Indian Journal of Advances in Chemical Science

Article

An Investigation on Spectral and Thermal Properties of Nickel Soaps of Higher Fatty Acids

M. K. Rawat[1], Mamta Gautam[1], Sangeeta[2]*

[1]Department of Chemistry, Agra College, Agra, Uttar Pradesh, India, [2]Department of Applied Science, IET Khandari, Dr. B.R. Ambedkar University, Agra, Uttar Pradesh, India

ABSTRACT

The present study aims to evaluate the spectroscopic and thermal properties of nickel soaps (myristate, palmitate, and stearate). The main methods of structural investigation such as infrared, X-ray diffraction, and thermogravimetric analysis (TGA) are examined in detail based on common synthetic routes, leading to the isolation of metal soaps. The results of IR spectra confirm its ionic nature and dimeric structure through intermolecular hydrogen bonding. The double-layer structure of nickel soaps is confirmed by X-ray diffraction measurements. Data of TGA show that the decomposition reaction of nickel soaps is zero order and activation energy was found to be 7.8–20.0 kcal/mol.

Key words: Activation energy and nickel soaps, Infrared spectra, Thermogravimetric analysis, X-ray diffraction.

1. INTRODUCTION

A saponification reaction is used for the synthesis of sodium and potassium soaps. Metal soaps were prepared by direct metathesis method. They do not form emulsion due to its insoluble properties in water. Metal soaps are used as waterproofing agent [1], sunscreen [2] catalyst [3,4], lubricants [5], corrosion inhibitor [6], thermal stabilizers [7], and gelling agent in many cosmetic [8]. The structural studies of metal soaps were carried out by White *et al*. [9]. The magnetic properties of cobalt(II) and manganese(II) carboxylates have been investigated by Kambe *et al*. [10]. A number of monomorphic metal carboxylates have been prepared [11,12], and recently, liquid crystal display of metal soaps was synthesized [13].

Considering the commercial significance of metal soaps and the appreciation of their molecular structures, attempts will be made in this manuscript to give a general overview of investigations on the structures and thermal behaviors of nickel soaps.

2. EXPERIMENTAL

2.1. Synthesis of Nickel Soaps

Nickel soaps (myristate, palmitate, and stearate) have been synthesized by indirect method in two steps. The first step is the synthesis of potassium soap (K-soap) through the saponification reaction of saturated fatty acids with potassium hydroxide; the second step is the synthesis of nickel soaps through the trans-saponification reaction of K-soap with its acetate salts. Typically, fatty acids (40 g) with 120 mL of 15% potassium hydroxide (KOH) solution (22 g of KOH in 120 mL distilled water) remained refluxed at 80°C for 4 h, and cooled at room temperature. After cooling, Whatman filter paper-40 was used to filter the mixture. The residue has been purified by salting it out. A 50 mL of 5% nickel acetate solution was added dropwise to the K-soap solution (10 g in 100 mL) at 60°C to get a precipitate. The residue has been filtered, washed with distilled water, and dried at 40°C in the oven for 2 days giving a solid nickel soap.

3. RESULTS AND DISCUSSION

3.1. Infrared Spectra

The infrared spectral bands [Figure 1] and their tentative assignments for nickel myristate, nickel palmitate, and nickel stearate are assigned and compared with nickel myristate, nickel palmitate, and nickel stearate as well as with corresponding fatty acid (myristic acid, palmitic acid, and stearic acid) Table 1. The absorption maxima near 2640VW–2650S (O-H stretching vibrations), 1700–1680 (C=O stretching vibrations), 950–930, 690, and 550 cm^{-1} in the spectra of fatty acids indicate that in the form of dimeric structure, a localized carboxylic group is present and the existence of intermolecular hydrogen bonding between two molecules of acid. Nickel soaps spectra show that the absorption band near 2650–2640 and 950–930 cm^{-1} corresponding to the –OH group in the spectra of fatty acids have completely disappeared. The absorption band observed at 1700–1650 cm^{-1} corresponding to the carbonyl group of the fatty acid is also observed in the spectra of nickel soaps with weak intensity which may be due to the incomplete resonance of the carbonyl group in the nickel soaps. The singlet band observed near 690–720 cm^{-1} is the characteristic of divalent metal soaps.

