

Physico Chemical Study on Manganese and Potassium Myristate and Stearate by IR spectrum

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Abstract - IR spectrum is used to determine the structure of fatty acid and manganese and potassium myristate and stearate soap. The important frequencies of absorption Maxima in IR spectra of fatty acids and manganese and potassium myristate and stearate soap are recorded and compare the result of corresponding myristic and stearic acid and potassium soaps. The IR result revealed that the fatty acid of myristate and stearate exist in dimeric state through hydrogen bonding and manganese soaps possess partial ionic character.

Keyword: Manganese, Myristate, Stearate, IR spectrum, Metallic soaps

INTRODUCTION

The study of metallic soaps is becoming increasingly important in technology and academic fields the application of these metal soaps depend largely on their physical state, stability chemical reactivity, nature of bonding and structure of the soaps. Several workers have studied on nature and structure of these soaps are of great importance for their use in industries and for explaining their character under different conditions. The current work deals with the infrared studies of manganese and potassium soaps in solid state initiated with a view to obtain structural information and nature of the metallic soaps. High metal content in metallic soaps make them unique in many diversified field. Metallic soaps are useful in many diversified field such as lubricating, softeners, cosmetic gel, intended to improve flow, coating smoothness, finishing, driers in paints, dry clean industry, heat stabilizers for plastic, anti-dusting, fungicide, pesticide, preservation and preparation of Nano films etc. The investigation of the above related categories of materials with infrared spectroscopy can provide an overall picture of the organic components' identity and demonstrate their condition and prehistory. The capability of investigating and distinguishing fatty acids and their metal soaps through their rich infrared features, such as the acidic

carbonyl, the carboxylate shifts, the variable splits of alkyl chain stretching, bending, twisting, wagging, and rocking vibrations, as well as the hydroxyl peak envelopes and acid dimer bands, allows for their direct detailed characterization. This paper reviews the infrared spectra of selected saturated fatty monoacids and di acids, and their corresponding manganese and potassium salts and, supported by newly recorded data, highlights the significance of their spectroscopic features.

Aim

The present work has been initiated with a view to obtain the information regarding the nature of bonding and structure of manganese and potassium myristate and stearate soap in solid state.

Experimental

1. Purification of Chemicals:

Fatty Acids:

Myristic and stearic acid were purified by distilling under reduced pressure and recrystallizing with alcohol. The purity of acids was checked by determining their melting point. The melting point of the purified acids were:

Myristic acid M.P.: 54.00C

Stearic acid M.P. : 71.50C

Solvents:

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 point of purified benzene was 80.10C.

Methanol was purified by keeping over potassium hydroxide 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 the purified methanol was 65.00C.

2. Preparation of Soaps:

Potassium myristate and stearate were prepared by refluxing equivalent amounts of corresponding fatty

acid and aqueous solution of potassium hydroxide for 6 – 8 hours on a water bath.

The soaps were purified by recrystallization with methanol and dried under reduced pressure.

Manganese and iron soaps were prepared by direct metathesis of corresponding potassium soap (myristate and stearate) with slight excess of the solution of manganese chloride under stirring. The precipitated soaps were washed several times with distilled water and acetone. The soaps were purified by recrystallization with benzene – methanol mixture. The purity of the soaps was confirmed by determining their melting points. The melting points of the purified soaps were:

Manganese myristate : 127°C

Manganese stearate : 110°C

Preparation of Soap Solutions:

The calculated amount of soap was weighed in a standard flask and the solution was made up by adding the required amount of solvent mixture of benzene and methanol. In this way, number of solutions of different concentrations of manganese myristate, manganese stearate were prepared.

Measurements:

Infrared absorption spectra:

The infrared absorption spectra of myristic and stearic acid and of corresponding potassium, manganese and iron soaps were obtained with a NICOLET 5 DXFT instrument (U.S.A.) in the region of 4000 – 200 cm⁻¹ using potassium bromide disc technique.

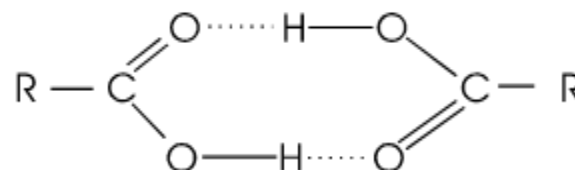
RESULT AND DISCUSSION

The important frequencies of absorption maxima in the infrared spectra of manganese with their assignments are recorded and compared with the result of corresponding fatty acids and potassium soaps (Table 1.1 to 1.2).

The absorption maxima characteristic of aliphatic portion of the acid molecule remain unchanged when fatty acids are converted to the corresponding potassium and manganese soaps (Figs 1.1 to 1.2). The absorption band of C – H stretching vibration, viz. the symmetric vibration of CH₂ at 2840 – 2860 cm⁻¹, the asymmetric stretching vibration of CH₂ at 2910 – 2920 cm⁻¹, the asymmetric stretching vibration of CH₃ at 2920 – 2960 cm⁻¹ and the deformation of CH₂ at 1450 – 1465 cm⁻¹ are observed in the spectra of potassium and manganese soaps as well as in corresponding fatty acid. The evenly spaced progressive bands near 1350 – 1110 cm⁻¹, which are

characteristic of the hydrocarbon chain, remain unchanged on preparing the soap from acid.

