

INFRARED ABSORPTION SPECTROSCOPIC ANALYSIS OF PRASEODYMIUM (Pr) SOAPS

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ABSTRACT

There is a great significance of the nature and structure of the metallic soaps. The praseodymium (Pr) soaps (butyrate, caproate and caprylate) were prepared by the direct metathesis of the corresponding sodium soaps with slight excess of the praseodymium nitrate under vigorous stirring and subjected to the Infrared absorption analysis. The IR spectra reveals that 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 550 cm^{-1} in the spectra of fatty acids have been indicated the presence of localized -COOH group in the form of dimeric structure and the existence of the intermolecular hydrogen bonding between two molecules of butyric acid, caproic acid and caprylic acid respectively. There were a complete resonance in the C=O bond of carboxyl group of soap molecule and two bonds become identical with the force constants assuming the value, those of normal double and single bonds, in between is intermediate. Therefore, it was concluded that the resonance character of the ionized carboxyl group was retained in soaps and the metal to oxygen bond is ionic in nature.

Key Words: benzene, butyric acid, Dimeric, methanol, oil paint, resonance.

1. INTRODUCTION

Metallic soaps are playing a very important role in human life, based on their importance and usefulness in various industries such as textiles, lubricants, greases, cements, cosmetics, emulsifiers, waterproofing agents etc. The metallic soaps are used not only in medicines and pharmaceuticals but also are used in germicides, printing inks, varnishes, catalysts, softeners, hardeners and stabilizers etc. Thus the consequences of metallic soaps are mostly depends upon the conditions and the methods of their preparations. Thus there is a great significance of the nature and structure of the metallic soaps for their uses in different industries [1]. Various methods and techniques have been used by several workers for studying the preparation, properties and uses of metal soaps. In addition infrared absorption spectroscopic studies of nickel butyrate, caproate and caprylate soaps reported that fatty acids exist with dimeric structure through hydrogen bonding and possess partial ionic character [2].

Further, infrared absorption spectra of nickel butyrate soap reported and also showed that the fatty acids are present in dimeric state[3]. Spectroscopic analysis of chromium (Cr) soaps investigated by Mitra and others and shown that IR spectra of chromium soaps (butyrate and caprylate) were exist in dimeric state through hydrogen bonding and soaps possess partial ionic character. They also shown that the decomposition reaction was found kinetically of zero order with energy of activation 0.180 Kcal/mole for butyrate and caprylate respectively[4]. The synthesis of new type of lead (Pb) and zinc (Zn) soaps, a source of informations for the study of oil paints degradation investigated by Hermanns and found that the results are a first step toward more accurate interpretations in paint sample analysis and a more detailed understanding of oil paint degradation of a molecular scale[5]. Infrared , thermal and X-rays diffraction analysis of dysprosium soaps reported and the X-rays diffractions measurements confirm the double layer structure of dysprosium soaps [6]. In addition, analysis of electrolytic behavior of dysprosium soaps solution reported by Upadhyay and shown that the excellent solubility of transition metallic soap in a methanol and benzene mixture (v/v) has necessitated this study on the conductance and micellar behavior of these compounds in this mixture and different temperatures (7).

The main aim of this paper deals the infrared absorption spectroscopic analysis of praseodymium (Pr) soaps (butyrate, caproate and caprylate). These soaps were preped by the direct metathesis of the corresponding sodium soaps with slight excess of the praseodymium nitrate under vigorous stirring and subjected to the IR analysis.

II. METHODOLOGY

Before preparation of praseodymium soaps, first fatty acids such as butyric acid, caproic acid and caprylic acid were purified by distilling under reduced pressure. The used solvents such as benzene and methanol were also purified by appropriate methods , see elsewhere. The purification of fatty acids and solvents followed by the preparation of sodium soaps (butyrate, caproate and caprylate) and then purified by recrystallization with methanol and dried under reduced pressure. Praseodymium soaps (butyrate, caproate and caprylate) were prepared by the direct metathesis of the corresponding sodium soap with slight excess of the solution of praseodymium nitrate under vigorous stirring, which followed by washing with water , methanol and acetone , then drying the soaps first in air oven and then under reduced pressure. Finally, the praseodymium soaps were purified by recrystallization with benzene-methanol mixture. The elemental analysis for C, H, and metal are further confirmed by the molecular formula of soaps. The melting points of purified praseodymium soaps were 96°C for praseodymium butyrate , 109°C for praseodymium caproate and 122°C for praseodymium caprylate.

Further, praseodymium soaps (butyrate, caproate and caprylate) and of corresponding fatty acids were investigated by Infrared Absorption spectroscopic analysis. The infrared spectra of praseodymium soaps (butyrate, caproate and caprylate) nd corresponding fatty acids were obtained with a Perkin-Elmer “577 Model” Grating Spectrometer in the region of 4000-400 cm⁻¹ using potassium bromide (KBr) disc method. .

III. RESULTS AND DISCUSSIONS

The infrared absorption maxima of praseodymium (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 in Table-1-3.

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

S.No.	Absorption	Butyric Acid	Sodium Butyrate	Praseodymium Butyrate
1.	CH_3 , C-H asymmetrical stretching	2940	2950	2964
2.	CH_2 , C-H asymmetrical stretching	2900	2910	2932
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	1551
7.	COO^- , C-O symmetrical stretching	ND	1430	1441
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	1310-1215
11.	CH_3 Rocking	1100	1070	1097
12.	OH out of plane deformation	930	ND	ND
13.	CH_2 , Rocking	720	730	758
14.	COOH, Bending mode	690	ND	ND

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15.	COOH, Wagging mode	550	ND	ND
16.	Ni-O bond	ND	ND	468

Table-2. Infrared absorption spectral frequencies with their assignment (cm⁻¹) of Praseodymium caproate soap.

