SUMMARY

This thesis deals with the synthesis, physico-chemical characterization and application of ammonium and potassium carboxylate as herbicides against moss and weeds. Potassium laurate, potassium myristate, ammonium laurate and ammonium myristate have been synthesized and investigated its different physical and chemical properties like IR, pH, conductivity, ultrasonic velocity and assessed its application as herbicides on weed and moss, also used ANOVA technique to compare the efficacy of prepared herbicides. The thesis comprises eight chapters and the content of each chapter a concise is delineated here under.

CHAPTER-1

INTRODUCTION

The survey of earlier work in this field covers the period from early fifties to the middle of 2013. It also presents the details regarding the characteristics of weed and moss plant, classification of pesticides, classification of weed and moss, chemical and physical control of weed and moss, their uses, commonly used herbicides, its uses, which one is effective which one is not, whether it is a contact or systemic, selective or non-selective, pre-plant or post emergent herbicides, mechanical, biological, cultural control of weed and moss, transport, distribution and degradation of pesticides in the environment (air, water, soils, humans), health effects and references.
CHAPTER-2

Review of literature and object of the present work

The review of literature of the present work is presented justifying the choice and significance of the work reported in the thesis.

OBJECTIVES

6. Synthesize and characterize the carboxylates of K and NH₄. They are-
   - Ammonium laurate (C₁₁H₂₃COONH₄)
   - Ammonium myristate (C₁₃H₂₇COONH₄).
   - Potassium laurate (C₁₁H₂₃COOK).
   - Potassium myristate (C₁₃H₂₇COOK).

7. Obtain structural information of (C₁₁H₂₃COONH₄, C₁₃H₂₇COONH₄, C₁₁H₂₃COOK and C₁₃H₂₇COOK) in solid state from IR spectra.

8. Determine the solubility of carboxylates of K and NH₄ in polar and non-polar solvents and evaluate various thermodynamic parameters for the solutions of carboxylates by conductometric and acoustic measurements.

9. Correlate the properties and structure of carboxylates with their applications as herbicide on weeds (Parthenium hysterophorus) and moss (Indian moss).

10. Compare the efficacy of potassium carboxylates (laurate and myristate) and ammonium carboxylates (laurate and myristate) as herbicides on weeds and moss through the statistical tool, ANOVA Technique.
CHAPTER-3

Experimental methods and techniques

This chapter describes the general experimental methods, various physical techniques that were employed in the characterization and preparation of potassium and ammonium soaps (laurate and myristate), structure, specification and equation. The following techniques were used:

a. pH by pH meter

b. Electrical Conductivity measurements by Conductivity meter

c. Infrared Spectral Analysis by FTIR

d. Ultrasonic Velocity by Ultrasonic Interferometer

e. Application technique of potassium carboxylate (laurate and myristate) and ammonium carboxylate (laurate and myristate) on weeds and moss plant.

CHAPTER-4

Results and Discussion

This chapter consists of datas and interpretation of different technique which were used for the analysis of our experiment one by one. The infrared absorption spectra of fatty acids (lauric acid and myristic acid) and of corresponding potassium and ammonium soaps were obtained with “Perkin Elmer, Spectrum RX-1 in region 4000cm⁻¹, 400 cm⁻¹ using KBr disc method. The absorption bands observed near 2650-2640, 1700, 950-930, 690-550 cm⁻¹ in the spectra of fatty acids have indicated
the presence of localized CH$_2$ group in the form of dimeric structure and the existence of intermolecular hydrogen bonding between two molecules of the acid.

The absorption bands observed near 2650-2640, 1700 and 950-930 cm$^{-1}$ corresponding to the -OH group in the spectra of fatty acids have completely disappeared in the spectra of corresponding potassium and ammonium carboxylates. The absorption maxima observed near 690 cm$^{-1}$ and 550 cm$^{-1}$ in the spectra of fatty acids are assigned to the bending and wagging modes of vibrations of the carboxyl groups of the fatty acids molecules which is not observed in the spectra of potassium and ammonium soaps.

The infrared spectra of potassium and ammonium carboxylates show marked differences with the spectra of corresponding fatty acids in some spectral regions. The complete disappearance of two absorptions bands of carbonyl group corresponding to the symmetric and asymmetric vibrations of carboxylates ion near 1470-1440 cm$^{-1}$ and 1625-1560 cm$^{-1}$ respectively in the spectra of potassium carboxylate indicates that there is a complete resonance in the C-O bonds of carbonyl group of the carboxylate molecules and the two bands become identical with force constant 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 carboxylates.

