

Spectroscopic and Thermal Behavior of Chromium Soaps

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Received June 15, 1995; in revised form October 6, 1995; accepted October 11, 1995

The physicochemical characteristics of chromium soaps (myristate and stearate) were investigated in the solid state (thermal, X-ray, and IR measurements) and in solutions (spectrophotometric measurements). The thermal measurements showed that the decomposition of chromium soaps is a two-step process. The soap decomposed into chromium oxycarboxylate, ketone, and carbon dioxide in the first step and the intermediate oxycarboxylate underwent further decomposition to chromium trioxide in the second step. The results showed that the second step is kinetically of zero order and the values of energy of activation for the first and second steps lie in the ranges 6–7 and 17–18 kcal mol⁻¹, respectively. The X-ray diffraction results showed that these soaps possess double-layer structure with molecular axes slightly inclined to the basal plane. The infrared results revealed that the fatty acids exist with dimeric structure through hydrogen bonding between two molecules of fatty acids whereas the metal-to-oxygen bonds in chromium soaps are not purely ionic but possess considerable covalent character. The results of spectrophotometric measurements also confirmed the somewhat covalent nature of chromium soaps in solutions in dichloromethane. © 1996 Academic Press, Inc.

INTRODUCTION

The transition metal soaps are used in various industries as catalysts, activators, stabilizers, plasticizers, detergents, hardeners, lubricants, driers, preservatives, adhesives, water repellents, water-proofing, oxidizing, and reducing agents, fungicides, bactericides, insecticides, herbicides, and medicines. However, the physicochemical characteristics and structures of soaps depend to an extent on the method and conditions of their preparation and so studies on the nature and structure of these soaps are of great importance for their uses in industries and for explaining their characteristics under different conditions. The infrared spectra of soaps of metals of the first transition series (V (1), Cr (2–5), Mn (6), Fe (7–10), Co (11–13), Ni (14–16), Cu (17–22), and Zn (23–27)) were investigated by several workers. The absorption spectra of transition metal (Cr, Mn, Co, Ni, and Cu) soaps in various solvents were investigated by Mehrotra *et al.* (16, 28–30), Malik and Ahmad (31), Zhumadylov *et al.* (32), and Jain *et al.* (33). The

crystal structures of transition metal soaps were studied by X-ray diffraction by Vold and Hattiangdi (34), Koga and Matsuura (35), and Mehrotra *et al.* (6, 16, 27). The thermal decomposition of transition metal (Cr (36), Mn (6, 37–41), Fe (41–44), Co (39, 45–51), Ni (15, 16, 39, 45–47, 52–57), Cu (18, 39, 53–59), and Zn (27, 38, 39, 60, 61)) soaps were investigated thoroughly.

The present work has been initiated with a view to investigate the physicochemical characteristics and structures of chromium soaps (myristate and stearate) in the solid state as well as in solutions using infrared, X-ray, spectrophotometric, and thermal measurements.

EXPERIMENTAL

Chromium soaps (myristate and stearate) were prepared by direct metathesis of the corresponding potassium soap with the required amount of chrome alum solution under vigorous stirring. The soaps were purified by recrystallization with a benzene–methanol mixture. The purity of the soaps was checked by elemental analysis (myristate: found C = 68.2, H = 10.9; calcd. C = 68.8, H = 11.0; stearate: found C = 71.8, H = 11.4; calcd. C = 71.9, H = 11.6) and determination of melting points (myristate: 61°C, and stearate: 69°C).

The thermal analysis was carried out with an STA-780 simultaneous thermal analyzer, Stanton, U.K., at a constant heating rate (10°C/min) in a nitrogen atmosphere and maintaining similar conditions throughout the investigations. The X-ray diffraction patterns were recorded with a Rigaku Geigerflex RBRU 200. The CuK α radiations were used over the diffraction angle range $2\theta = 3^\circ$ – 65° . The infrared absorption spectra of fatty acids and chromium soaps were obtained with a Nicolet 50XFT Instrument, USA, grating spectrophotometer in the region 4000–400 cm⁻¹ using the potassium bromide disk method. The spectrophotometric measurements were carried out in the region 350–940 nm with a digital Toshniwal visible spectrophotometer (Model CL.10A3).

