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# Spectroscopic Analysis of Chromium Soaps

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*Abstract-* The spectroscopic characteristics of chromium soaps (butyrate and caprylate) in solid state were investigated by IR, X-ray diffraction and thermal measurements. The IR results reveal that the fatty acids exist in dimeric state through hydrogen bonding and soaps possess partial ionic character. The X-ray diffraction measurements were used to calculate the long spacings and the results confirm the double layer structure of chromium soaps. The decomposition reaction was found kinetically of zero order with energy of activation .275 and .180 kcal mol-1 for butyrate and caprylate, respectively.

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## I. Introduction

The survey of literature reveals that the physico-chemical characteristics of transition soaps have not yet been studied thoroughly in spite of the wide range of applications of these soaps in various industries and academic field [1-18]. The applications of the soaps depend largely on their physical state, stability and chemical reactivity together with their volalitity and solubility in common solvents. The present work deals with infrared, x-ray and thermal studies of chromium Soaps and have been used to determine structural information in solid state.

## II. Experimental

All the chemicals used were of BDH /AR grade. Chromium soaps (butyrate and caprylate) were prepared by direct metathesis of corresponding potassium soap with slight excess of the solution of chromium nitrate at 50-55oC under vigorous stirring. The precipitated soap was filtered and washed with distilled water and acetone and recrystallized with a mixture of benzene and methanol and dried under reduced pressure.

The infrared absorption spectra of fatty acids and their corresponding chromium soaps were recorded with a Perkin-Elmer "577 model" grating spectrophotometer in the region of 4000-200 cm-1 using potassium bromide disc method.

The X-ray diffraction patterns were obtained with a Richseifert "2002 D" Isodebyeflex Diffractormeter using Cu-Kα radiations filtered by a nickel foil over the range of diffraction angle, $2\theta = 30$ to 650 where $\theta$ is Bragg's angle. The readings of the diffraction angle were made up to 0.001° and the wavelength of the radiation was taken as 1.542Å. The thermogravimetric Analyses of chromium soaps were carried out by Perkin-Elmer thermogravimetric analyzer TG-S-2 at a constant heating rate of 10o/min in nitrogen atmosphere and maintaining similar conditions throughout the investigations.

## III. Results and Discussion

### a) *Infrared Spectra*

The wave numbers of some important absorption bands in infrared absorption spectra of chromium (butyrate and caprylate) were assigned and compared with those of corresponding fatty acids (Table-1). The absorption bands observed at 2660-2580, 1700, 1430-1390, 930-910, 690 and 550 cm-$^{1}$ in the spectra of fatty acids 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 acid. The evenly spaced progressive bands at 1330-1140 cm-$^{1}$ also observed which are characteristic of the hydrocarbon chain and remain unchanged during the preparation of the soap. The complete disappearance of, the carbonyl frequency at 1700 cm-$^{1}$ in the spectra of chromium soaps indicates that there is a complete resonance between the two C=O bonds of the carboxylic groups of the soap molecule and the two bonds become identical with their force constant assuming an intermediate value between the normal double and single bonds. The appearance of two absorption bands corresponding to symmetric and antisymmetric stretching vibrations of carboxylate ion at 1470-1436 cm-$^{1}$ and 1600-1550 cm-1 regions, respectively, in the spectra of chromium soaps place of one band of carbonyl frequency near 1700 cm-1 confirms the partial ionic nature of these soaps.

The results show that the fatty acids in the solid state exist with dimeric structure through hydrogen bonding between carboxyl group of the two acid molecules whereas metal-to-oxygen bonds in chromium soaps are not purely ionic, but somewhat covalent in character. The assigned frequencies are in agreement with the results of other workers [6-19].

