CHAPTER - I

INTRODUCTION

1.1 GENERAL INTRODUCTION

Electrochemistry in fused salt media has definite advantages over electrochemistry in aqueous and non-aqueous media. The development of chemistry, in the beginning, has been shaped largely on the use of water and other room temperature liquids as solvents. This fact and the influence of the conventional chemistry has impeded the progress in many preparative problems. Actually molten salts are often much better and more versatile solvents than room temperature solvents, being capable of dissolving such diverse substances as organic compounds, metals, oxides and non-metallic elements. In fact molten salts are now extensively used in electrometallurgy, in the field of nuclear technology as coolants in reactors, in fuel reprocessing systems, in salt extraction systems etc.

Modern electrochemistry has introduced many organic liquids as solvents and this has extended the range of potentials which could be applied. Even there the limitation was temperature range which normally would have to be kept within 60 - 70 K from the room temperature. The use of molten salts have allowed the use of as large a temperature range as 500 K and temperatures as low as 362 K and as high as 1273 K. This together with the fact that the range of potential is variable from 0 to -3 V, a range much higher than what can be obtained with organic solvents, has embellished the use of molten salts as electrochemical solvents. These molten salts have higher electrical conductivities arising from their high degree of ionisation and mobilities of ions. Other properties are also important such as faster electrode kinetics indicated by high exchange current densities without the need to use excessive cell voltage, absence of H^+ and OH^- ions from the solvent enabling electrolytic recovery of metals that are high in electrochemical series. The above mentioned advantages make molten salts versatile electrochemical solvents.

The molten salts have also been used with advantage in not only electrochemistry, but also in electroanalytical chemistry. However most of the work has been done working with high temperature eutectics. Excellent reviews of such work are available; a short summary of the work done in the field will be given below.

1.2 ELECTROANALYTICAL CHEMISTRY IN FUSED SALTS

Thomas B. Reddy[1] has made an extensive review of the electrochemistry of molten salts. He has shown that studies of transport processes have served to elucidate the nature of some ligands. The application of modern techniques to study the electrode kinetics in fused salts has proved necessary because of high values of exchange currents for electrode reactions at high temperature. Electroanalytical methods have been used to the study of electrode processes under conditions where the mass transport is limiting. Fused salt electrolytic procedures hold considerable promise for preparation of several compounds, metal and alloys. There has been much recent research on high temperature power systems. Advances have been made in the field of fused salt fuel cells but many practical engineering problems must be solved before long term trouble-free operation with inexpensive fuel is possible. Thermally regenerated galvanic cells using molten salts are in early stage of development.

Gaur and Sethi(2) in an extensive review have observed the methodology of polarography in molten salts. They have described the various methods of preparation of solvents, indicator electrodes and reference electrodes. The theory of polarography in molten salts in unstirred and stirred solutions has been given in detail, as well as the technique of oscilloscopic polarography. Various applications of this method have been cited together with studies of polarography of complexes in molten salts, anodic, derivative, oscillographic polarography and polarography with rotating disc electrode.

Electroanalytical chemistry of molten salts has been extensively reviewed by Liu, Johnson and Laitinen(3). The authors have reviewed the subject thoroughly with respect to polarography, chronopotentiometry, titrimetry and coulometry. On the theoretical side, they have paid emphasis on electrical double layer and electrode kinetics.

An excellent review by Inman[4] on the subject covers the work in the field upto 1968 and larger part of 1969. Studies have included transport processes, determination of transport numbers, self-diffusion coefficients and electrical conductances. Processes at equilibrium have been studied in detail with respect to electrode potentials and electromotive forces. Solubility and complex formation have also been studied in detail. The acidic and basic characteristics of these melts have been exploited in the potentiometirc titrations. In non-equilibrium systems, various techniques of polarography, voltammetry, chronopotentiometry etc. have been used.

Laitinen[5] briefly reviewed polarography in melts. The subject has been studied in detail with reference to gas electrodes and passivation.