S.No.	Absorption	Caproic Acid	Sodium Caproate	Praseodymium caproate
1.	CH ₃ , C-H asymmetrical stretching	2950	2950	2959
2.	CH ₂ , C-H asymmetrical stretching	2920	2925	2931
3.	CH ₂ , C-H symmetrical stretching	2865	2870	2866
4.	OH, stretching	2660	ND	ND
5.	C=O stretching	1690	ND	ND
6.	COO ⁻ , C-O asymmetrical stretching	ND	1550	1551
7.	COO ⁻ , C-O symmetrical stretching	ND	1430	1438
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	1306-1226
11.	CH ₃ Rocking	1100	1105	1107
12.	OH out of plane deformtion	950	ND	ND
13.	CH ₂ , Rocking	720	730	726
14.	COOH, Bending mode	690	ND	ND
15.	COOH, Wagging mode	550	ND	ND
16.	Ni-O bond	ND	ND	471

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

S.No.	Absorption	Caprylic Acid	Sodium Caprylate	Praseodymium Caprylate
1.	CH ₃ , C-H asymmetrical stretching	2950	2950	2957
2.	CH ₂ , C-H asymmetrical stretching	2920	2925	2938
3.	CH ₂ , C-H symmetrical stretching	2865	2870	2863
4.	OH, stretching	2660	ND	ND
5.	C=O stretching	1690	ND	ND
6.	COO ⁻ , C-O asymmetrical stretching	ND	1550	1565
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	1307-1225
11.	CH ₃ Rocking	1100	1105	1111
12.	OH out of plane deformation	950	ND	ND
13.	CH ₂ , Rocking	720	730	727
14.	COOH, Bending mode	690	ND	ND
15.	COOH, Wagging mode	550	ND	ND
16.	Ni-O bond	ND	ND	482

The vibrational frequencies characteristics of the aliphatic portion of the fatty acids do not vary even when acid is converted into sodium or praseodymium soaps. The absorption bands of –C-H stretching vibrations viz. the symmetrical vibrations of –CH₂, the asymmetrical stretching vibrations of –C-H₂, the asymmetrical vibrations

of $-\text{CH}_3$, and the deformation of $-\text{CH}_3$ were observed at $2850\text{-}2877\text{ cm}^{-1}$, $2910\text{-}2938\text{ cm}^{-1}$, $2940\text{-}2960\text{ cm}^{-1}$, and $1280\text{-}1310\text{ cm}^{-1}$ respectively in the spectra of metal soaps as well as in corresponding fatty acids. The progressive bands of weak intensity were observed near $1340\text{-}1040\text{ cm}^{-1}$, in the spectra of praseodymium soaps, corresponding to the wagging and twisting vibrations of chains of successive methylene groups in their molecules.

The absorption bands have been observed near $2660\text{-}2650\text{ cm}^{-1}$, $1700\text{-}1670\text{ cm}^{-1}$, $1470\text{-}1460\text{ cm}^{-1}$, $960\text{-}930\text{ cm}^{-1}$, 690 and 550 cm^{-1} in the spectra of fatty acids have been indicated the presence of localized $-\text{COOH}$ group in the form of dimeric structure and the existence of the intermolecular hydrogen bonding between two molecules of acids respectively. The absorption maxima near 690 cm^{-1} and 550 cm^{-1} in the spectra of fatty acids were assigned to bending and wagging mode of vibrations of carboxylic group of acids molecules and were not observed in the spectra of praseodymium soaps.

The IR spectra of sodium and praseodymium soaps showed marked differences with the spectra of corresponding fatty acids in some spectral regions. From, the spectra of sodium and praseodymium soaps indicate that there were a complete resonance in the $\text{C}=\text{O}$ bond of carboxyl group of the soap molecule and two bonds become identical with the force constants assuming the value intermediate between those of normal double and single bonds. Therefore, it was concluded that the resonance character of the ionize carboxyl group was retained in these metal soaps and the metal to oxygen bond is ionic in nature.

IV. CONCLUSIONS

On account of the significant role of metallic soaps in several industries, in this study, the praseodymium soaps (butyrate, caproate and caprylate) were prepared by the direct metathesis of the corresponding fatty acids such as butyric acid, caproic acid and caprylic acid as per as standard method followed by purification and recrystallization of these metallic soaps. Further, sodium and praseodymium soaps were investigated by the IR absorption analysis with Perkin-Elmer "577 Model" Grating Spectrometer in the region of $4000\text{-}400\text{ cm}^{-1}$, using potassium bromide (KBr) disc method. The IR spectra of sodium and praseodymium soaps shown the progressive bands of weak intensity corresponding to the wagging and twisting vibrations of chains of successive methylene groups in their molecule. It was also indicated that the presence of localized $-\text{COOH}$ group in the form of dimeric structure and the existence of the intermolecular hydrogen bonding between two molecules of acids. The bending and wagging mode of vibrations of carboxylic group of acids molecules and were not observed in the spectra of praseodymium soaps. The IR spectra of sodium and praseodymium soaps showed marked differences with the spectra of corresponding fatty acids in some spectral regions. It was also concluded that the resonance character of the ionize carboxyl group was retained in these metal soaps and the metal to oxygen bond is ionic in nature.

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