RESULTS AND DISCUSSION

Thermal Analysis

The results of thermogravimetric analysis (TGA) of chromium soaps (myristate and stearate) show that the

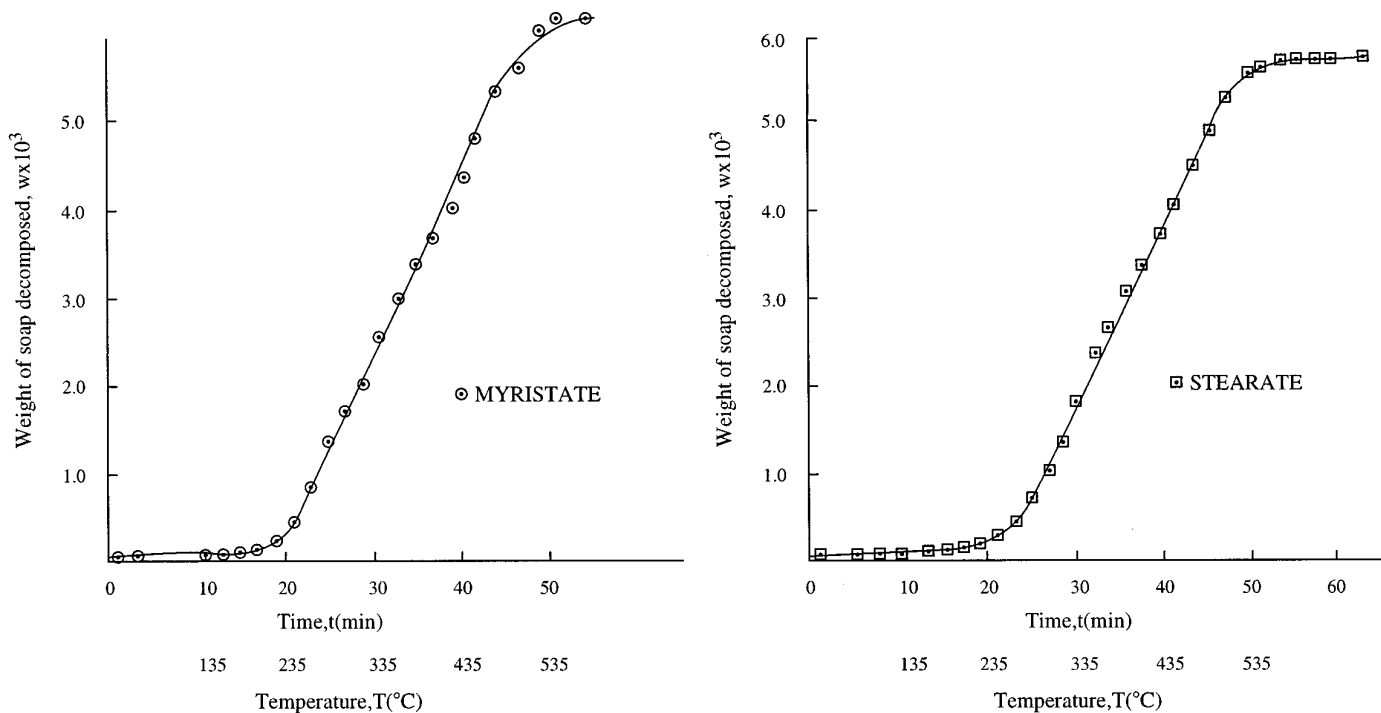


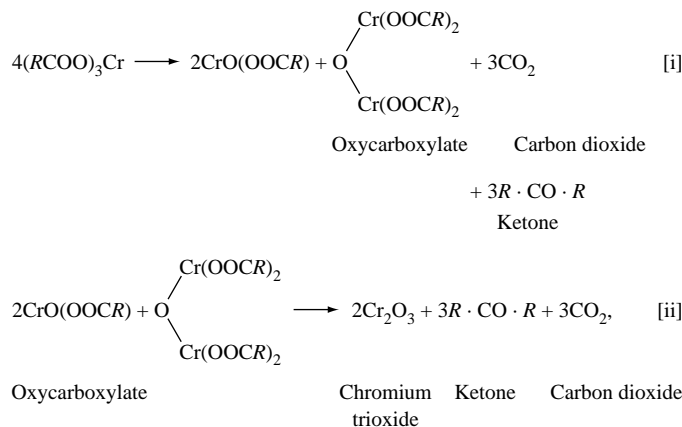
FIG. 1. Weight of soap decomposed vs time.

