

INFRARED ABSORPTION SPECTROSCOPIC STUDIES OF NICKEL (Ni) BUTYRATE, CAPROATE, AND CAPRYLATE SOAPS

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ABSTRACT

Alkaline earth metals and heavy metals salts of fatty acids which are referred as metallic soaps. Nickel soaps (butyrate, caproate and caprylate) were prepared by means of fusion method as per the standard method followed by the elementary analysis and IR Spectroscopy analysis. The IR spectra of Nickel soaps (butyrate, caproate and caprylate) confirm that fatty acids exist with dimeric structure through H-bonding and these soaps possess partial ionic character.

Key Words: caprylic acid, fusion, hydrogen bonding, ionic character, and fatty acids.

INTRODUCTION

Alkaline earth and heavy metals salts of fatty acids which are insoluble in water and either soluble in or solvated by organic solvents, are referred as metallic soaps. Ralston prepared the lithium soaps of lauric, myristic, palmitic, and stearic acids and shown that these metallic soaps of long chain fatty acids are sparingly soluble in water and somewhat were soluble in ethanol (1). Lithium stearate, palmitate, myristate, laurate, caproate and caprylate were prepared by means of fusion method by Shoeb and reported that the ionic character of the metal to oxygen bond was enhanced with the number of carbon atoms as shown by infrared spectroscopy (2). In addition, infrared absorption spectra of Ni butyrate soap shown by Babita Rani and found that the fatty acids exist with dimeric structure through hydrogen bonding where as the metal to oxygen bond in the metal soap possess ionic character (3). Furthermore, infrared analysis of Dysprosium soaps reveal that the fatty acid exist in dimeric state through H-Bonding and soaps possess partial ionic character (4).

In the whole world the metallic soaps are being used increasing in various industries such as textiles, paints lubricants, greases, cements, cosmetics, emulsifiers, water-proofing agents, medicines, pharmaceuticals, germicides,

printing inks, varnishes, catalysts, softeners, hardners and stabilizers etc. Therefore, the applications of metallic soaps are mostly depend on the conditions and the methods of the preparations of the metallic soaps, thus there is a great significance of the nature and structure of the metallic soaps for their uses in various industries under different conditions. On account of their unique characteristics, metallic soaps have vast importance and play an important role in technological and academic fields. However, the applications of the metallic soaps are based on the empirical knowledge and the selection of for a specific purpose is mainly governed by economic factors. Several studies have been done on the alkali, alkaline and transition metal soaps but less work has been done on the Nickel (Ni) butyrate, caproate and caprylate soaps. Various methods and techniques have been used by several workers for studying the preparation, properties and uses of metal soaps. The methods of preparation of rare earth metal soaps were reported by several workers (5-9). Ralston (1) prepared the lithium soaps of lauric, myristic, palmitic, and stearic acids by adding the calculated amount of lithium acetate to ethanol solution of the respective fatty acids and determined the solubility of those soaps in a number of solvents. The soaps of second series of transition metals were prepared by several workers (10) by treating the halides (generally chlorides) with carboxylic acids. Several workers reported the methods of preparation of transition metal soaps by double decomposition, metathesis and fusion or by direct reaction of metal oxide with an organic acid (11-16).

In this paper we describe the preparations of three Nickel soaps (butyrate, caproate and caprylate) with fatty acids (butyric acid, caproic acid and caprylic acid) having long chain of carbon atoms. These soaps were prepared by fusion method and subjected to elementary analysis and Infrared Absorption Spectroscopy analysis.

II. METHODOLOGY

In this study, first the fatty acids were purified by distilling under reduced pressure. The purity of acids was checked by determining their boiling points, melting points. The m.p. of purified acids were; 162^o C of butyric acid, 185^o C of caproic acid, 238^o C of caprylic acid. Then used solvent benzene was purified by keeping over sodium for a couple of days and then distilling. The distillate was refluxed over sodium metal and then redistilled. The boiling points of purified benzene was 80.1^o C. Methanol was purified by keeping over KOH for twenty four hours and then distilling. The distillate was refluxed with 1% of calcium metal for about eight hours and redistilled. The boiling point of purified methanol was 65.0^o C.