Another field in which lot of work has been done is the electrodeposition of refractory metals. Again in the field of electrolysis, batteries and fuel cells, also molten salts have found application. The theoretical side has been restricted to double layer and rapid charge transfer processes.

1.3 ELECTROANALYTICAL CHEMISTRY IN NITRATE MELTS

The literature on the chemistry, electrochemistry and electroanalytical chemistry of fused salts or melts is too extensive to be quoted here fully. No justice can be done to this subject unless a full review of the work is reported. And this will be out of context in the present case. Hence the present review is restricted to the literature on nitrate melts.

Molten nitrates have been widely used as solvents for electrochemical studies. The low melting characteristics coupled with the relatively non-hygroscopic nature of nitrates have made these melts popular. The disadvantages of using these melts are a limited potential span and their oxidising properties. The purity of the melt is easily obtained by simply melting the dried recrystallised salts under vacuum and continuing the evacuation for several hours.

Inman et. al[6-8] have studied the nitrate melts extensively using dropping mercury electrode. In the first part of the series half-wave potentials and diffusion coefficients for the reduction of Pb^{++}, Cd^{++}, Ni^{++} & Co^{++} have been determined at a dropping mercury electrode in molten (Li, Na, K) NO_3 eutectic at 418 K. The results were compared with those obtained previously by other workers. The discrepancies, where they exist, were related to the effects of appreciable quantities of water, arising from the use of incompletely dried solvents and solutes added as hydrates, and chloride present in the melt used in previous investigations.

In the second part of the series, they studied the stability constants of halide complexes in (Li, Na, K) NO_3 eutectic. Some preliminary experiments were carried out in melts containing fluoride and cyanide ions. The stability constants of chloro and bromo complexes of Ni^{++}, Co^{++}, Pb^{++} and Cd^{++} were calculated. They used the method of ' half wave potential shift ' to measure these stability constants of complexes.

In the third part of the series, they studied the adsorption of complex ions at dropping mercury electrode. The systems Cd^{++}, Pb^{++}, Co^{++} and Ni^{++} with Cl^-, Br^- ion ligands in (Li, Na, K) NO_3 at 418 K. It was difficult to measure the stability constants because of the formation of polarographic maxima. It was concluded that the maxima was pronounced as a result of adsorption of complex ions on mercury surface.

Gaur[9] has studied the association equilibria with precipitation of single and combined halide complexes with Ag^+, Pb^{++} and Cd^{++} in melts of molten alkali and alkaline earth nitrates.

Barker and Faircloth[10] have made the application of square-wave polarograph to study the electrode reactions taking place at a dropping mercury electrode in molten nitrate electrolyte. The diffusion coefficients of a number of ions which are reversibly reduced have been measured and the variation, with potential, of the differential double layer capacity of the mercury surface in contact with the melt has been investigated.

Francini, Martini and co-workers[11-17] have studied the classical and linear sweep polarography with dropping mercury electrode at temperatures upto 543 K. Their review[14] on molten alkali metal nitrates includes an assessment of method of determining stability constants. The reduction of Tl^{+}, Cd^{++}, Pb^{++}, Zn^{++}, Ni^{++}[11] and Eu^{++}[13] in (Li, Na, K) NO_3 melt, Tl^{+}, Pb^{++} and Cd^{++} and the oxidation of Cl^{-}, Br^{-} and I^{-}[12] in (Na, K) NO_3 melt were described and diffusion data presented for each system. All the systems obeyed the simple theory at sweep rates upto $10\,V\,s^{-1}$, although Zn^{++} and Ni^{++} in the ternary melt and Pb^{++} and Cd^{++} in the binary melt began to show some irreversibility at this point.

Braunstein and co-workers[18,19] have extensively studied associated equilibria in molten nitrates. Lammers and Braunsten[18] determined the association constants for the complexes formed between cadmium ions and bromide ions in molten equimolar $LiNO_3 - KNO_3$ containing various concentrations of water at 391 K and 441 K. The decrease in association constants when water content was increased was attributed by them to the competition between hydration and association equilibria in aqueous melts. Flaherty and Braunstein[19] determined the association constants for complexes formed between Cd^{++} and Cl^- ions in molten $LiNO_3$ and in mixture of $LiNO_3 - KNO_3$. This was worked out from measurement of solubility of silver chloride.

