C H A P T E R - V

D I S C U S S I O N

5.1 GENERAL INTRODUCTION

In the foregoing chapters were described the general electroanalytical techniques of chronopotentiometry, cyclic voltammetry, chronoamperometry and sampled current voltammetry together with the experiments and the results obtained by these techniques on the redox reactions of Pb^{++}, Co^{++}, Ni^{++}, Fe^{+++} and Cu^{++} ions in (Li, Na, K) NO_3 melt at 423 K. A detailed discussion of the results obtained together with the conclusions drawn is given in the various sections of this chapter.

5.2 DIFFUSION COEFFICIENTS

Table 5.1 lists the values of the diffusion coefficients of the various ions by different techniques already mentioned. Among these chronopotentiometry is unique in that the reverse chronopotentiometric data can yield the reverse diffusion coefficients, i.e., the diffusion coefficient of the reduced species to the electrode. Of course, cyclic voltammetry also yields this data, provided the reverse or anodic cyclic voltammograms are obtained. The only useful data that can be computed from chronoamperometry is the diffusion coefficient of the cathodic reaction. Chronoamperometry on the reverse track has seldom been used, but when used can yield the respective values of the diffusion coefficients. In the present case in most of cyclic voltammograms no reverse peaks were obtained.

Table 5.1

Values of Forward and Reverse Diffusion Coefficients of Various Ions by Different Techniques in (Li, Na, K)NO_3 Eutectic at 423 $\pm$ 2 K

Forward $(D_o)_f \times 10^6$ cm^2 s^{-1} *

Technique	Ions				
	Pb^{++}	Co^{++}	Ni^{++}	Fe^{+++}	Cu^{++}
Chronopotentiometry	7.5	4.3	4.7	10.5	3.3 4.9
Cyclic voltammetry	2.1	4.4	7.2	1.3	1.6
Chronoamperometry	2.0	2.1	0.36	63.3	5.2

Reverse $(D_o)_r \times 10^6$ cm^2 s^{-1} *

Technique	Ions				
	Pb^{++}	Co^{++}	Ni^{++}	Fe^{+++}	Cu^{++}
Chronopotentiometry	1.7	1.7	1.7	2.1	1.3 1.9

* Mean of several determinations varying relevant parameters

None of these methods, in principle, is a good method for determining diffusion coefficients as too many factors or parameters are included in the Sand's equation, Randle - Sevcik equation and the Cottrell equation. However, other diagnostic criteria being satisfied, this is not so in general practice, particularly so due to the agreement in the present values by different techniques, as also from whatever values available in literature by other methods. Perhaps the Pb^{++} ion holds the credit of being the most studied in nitrate melts. Tables 5.2 and 5.3 reproduce the data obtained by different techniques on Pb^{++} ion in (Li, Na, K) NO_3 at different temperatures and in various nitrate melts respectively. Considering that all these data have been obtained on either a dropping mercury electrode or a hanging mercury electrode, while in the present case a platinum electrode has been used, the agreement should be deemed as excellent. In general the values have been in the range of $2 - 9 \times 10^{-6}$ cm^2 s^{-1}, except in the case of Cu^{++} and Fe^{+++} ions by the technique of chronoamperometry. An explanation for this anomaly is not immediately available, but such variations have been reported in literature. Lowering and Oblath[(24)] have reported that the diffusion coefficient of Ni^{++} ions in a (La, K)NO_3 melt at 415 K (using a d.m.e and d.c. polarography) varies from 2.2×10^{-7} at very small concentrations of water to 4.5×10^{-6} cm^2 s^{-1} at a

Table 5.2

Values of Diffusion Coefficients of Pb^{++} Ion in (Li, Na, K) NO_3 Melt

Temperature K	Technique	Diffusion coefficient $D_o \times 10^6$ $cm^2\ s^{-1}$	Reference
433	D.C. Polarography	1.80	46
429	Square Wave Polarography	0.78	10
438	Cathodic Ray Polarography	1.00	17
422	Polarography	0.92	6
403	Cyclic voltammetry	3.00	143

Table 5.3

Diffusion Coefficients of Pb^{++} Ion in some Nitrate Eutectics from Cyclic Voltammetric Data*

Eutectic	Temperature K	Diffusion coefficient $D \times 10^6$ cm^2 s^{-1}
$CO(NH_2)_2$ + NaCl + $NaNO_3$	359	8.8
$NaNO_3$ + NH_4NO_3	403	8.1
$CO(NH_2)_2$ + KNO_3	391	4.0

* Ref. 143

water concentration, in the melt, of 3.36 M. Khasgiwale et. al[144] have obtained values as high as $8.4 \times 10^{-5}\ cm^2\ s^{-1}$ for the diffusion coefficient of Ni^{++} ion in a(LiCl - KCl) melt at 723 K.