The result confirm that the fatty acids exist with dimeric structure through hydrogen bonding whereas the metal to oxygen bonds in these metal
carboxylates are ionic in character. It is also confirmed that the molecules of carboxylates retain the resonance character of the carboxyl group.

The infrared spectra of potassium and ammonium carboxylates do not show any absorption maxima in the region of 3500-3300 cm$^{-1}$ which confirms the absence of any coordinated water molecules in these carboxylates molecules.

The specific conductance, k of the solution of soap (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) in distilled water increases with increasing soap concentration, C. The increase in specific conductance may be due to ionization of metal carboxylates (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) into simple metal cations ($K^+$ and $NH_4^+$) and fatty acid anions ($C_{11}H_{23}COO^-$, $C_{13}H_{27}COO^-$) in dilute solution and due to the formation of ionic micelles at higher soap concentration. The plots of specific conductance, k Vs soap concentration, C of (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) in distilled water are characterized by an intersection of two straight line at a definite soap concentration corresponding to the CMC of soap in these solution. The results show that the values of the CMC decrease with increasing tail of soap. The micellization occurs when the energy released as a result of aggregation of hydrocarbon chains of the monomers is sufficient to overcome the electrical repulsion between the ionic head groups and to balance the decrease in entropy accompanying aggregation. The CMC increases with the increase in soap concentration since the kinetic energy of the monomers increases with concentration.
The molar conductance, \( \mu \) of the solution of soap (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) decreases with increasing soap concentration. The decrease in molar conductance is attributed to the combined effect of ionic atmosphere, solvation of ions and decrease of mobility and ionization with the formation of micelles. The plot of molar conductance, \( \mu \) Vs \( C\mu^2 \) are not linear which indicates that the soap behaves as a weak electrolyte in distilled water.

The values of the degree of dissociation, \( \alpha \) at different soap concentrations (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) have been calculated by assuming it as equal to the conductance ratio, \( \mu / \mu_0 \) and using the value of \( \mu_0 \) obtained from the plots of \( C\mu^2 \) Vs \( \mu \). The values of degree of dissociation, \( \alpha \) decreases with increasing soap concentration (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) which shows that the potassium and ammonium soaps behaves as a weak electrolyte in these solutions.

The values of the dissociation constant, \( K \) have been calculated. The calculated values of dissociation constant, exhibit a drift with increasing soap concentration which may be partly due to the fact that the degree of dissociation, \( \alpha \) is not exactly equal to the conductance ratio \( \mu / \mu_0 \) but mainly due to the activity coefficients of the ions are not equal to unity. The deviation at higher soap concentrations may be due to the failure of Debye-Hückel’s, activity equation.
It is therefore, concluded that potassium soaps [laurate and myristate] and ammonium soaps [laurate and myristate] are weak electrolytes in distilled water.

The ultrasonic velocity, \( v \) of the solution of potassium (laurate and myristate) and ammonium soap (laurate and myristate) in distilled water increases with increasing soap concentration. The variation of ultrasonic velocity, \( v \) with soap concentration, \( C \) can be expressed in terms of the concentration derivatives of density, \( \rho \) and adiabatic compressibility, \( \beta \).

The result indicates that the density increases while adiabatic compressibility decreases with increasing soap concentration and so the quantity \( (\partial \rho / \partial C) \) is positive while \( (\partial \beta / \partial C) \) is negative. Since, the values of \( [1/\beta (\partial \beta / \partial C)] \) are larger than the values of \( 1/ \rho (\partial \rho / \partial C) \) for the soap solution, the concentration derivatives of velocity; \( (\partial v/\partial C) \) is positive which is in agreement with the results of other workers reported for electrolytic solution.

The adiabatic compressibility, \( \beta \) for the solution of soap (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) decreases with increase in soap concentration. The decrease in adiabatic compressibility is attributed to the fact that the soap molecules in dilute solutions are ionized into simple metal cations, \( K^+ \) and \( NH_4^+ \) and anions (laurate and myristate). These ions in solutions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of ions and thus the internal pressure increases which lowers the compressibility of solutions i.e the solutions become harder to compress.
The plots of adiabatic compressibility $\beta$ Vs soap concentration, $C$ indicate a break at a definite soap concentration which corresponds to the CMC of the potassium (laurate and myristate) and ammonium soap (laurate and myristate).