Mazzocchin, Bombi and Fiorani[20] determined the standard electrode potentials of Hg/Mg^{I} and Hg/Mg^{II} in molten $(Li, K)NO_3$ in the temperature range of 420 - 480 K. The Hg^{I} oxidation state at 450 K was slightly more stable than in water at room temperature. The difference increased if data given were extrapolated to room temperature. They also observed that equilibrium constant for the reaction $Hg + Hg^{+2} \rightleftharpoons Hg_2^{+2}$, if extrapolated to room temperature, was more than one order of magnitude different from that in water.

Sacchetto, Bombi and Fioran[21] determined the standard potential for redox couples I_2/I^-, I_2/I_3^- in molten $(Li, K)NO_3$ in temperature range of 435 - 490 K, by employing cells of the following type

$$Pt / Ag / \frac{AgNO_3}{(Li, K)NO_3} / \text{glass} / \frac{KI}{(Li, K)NO_3} / I_2(g) / C / Pt$$

They also determined the equilibrium constants for the reactions

$$I_2(g) \rightleftharpoons I_2 \text{ (soln.)}$$
$$I_2(g) + I^{-1} \rightleftharpoons I_3$$
$$I_2(\text{soln.}) + I^- \rightleftharpoons I_3^-$$

and thermodynamic parameters (ΔG^o, ΔH^o, ΔS^o). Comparison was made with the results obtained in molten nitrates by other workers.

Forcheri and Monfrini[22] have measured the mobilities of some alkali metals and alkaline earth metals in variety of nitrate melts. They employed thin layers of melts supported by alumina powder sprayed onto a non-porous alumina support. No correction was made for labyrinth factor. However their results agreed with those obtained by other techniques. Two interesting observations were made. In the ternary eutetic (Li, Na, K) NO_3 containing one mole of KCl at 433 K, two ill defined bonds of ^{36}Cl were obtained. On repeating the experiment at 513 K these two bonds were not observed, only that due to normal ^{36}Cl migration was seen. The results were tentatively interpreted in terms of ionic association involving ^{36}Cl. It is unlikely that this is an adsorption effect since no adsorption of ^{36}Cl on γ-Al_2O_3 is reported.

Berlin et. al[23] observed that migration of Cd^{++} ion in (Li, Na, K) NO_3 melt containing 0.8 M KCl and 0.1 M $Cd(NO_3)_2$ was towards anode, whereas in pure melt the cadmium migrated to the cathode. The results are in agreement with other studies on such a reciprocal system where complex ions are postulated.

Lovering and Oblath[24] have studied the influence of water on Ni (II) /Ni (Hg) electrode process in molten $LiNO_3$ - KNO_3 eutectic. The D - C pulse, differential pulse and linear sweep polarographic methods have been used to characterise the Ni (II) / Ni (Hg) reduction as a function of water content in (Li - K) NO_3 eutectic melt at 418 K .

Miles and Fletcher[25] have studied the cation effects on the electrode reduction of molten nitrates. Cyclic voltammetric, potentiostatic and galvanostatic methods have been employed using a platinum electrode. The cation of nitrate salt plays an important role in reduction reaction as well as in determining the ultimate fate of the oxide ion produced. Nitrate reduction occurs most readily in $LiNO_3$ melts and Li_2O formed appears to be relatively stable. Overvoltages for nitrate reduction increases with increasing size of metal cation involved and the oxide ions produced by the reduction become more prone to oxidation to form peroxide or superoxide. The rate of removal of water by purging the nitrate melt with helium gas was monitored by the water - wave on platinum. Surprisingly no water - wave was detected using a nickel electrode. The solubilities of several substances were determined in $LiNO_3$ and KNO_3 and compared with ideal solubility calculations.