### b) *X-ray Diffraction analysis*

Since the metal soaps do not give large crystals for a detailed single crystal examination, so the X-ray powder diffraction patterns of chromium soaps have been investigated to characterize the structure of these soaps.The intensities of the diffracted X-ray as a function of the diffraction angle, $2\theta$ for chromium soaps were observed and the interplanar spacings, d, have been calculated from the positions of the intense peaks

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using Bragg's relationship, $n\lambda = 2d \sin \theta$, where $\lambda$ is the wavelength of the radiation. The calculated spacings together with the relative intensities with respect to the most intense peaks are recorded (Tables 2 and 3). The appearance of the diffractions up to the 5th order in chromium butyrate and up to 12th order in chromium caprylate confirms good crystallinity for these soaps. The average planar distance, i.e., long spacing of chromium caprylate and butyrate are 24.12 and 14.893 A respectively. The difference in the observed values of long spacings for chromium caprylate is 9.227 Å which corresponds to twice the length of the additional methylene (-$CH_2$-) groups in the fatty acid radical constituent of the soap molecules. The values of the long spacings for these soaps are approximately equal to double the length of the fatty acid radical of the soap molecules. It is therefore, suggested that the zig-zag chains of fatty acid radicals extended straightforward in these soap molecules.

*Table 1 :* Iinfrared Absorption Spectral Frequencies (Cm-1) of Acids and Their Soaps

| S. | Assignments | Butyric Acid | Chromium Butyrate | Caprylic Acid | Chromium Caprylate |
|---|---|---|---|---|---|
| 1 | $CH_3$, C—H asymmetrical stretching | 2960 W | 2960 W | 2950 W | 2950 VS |
| 2 | $CH_2$, C—H asymmetrical stretching | 2910 M | 2930 S | 2920 S | 2920 S |
| 3 | $CH_2$, C—H symmetrical stretching | 2855 S | 2860 M | 2850 S | 2840 VS |
| 4 | OH, stretching | 2660 S | — | 2580 W | — |
| 5 | C = O, stretching | 1700 S | — | 1700 VS | — |
| 6 | COO–, C—O asymmetrical stretching | — | 1550 S | — | 1560 MS |
| 7 | $CH_2$, deformation | — | — | 1470 M | 1440 M |
| 8 | C—O Stretching + O—H inplane deformation | 1390 M | — | 1430 M | — |
| 9 | COO, C-O symmetrical stretching | — | 1460 W | — | 1400 S |
| 10 | $CH_2$ (adjacent to COOH group) deformation | 1410 S | 1440 S | 1370 S | 1400 S |
| 11 | $CH_3$, symmetrical deformation | 1350 W | 1340 W | 1340 S | — |
| 12 | Progressive bands ($CH_2$ twisting and wagging) | 1270-1220M | 1330-1180W | 1320-1140M | 1180W |
| 13 | $CH_3$ rocking | 1100 VS | 1120 W | 1110 VS | 1100 S |
| 14 | OH, out-of-plane deformation | 930 S | — | 910 S | — |
| 15 | $CH_2$ rocking | 720 S | 722 M | 720 M | 720 VS |
| 16 | COOH bending mode | 690 M | — | 690 M | — |
| 17 | COOH wagging mode | 550 M | — | 550 M | — |
| 18 | Cr — O bond | — | 425 M | — | 420 M |

*Key to abbreviation: VW = Very weak*
*VS = Very sharpS = Sharp*
*M = Medium W = Weak*

The observed values of the long spacing for caprylate (24.12 Å) and butyrate (4.893 Å) of chromium are smaller than the calculated dimension of caprylate (27.0 Å) and butyrate (17.0 Å) ions from Pauling's values of atomic radii and bond angles and this suggests that the molecular axes of these soaps are somewhat inclined to the basal planes. The metal ions fit into spaces between oxygen atoms of the ionized carboxyl group without a large strain of the bonds. A number of diffraction peaks in the intermediate range of the diffraction angles are also observed in the diffraction patterns of chromium soaps and these are attributed to the diffraction of X-ray by planes of atoms of much smaller separation than the basal planes. The calculated spacings from these peaks correspond to the shorter side spacings, i.e., the lateral distances between one soap molecule and the next in a layer. It is observed that the long spacing peaks are fairly intense while the short spacing peaks are relatively weak. On the basis of long and short spacings, it is proposed that the metal ions in chromium soaps are arranged in a parallel plane, i.e., a basal plane is equally spaced in the soap crystal with fully extended zig-zag chains of fatty acid radicals on both side of each basal plane and chromium soaps have double layer structure as proposed by Vold and Hattiangdi [20].