The values of intermolecular free length, $L_f$ decreases while those of specific acoustic impedance, $Z$ increases with the increase in soap concentration, $C$ which can be explained on the basis of lyophobic interaction between the soap and solvent molecules which increases the intermolecular distance leaving relatively wider gaps between the molecules and thus becoming the main cause of impediment to the propagation of ultrasound waves.

The values of the solvation number, $S_n$ at first decrease (up to the CMC) and exhibit an increase above the CMC, which may be due to more intake of solvent molecules above the CMC to reduce repulsive forces acting between heads of ionic micelles.

The ultrasonic velocity results confirm that there is a significant interaction between the solute-solvent molecules in dilute solutions and the carboxylate molecules do not aggregate appreciably in dilute solutions. The values of the CMC for potassium carboxylate are in agreement with those obtained by other physical measurements.

There are many herbicides available for the control of weeds and moss, but all of them have negative impact on the crops as well as in environment. Hence an attempt has been made to develop an eco-friendly economical product for integrated herb management strategy. Therefore, the present study was carried out to evaluate
the efficiency of soap based herbicide containing potassium laurate, potassium myristate, ammonium laurate and ammonium myristate on weed plants as there is an urgency in the search for eco-friendly alternative approaches for the removal of weed and moss.

These four soap based herbicides of different concentration were prepared and sprayed on the weeds. It can be used as a good herbicide because it does not have negative impact on the crops. Parthenium seeds were sown in a chamber which is divided into four sections and first plant on every section was kept as control and first, second, third, fourth, section were sprayed with potassium laurate, potassium myristate, ammonium laurate and ammonium myristate respectively of various pH and concentrations.

These four soap based herbicides of different concentration were prepared and sprayed on the weed and moss. Parthenium moss plants were grown in chamber of 24x30 cm diameter each containing 5 kg of sandy loam soil having organic matter 0.9%, pH 8.2, nitrogen 0.05%, available phosphorous 14 mg kg\(^{-1}\) and available potassium 210 mg kg\(^{-1}\),were arranged in a completely ordered manner under natural conditions. There was fifteen plants of parthenium and moss in each section of chamber.

The plants of first section were treated with soap solution of potassium laurate, second section of the row was treated with the soap solution of potassium myristate, third and fourth section of the row were treated with the soap solution of
ammonium laurate and ammonium myristate respectively. First plant on every section was kept as control.

Fourteen spray solutions of potassium laurate in water of different concentration having pH 4.2-8.8 have been prepared and sprayed on weeds.

The first section of the chamber was control and was healthy. The solution of potassium laurate having pH 5.8 was found to be more effective for the control of weed as the mortality of this solution was the highest among various solutions of potassium laurate.

The second, third and fourth plant of second section were treated with the herbicidal solution containing potassium myristate having pH 4.6-5.4. Sprays were applied bi-weekly in the beginning and weekly (after four weeks of application). After bi-weekly application the leaves were found to be unhealthy but plant needed frequent application of spray.

In our experiment we conclude that, the liquid spray herbicide contains potassium myristate having pH 5.8 is found to be most effective than other solutions of potassium myristate as their mortality was high as 58.9%. They cause “leaf burning” and eventually death of the plant.

In the, third and fourth plant of third section was subjected to the herbicide solution of ammonium laurate having pH 8.93-7.10. Even after the fourth week of bi-weekly application the weed growth remained the same as the mortality of these solutions were very low, the plant needed frequent application for the control of weed.
In our experiment we conclude that, the liquid spray herbicide, ammonium laurate of pH 4.33 is found to be more effective than other solutions of ammonium laurate as their mortality was high as 60%

The advantage of ammonium carboxylate is that it decomposes within a short period after application. This is desirable as it allows crops which may be affected by the herbicide to be grown on the land in future seasons.

First weed plant in the first section was control, healthy and grew normally. In the second and third plant of fourth section which were subjected to the herbicide solution of ammonium myristate having pH 8.93-8.87. After bi-weekly in the beginning and weekly application, these solutions do not have any significant impact on the plant as their mortality was very low. (30-32%)

However, herbicides like ammonium carboxylates with low residual activity often do not provide season-long weed control. Potassium and ammonium carboxylates are post-emergence herbicide. It performs by its increasing herbicide activity by absorption and reducing surface tension. Thus helps carboxylate solution to spread evenly and to get absorbed on the weed plant. Potassium carboxylates are a contact herbicides, it kills the weed part by contact by the chemical by destroying cell membranes. They appear to burn plant tissues within days of application. Good coverage of the plant tissue is necessary for maximum activity of these herbicides, Muniappa T.V, et.al (1980).