S. Casadio et. al[26] studied the reduction of Cd^{++} ions at platinum microelectrodes in fused alkali nitrates.

Current reversal chronopotentiometry was used to investigate the cathodic reduction of Cd^{++} in molten (Na, K) NO_3 at different temperatures. The high rate of irreversible oxidation of cadmium metal by the nitrate solvent made it difficult to interpret data quantitatively.

W.E. Triaca[27] studied electrochemical oxidation of iodide dissolved in (Na, K) NO_3 eutectic melt on platinum rotating disc electrode. The E / I curves related to the electrochemical oxidation of iodide dissolved in molten nitrates involves two anodic waves. The first corresponds to a reversible two electron process. A definite ratio between the anodic limiting currents is established suggesting that the second anodic wave is not independent from the first one. The parameters related to the diffusion of the species participating in the reaction are evaluated.

Susic et. al[28] studied the polarographic behaviour of some metal ions in molten (Li, K) NO_3 in presence of complexone - III.

Narayan and Valsraj[29] studied the reduction of Pb^{++} ion in molten $Ca(NO_3)_2.4H_2O$ and the influence of bromide, chloride and thiourea on their reduction. They also investigated the electrochemistry in molten acetamide.

1.4 DISCREPANCIES IN THE REDOX PROCESS OF METALS IN NITRATE MELTS

In spite of the obvious advantages cited above, of using nitrate melts as solvents in electroanalytical chemistry, many fundamental aspects of the problem are still controversial. This is, primarily, due to the fact that the nitrate ion of the melt itself often takes part in electrolysis process. The role of other electroactive cations, other than those which are present in the melt itself, is shrouded in controversy. The nitrate ions in the melt often form complexes with these electroactive ions and may get reduced, thus complicating the issues. A comprehensive study of "oxide chemistry" in molten sodium potassium nitrate eutectic was made by Zamborin and Jordan[30]. In this study, the results were critically dependent on the moisture in the melt and the container material. They used a rotating electrode in a specially designed cell made from platinum; the moisture level was decreased to less than 10^{-6} M to avoid the side reactions of oxide ions with silica and water. Oxide ions added to the melt as Na_2O were almost completely converted to peroxide and superoxide ions in accordance with the equation

$$NO_3^- + O_2^- \rightleftharpoons O_2^{2-} + NO_2^- \qquad 1.1$$

$$O_2^{2-} + NO_3^- \rightleftharpoons 2\,O_2 + 2NO_2^- \qquad 1.2$$

The presence of O_2^{--}, O_2^- and NO_2^- was deduced from the comparison of the voltammetric results with the voltammograms obtained by dissolving Na_2O_2, KO_2 and $NaNO_2$, respectively, in the pure melt. The peroxide ion could be converted almost completely to superoxide ions by bubbling oxygen through the melt.

$$O_2^{--} + O_2 \rightleftharpoons 2\,O_2^-$$

In view of the work of Zambonin and Jordon, previous and some recent results[31-33] pertaining to the behaviour of oxide ions in molten nitrates are apparently incorrect.

Zambonin[34] carried on further studies in pure molten sodium potassium nitrate eutectic and in the melt containing species produced in situ by massive electrolysis. The temperature range was 500 - 555 K and he concluded that the electrochemical reduction of NO_3^- at a platinum cathode can be substantiated by the following processes.

$$NO_3^- + 2\,e^- = NO_2^- + O^{2-} \qquad 1.3$$

$$O^{2-} + 2Na^+ = Na_2O \text{ (solid.)} \qquad 1.4$$

$$O^{2-} + NO_3^- = NO_2^- + O_2^{2-} \qquad 1.5$$

$$O_2^{2-} + 2NO_3^- = 2NO_2^- + 2\,O_2^- \qquad 1.6$$

According to him the oxide ions, produced according to equation 1.3 precipitate on the electrode because of the low solubility of Na_2O and the kinetic prevalence of process 1.6 over process 1.5. On the other hand, process 1.5 is sufficiently fast to accelerate considerably (subtracting oxide ions) the physical redissolution in the melt of Na_2O accumulated on the electrode. Equation 1.6 represents a slow reaction which cannot influence the processes at the electrode. The Na_2O formed on the electrode surface can be electrooxidised according to the consecutive reactions $2Na_2O$ (solid.) $= 2Na^+ + O_2^- + 3e^-$ and $O_2^- = O_2 + e^-$, responsible for two distinct anodic peaks.

