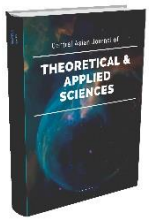

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X-Ray Diffraction Studies on Carboxylates of Zirconium in Solid State

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Abstract: *The x-rays diffraction studies were used to determine the structure of Zirconium carboxylates (myristate, palmitate and stearate) in solid state. The x-ray diffraction measurements confirm that Zirconium carboxylates possess double layer structure with long spacings.*

Keywords: *Metal Carboxylates, X-Ray Diffraction.*

Introduction

Metal carboxylates are chemical compounds consisting of metal and the long-chain fatty acid. The non alkali metal salts of higher fatty acids containing at least six or seven carbon atoms are called Metal carboxylates or Metal soaps. The transition metal carboxylates are being widely used in industry, technology and allied sciences. The uses of metal soaps largely depend on their physical state, stability, chemical reactivity and solubility in polar and non polar solvents. These metal carboxylates has been a subject intense investigation in the recent past on account of its role in such diversified field as medicine, cosmetic emulsifier, lubricant, germicides and anti-oxidant. The transition and inner transition metal carboxylates were prepared by **several workers**(1-6)by double decomposition and metatheses. Mohd. Aftab Khan *et al.*(7) worked on computation of elastic, ultrasonic and thermal properties of B2 structured AuRE (RE= Sm, Tb, Ho, Tm) intermetallics in temperature rang 300K-900K. The infrared absorption spectra, x-ray diffraction studies and thermal behaviour of cerium and thorium laurate were studied by Gupta et al.(8). Corbeil(9) reported the comparative crystal structure study of zinc, copper and lead soaps with saturated and unsaturated fatty acids. Galli *et al.*(10)studied the structural and magnetic behaviour of molecular soap by using X-ray powder diffraction method. Robinet *et al.*(11) Characterized the metal soaps found in paint films or on metal surfaces, many metal soaps were synthesized and their X-ray diffraction pattern, Fourier transform infrared and raman spectra was measured. Wanjun *et al.*(12)characterised the stearates of metal soaps. The studies on micellar properties of scandium and yttrium metal soaps was studied by Khirwar (13). The studies of ultrasonic velocity and allied properties of manganese, cobalt and copper soaps in non-aqueous medium Rawat (14). Surface tension of titanium soaps solutions in mixed organic solvents has been measured at 313 K and the data have been discussed on the basis of Langmuir's approximate equation was studied by H.S.Verma et al.(15).In the present work attempts have been made to determine the structure of Zirconium carboxylates (myristate, palmitate and stearate) in solid state through X-Rays diffraction analysis.

Aim of the Study

The results of the survey of literature reveals that the physico-chemical properties of Zirconium carboxylates have not been systematically investigated while they have many uses in industrial areas and academics. The aim of this research work is to study the structure of Zirconium carboxylates in solid state through x-rays diffraction analysis.

Experimental

The Zirconium carboxylates (myristate, palmitate and stearate) were synthesized by direct metathesis of corresponding potassium carboxylates with the required amount of aqueous solution of Zirconium (III) chloride at 50-55°C under vigorous stirring. The precipitated soaps were washed several times with distilled water and then acetone to remove the fatty acid and metal nitrate. The soaps were purified by recrystallization with the benzene and cyclohexane mixture, dried in an air oven at 50-60°C and the finally drying of the carboxylates were carried out under reduced pressure.

The X-ray diffraction patterns of Zirconium carboxylates (myristate, palmitate and stearate) were obtained with a Rich-Seifert 2002D isodebyeflex diffractometer using cu-k_0, radiations filtered by a nickel foil over the range of diffraction angle, $2\theta = 3^0$ to 65° (where θ is Bragg's angle). The XRD curves were recorded under the applied voltage of 35KV using scanning speed of 1^0 per minute and chart speed of 1 cm per minute. The wave length of radiations was taken as 1.543Å.

Review of Literature

Present research work reviews the literature relevant with the aim of study. The spectroscopic studies of metallic carboxylates have been studied by several workers. Some of them are listed below.

Kamal Kishore (2017) was studied the spectroscopic and Thermogravimetric analysis of Terbium Myristate.

Khirwar (2016) was studied the Infrared absorption spectra and X-Ray Differaction on yttrium soaps in solid state.

Anushri Gupta (2012) was studied the infrared absorption spectra, x-ray diffraction studies and thermal behaviour of cerium, and thorium laurate.

