Recl. Trav. Chim. Pays-Bas 106, 625-627 (1987)

# Physico-chemical studies on calcium soaps

K. N. Mehrotra and S. K. Upadhyaya

Department of Chemistry, Agra University, AGRA-282004, India (Received May 18th, 1987)

Abstract. Calcium soaps were prepared by the metathesis of the corresponding potassium soap with an aqueous solution of calcium acetate. The IR results showed that the fatty acids exist in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two acid molecules, whereas calcium palmitate has an ionic character. The X-ray analysis indicated that the zig-zag chains of the fatty acid radical constituent of the soap molecules extend straightforward on both sides of each basal plane and that the molecular axes of the soaps are slightly inclined to the basal plane. The thermal decomposition of calcium palmitate was found to be kinetically of zero order and the energy of activation for the decomposition reaction was in the region of 3 KJ/mole.

### Introduction

The non-alkali metal salts of higher fatty acids are known as "metal soaps" due to their molecular similarity to alkali metal soaps which are the alkali metal salts of the corresponding fatty acids. The alkaline-earth metal soaps are being widely used in industry as detergents, softners, plasticizers, greases, lubricants, cosmetics and medicines. The physico-chemical characteristics and the structure of these soaps depend on the method and conditions of their preparation.

The physico-chemical properties of alkaline-earth metal soaps in the solid state have been investigated by several workers<sup>1-10</sup>. The present work deals with studies of infrared, X-ray and thermogravimetric analysis of calcium palmitate carried out in order to investigate the structure of calcium soaps in the solid state.

# Experimental

Calcium soaps were prepared by the direct metathesis of the corresponding potassium soaps with the required amount of calcium acetate solution. The soaps were analysed for carbon, hydrogen and metal content and the results were found to be in agreement with the theoretically calculated values. The infrared spectrum showed the absence of free fatty acid and co-ordinated water molecules in the soap.

The IR spectra of calcium soaps and fatty acids were recorded using a Perkin-Elmer "Model 577" grating spectrophotometer.

The X-ray diffraction patterns were obtained with a Rich-Scifert 2002 D Isodebyeflex Diffractometer using  $Cu-K_{\alpha}$  radiations filtered by a nickel foil over the range of diffraction angle, 20 from 4° to 55°. Diffraction angles were measured to 0.01°.

The thermogravimetric analysis of calcium soap was carried out at a constant rate of heating  $(20^{\circ}C/min)$  under nitrogen atmospheric conditions in a thermobalance (Mettler TG 50).

### **Results and discussion**

## (i) Infrared absorption spectra

The infrared absorption bands for calcium palmitate (hexadecanoate) were assigned and compared with those of

palmitic acid. The absorption maxima, which are characteristic of the aliphatic portion of the acid molecule, remain essentially unchanged when the palmitic acid is converted into calcium palmitate. The absorption maxima observed near 2650, 1700, 930, 680 and 550 cm<sup>-1</sup> are associated with the localised COOH group of the acid molecule in the dimeric form and confirm the presence of hydrogen bonding between two molecules of palmitic acid.

$$C_{15}H_{31} - C / C - H_{31} - C / C - C_{15}H_{31}$$

The complete disappearance of the strong absorption bands near 1700 cm<sup>-1</sup> in the spectrum of calcium palmitate indicates that there is a complete resonance between the two carbonyl bonds of the carboxylic group of the soap molecule and the two C-O bonds such that they become identical with their force constant, assuming an intermediate value between those of normal double and single bonds. The appearance of two absorption bands of the carboxyl group corresponding to the symmetric and asymmetric stretching vibrations of carboxylate ion near 1410 and 1530 cm<sup>-1</sup> in the spectrum of calcium palmitate, instead of one band near  $1700 \text{ cm}^{-1}$ , confirms that the soap possesses an ionised structure and that the metal-oxygen bonds in the soap have an ionic character. The absorption maxima near 680 and  $550 \text{ cm}^{-1}$  in the spectrum of palmitic acid are assigned to the bending and wagging modes of the vibrations of the carboxylate group of the acid molecules, respectively. These maxima are not observed in the spectrum of calcium palmitate. The assigned frequencies are in good agreement with the results of other workers<sup>1,11,12</sup>.