In the present study since the test herbicides were found effective even at a lower dosage, there are comparatively less environmental risks in their usage.
Furthermore, since weed did not regenerate after death of the top that also increases the importance of these herbicides for their selections against parthenium. Thus in light of the results of the present study it is recommended that parthenium should be managed using lowest doses of these herbicides especially those which take comparatively less time to kill this alien weed species.

Mosses were sown in a lawn, which is divided into four sections and first plant on every section was kept as control and first, second, third, fourth, section were sprayed with potassium laurate, potassium myristate, ammonium laurate and ammonium myristate respectively of various pH concentrations.

These four soap based herbicides of different concentration were prepared and applied on moss plant. There were fifteen moss plants in each section.

Suspensions of four chemical herbicides namely potassium laurate, potassium myristate, ammonium laurate and ammonium myristate of different pH and concentrations were prepared in water. Different doses of test herbicides were sprayed with a hand atomizer on 1 and 2 weeks grown moss plants. The control treatment was sprayed with water. Effect of herbicides were monitored till all the plants in herbicidal treatments become dead.

The plants of first section were treated with soap solution of potassium laurate, second section of the row was treated with the soap solution of potassium myristate, third and fourth section of the row were treated with the soap solution of ammonium laurate and ammonium myristate respectively. First plant on every section was kept as control.
Fourteen spray solutions of potassium laurate of different concentration having pH 4.6-8.8 have been prepared and sprayed on moss.

The first section of the first plant of the lawn was control and was healthy. The second, third, fourth, fifth, sixth, seventh, eighth, ninth, tenth, eleventh, twelfth, thirteenth and fourteenth plants which were treated with potassium laurate solution having pH 4.6-8.8. Sprays were applied bi-weekly in the beginning and weekly after four weeks of application. After bi-weekly application the mosses were found healthy and it needed frequent application of spray. So, the soap based solution of potassium laurate having pH 4.6-8.8 needs frequent application. The mortality of this formulation was low (20.6-9.6%).

The second, third, fourth, fifth, sixth, seventh and ninth ,tenth, eleventh, twelfth, thirteenth and fourteenth plant of second section were treated with the herbicidal solution containing potassium myristate having pH 4.6-8.8. Sprays were applied bi-weekly in the beginning and weekly after four weeks of application. After bi-weekly application the leaves were found healthy but plant needed frequent application of spray and also less effective. Even after the fourth week of application there were not much improvement on the structure of the plant as their mortality was low. (27.2-10.1%)

In the second, third, fourth, fifth sixth, seventh, eighth, ninth, tenth, eleventh, twelfth, thirteenth and fourteenth plant of third section was subjected to the herbicide solution of ammonium laurate having pH 4.33-8.93. (10.1-27.7%). Even after the fourth week of bi-weekly application the moss growth remained the same.
In the present study since the most of the test herbicides were found to be less effective, though it could kill a very small fraction of moss plant. The recurrence of the moss with the availability of the moisture, decomposition of herbicide within a short period after application and the lack of rain fastness made this herbicide a less effective to treat moss and to control its population.

Descriptive statistics for mortality due to different carboxylates solution (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) reveals that average mortality by potassium laurate, potassium myristate, ammonium laurate and ammonium myristate is 44.0±9215, 42±1177, 40±1326 and 47±1388 respectively.

ANOVA to compare mortality on weed due to different soap solution (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) concluded that there is no significant difference between the mortality on weed due to different test solution (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) as P>0.05. All these carboxylates are equally effective herbicides to destroy weeds.

Descriptive statistics for mortality on moss plant due to different soap solution (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) showed that average mortality by potassium laurate, potassium myristate, ammonium laurate and ammonium myristate is 19.7±6125, 26.7±1891, 19.6±7718 and 22±6316 respectively.
ANOVA to compare mortality on moss due to different soap solution (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) concluded that there is a significant difference between the mortality on moss due to different solution (potassium laurate, potassium myristate, ammonium laurate and ammonium myristate) $P<0.1$

Though test herbicidal solution are not good enough to kill moss permanently, but ANOVA technique show that on comparing the efficacy of four of these herbicides, potassium myristate is better option as a herbicide on moss than other carboxylate solution.