The absorption bands observed near 2640 – 2650, 1700, 940 – 945, 680 – 690 and 550 cm⁻¹ in the spectrum of myristic and stearic acid has indicated the presence of localized -COOH group in the form dimeric structure and existence of intermolecular hydrogen bonding between two molecule of myristic and stearic acid.



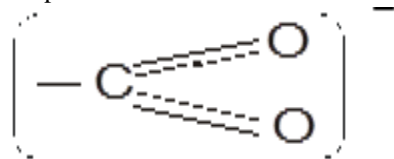
[Dimeric structure of myristic and stearic acid]

Where, R = C₁₃H₂₇ and C₁₇H₃₅ for myristic and stearic acid.

The absorption bands observed near 2640 – 2650, 1700 and 940 – 945 cm⁻¹ corresponding to the – OH groups in the spectrum of myristic and stearic acid have completely disappeared in the spectra of potassium, manganese soaps of myristic and stearic acid. The absorption maxima corresponding to 680 – 690 and 550 cm⁻¹ in the spectrum of myristic and stearic acid have been assigned to the bending and wagging modes of vibrations of carbonyl group of both acid molecules. These assigned frequencies are not observed in the spectra of potassium and manganese soaps. The infrared spectra of potassium, manganese and iron soaps shows marked differences with the spectra of corresponding myristic and stearic acid in some spectral regions.

The characteristic vibrations of myristic and stearic acid were found completely absent in the spectra of potassium, manganese soaps. The complete disappearance of carbonyl frequency in the vicinity of 1700 cm⁻¹ and the appearance of absorption bands of carboxyl group corresponding to the symmetric vibrations of carboxylate ion near 1415 – 1445, 1430 – 1415, 1350 – 1440 cm⁻¹ and for asymmetric vibrations 1540 – 1560, 1550 – 1560 and 1540 – 1560 cm⁻¹ in potassium and manganese soaps, respectively, 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

ionized carboxyl group is retained in these metal soaps.



(Resonance hybrid structure of carboxylate ion)

It may be pointed out that the metal to oxygen bonds in the ionized structure of these soaps should have an ionic character. The band observed near 440 – 460 cm⁻¹ assigned to Mn – O bond in the spectrum of manganese soaps of myristic and stearic acid.

Table 1.1-IR ABSORPTION FREQUENCIES (cm⁻¹) TOGETHER WITH THEIR ASSIGNMENTS

| S. No. | Assignment | Myristic acid | Potassium myristate | Manganese myristate |
|--------|--|---------------|---------------------|---------------------|
| 1. | CH ₃ , C – H asymmetric stretching | 2950 vw | 2940 w | 2920 vw |
| 2. | CH ₂ , C – H asymmetric stretching | 2920 vs | 2910 vs | 2900 w |
| 3. | CH ₂ , C – H symmetric stretching | 2850 s | 2850 vs | 2855 vs |
| 4. | OH, stretching | 2640 vw | -- | -- |
| 5. | C=O, stretching | 1700 vs | -- | -- |
| 6. | COO ⁻ , C – O asymmetric stretching | -- | 1600 w | 1560 m |
| 7. | CH ₂ , deformation | 1460 m | 1450 w | 1450 w |
| 8. | COO ⁻ , C – O symmetric stretching | -- | 1420 s | 1430 vw |
| 9. | CH ₂ (adjacent to COOH group) deformation | 1410 w | -- | -- |
| 10. | CH ₃ , symmetric deformation | 1370 w | -- | -- |
| 11. | Progressive bands (CH ₂ twisting and wagging) | 1350 – 1180 w | 1185 – 1100 w | 1880 – 1080 s |
| 12. | CH ₃ , rocking | 1120 w | 1100 w | 1080 s |
| 13. | OH, out of plane deformation | 940 m | -- | -- |
| 14. | CH ₂ rocking | 730 w | 720 s | 720 vs |
| 15. | COOH, bending mode | 690 m | -- | -- |
| 16. | COOH, wagging mode | 550 | -- | -- |
| 17. | Mn – O bond | -- | -- | 440 vs |