## (ii) X-ray diffraction patterns

The intensities of the diffracted X-rays as a function of the diffraction angle,  $2\theta$ , for calcium soaps were observed and interplanar spacings (d) were calculated from the positions of the intense peaks using *Bragg's* relationship,

 $n \cdot \lambda = 2d \cdot \sin(\theta)$ , where  $\lambda$  is the wavelength of the radiation. A number of peaks arising from the diffraction of X-rays by planes of metal ions (known as basal planes) have been observed over the range of 4° to 55° of the diffraction angles in the diffraction patterns of calcium soaps. The appearance of the diffractions up to 23rd order suggests good crystallinity for calcium soaps. The interplanar spacings for 3rd, 4th, 7th, 8th, 10th, 13th, 16th, 17th, 19th, 20th, 21st, 22nd and 23rd order diffractions for calcium palmitate are 43.95, 43.96, 43.54, 44.08, 44.00, 44.46, 44.00, 44.35, 44.27, 44.00, 44.31, 43.56 and 43.47 Å, respectively. The average planar distance, i.e. the long spacing for calcium palmitate, is 43.92 Å. The difference in the long spacings for calcium stearate (48.81 Å)<sup>13</sup> and calcium palmitate (43.92 Å) is 4.89 Å, which approximately corresponds to double the length of two additional methylene groups in the fatty acid radical constituent of the soap molecules. It is, therefore, suggested that the zig-zag chains of the fatty acid radical constituent of the soap molecule extend straightforward on both sides of each basal plane. The values of the long spacings for calcium stearate (48.81 Å) and palmitate (43.92 Å) are smaller than the calculated dimensions of stearate (52 Å) and palmitate (47 Å) ions from Pauling's values for atomic radii and bond angles. This suggests that the molecular axes are somewhat inclined to the basal planes. The metal ions,  $Ca^{++}$ , fit into spaces between oxygen atoms of the ionised carboxyl group without a large strain of the bonds.

Comparison of the long spacings of palmitates of calcium (43.92 Å), strontium (42.20 Å) and barium (41.42 Å)<sup>14</sup> shows that the long spacings decrease in the order of calcium, strontium and barium, although the ionic radii of the metal ion constituent of the soap molecules exhibit the opposite trend. It is, therefore, concluded that the angle of inclination of the molecular axes of the soap molecule to the basal plane is affected by the metal ions. A number of diffraction peaks in the intermediate range of the diffraction angle of 20–30° are also observed in the diffraction pattern of calcium palmitate and are attributed to the diffraction than the basal planes. The calculated spacings from these peaks correspond to the shorter side spacings.

On the basis of long and short spacings, it is proposed that the metal ions  $(Ca^{++})$  in the calcium soap are arranged in a parallel plane, equally spaced in the soap crystal with fully extended zig-zag chains of the fatty-acid radical on both sides of each basal plane.

#### (iii) Thermogravimetric analysis

The results of the thermogravimetric analysis of calcium palmitate and the treatment of the data are recorded in Table I. The results show that the final residue is calcium carbonate since the weight of the residue is in agreement with the theoretically calculated weight of calcium carbonate from the molecular formula of calcium palmitate. The substance which condensed at the cold part of the tube on heating of the soap was identified as palmitone (16-hentriacontanone). The thermal decomposition of calcium palmitate can be represented as:

$$(C_{15}H_{31}COO)_2Ca$$

calcium palmitate

 $C_{15}H_{31} \rightarrow CO \rightarrow C_{15}H_{31} + CaCO_3 + CO_2$ palmitone calcium carbonate

The results of the thermal decomposition of calcium soaps have been explained in terms of *Freeman-Carroll*'s<sup>15</sup> and *Horowitz-Metzger*'s<sup>16</sup> equations. *Freeman* and *Carroll*'s rate expression for the thermal decomposition of soap, where the soap disappears continuously with time and temperature and where one product is gaseous, can be expressed as:

$$\frac{\Delta[\log(dw/dt)]}{\Delta[\log(W_r)]} = -\frac{E}{2.303 \cdot R} \cdot \frac{\Delta(1/T)}{\Delta[\log(W_r)]} + n$$

where T, R, E, n,  $W_r$  and dw/dt are the temperature on the absolute scale, the gas constant, the energy of activation, the order of reaction, the difference between the total loss in weight and the loss in weight at time  $(t, i.e. W_0 - W_t)$ , and the value of the rate of weight loss obtained from the loss in weight vs. time curves at appropriate times, respectively.

The treatment of thermogravimetric results, according to *Freeman-Carroll*'s equation, is given in Table I. It was found that the order of reaction for the thermal decomposition of calcium soap is zero and that the value of energy of activation for the thermal decomposition of calcium palmitate is 3 KJ/mole.

It is therefore suggested that the surface of the soap molecules remains completely covered at all times by the molecules of the gaseous product, since the decomposition is fast and thus the rate of decomposition is kinetically of zero order.