Result and Discussion

The x-ray diffraction patterns of Zirconium carboxylates (myristate, palmitate and stearate) have been investigated with a view to characterize in solid state. The intensities of diffracted x-ray as a function of diffraction angle, 2θ for scandium soaps are recorded over the range of 4-75°. The inter planer spacings, d, have been calculated from the position of the intense peaks using Braggs relation-ship.

$n\lambda = 2d \sin\theta$

where λ is the wave length of radiation.

The calculated spacings and relative intensities with respect to the most intense peaks are recorded (Table:1-3). A large number of peaks arising from the diffraction of x-ray by planes of metal ion (known as basal planes) are observed in the diffraction patterns of Zirconium carboxylates. The appearance of diffraction for Zirconium myristate up to the 15th order, Zirconium Palmitate up to the 12th and Zirconium stearate up to the 9th order confirms good crystallinity for scandium soaps.

The long spacings average planer distance for Zirconium myristate, Zirconium palmitate and Zirconium stearate are 38.04, 35.74, 33.21 A^0, respectively. The difference in long spacings of Zirconium carboxylates (myristate and palmitate 2.35A^0; palmitate and stearate is 0.51A^0) correspond almost to the

length of methylene Zig-Zag chains of the fatty acid radical constituent of the carboxylate molecules extend straight forward on the both sides of each basal plane. The values of long spacings for metal soaps are very smaller then calculated dimensions of anions (myristate 47.0, palmitate: 47.0 and stearate is 52.0) from the Paulings values of atomic radii and bond angles. It is therefore, concluded that the molecular axes of these carboxylates are somewhat inclined to the basal planes. The metal ions, Ti^{3+} fit into spaces between oxygen atoms of the ionized carboxyl group without a large strain of the bond.

A number of diffraction peaks in the intermediate range are also observed in the diffraction patterns of Zirconium carboxylate and are attributed to the diffraction of x-ray by plans of atoms of much smaller separation than the basal planes. The calculated 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.

Conclusion

The values of the long spacings for Zirconium carboxylate are agreement with the double layer structure of the soaps proposed by Vold and Hattiangdi(16). On the basis of long and short spacings, it is suggested that the metal ions are arranged in parallel planes equally spaced in the carboxylate crystal with fully extended Zig-Zig chains of fatty acid radicals on both sided of each basal plane.The results suggest that scandium soaps possess double layer structure with molecular axes somewhat inclined to the basal planes.

TABLE:1 X-RAY DIFFRACTION ANALYSIS OF ZIRCONIUM MYRISTATE

S.NO	2θ	θ	Sin θ	D	d(A^0)	n
1.	2.975	1.487	.0259	17.966	35.892	1
2.	4.409	2.204	.0385	11.416	34.178	2
3.	7.566	3.283	.0572	8.993	35.872	3
4.	9.453	4.726	.0823	7.043	35.085	4
5.	10.833	5.915	.1030	6.235	37.250	5
6	18.295	9.147	.1589	3.893	38.650	8
7.	19.291	9.645	.1675	2.395	39.495	9

Average value of d=36.06A^0

TABLE:2 X-RAY DIFFRACTION ANALYSIS OF ZIRCONIUM PALMITATE

S.NO	2θ	θ	Sin θ	D	d(A^0)	n
1.	3.149	1.578	0.0239	18.386	36.733	1
2.	4.243	2.121	0.0370	11.946	35.769	2
3.	6.349	3.174	0.0553	8.422	34.587	3
4.	5.948	2.474	0.0431	6.948	34.598	5
5.	0.903	0.451	0.0078	4.999	29.995	6
6	0.572	0.286	0.0049	3.997	31.215	8
7.	0.250	0.125	0.0022	2.889	34.448	10

Average value of d=33.76A^0

TABLE:3 X-RAY DIFFRACTION ANALYSIS OF ZIRCONIUM STEARATE

S.NO	2θ	θ	Sin θ	D	d(A^0)	n
1.	3.946	1.973	0.0344	13.982	41.897	3
2.	6.235	3.117	0.0543	8.253	41.161	5
3.	18.933	9.466	0.1644	2.969	32.479	10
4.	19.536	9.768	0.1696	2.871	34.357	11
5.	32.138	16.069	0.2767	1.988	37.395	20
6	34.255	12.127	0.2100	1.546	30.633	21
7.	35.647	17.823	0.2970	0.997	21.644	22

Average value of d=34.22A^0

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