The appearance of two absorption bands observed near 1450–1460 cm^{-1} and 1540–1530 cm^{-1} in the spectra of nickel soaps correspond to symmetric and asymmetric vibrations of carboxylate ion. The band observed near 478–477 cm^{-1} in the spectra of nickel soaps correspond

***Corresponding author:**
Sangeeta,
E-mail: sangeeta.kumar47@rediffmail.com

ISSN NO: 2320-0898 (p); 2320-0928 (e)
DOI: 10.22607/IJACS.2024.1203011

Received: 31st May 2024;
Revised: 04th July 2024;
Accepted: 27th August 2024
Published: 05th September, 05 2024

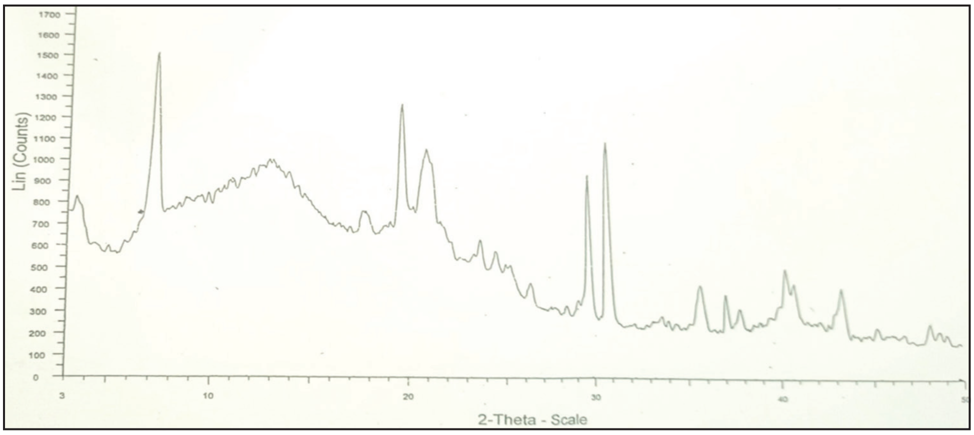

Figure 1: X-ray diffraction of nickel palmitate.

Table 1: Infrared absorption frequencies (cm^{-1}) maxima with their assignments.

S. No.	Absorption	Myristic acid	Nickel myristate	Palmitic acid	Nickel palmitate	Stearic acid	Nickel stearate
1.	CH_3, C-H asymmetrical stretching	2960VW	2960VW	2960VW	2954VW	2960W	2957V
2.	CH_2, C–H asymmetrical stretching	2920VS	2916W	2920S	2916S	2920VS	2917VS
3.	CH_2, C–H symmetrical stretching	2855S	2849VS	2860S	2850S	2850S	2850S
4.	OH, stretching	2640VW	---	2650VS	----	2650S	-----
5.	C=O stretching	1700VS	---	1680VS	----	1700VS	----
6.	COO–, C–O asymmetrical stretching	-	1552M	-	1551S	-	1552S
7.	CH_2 deformation	1465MS	1467VS	1470M	1467W	-	1467W
8.	COO–, C–O symmetrical stretching	---	1413VW	-	1422S	-	1422W
9.	CH_2, (adjacent to COOH group) deformation	1410W	---	-	---	1412VS	--
10.	CH_3, symmetrical deformation	1375VW	1333W	1350M	---	1375W	---
11.	Progressive bonds (CH_2 twisting and wagging)	1350-1090W	1380-1190S	1370-1090W	1320-1200W	1350-1202M	1330-1170M
12.	CH_3, rocking	1110W	1110S	1220W	1116	1110M	1113W
13.	OH, out-of-plane deformation	950S	--	930VS	--	930M	720MS
14.	CH_2, rocking	720MS	720VS	720S	690VS	740M	
15.	COOH. Bending mode	690M	----	690M	---	689S	---
16.	COOH wagging Mode	550M	---	550M	---	550S	---
17.	Ni–O bond	-	477VS	-	477W	-	478M

to Cr-O bonds. The absence of water molecules in nickel soaps confirms by the disappearance of the absorption band near 3500–3000 cm^{-1}.

