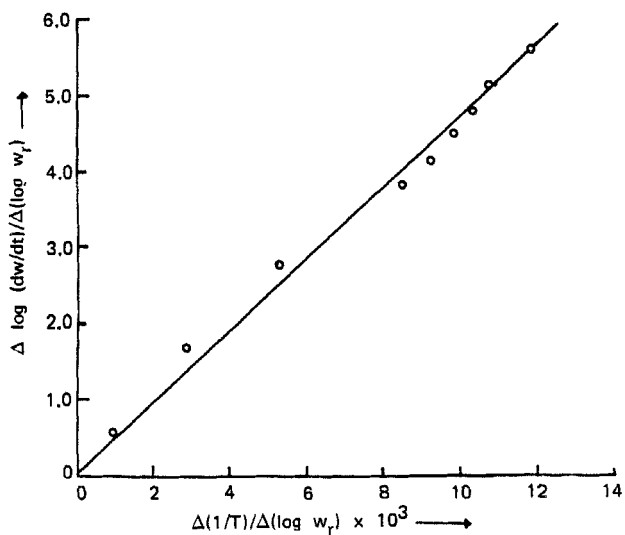


FIG. 2. Freeman and Carroll's equation.

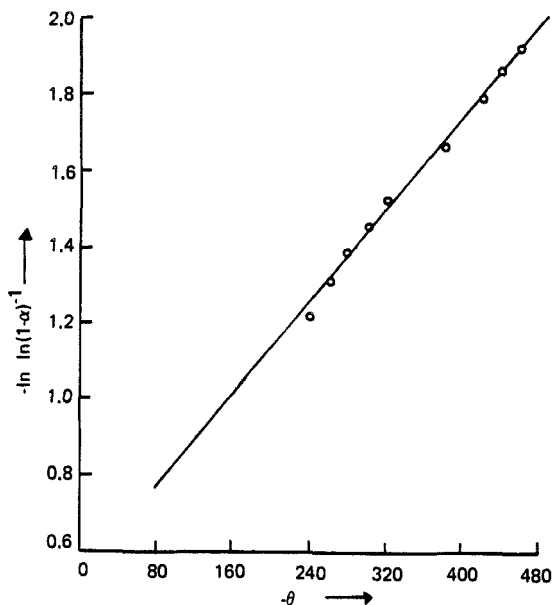


FIG. 3. Horowitz and Metzger's equation.

It is found that the energy of activation for the decomposition of cesium stearate is 2.23 kcal/mol and the order of the decomposition reaction is zero. It is suggested that the surface of the soap molecules remains completely covered at all times by the molecules of the gaseous product because the decomposition is fast and thus the rate of decomposition is constant and the process of decomposition is kinetically of zero order.

The energy of activation for the thermal decomposition of cesium stearate has also been calculated by using the following other equations.

Horowitz and Metzger's equation [18] is

$$\ln \ln (1 - \alpha)^{-1} = \frac{E}{RT_s^2} \theta$$

where α is the fraction of the soap decomposed, T_s is the temperature of maximum rate of decomposition, θ is $T - T_s$, and E is the energy of activation.

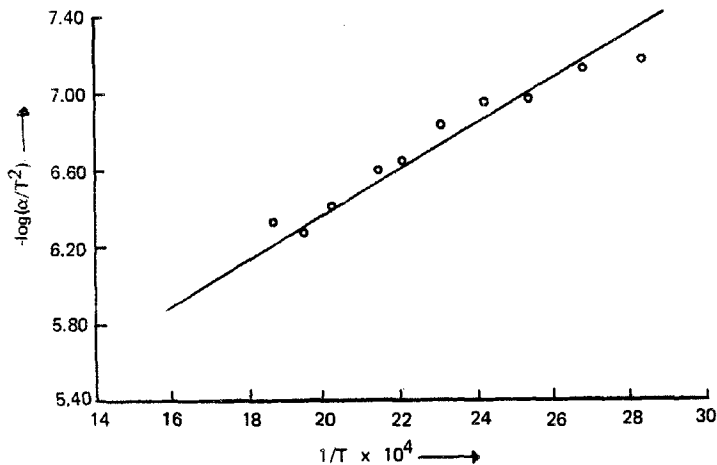


FIG. 4. Coats and Redfern's equation.

Coats and Redfern's equation [19] for a zero-order reaction is

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

where a is the rate of heating in $^{\circ}\text{C}$ per minute, α is the fraction of the soap decomposed, A is the frequency factor, and E is the energy of activation.

The plots of $\ln \ln (1 - \alpha)^{-1}$ vs θ (Horowitz and Metzger's equation) and of $\log (\alpha/T^2)$ vs $1/T$ (Coats and Redfern's equation) are shown in Figs. 3 and 4, respectively. The values of the energy of activation for the decomposition of cesium stearate are 5.68 and 5.53 kcal/mol according to Horowitz and Metzger's equation and Coats and Redfern's equation, respectively, and the decomposition reaction is kinetically of zero order.

The activation energies for the decomposition of other metal soaps lie in the range of 3 to 6 kcal/mol, and the values are almost independent of the nature of the cation and anion in the soap molecule [20]. The energy of activation for zinc stearate was found to be 9.83 kcal/mol by Rasheed and Bhohe [21]. The small difference may be due to the different experimental conditions which must be maintained constant to reproduce the kinetic data.

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