Sodium soaps (butyrate, caproate and caprylate) was prepared by refluxing equivalent amounts of corresponding fatty acid aqueous solution of sodium hydroxide for 6-8 hours on a water bath. The soaps were purified by recrystallization with methanol and dried under reduced pressure. The purity of soaps was checked by the determination of their melting points. Nickel butyrate, caproate and caprylate soaps were prepared by direct metathesis of the corresponding sodium soap with slight excess of the solution of nickel nitrate under vigorous stirring. The precipitated soaps were washed with water, methanol and acetone to remove the excess of metal salts, sodium soap and unreacted fatty acid. The soap thus obtained was dried in an air oven and the final drying

of the soaps were carried out under reduced pressure. The soaps were purified by recrystallization with benzene-methanol mixture. The purity of the soaps were confirmed by determination of their melting point. The elemental analysis for C, H, and metal are further confirmed by the molecular formula of soaps. The melting point of Nickel butyrate, nickel caproate and caprylate soaps are 112°C, 124 °C and 135 °C respectively.

The calculated amount of soaps were weighted in a standard flask and the solutions was made by adding the required amount of solvent. In this way different amount of Nickel soaps was prepared. Care was taken to avoid trace of water, which were found to hydrolysis these soaps. Further, IR Absorption Spectra of Nickel butyrate, nickel caproate and nickel caprylate soaps and of corresponding fatty acids were obtained with a Perkin-Elmer 577 Model Grating Spectrometer in the region of 4000-400 cm⁻¹ using KBr disc method.

III. RESULTS AND DISCUSSIONS

The infrared absorption maxima of nickel (butyrate, caproate and caprylate) soaps and of corresponding fatty acids were obtained with a Perkin-Elmer 577 Model Grating Spectrometer in the region of 4000-400 cm⁻¹. And have been assigned and recorded. Further, these were compared with those of corresponding fatty acids and sodium soaps. The vibrational frequencies characteristics of the aliphatic portion of the fatty acid do not vary even when acid is converted into sodium or nickel soaps.

The absorption bands of -C-H stretching vibrations(17-18) viz. the symmetrical vibration of -CH₂, the unsymmetrical stretching vibrations of -CH₂, the asymmetrical vibrations of -CH₃ and the deformation of -CH₃ are observed at 2865-2850 cm⁻¹, 2930-2900 cm⁻¹, 2955-2940 cm⁻¹ and 1370-1350 cm⁻¹ respectively in the spectra of metal soaps as well as in corresponding fatty acids.

The progressive bands (19-20) of weak intensity are observed near 1340-1040 per cm in the spectra of nickel soaps corresponding to the wagging and twisting vibrations of chains of successive methylene groups in their molecules. The absorption bands have been observed near 2660-2650 cm⁻¹, 1700-1670 cm⁻¹, 1470-1460 cm⁻¹, 960-930 cm⁻¹, 690 and 550cm⁻¹ in the spectra of fatty acids have indicated the presence of localizes -COOH group(21-24) in the form of dimeric structure and the existence of the intermolecular hydrogen bonding between two molecules of acids.

The absorption bands observed near 2660-2650 cm⁻¹, 1700-1670 cm⁻¹ and 960-930 cm⁻¹ corresponding to the -COOH group in the spectra of fatty acid having completely disappeared in the spectra of corresponding sodium and nickel soaps. The absorption maxima near 690 cm⁻¹ and 50 cm⁻¹ in the spectra of fatty acids were assigned to bending and wagging mode of vibration of carboxyl group of acid molecules and were not observed in the spectra of metal soaps. The IR spectra of nickel and sodium soaps show marked differences with the spectra of corresponding fatty acids in some spectral regions.

The IR spectra of nickel butyrate, caproate and caprylate soaps does not show any absorption maxima in the regions of 3500-3300 cm^{-1} which indicate the absence of any coordinated water molecules in the soap molecules. The infrared absorption spectral frequencies (cm^{-1}) of Nickel butyrate, caproate and caprylate soaps with their assignment were given below in Table-1- 3. From the tables 1-3, it was absorbed that the infrared absorption spectral frequencies with their assignment were great agreement with those of the sodium soaps of the fatty acids such as butyric acid, caproic acid and caprylic acid respectively.

Table-1. Infrared absorption spectral frequencies with their assignment (cm^{-1}) of Nickel butyrate soap.