3.2. X-ray Diffraction Analysis

The X-ray diffraction studies of nickel myristate, nickel palmitate, and nickel stearate have been used to characterize the structure in the solid state. The calculated spacing together with the relative intensities with respect to the most intense peaks are recorded in Tables 2-4. The intensity and sharpness (half-width; that is, the angular width of the peak at half its maximum intensity) of the peaks are the measures of the degree of crystallinity of the metal soaps. The appearance of diffraction up to 13, 15, and 16th orders for myristate, palmitate, and stearate, respectively, confirms the good crystallinity of these metal soaps. The average planar distances, that is, long spacing for nickel myristate, nickel palmitate, and nickel stearate were found to be 42.1902, 47.3696, and 51.8217 (Å), respectively.

The difference in the observed values of long spacing for nickel in palmitate and stearate corresponds to the double length of methylene groups (-CH_2) in the fatty acid radical constituent soap molecules (myristate and palmitate: 5.1793, palmitate and stearate: 4.4521). It is, therefore, suggested that the zig-zag chains of the fatty acid radical constituent of the soap molecules extend straight forward on both sides of each basal plane. The values of long spacing for nickel myristate 41.7247 (Å), palmitate 46.8786 (Å), and stearate 51.7978(Å) are

Table 2: X-ray diffraction analysis of nickel myristate.

No.	2Θ	Θ	Sin Θ	D	d(Å)	*n*
1	4.83	2.41	0.0421	42.1235	42.1235	1
2	5.98	2.99	0.0521	20.4907	41.3956	2
3	8.50	4.25	0.0741	14.0894	42.2682	3
4	10.24	5.12	0.0892	10.6063	42.4252	4
5	12.98	6.49	0.1130	8.4600	42.3000	5
6	22.13	11.06	0.1919	7.1609	42.9654	6
7	25.18	12.59	0.2179	6.1442	43.0094	7
8	26.04	13.02	0.2252	5.2781	42.2248	8
9	32.56	16.28	0.2803	4.6380	41.7420	9
10	36.84	18.42	0.3159	3.1883	41.4479	10

Average value of d(Å)=42.1902

Table 3: X-ray diffraction analysis of nickel palmitate.

No.	2Θ	Θ	SinΘ	D	d(Å)	*n*
1	7.62	3.81	0.0664	47.7133	47.7133	1
2	10.09	5.04	0.0879	24.0680	48.1360	2
3	12.39	6.19	0.1079	15.7274	47.1822	3
4	14.21	7.10	0.1236	11.5477	47.0192	4
5	15.15	7.57	0.1318	9.2696	47.3835	5
6	16.38	8.19	0.1424	7.8198	46.9180	6
7	18.94	9.47	0.1645	6.7843	47.4901	7
8	23.35	11.67	0.2023	4.2426	46.6685	11
9	28.62	14.31	0.2471	3.6213	47.0769	13
10	38.54	19.27	0.3300	3.4142	48.1065	15

Average value of palmitate d(Å)=47.3696

smaller than calculated dimensions of anions [myristate 42 (Å), palmitate 47 (Å), and stearate 52 (Å)] from Pauling's value of atomic radii and bond angle, which suggests that the molecular axes of soap molecules are somewhat inclined to the basal plane. The metal ion, Ni^{2+} fit into spaces between oxygen atoms of the ionized carboxyl group without large strain of the bond. As a significance, X-ray spectroscopy is a very useful technique to characterize an extensive variety of materials.

3.3. Thermal Analysis (Thermogravimetric Analysis [TGA])

The TGA technique was used for the analysis of the thermal decomposition of nickel soaps (laurate, myristate, and palmitate) and the results are given in Figure 2. The theoretically calculated weights of nickel dioxide from the molecular formulas of the soaps are in agreement with the weight of the final residue. The thermal decomposition of nickel soaps may be written as.

$$(RCOO)_2Ni \quad Ni^{2+} + 2RCOO^-$$

$$2(RCOO)_2Ni \quad 2RCOR + NiO + 2CO_2$$

Where R = $C_{13}H_{27}$, $C_{15}H_{31}$ and $C_{17}H_{35}$.

The results of the thermal decomposition of nickel soaps have been explained in the light of some well-known equations, Freeman and Carroll's [14] and Coats and Redfern's [15] equations expressed as follows:-

Table 4: X-ray diffraction analysis of nickel stearate.