The solubility and detection of water in molten (Na, K) NO_3 eutectic were studied by Zambonin and co-workers[35] using a rotating platinum electrode. Zambonin[36] also reported the voltammetric study of the interaction between O_2^- and H_2O ($4O_2^- + 2H_2O \rightleftharpoons 4OH^- + 3O_2$) in the same solvent. He demonstrated the possibility of determining the four species in the above equlibrium. The presence of NO_2^+ in the melt[37] formed by self-dissociation, $NO_3^- \rightleftharpoons NO_2^+ + O_2^-$, which cannot be detected by direct measurement because of its extremely low concentration was shown indirectly by Zambonin by measuring the concentration of OH^- obtained from O_2^-.

The complex nature of the electrolysis of nitrate melts is clearly understandable from the above discussion. The precautions which are to be taken consists mainly of the use of a limited potential range at which the nitrate ions are not reducible. Use of pyrex vessels will not cause any serious problem, because the electroactive species added will be more reducible and such reactions will have kinetic prevelence over the chemical reaction. In spite of these complexities these melts have been widely used in electroanalytical chemistry . To the list of references about the redox reactions of metals in nitrate melts, already cited in the earlier section, could be added some more work(38-46) which has been published.

A pecularity which is most noticable in these publications is that most of the workers have used either a stationary (hanging) or a dropping mercury electrode as the indicator electrode and the common techniques used were d.c. polarography, oscillographic polarography and in a few cases, chronopotentiometry and cyclic voltammetry. Two opinions exist on the redox process. While one school insisted that the cathodic reaction led to the reduction of these metal ions to the metal which got deposited on the electrode, another school insists that there is no firm evidence for the deposition of any element in nitrate medium in the electrostability region of the melt of course, Ag^+ ions are quoted as a striking exception by the second school. According to some in the second school(26,42-44) the postulation is that the reduction to the metal is followed by the rapid oxidation of the deposited metal phase by the nitrate melt, according to the reaction

$$M + NO_3^- = MO + NO_2^- \qquad 1.7$$

In a very recent study, Miles[47] refutes this statement in a detailed cyclic voltammetric study of Pb^{++} and Cd^{++} on platinum and mercury electrodes. He suggests that the cathodic deposition of the metal does not occur in (Na, K) NO_3 melt and the cathodic wave produced by the addition of these metal ions to the melt is due to the irreversible reduction of the nitrato complex according to the equation

$$(MONO_2)^{+} + 2\,e^{-} \longrightarrow MO + NO_2^{-} \qquad 1.8$$

In a previous study[48] involving (Li, K) NO_3 melt also, it was shown that reduction to the free metal never occurs for Pb^{++} or Cd^{++} ions. Reactions 1.7 and 1.8 yield the same final products but do not involve any change in the oxidation state of the metal ion. The investigations[49] of Miles of Tl^{+}, Cd^{++}, Pb^{++}, Zn^{++} and In^{+++} metal ions in (Li, K) NO_3 melts yielded similar conclusions.

However, recent studies reported by Inman[50] and Baret[51] have challenged the nitrato complex reduction model. Evidence for the direct electrodeposition of Pb^{++} and Cd^{++} metals is claimed from linear sweep voltammetric and chronopotentiometric experiments on mercury electrodes in the equimolar (Na, K) NO_3 melts at 533 K [50]. However, in response to this claim of metal deposition, Miles[47] has focussed his studies of Pb^{++}, Cd^{++} and Ag^{+} ions on both platinum and mercury electrode in the equimolar (Na, K) NO_3 melts. He has, by exhaustive electrolysis of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in the molten electrolyte using a mercury cathode, shown that no appreciable quantity of metal is deposited on the electrode. Thus the situation remains very complex.