*Table 2 :* X-Ray Diffraction Analysis of Chromium Butyrate

| S.No. | 2θ | θ | Sin θ | $\frac{\lambda}{2\sin\theta}$ | d | n | $I/I_{max}$ |
|---|---|---|---|---|---|---|---|
| 1. | 5.94 | 2.97 | 0.0518 | 14.8649 | 14.865 | 1 | 1.00 |
| 2. | 11.89 | 5.95 | 0.1037 | 7.4253 | 14.851 | 2 | 0.16 |
| 3. | 17.89 | 8.95 | 0.1556 | 4.9486 | 14.846 | 3 | 0.06 |
| 4. | 23.72 | 11.86 | 0.2055 | 3.7469 | 14.988 | 4 | 0.03 |
| 5. | 29.79 | 14.90 | 0.2571 | 2.9949 | 14.975 | 5 | 0.05 |
| 6. | 42.61 | 21.31 | 0.3634 | 2.1189 | 14.832 | 7 | 0.01 |

*Average value of d = 14.893Å*

*Table 3 :* X-Ray Diffraction Analysis of Chromium Caprylate

| S.No. | 2θ | θ | Sin θ | $\frac{\lambda}{2\sin\theta}$ | d | n | $I/I_{max}$ |
|---|---|---|---|---|---|---|---|
| 1. | 7.31 | 3.66 | 0.0638 | 12.069 | 24.138 | 2 | 0.59 |
| 2. | 11.03 | 5.51 | 0.0960 | 8.007 | 24.021 | 3 | 1.00 |
| 3. | 14.69 | 7.35 | 0.1279 | 6.027 | 24.108 | 4 | 0.17 |
| 4. | 18.34 | 9.17 | 0.1594 | 4.832 | 24.160 | 5 | 0.18 |
| 5. | 22.23 | 11.12 | 0.1929 | 3.995 | 23.970 | 6 | 0.02 |
| 6. | 25.61 | 12.80 | 0.2215 | 3.476 | 24.332 | 7 | 0.11 |
| 7. | 29.90 | 14.95 | 0.2580 | 2.985 | 23.880 | 8 | 0.16 |
| 8. | 33.36 | 16.68 | 0.2870 | 2.684 | 24.156 | 9 | 0.09 |
| 9. | 41.69 | 20.85 | 0.3559 | 2.164 | 23.804 | 11 | 0.10 |
| 10. | 44.56 | 22.28 | 0.3791 | 2.031 | 24.372 | 12 | 0.13 |
| 11. | 64.99 | 32.50 | 0.5373 | 1.433 | 24.361 | 17 | 0.03 |

*Average value of d = 24.12Å*

### *c) Thermogravimetric Analysis*

The results of thermogravimetric analysis of chromium soaps (caprylate and butyrate) show that the final residue is metal oxide and the weights of the residues are in agreement with the theoretically calculated weight of chromium oxide from the molecular formulae of the soaps. A white substance is found deposited at the cold part of the sample tube surrounding the sample and it is identified as caprylone (m.p. 39oC) and butanone (b.p. 79.6oC) in case of caprylate and butyrate, respectively.

The thermal decomposition of chromium soaps can be expressed as:

$2(RCOO)_3Cr \rightarrow 3RCOR + 3CO_2 + Cr_2O_3$
chromium Ketone
Soap

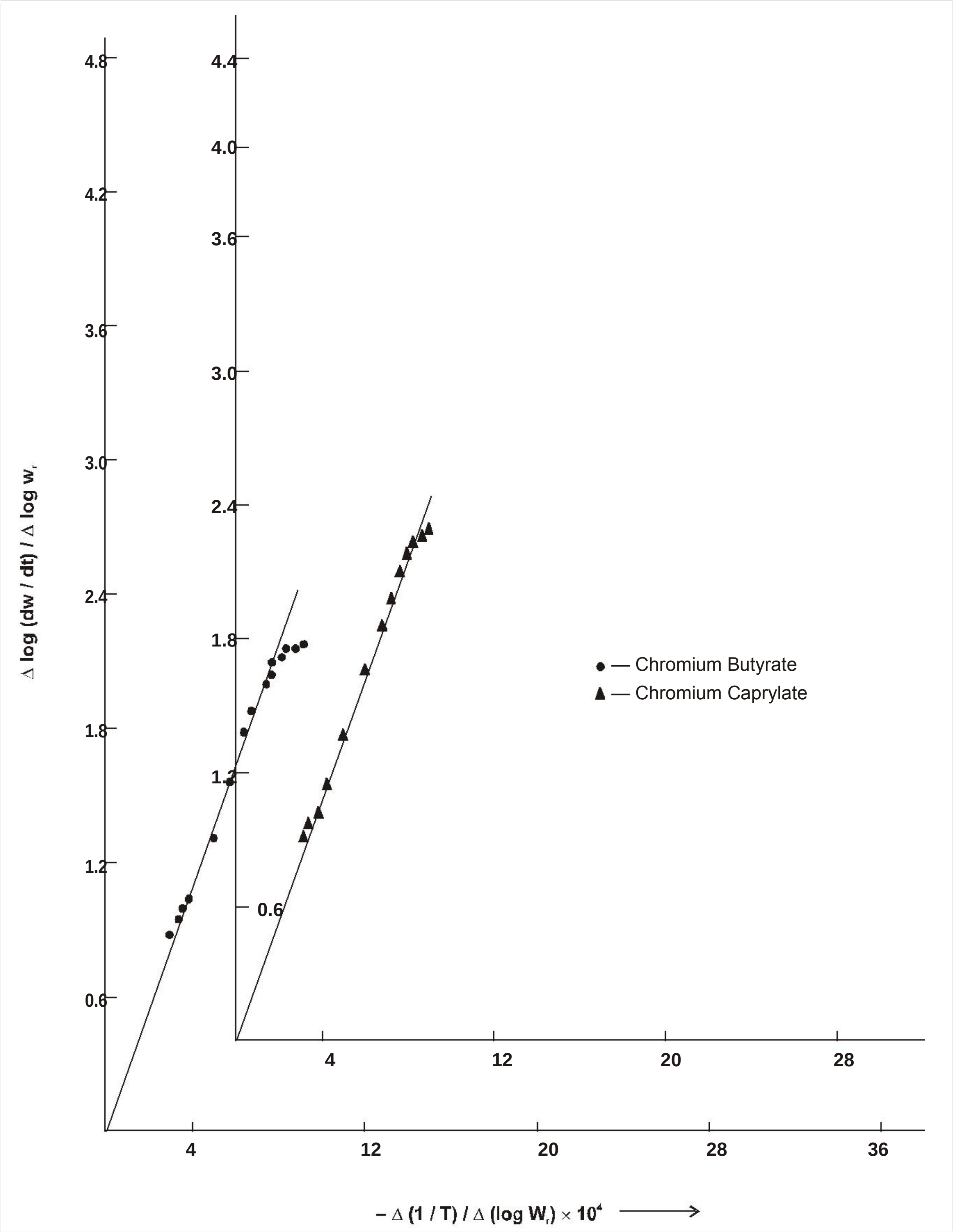
The thermogravimetric data have been used to calculate the energy of activation and to find the order of reaction for decomposition of chromium soaps using the equation of Freeman-Carroll [19] which may be written as:

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

Where E = energy of activation, R = gas constant, n = order of decomposition reaction, T = temperature on absolute scale, $W_r$ = difference between the total loss in weight and loss in weight at time, t, i.e., W0 – Wt, and dw/dt = value of rate of weight loss obtained from the loss of weight Vs time curves at appropriate times.

The plots of [log dw/dt)/log $W_r$] vs. [(1/T)/log $W_r$] have been found to be linear with the intercept equal to zero (Fig.1). It is, therefore, concluded that the order of reaction for the decomposition of chromium soaps is zero and the value of energy of activation from the slope (-E/2.303R) of the plots (Fig. 1) are .275 and .180 kcal.mol-1 for chromium (butyrate and caprylate) respectively.

*Fig. 1 :* Freeman – Carroll's Type Plots



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