soaps are stable up to 200°C, at which the decomposition of soaps starts (Fig. 1). The weights of the final residue are in agreement with the theoretically calculated weights of chromium trioxide from the molecular formulas of the soaps. The results of thermogravimetric analysis were explained in terms of Freeman–Carroll’s equation (62),

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

where dw/dt , W_r , E , T , R , and n are the rate of weight loss, the difference between the total loss in weight and the loss in weight at time (t), the energy of activation, the absolute temperature, the gas constant, and the order of the decomposition reaction, respectively.

The plots of $[\Delta \log (dw/dt)/\Delta (\log W_r)]$ vs $[\Delta(1/T)/\Delta (\log W_r)]$ (Fig. 2) show a break at a temperature of about 255 and 265°C for myristate and stearate, respectively, indicating that the decomposition of soaps takes place in two steps. In the first step, the soaps decomposed into oxycarboxylate, ketone, and carbon dioxide and in the second step, the intermediate oxycarboxylates underwent further decomposition into chromium trioxide and corresponding ketone. The ketones undergo further decomposition at higher temperatures,



where R is $C_{13}H_{27}$ for myristate and $C_{17}H_{35}$ for stearate. The results show that the order of reaction for the thermal decomposition of chromium oxycarboxylates is zero. The calculated values of energy of activation from the slope ($-E/2.303R$) of the plots (Fig. 2) are 6.7 and 7.1 kcal mol⁻¹ for the first step and 17.1 and 18.3 kcal mol⁻¹ for the second step for myristate and stearate, respectively.

Rai and Parashar (36) also reported two equal depressions in DTG curves of chromium soaps and suggested two-step decomposition for these soaps.

The DTA curves (Fig. 3) for chromium myristate and stearate also show broad exothermic peaks at about 265

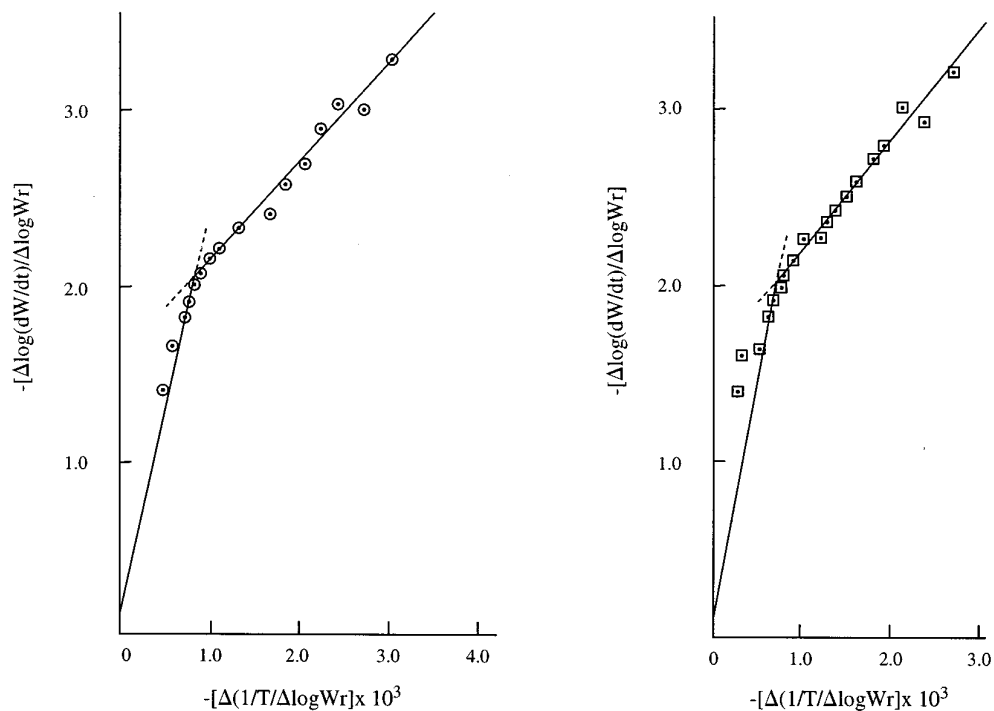


FIG. 2. Freeman-Carroll type plot.