S.No.	Absorption	Butyric Acid	Sodium Butyrate	Nickel Butyrate
1.	CH_3 , C-H asymmetrical stretching	2940	2950	2964
2.	CH_2 , C-H asymmetrical stretching	2900	2910	2931
3.	CH_2 , C-H symmetrical stretching	2850	2860	2877
4.	OH, stretching	2650	ND	ND
5.	C=O stretching	1670	ND	ND
6.	COO^- , C-O asymmetrical stretching	ND	1550	169
7.	COO^- , C-O symmetrical stretching	ND	1430	1418
8.	CH_2 , (adjacent to COOH group)	1410	1420	ND
9.	C-O stretching, OH in plane deform	1460	ND	ND
10.	Progressive bands (CH_2 twisting and wagging)	1280-1040	1320-1060	1311-1218
11.	CH_3 Rocking	1100	1070	1102
12.	OH out of plane deformation	930	ND	ND
13.	CH_2 , Rocking	720	730	769
14.	COOH, Bending mode	690	ND	ND
15.	COOH, Wagging mode	550	ND	ND

16.	Ni-O bond	ND	ND	455
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Vibrations of carboxylate ions near $1460\text{-}1430\text{ cm}^{-1}$ and $1555\text{-}1550\text{ cm}^{-1}$ in the spectra of sodium and nickel soaps indicate that there is a complete resonance in the C=O bonds of carbonyl group of the soap molecules and the two bonds become identical with the force constants assuming the value intermediate between those of normal double and single bonds. It is therefore, concluded that the resonance character of the ionized carboxyl group is retained in these metal soaps and the metal to oxygen bond is ionic in nature.

Table-2. Infrared absorption spectral frequencies with their assignment (cm^{-1}) of Nickel caproate soap.

S.No.	Absorption	Caproic Acid	Sodium Caproate	Nickel caproate
1.	CH ₃ , C-H asymmetrical stretching	2950	2950	2958
2.	CH ₂ , C-H asymmetrical stretching	2920	2925	2929
3.	CH ₂ , C-H symmetrical stretching	2865	2870	2867
4.	OH, stretching	2660	ND	ND
5.	C=O stretching	1690	ND	ND
6.	COO ⁻ , C-O asymmetrical stretching	ND	1550	1578
7.	COO ⁻ , C-O symmetrical stretching	ND	1430	1415
8.	CH ₂ , (adjacent to COOH group)	1410	1430	ND
9.	C-O stretching, OH in plane deform	1465	-ND	ND
10.	Progressive bands (CH ₂ twisting and wagging)	1310-1180	1320-1210	1303-1223
11.	CH ₃ Rocking	1100	1105	1112
12.	OH out of plane deformtion	950	ND	ND
13.	CH ₂ , Rocking	720	730	771
14.	COOH, Bending mode	690	ND	ND

15.	COOH, Wagging mode	550	ND	ND
16.	Ni-O bond	ND	ND	473

It is also shown by the infrared spectra of nickel soaps that the absence of any coordinated water molecules in the soaps molecule.

Table-3. Infrared absorption spectral frequencies with their assignment (cm⁻¹) of Nickel caprylate soap.

S.No.	Absorption	Caprylic Acid	Sodium Caprylate	Nickel Caprylate
1.	CH ₃ , C-H asymmetrical stretching	2950	2950	2960
2.	CH ₂ , C-H asymmetrical stretching	2920	2925	2927
3.	CH ₂ , C-H symmetrical stretching	2865	2870	2857
4.	OH, stretching	2660	ND	ND
5.	C=O stretching	1690	ND	ND
6.	COO ⁻ , C-O asymmetrical stretching	ND	1550	1570
7.	COO ⁻ , C-O symmetrical stretching	ND	1430	1413
8.	CH ₂ , (adjacent to COOH group)	1410	1430	ND
9.	C-O stretching, OH in plane deform	1465	ND	ND
10.	Progressive bands (CH ₂ twisting and wagging)	1310-1180	1320-1210	1301-1159
11.	CH ₃ Rocking	1100	1105	1114
12.	OH out of plane deformtion	950	ND	ND
13.	CH ₂ , Rocking	720	730	722
14.	COOH, Bending mode	690	ND	ND
15.	COOH, Wagging mode	550	ND	ND

16.	Ni-O bond	ND	ND	473
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IV. CONCLUSIONS

The infrared spectra of sodium, and Nickel soaps (butyrate, caproate and caprylate) show marked differences with the spectra of corresponding fatty acids in some spectral regions. It is therefore, concluded that the resonance character of the ionized carboxyl group is retained in these metal soaps and the metal to oxygen bond is ionic in nature. The infrared spectra of nickel soaps does not show any absorption maxima in the regions of 3500-3300 per cm which indicate that the absence of any coordinated water molecules in the soap molecules. Thus the results confirm that the fatty acid exist with dimeric structure through hydrogen bonding where as the metal to oxygen bonds in the metal soaps possess ionic character.

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