Table 1.2-IR ABSORPTION FREQUENCIES (cm⁻¹) TOGETHER WITH THEIR ASSIGNMENTS

| S. No. | Assignment | Stearic acid | Potassium stearate | Manganese stearate |
|--------|--|---------------|--------------------|--------------------|
| 1. | CH ₃ , C – H asymmetric stretching | 2950 s | 2950 ms | -- |
| 2. | CH ₂ , C – H asymmetric stretching | 2920 vs | 2910 vs | 2880 s |
| 3. | CH ₂ , C – H symmetric stretching | 2860 s | 2860 s | 2860 s |
| 4. | OH, stretching | 2650 w | -- | -- |
| 5. | C=O, stretching | 1700 vs | -- | -- |
| 6. | COO ⁻ , C – O asymmetric stretching | -- | 1560 vs | 1550 vs |
| 7. | COO ⁻ , C – O symmetric stretching | -- | 1440 m | 1445 s |
| 8. | CH ₂ , deformation | 1465 ms | 1465 ms | 1460 s |
| 9. | C – O, stretching, OH in plane deformation | 1430 vs | -- | -- |
| 10. | CH ₂ (adjacent to COOH group) deformation | 1410 m | -- | -- |
| 11. | CH ₃ , symmetric deformation | 1370 w | 1370 m | 1340 s |
| 12. | Progressive bands (CH ₂ twisting and wagging) | 1350 – 1100 m | 1320 – 1190 m | -- |
| 13. | CH ₃ , rocking | 1110 w | 1110 w | 1110 w |
| 14. | OH, out of plane deformation | 940 w | -- | -- |
| 15. | CH ₂ rocking | 720 s | 715 ms | 710 s |
| 16. | COOH, bending mode | 680 w | -- | -- |
| 17. | COOH, wagging mode | 550 w | -- | -- |
| 18. | Mn – O bond | -- | -- | 460 vs |

FIG. 1.1 : INFRARED ADSORPTION SPECTRUM OF MANGANESE MYRISTATE

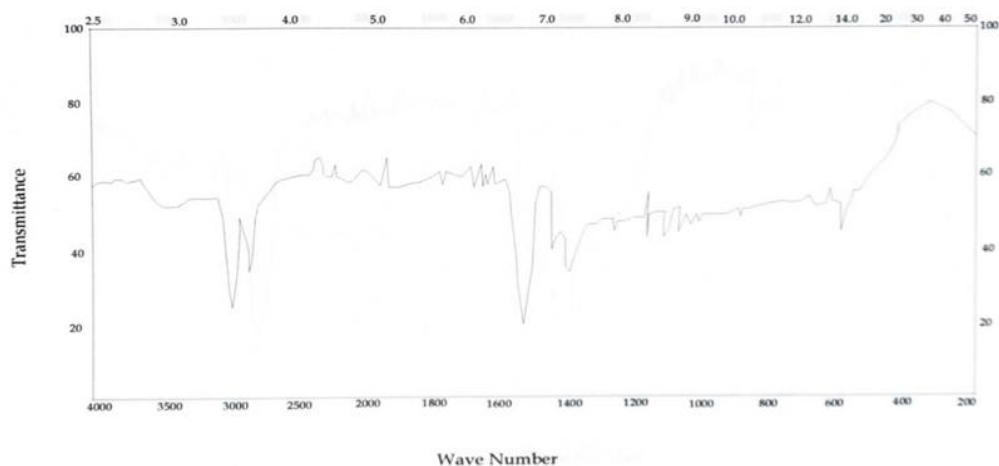
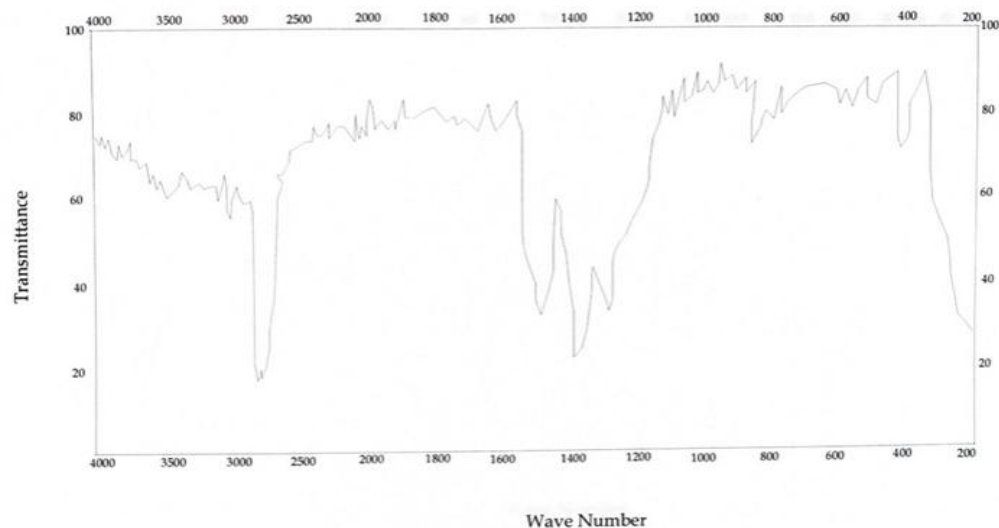


FIG. 1.2 : INFRARED ADSORPTION SPECTRUM OF MANGANESE STEARATE



CONCLUSION

The results confirm that:

- The formation of the soaps from corresponding acids does not alter the absorption maxima

characteristic of the aliphatic portion of the acid molecule.

- The fatty acids in the solid or liquid state exist with dimeric structure through hydrogen bonding between the carboxyl group of two acid molecules

whereas the metal-to-oxygen bonds in these metal soaps are partially ionic in character.

- The soap molecules retain the resonance character of carboxyl group
- The infrared spectra of Potassium and manganese soaps do not show any absorption maxima in the region of $3500 - 3300 \text{ cm}^{-1}$, which confirms the absence of any co-ordinate water molecules in these soap molecules.

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