and 300°C and endothermic peaks at 600 and 645°C, respectively.

The results of thermal analysis (TGA, DTG, and DTA) of chromium soaps confirm that the soaps are stable up to 200°C, at which the decomposition of soaps starts with the formation of oxycarboxylate, ketone, and carbon dioxide. The intermediate oxycarboxylates undergo further decomposition into chromium trioxide and corresponding ketones at higher temperatures. It is concluded that thermal decomposition of chromium soaps occurs in two steps.

X-Ray Diffraction Analysis

Since the metal soaps do not give large crystals for a detailed single-crystal examination, the X-ray diffraction patterns of chromium soaps (myristate and stearate) have been investigated to characterize the structure of these soaps. The intensities of the diffracted X-rays as a function of diffraction angle, 2θ , for chromium soaps were measured and the interplanar spacings, d , have been calculated from the positions of intense peaks using Bragg's relationship, $n\lambda = 2d \sin \theta$, where λ is the wavelength of radiation. The calculated spacings together with the relative intensities with respect to the most intense peak are recorded in Table 1. The X-ray diffraction patterns of chromium soaps show few peaks over the diffraction angles range 3°–65°, which suggests poor crystallinity of chromium soaps (Fig. 4). The

noncrystalline nature of chromium soaps has also been reported by Koga and Matsuura (35). The average planar distances, i.e., long spacing, for chromium myristate and stearate were found to be 41.58 and 50.10 Å, respectively. The difference in the observed values of long spacings for chromium myristate and stearate is 8.52, which corresponds approximately to double the length of methylene groups ($-\text{CH}_2$) in the fatty acid radical constituent of soap molecules. It is therefore suggested that the zig-zag chains of the fatty acid radical constituent of the soap molecule extend straight forward on both sides of each basal plane. The values of long spacings for chromium soaps (myristate, 41.58 Å, stearate, 50.10 Å) are smaller than the calculated dimensions of anions (myristate, 42 Å, stearate, 52 Å) from Pauling's values of atomic radii and bond angle, which suggests that the molecular axes of soap molecules are somewhat inclined to the basal plane. The metal ions, Cr^{3+} , fit into spaces between oxygen atoms of the ionized carboxyl group without large strain of the bond.

Some diffraction peaks in the intermediate range of diffraction angles, 6°–40°, are also observed in diffraction patterns of chromium soaps and these are attributed to the diffraction of X-rays 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 distance between one soap molecule and the next in a layer. On the basis of short and long spacings,

