The summary of the thesis entitled

" Electrochemistry of certain Ions in a Low Melting Nitrate Eutectic "

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Electrochemistry in fused salt media has definite advantages over electrochemistry in aqueous and non-aqueous media. Some of these can be listed as the large temperature range, the wide potential range, higher electrical conductivities, enhanced kinetics etc. Low temperature eutectics form a part of the series, enabling ease of operation due to the low melting point. Among these nitrate melts have been widely used as solvents for electrochemical studies. In fact, the (Li, Na, K) NO_3 melt is the most widely used eutectic. However, a lot of discrepancies in the elucidation of the redox processes of metals in nitrate melts have been noticed in literature. There is marked difference in the behaviour of these reactions when different types of electrodes like mercury, platinum, vitreous carbon etc. are used. One school maintains that the reduction of the particular ion to the metal occurs while the other school is of the opinion that it is the nitrato complex of the particular metal ion take place.

In order to get the clearer view of these controversial mechanism the present work was undertaken.

In the present study the redox reactions of Pb^{++}, Co^{++}, Ni^{++}, Fe^{+++} and Cu^{++} ions have been studied by the techniques of (1) chronopotentiometry (2) cyclic voltammetry (3) chronoamperometry and (4) sampled current voltammetry in a (Li, Na, K) NO_3 eutectic at 423 $\pm$ 2 K using platinum electrode, cylindrical or planar. The apparatus and cell assembly were all fabricated in the laboratory. The apparatus was a multipurpose one which could yield the different parameters required for these different techniques. A three-electrode system consisting of platinum as working electrode, a small platinum wire as the auxiliary electrode and Ag/Ag^{+} electrode as the reference electrode was used.

In chronopotentiometry the parameters changed for the study were current densities and concentrations, while in cyclic voltammetry the voltage sweep rates and concentrations were changed. In chronoamperometry various potential steps were used and the currents were measured as a function of time and the data was used to compute the sampled current voltammograms for the various metal ions. In the first two techniques reverse reactions were also attempted. The parameters measured in chronopotentiometry were the transition time, quarter - wave potential etc., while in cyclic voltammetry the peak potentials, half-peak potentials, peak currents etc. were measured. The current values at any time 'τ' were calculated for constructing the sampled current voltammograms for these ions. The half-wave potentials, diffusion currents etc. were calculated for all these voltammograms. In all these experiments it was first of all ascertained that the reactions proceeded in diffusion controlled conditions.

All the redox reactions were found to be either irreversible or quasi-reversible. In cyclic voltammetry this was evident from the absence of the reverse peaks while the diagnostic criteria of potential-time relationship in chronopotentiometry were looked into to verify the reversibilities of the redox reactions. Under these conditions the transfer coefficients $\alpha_c n_\alpha$ for the reduction of these elements under varying conditions were calculated and the significance of these values discussed. These values were used to calculate the heterogeneous rate constants at 0.0 V vs NHE and from these values the standard electron transfer rate constants were computed. The values of the rate constants were of the range of quasi-reversible and irreversible reactions. After having ascertained that the reactions are diffusion controlled, the diffusion coefficients of these ions at 423 $\pm$ 2 K under varying conditions of electrolysis were calculated.

A full discussion on the significance of the measured quantities and the computed values has been given. The diffusion coefficients were found to be of the order of 10^{-6} cm^2 s^{-1} in all the cases for all the elements. These values agree with the values in aqueous media, while it is expected to be much higher in molten salts. This has been explained as due to the large nitrato-metal ion diffusing to the electrode rather than simple ion. The theory of reduction of the nitrato complex has been delved into and the conclusion has been drawn that the most probable reactions are

$$M^{++} + 2\,e \longrightarrow M^{0}$$

and $$M + NO_3^{-} \longrightarrow MO + NO_2^{-}$$

or $$(MO\,NO_2)^{+} + 2\,e \longrightarrow MO + NO_2^{-}$$

A firm conclusion could not be arrived at; the data provided in this work point out to the first mechanism as the most probable one. A complete and quantitative proof can be provided by only hyphenated methods, a combination of electrochemistry and spectroscopy. Suggestions for the further work are given.

A total of 183 references has been given.