No.	2Θ	Θ	SinΘ	D	d(Å)	*n*
1	3.60	1.80	0.0314	25.9319	51.8638	2
2	5.20	2.60	0.0453	17.4972	52.4916	3
3	7.53	3.76	0.0656	13.1104	52.4416	4
4	11.42	5.71	0.0994	10.9033	50.0190	5
5	12.19	6.09	0.1061	8.7800	52.6800	6
6	17.38	8.69	0.1510	7.5374	52.7618	7
7	18.42	9.21	0.1600	6.5019	52.0152	8
8	27.63	13.81	0.2337	4.6380	51.0180	11
9	31.69	15.84	0.2730	3.2071	51.3136	16

Average value of palmitate=d(Å) = 51.7978

Table 5: Energy of activation of nickel soaps.

Name of metal soaps	Freeman-Carroll	Coats Redfern's
Nickel myristate	7.8	14.06
Nickel palmitate	11.8	15.00
Nickel stearate	14.7	20.00

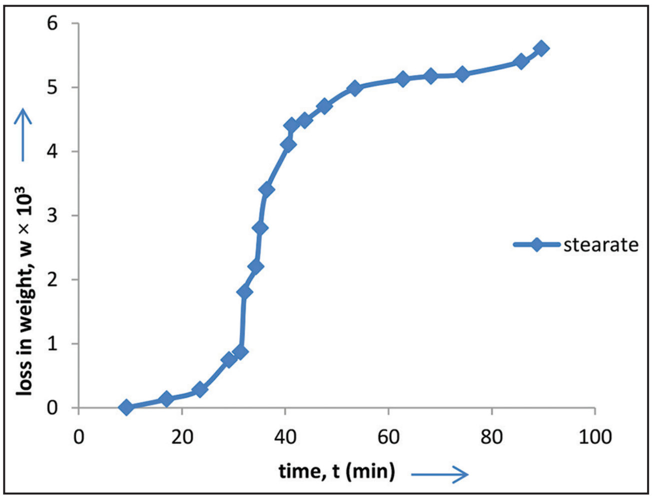

Figure 2: Thermogram of nickel stearate.

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

Where, E = energy of activation, n = order of reaction, T = temperature on the absolute scale, Wr = difference between the total loss in weight and loss in weight at time t, that is, W_o–W_v, dw/dt = rate of weight loss calculated from the loss in weight of soaps and the loss at pre-determined time.

The values of activation energy (E) are calculated from the slope (−E/2.303R) of the plots of log (dw/dt) versus (1/T) and are found in the range of 7.8–20.0 kcal/mol [Table 5].

4. CONCLUSION

The existence of fatty acid in a dimeric structure confirm by infrared as a result of hydrogen bonding between the carboxyl group of two fatty acid molecules and nickel soaps possess ionic character. The double-layer structure of nickel soaps with molecular axes slightly inclined to the basal plane was confirmed by X-ray analysis. The thermal decomposition of these soaps was found to be zero order and the energy of activation for the decomposition process was in the range of 7.8–20.0 kcal/mol.

5. ACKNOWLEDGMENT

The authors are thankful to the Department of Chemistry, Agra College, Agra for providing all necessary facilities.