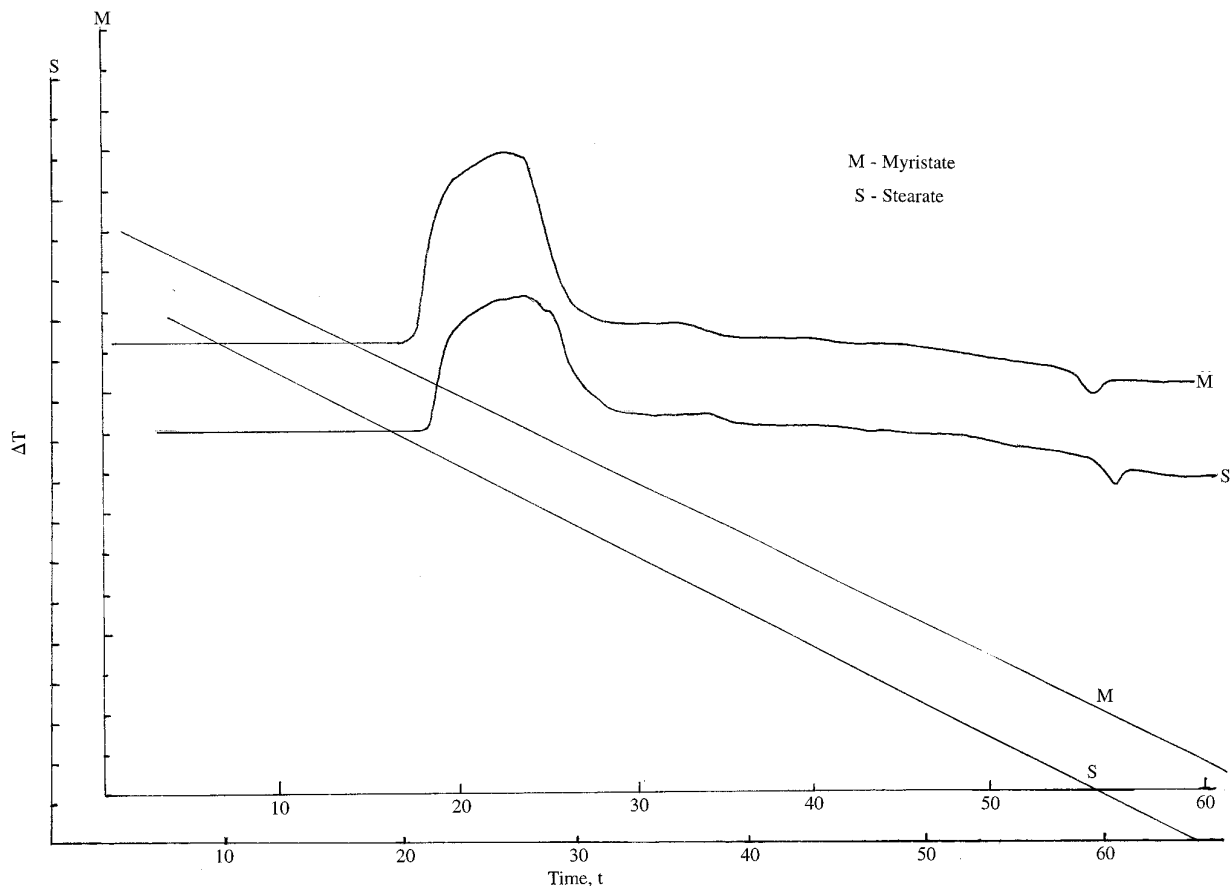


FIG. 3. DTA curves for chromium myristate and stearate.

TABLE 1
X-Ray Diffraction Analysis of Chromium Soaps

No.	2θ	D (Å)	d/n (Å)	n	(I/I_0) (%)
Myristate					
1	6.6	13.380	40.140	3	19
2	8.3	10.643	42.572	4	9
3	10.3	8.580	42.900	5	5
4	12.9	6.856	41.136	6	6
5	14.8	5.980	41.860	7	5
6	17.2	5.150	41.200	8	5
7	19.4	4.571	41.139	9	28
8	21.5	4.129	41.290	10	100
9	23.3	3.814	41.954	11	4
Stearate					
1	20.30	4.370	48.070	11	34
2	21.05	4.216	50.592	12	100
3	21.75	4.082	53.066	13	18
4	29.30	3.045	48.720	16	23
5	30.35	2.942	50.014	17	27

it is proposed that the metal ions in chromium soaps are arranged in a parallel plane and the soaps have double-layer structure as proposed by Vold and Hattiangdi (34).

Infrared Absorption Spectra

The wavenumbers of important absorption in the IR spectra of chromium soaps (myristate and stearate) are compared with those of corresponding fatty acids (myristic/stearic) (Table 2). The absorption maxima near 2650–2640, 1700, 940, 690, and 550 cm^{-1} in the spectra of fatty acids indicate the presence of a localized carboxyl group in the form of dimeric structure and the existence of intermolecular hydrogen bonding between two molecules of acids.