1.5 SCOPE OF THE THESIS

In spite of the obvious advantages of using a ternary nitrate (alkali metal) as an electrochemical solvent, there exist serious complexities in their use in electroanalytical chemistry, as explained in the earlier section. These complexities pertain to the region where the cathodic and anodic background limits are transgressed. The behaviour of these electrolytes and the potential limits of cathodic and anodic background are a matter, yet to be studied, when an electroactive substance is present in the melt, which could be an impurity in the salts of the ternary eutectic itself or which is added as a solute. These effects, even though to a slight extent, may be visible, under these conditions, in the electrostability region, itself and cannot be corelated to the experimental results obtained in the absence of these electroactive solutes. The appearance of the waves for peroxides and superoxides ions is another phenomenon connected with the presence of the solutes. In fact of more importance is the mechanism of the actual redox reactions taking place. In the earlier section a clear picture of the discrepancies that exist in the exposition of the mechanism of not only nitrate reduction but also of the redox reactions of electroactive solutes in the nitrate melt has been given. One school of thought has gone to the extent that all the electrochemical work using nitrate melts must be invalidated due to the present controversy about the mechanisms. Doubts have been expressed about the very nature of reaction product itself. One school of thought has already relegated to the background the theory of metal deposition, after a decade of work confirming the same and switched on to the theory of an instantaneous production of metal immediately followed by the reduction of the metal to the nitrato-complex. The other school is not even ready to acknowledge the formation of a zero valance state and insists on a complex formation theory in which metal formation is not envisaged. Most of the discrepancies have come to the fore-front from the use of mercury (either dropping or hanging drop) as the working electrode and from the use of the transient technique of cyclic voltammetry. Earlier work in this laboratory has shown that this eutectic (Li, Na, K) NO_3 can be successfully used as electrochemical solvent for anodic stripping voltammetry, which would be possible only if metal deposition takes place. In the light of the above discrepancies it was thought that a more comprehensive study and investigation of redox reactions in nitrate melts was desirable not only with respect to more elements but also with respect to more electrochemical techniques.

Hence the techniques of chronopotentiometry, cyclic voltammetry, chronoamperometry and sampled current voltammetry were chosen for the study of redox reactions of Pb^{++}, Co^{++}, Ni^{++}, Fe^{+++} and Cu^{++} ions in nitrate melt at 423 K. Of these elements, some work has been done on Pb^{++} ions using polarography and cyclic voltammetry; practically no work exists on the redox reactions of Co^{++}, Ni^{++}, Fe^{+++} and Cu^{++} ions in nitrate melts by any electrochemical method. Chronoamperometry and sampled current voltammetry have been used for the first time to study any system in nitrate melts. Fe^{+++} was specially chosen because unlike other elements under study, here, no metal formation was envisaged. Co^{++} and Ni^{++} exhibit special peculiarities in electroanalytical chemistry and Cu^{++} is a system in which some reversibility was predicted. The foregoing statements justify the present investigation.

The thesis is divided into 5 chapters, with the first chapter dealing with a short introduction on electroanalytical chemistry in melts and in nitrate melts, paying special emphasis on the discrepancies that are reported in redox processes in these melts. Chapter 2 deals with the fundamentals on the four electrochemical techniques used in the present investigation, viz., chronopotentiometry, cyclic voltammetry, chronoamperometry and sampled current voltammetry. The bulk of the thesis pays emphasis on the experimental work, results and conclusions. The apparatus and the cell assembly were all home made and thus lacked the sophistication of computer or microprocessor based modern instruments. But this disadvantage was easily matched by the advantages accrued from the full knowledge of the working of the apparatus. The present work should be appreciated to the extent that the whole apparatus was home made. Chapter 3 gives the full details of the circuitry of the apparatus, cell assembly etc. While chapter 4 details the extensive results obtained on these 5 elements by the 4 electrochemical techniques, the 5^{th} and final chapter contains a comprehensive discussion of the results with conclusions on the results obtained and some suggestions for future work.