The values, obtained in the present work, for the diffusion coefficients are not in variation from the values obtained in aqueous solutions. These values are expected to be much higher in nitrate melt than in aqueous media. The most probable and logical explanation is that these ions do not migrate to the electrode as pure ions, but as large nitrato complexes. The effective size of the nitrato complexes causes to reduce the magnitude of the diffusion coefficient, in spite of the higher temperatures involved and the consequent higher electrical conductivity, higher exchange current densities, faster electrode kinetics etc. It should be taken into account, without consideration of the actual mechanism of the redox reaction of these ions, that there are differences in complexity between inorganic and organic processes, especially with regard to chemical follow - up reactions. In the charge transfer process

$$M^{n+} + e \longrightarrow M^{(n-1)+}$$

the process is not just the simple injection of an electron into a M^{n+} ion. The solvation atmosphere of M^{n+} and $M^{(n-1)+}$ ions may be markedly different and a considerably rearrangement of bonds accompanies this apparently elementary act.

The resulting $M^{(n-1)+}$ species is, nevertheless, easily recognised as the same metallic species - only now in a different oxidation state and with a new solvation sheath.

5.3 TRANSFER COEFFICIENTS $\alpha_c\ n_\alpha$

Transfer coefficient $\alpha_c\ n_\alpha$ or simply αn_a, as it is sometimes referred to, determines the wave shape obtained when the electrode surface concentrations are determined by kinetics instead of thermodynamics. Such behaviour is called " non - Nernstian " or depending upon the extent of deviation from reversible behaviour, irreversible or quasi - reversible behaviour. The steady - state slope of the concentration profile is determined entirely by the steady - state concentration at the electrode surface. This is determined by the rate of charge transfer at that potential. If the electrode concentration of the reactant is determined by kinetics instead of thermodynamics at a given potential, the surface concentration of this substance will be greater than it would have been if the charge transfer rate were fast enough to maintain the laws of thermodynamics. Thus the kinetically - controlled current at a given potential is less than the reversible current at the same potential. In such cases the limiting currents or transition times are not achieved as easily as in the case of reversible waves and the half - wave potential $E_{\frac{1}{2}}$ no longer corresponds to E_o, since $E_{\frac{1}{2}}$ or $E_{\tau/4}$ is now determined by charge transfer kinetics. The measurement of this potential provides information instead of thermodynamic information. A measure of this kinetic information is given the factor $\alpha_c n_\alpha$ and thus this is a factor depending on the electrolysis conditions and on the electrode reaction. The foregoing discussion clearly points out that this factor need not be the same when a particular redox reaction is investigated by different electroanalytical techniques.

Table 5.4 lists the values of $\alpha_c n_\alpha$ obtained for the various redox reactions by different techniques. It can be seen that the values of $\alpha_c n_\alpha$ obtained from cyclic voltammetry are invariably higher than the values obtained by the other two techniques for all the ions. In cyclic voltammetry the value of $\alpha_c n_\alpha$ depends on the scan rates used. At the relatively small values of scan rates used in the present work, it is expected that the values of $\alpha_c n_\alpha$ are expected to be higher. This quantity is calculated in cyclic voltammetry by two equations, viz.,

$$\left| E_p - E_{p/2} \right| = -1.857 \frac{RT}{\alpha_c n_\alpha F} \qquad 5.1$$

and

$$(E_p)_2 - (E_p)_1 = \frac{RT}{\alpha_c n_\alpha F} \ln \sqrt{\frac{\nu_1}{\nu_2}} \qquad 5.2$$

For the proper computation of $\alpha_c n_\alpha$ using the second equation ν_2 must be orders higher than ν_1. Even in the small range of