The absorption bands observed near 2650–2640 and 940 cm^{-1} corresponding to the $-\text{OH}$ group in the spectra of fatty acids have completely disappeared in the spectra of chromium soaps. The absorption band observed at 1700 cm^{-1} corresponding to the carbonyl group of the fatty acid is also observed in the spectra of chromium soaps with weak intensity, which may be due to the incomplete resonance of the carbonyl group in chromium soaps. The singlet

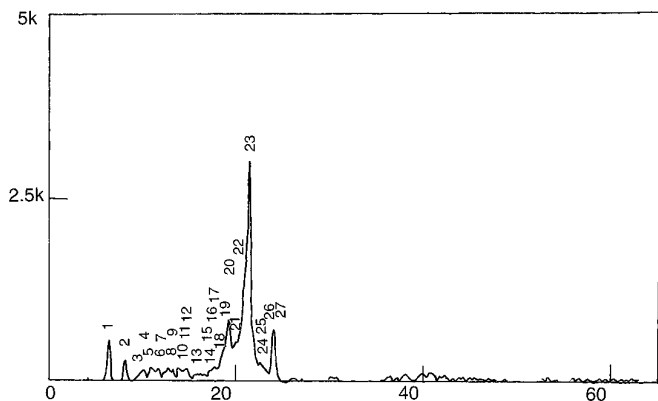


FIG. 4. X-ray diffraction analysis of chromium myristate.

band observed near $715\text{--}710\text{ cm}^{-1}$ is the characteristic of trivalent metal soaps.

The two absorption bands observed near 1450 and $1560\text{--}1530\text{ cm}^{-1}$ in the spectra of chromium soaps correspond to symmetric and asymmetric vibrations of carboxylate ion.

The band observed near $417\text{--}415\text{ cm}^{-1}$ in the spectra of chromium soaps correspond to Cr–O bonds. The chromium soaps do not exhibit any absorption band near $3500\text{--}3000\text{ cm}^{-1}$, which suggests the absence of any coordinated water molecules in these soap molecules.

Spectrophotometry

The solutions of chromium soaps (myristate and stearate) in dichloromethane exhibit well-defined maxima at

575 nm ($17,391\text{ cm}^{-1}$) and 420 nm ($23,809\text{ cm}^{-1}$). The absorption studies have also been carried out for aqueous solutions of chrome alum, and maxima were observed at 590 nm ($16,949\text{ cm}^{-1}$) and 420 nm ($23,809\text{ cm}^{-1}$). The results show that the behavior of chromium soaps in dichloromethane is quite similar to that of aqueous solutions of chrome alum.

Chromium(III) possesses the d^3 electronic configuration and permits three electronic transitions (63). The electronic band observed at $17,391\text{ cm}^{-1}$ is assigned to the first transition, ν_1 , $\{^4A_{2g}(F) \rightarrow ^4T_{2g}(F)\}$, and the second transition, ν_2 , lies at $23,809\text{ cm}^{-1}$, $\{^4A_{2g}(F) \rightarrow ^4T_{1g}(F)\}$. The third transition, ν_3 , $\{^4A_{2g}(F) \rightarrow ^4T_{1g}(P)\}$, which usually occurs at about $37,000\text{ cm}^{-1}$ is beyond the range of our instrument.

The crystal field splitting energy parameter (Dq) (63), Racah (64) interelectronic repulsion parameter (B), nephelauxetic ratio (65) (β), percentage covalency (δ), and bonding parameter (66) ($b^{1/2}$) have been evaluated using the relationships