6. REFERENCES

1. E. Loncar, G. Lomic, R. Malbasa, L. Kolarov, (2003) Preparation and characterization of aluminum stearate, ***Acta Periodica Technologica***, **34:** 55.
2. S. Sutrisno, H. W. Wijaya, D. Sukarianingsih, M. N. D. Santiaji, (2021) Synthesis and characterization of metal soap (Zn, Al, and Mg-soap) from sunflower oil and its potential as sunscreen, ***AIP Conference Proceedings***, **2349:** 020042
3. D. M. Reinoso, D. E. Damiani, G. M. Tonetto, (2012) Zinc carboxylic salts used as catalyst in the biodiesel synthesis by esterification and transesterification: Study of the stability in the reaction medium, ***Applied Catalysis A General***, **449:** 88-95.
4. S. A. Maruyama, L. R. S. Kanda, F. Wypych, (2017) Isopropyl octanoate synthesis catalyzed by layered zinc n-octanoate, ***Journal of the Brazilian Chemical Society***, **28:** 985-994.
5. G. Poulent, S. Sentenac, Z. Mouloungui, (2004) Double decomposition reactions for the production of alkaline and alkaline-earth oleic soaps under salting-out conditions, ***Industrial and Engineering Chemistry Research***, **43:** 1574.
6. O. M. Folarin, O. N. Enikanoselu, (2010) Evaluation of the effect of temperature on the stability of metal soaps of ***Trichosanthes cucumerina*** seed oil, ***Journal of Applied Sciences and Environmental Managemen***t, **14:** 1604.
7. T. O. Egbuchunam, D. Balköse, F. E. Okieimen, (2007) Effect of zinc soaps of rubber seed oil (RSO) and/or epoxidised rubber seed oil (ERSO) on the thermal stability of PVC plastigels, ***Polymer Degradation and Stability***, **92:** 1572-1582.
8. D. Balköse, T. O. Egbuchunam, F. E. Okieimen, (2010), Thermal behaviour of metal soaps from biodegradable rubber seed oil, ***Journal of Thermal Analysis and Calorimetry,*** **101:** 795-799.
9. N. A. S. White, H. A. Ellis, P. N. Nelson, P. T. Maragh, (2011) Thermal and odd-even behaviour in a homologous series of lithium n-alkanoates, ***The Journal of Chemical Thermodynamics***, **43:** 584-59.
10. H. Kambe, T. Ozawa, M. Onoue, S. Igarashi, (1962) Physicochemical studies on cobalt salts of higher fatty acids. VI. Some observations on thermal transitions of cobalt soaps, by differential thermal analysis, thermogravimetry, and magnetic measurement, ***Bulletin of the Chemical Society of Japan***, **35:** 81-85.
11. G. Klose, F. Volke, M. Hentschel, A. Mops, (1983) Molecular motions and mesophases in anhydrous thallium (I) soaps studied by 1H- and 205TL-NMR. The 205TL chemical shift tensor, ***Molecular Crystals and Liquid Crystals***, **90:** 245-254.
12. S. J. Lee, S. W. Han, H. J. Choi, K. Kim, (2002) Structure and thermal behaviour of a layered silver carboxylate, ***The Journal of Physical Chemistry B***, **106:** 2892-2900.
13. J. S. Wilkes, (2002) A short history of ionic liquids-from molten salts to neoteric solvents, ***Green Chemistry***, **4(2):** 73-80.
14. E. S. Freeman, B. J. Caroll, (1958) The application of thermoanalytical techniques to reaction kinetics: The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate, ***The Journal of Physical Chemistry***, **62:** 394-394.
15. A. W. Coats, J. P. Redferns, (1964) Kinetic parameters from thermogravimetric data, ***Nature***, **201:** 68-69.

***Bibliographical Sketch**

Prof. M.K. Rawat is the head of the Chemistry department at Agra College, Agra. In 1990, he obtained Ph.d degree from Agra University, Agra. He was awarded the Young Scientist Award in 1996 for his research work. He has completed D.Sc in 2014 from Dr. B.R. Ambedkar University, Agra. Under his guidance, 29 researchers have obtained Ph.d degrees, his more than 60 research papers have been published in national and international journals. Dr. Rawat has also Published 09 books on various topics.He has participated in more than 70 National and International conferences. He also served as Principal of Agra College, Agra, from 2009-2016 selected by U.P. Higher Education selection commission.He is members of many academic and social bodies.

Dr. Mamta Gautam has completed her Ph.D from the department of Chemistry, Agra College, Dr. Bhimrao Ambedkar University, Agra, India. She has participated in national and international conferences.

Dr. Sangeeta is an assistant professor at the Department of Applied Chemistry, Institute of Engineering and Technology, Dr. B.R. Ambedkar University, Agra, India. She has more than 12 years of experience in teaching chemistry. She has published more than 14 research papers in various reputed journals, and her 03 chapters have also been published in esteemed publications. She was awarded a Ph.D. in chemistry from Dr. B.R. Ambedkar University, Agra, India. After Ph.D., she was awarded as a Post-doctoral Fellow (PDF) from UGC, Delhi. She has presented more than 20 research papers in various national and international conferences.