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SYNOPSIS OF THE THESIS SUBMITTED TO THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

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Molten salts are versatile solvents for many electrochemical processes e.g. electrometallurgical, electroanalytical etc. The advantages of using molten salts in electrochemistry range from high solubility to the use of wide temperature ranges. They can be obtained as oxidising and reducing, with either acidic or basic properties. Molten salts generally satisfy the fundamental requirements for application of electroanalytical techniques over a greater range of conditions than their aqueous and organic counter parts. They tend to exhibit ideal solution behaviour over more extensive solute concentration range, they have an inbuilt excess of supporting electrolyte to satisfy the transport requirements and double layer electrode capacitances seldom achieve high values. Their use in electroanalytical chemistry is widespread as the range of potential which can be applied is much wider than what could be applied in aqueous media. They provide fast reaction rates and problems of hydration of electroreducible ions are avoided. The obvious disadvantage of using molten salts is difficulty of operation at high temperature and the recent introduction of low melting eutectics into electrochemistry has obviated the necessity of using high temperature and produced ease of operation.

Low melting eutectics offer all advantages of molten salts and in addition are of special significance because in many cases the versatile dropping mercury electrode can be used. In spite of these advantages the use of low melting eutectics in electroanalytical chemistry has been limited. The present thesis is an attempt to study the redox reactions of certain metal ions in a nitrate low melting eutectic.

Molten nitrates[1] have been widely used as a solvent for electrochemical studies. Advantages of low liquidus temperature and relatively non-hygroscopic nature of molten nitrates have outweighed the disadvantages of these melts e.g. limited potential span and oxidising properties. A fairly pure melt can be obtained by simply melting the dried, recrystallised salts under vacuum and continuing evacuation for several hours.

A ternary low melting eutectic viz. $LiNO_3 - NaNO_3 - KNO_3$ is particularly advantageous in this respect as it has a low eutectic temperature of 393 K. This eutectic was used by Inman et. al[2] as an electrochemical solvent for study of redox reactions of Cd^{++}, Co^{++}, Ni^{++} and Pb^{++} by conventional polarography using a dropping mercury electrode. Later Francini and Martini[3,4] examined the electrochemical behaviour of Cd^{++}, Ni^{++}, Pb^{++}, Tl^{+} and Zn^{++} by conventional and linear sweep polarography. An excellent review of electroanalytical chemistry in molten salts including low melting eutectics has been given by Fung and Mamantov[5].

In the present thesis an attempt has been made to investigate the redox reactions of Pb^{++}, Ni^{++}, Fe^{+++}, Co^{++} and Cu^{++} in ternary nitrate eutectic at 423 K using a platinum disc as working electrode employing several electroanalytical techniques. The earlier authors[1-4] have used a dropping mercury electrode as working electrode and it was expected that the change over from the dropping mercury electrode to the platinum electrode would exhibit significant changes in the electrochemical reactions, as was borne out in the present study.

Further the earlier authors have taken recourse only to conventional and linear sweep polarography, while in present work several electrochemical techniques have been employed and in addition the ions Cu^{++} and Fe^{+++} have also been investigated.

The ternary low melting eutectic $LiNO_3 - NaNO_3 - KNO_3$ (wt. % 23.3 - 16.3 - 60.4, mole % 30.0 - 17.0 - 53.0) was used as the electrochemical solvent. The ternary eutectic was prepared by homogenising stoichiometric amounts of anhydrous, dry salts in an argon dry box using mortar and pestle and melting them slowly under vacuum for 48 hours.

The apparatus used for electrochemical experiments was fabricated in the laboratory and was a potentiostat-sweep generator capable of controlling any desired potential between + 2.5 V and - 2.5 V with a precision of $\pm$ 1 mV and which could generate ramp with slopes upto 100 mV $sec.^{-1}$. The apparatus was found most suitable for cyclic voltammetry and chronoamperometry. The apparatus used for chronopotentiometric experiments was also fabricated in the laboratory and could generate currents upto 1 mA. The measuring systems used were described in the literature[5].

The electrochemical cell was designed to have provision of connection to temperature monitoring facility apart from containing three electrode system and inlet as well as outlet for inert gas. The whole assembly was put in a controlled temperature furnace maintained at $\pm$ 2 K.

It was found that as long as the dimensions of electrode area were considerably greater than the diffusion layer thickness, linear diffusion prevails; hence a platinum disc of known dimensions and sealed in glass was used as the working electrode. The counter electrode was a platinum wire and the reference electrode used was a Ag/Ag Cl electrode after addition of a small amount of chloride in the melt.

In the present thesis the redox systems viz., Pb^{++}, Ni^{++}, Fe^{+++}, Co^{++} and Cu^{++} were studied in the above mentioned ternary nitrate melt at a temperature of 423 K using the electrochemical techniques viz. cyclic voltammetry, chronoamperometry, chronopotentiometry and sampled current voltammetry and with reference to variable parameters like concentration, scan rates and current applied etc.

Extensive relevant data like peak potentials, peak currents, transition times, quarter wave potentials etc. of these ions have been obtained. Efforts have been made to characterise the redox reaction and parameters like diffusion coefficients, α_{na}, heterogeneous rate constants etc. have been computed.

Recent studies reported by Inman[6] and Baret[7] have shown evidence for direct electrodeposition of Pb^{++}

and Cd^{++} for linear sweep voltammetry and chronopotentiometric experiments on mercury electrode in the equimolar $NaNO_3$ - KNO_3 melt at 533 K. On the other hand in a recent publication Miles[8] has suggested a nitrato - complex reduction model for the above reactions and has challenged direct electrodeposition model. Analysis of the data in view of these contradictory reports has been made with reference to the findings of the present work and a detailed discussion of the results included in the concluding chapter.

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