$$\nu_1 = 10Dq \quad [1]$$

$$(Dq/B) = 2.45 \quad [2]$$

$$\beta = (B/B_0) \quad [3]$$

$$\delta = \{(1 - \beta)/\beta\} \times 100 \quad [4]$$

$$b^{1/2} = \{(1 - \beta)/2\}^{1/2}, \quad [5]$$

where ν_1 is the wavenumber of the electronic band due to

TABLE 2
Infrared Absorption Spectral Frequencies (cm^{-1}) with Their Assignment

No.	Assignment	Myristic acid	Chromium myristate	Stearic acid	Chromium stearate
1	CH ₃ , C–H asym stretch	2960 VW	2980 M	2960 S	2970 W
2	CH ₂ , C–H asym stretch	2920 VS	2920 S	2910 VS	2920 S
3	CH ₂ , C–H sym stretch	2855 S	2850 S	2850 S	2850 S
4	OH stretch	2640 W	—	2650 W	—
5	C=O, stretch	1700 VS	1700 W	1700 VS	1700 W
6	COO [−] , C–O asym stretch	—	1540 S	—	1560–1530 M
7	COO [−] , C–O sym stretch	—	1450 S	—	1450 M
8	C–O, stretch, OH-in-plane deformation	1410 W	—	1432 VS	—
9	CH ₂ , (adjacent to COOH group) deformation	1375 VW	1400 S	1412 M	1400 M
10	CH ₃ , sym deformation	1340 W	1380 S	1350 W	1380 M
11	Progressive bands (CH ₂ twisting and wagging)	1350–1190 WB	1315–1200 M	1350–1100 M	1315–1170 M
12	OH, out-of-plane deformation	940 M	—	940 W	—
13	CH ₃ , rocking	1120 W	1100 W	1110 W	1120 SB
14	CH ₂ , rocking	725 MS	710 W	730 S	715 S
15	COOH, rocking	690 M	—	689 W	—
16	COOH, wagging mode	550 M	—	550 W	—
17	Cr–O, bond	—	415 S	—	417 S

Note. VW, very weak; VS, very strong; S, strong; W, weak; WB, weak broad; M, medium; SB, strong broad.

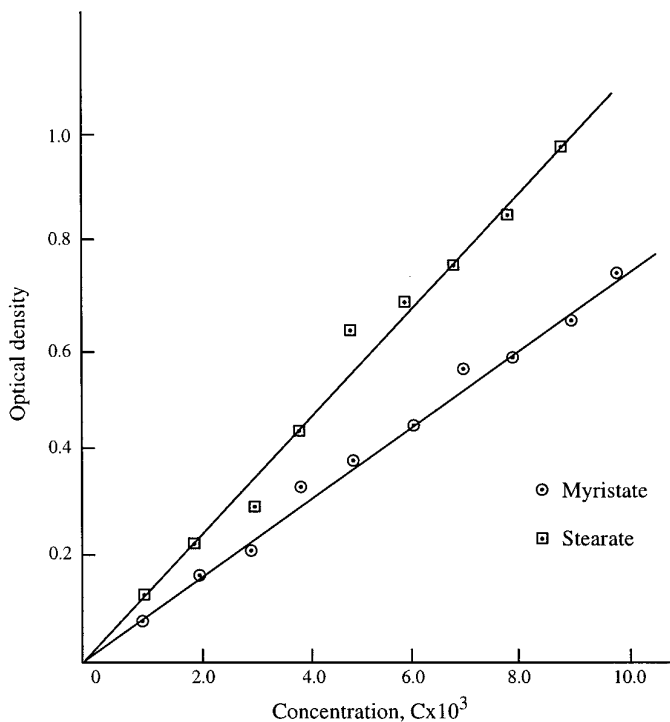


FIG. 5. Optical density vs concentration.

$\{^4A_{2g}(F) \rightarrow ^4T_{2g}(F)\}$ and B_0 is the value of the interelectronic repulsion parameter for Cr(III) ion and is equal to 1030 cm^{-1} .

The values of β (0.69) for chromium soaps are less than unity, which suggests that the metal-to-oxygen bond in soaps are not purely ionic but have considerable covalent character. The values of percentage covalency ($\delta = 45\%$) and the bonding parameter ($b^{1/2} = 0.39$) also indicate that these soaps are partly covalent in character.

The plots of optical density vs soap concentration (Fig. 5) are linear with intercept equal to zero, which proves the validity of Beer-Lambert's law for solutions of chromium soaps in dichloromethane. It is evident that the spectroscopic method can be used to estimate chromium content at λ_{max} in dilute solutions of these soaps.

ACKNOWLEDGMENTS

The authors are thankful to the CSIR, New Delhi, for financial support and for awarding SRF to one of them (M.J.).

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