Sample No.	Temp. T(Å)	Time t (min)	Weight of the soap decomposed $W \times 10^5$ (g)	$dw/dt \times 10^6$	Freeman-Carroll's eqn.		Horowitz-Metzger eqn.	
					$\frac{\Delta(1/T)/}{\Delta[\log(W_r)]} \times 10^3$	$-\Delta[\log(dw/dt)]/\Delta[\log(W_r)]$	$\theta = T - T_{\rm s}$	$\ln\left[\ln\left(1-\alpha\right)^{-1}\right]$
1.	373	0	_	-	1.3266	-	- 440	_
2.	413	2		- 1	1.1981	-	- 400	-
3.	453	4	-	-	1.0923	-	- 360	-
4.	493	6	6	10.00	1.0023	2.4701	- 320	- 5.2617
5.	533	8	9	11.25	0.9265	2.4439	- 280	- 4.8575
6.	573	10	13	13.00	0.8610	2.4106	- 240	- 4.6612
7.	613	12	18	15.00	0.8039	2.3777	- 200	- 4.1619
8.	653	14	21	15.00	0.7542	2.3756	- 160	- 4.0045
9.	693	16	39	24.38	0.7077	2.2623	- 120	- 3.3810
10.	733	18	140	77.78	0.6528	1.9661	- 80	- 2.0554
11.	773	20	710	355.00	0.4948	1.3195	- 40	- 0.0617
12.	813	22	920	418.18	0.3533	0.9704	0	- 0.4442
13.	853	24	953	397.08	-	-	40	0.5329
14.	893	26	953	366.54	_	-	80	0.5329

Table I Freeman-Carroll's and Horowitz-Metzger's treatment of thermogravimetric data of calcium palmitate.

The energy of activation for the thermal decomposition of calcium palmitate has also been calculated by using Horowitz-Metzger's equation:

$$\ln\left[\ln\left(1-\alpha\right)^{-1}\right] = \frac{E}{R \cdot T_s^2} \cdot \theta$$

where  $\alpha$ , E, T<sub>s</sub> and  $\theta$  are the fraction of soap decomposed at time t, the energy of activation, the absolute temperature at which the rate of decomposition is maximum and the difference between the heating temperature and the temperature at which the rate of decomposition is maximum, respectivelv.

The energy of activation calculated from the slope of the plot of  $\ln \left[ \ln (1 - \alpha)^{-1} \right]$  vs.  $\theta$ , for the thermal decomposition of calcium palmitate, is 3.3 KJ/mole, which is in agreement with the value obtained from *Freeman-Carroll's* equation.

## Summary

The IR results confirm that palmitic acid exists in a dimeric structure as a result of hydrogen bonding between the carboxyl groups of two acid molecules, whereas calcium palmitate has an ionic character. The X-ray analysis revealed that the molecular axes of calcium soaps are slightly inclined to the basal plane. The thermal decomposition of calcium palmitate was found to be kinetically of zero order and the energy of activation for the decomposition reaction is in the region of 3 KJ/mole.

# Acknowledgements

The authors wish to express their sincere thanks to Prof. S. K. Agarwal, Vice-Chancellor, Agra University, Agra, for providing facilities. Thanks are also due to RSIC (IIT Kanpur) and the National Physical Laboratory for recording X-ray spectra and for TGA analysis, respectively.

### References

- <sup>1</sup> Y. Koga and R. Matuura, Mem. Fac. Sci. Kyushu Univ. Series C Chemistry 4, 1 (1961).
- B. Seymour, J. Am. Chem. Soc. 62, 374 (1940).
- <sup>3</sup> C. L. Andrew, Rev. Sci. Instruments 11, 111 (1940).
- <sup>4</sup> M. J. Vold and R. D. Vold, J. Am. Oil Chemist's Soc. 26, 520 (1949).
- <sup>5</sup> D. C. Bisset and J. Iball, Trans. Faraday Soc. 50, 421 (1954).
- <sup>6</sup> P. Spegt and A. Skolios, J. Chem. Phys. 62, 418 (1965).
- <sup>7</sup> P. Spegt and A. Skolios, Acta Crystallogr. 17, 198 (1965).
- <sup>8</sup> K. N. Mehrotra and R. P. Varma, Indian J. Chem. 9, 703 (1971).
- <sup>9</sup> K. N. Mehrotra, R. P. Varma and H. K. Bhargava, Cellulose Chem. Technol. 9, 657 (1975).
- <sup>10</sup> K. N. Mehrotra and S. K. Upadhyaya, Tenside Detergents 24, 90 (1987).
- <sup>11</sup> C. Duval, J. Leocomte and F. Douville, Ann. Phys. 17, 5 (1942).
- <sup>12</sup> R. K. Kagarise, J. Phys. Chem. 59, 271 (1955).
- <sup>13</sup> S. K. Upadhyaya, Ph.D. Thesis, Agra University, Agra, 1987.
  <sup>14</sup> K. N. Mehrotra and S. K. Upadhyaya, (Communicated).
- <sup>15</sup> E. S. Freeman and B. Carroll, J. Phys. Chem. 62, 394 (1958).
- <sup>16</sup> H. H. Horowitz and G. Metzger, Anal. Chem. 35, 1464 (1963).