Table 5.4

Values of the Transfer Coefficients $\alpha_c n_\alpha$ of various Ions by Different Techniques in (Li, Na, K) NO_3 Eutectic at 423 $\pm$ 2 K

Technique	Transfer Coefficient $\alpha_c n_\alpha$				
	Ions				
	Pb^{++}	Co^{++}	Ni^{++}	Fe^{+++}	Cu^{++}
Chronopotentiometry	0.164	0.446	0.718	0.123	0.406
Cyclic voltammetry	0.431	0.972	1.143	1.221	0.772(c) 0.992(a)
Sampled Current voltammetry	0.114	0.201	0.315	0.269	0.475

scan rates used in the present work it was found that the values of $\alpha_c n_\alpha$ calculated from the two equations showed good agreement. The values of $\alpha_c n_\alpha$ can be increased or decreased sharply by the use of different scan rates and a totally irreversible reaction can be brought under thermodynamic conditions by the use of suitable scan rates. The values given in Table 5.4 are the mean of several determinations or the so - called chosen values; in each technique the parameters varied have been mentioned, e.g., in chronopotentiometry the parameters varied were the concentration and current densities and so on. The given values only clearly indicate the irreversible nature of the redox reactions. The values of $\alpha_c n_\alpha$ are high in cyclic voltammetry, but values nearing or greater than unity are seldom observed. The exceptions, here, are Ni^{++}, Co^{++} and Fe^{+++}. As early as in 1954, Delahay and Mattax[(64)] have reported that the value of $\alpha_c n_\alpha$ of Co^{++} ion in 0.1 N KCl was 0.82 from chronopotentiometric data. Lowering and Oblath[(24)], in their d.c. polarographic studies of Ni^{++} ions in a nitrate melt using a dropping mercury electrode, have shown that the values of $\alpha_c n_\alpha$ increased sharply from 1.83 from a very dry melt to a totally irreversible value of 2.0 at a water content of 4.5×10^{-3} M before falling again to only 1.35 at 3.36 M of water, i.e., approaching a totally irreversible behaviour in non-complexing media[(145)]. The magnitude of the transfer coefficient has, thus, always been found to be high for both Ni^{++} and Co^{++} and this is confirmed for Fe^{+++}, too. This is a situation particular to the transition metals and a clear cut reason is still lacking. The importance of the values of $\alpha_c n_\alpha$ will be evident in the next section where the heterogeneous electron transfer rate constants are discussed.

5.4 KINETICS AND THE CALCULATION OF STANDARD ELECTRON TRANSFER RATE CONSTANTS

The kinetics of a totally irreversible electrochemical redox reaction can, normally, be defined by three times, viz., $k_{f,h}$, $k^o_{f,h}$ and $k_{s,h}$. $k_{s,h}$ is defined as the heterogeneous electron transfer rate constant or coefficient at any potential for unit concentration and unit electrode area. The corresponding constant for the backward reaction is defined as $k_{b,h}$. When the potential is 0.000 V vs NHE, the constant is called as $k^o_{f,h}$ and similarly for the backward reaction it is $k^o_{b,h}$. If the formal thermodynamic potential E_o for a process is known or can be evaluated then $k^o_{f,h}$ and $k^o_{b,h}$ may be converted into a simplified rate constant $k_{s,h}$ which is a measure of the rate of electron transfer at the formal potential E_o.

The relation between $k^o_{f,h}$ and $k_{s,h}$ can be written as

$$k_{s,h} = k^{o}_{f,h}\, e^{\frac{-\alpha_c n_\alpha F E_o}{RT}}$$

$$= k^{o}_{b,h}\, e^{\frac{-(1-\alpha_c) n\ F E_o}{RT}} \qquad 4.5$$

Greef[75] quoting from the work of Nicholson and Shain[76] has simplified the equation to be used in cyclic voltammetry. His equation

$$K = E_o - \frac{R\ T}{\alpha_c n_\alpha F}\left[0.78 - \frac{2.303}{2}\log\frac{\alpha_c n_\alpha F D_o}{k^2_{s,h} RT}\right] \qquad \ldots\ldots\ldots \quad 2.33$$

Again Gokhshtein[146] derived an equation, for a totally irreversible cyclic voltammetric redox reaction, where the peak current is equated as given below.

$$i_p = 0.227\ n F A C_o^{\infty}\ k_{s,h} \exp\left[\left(\frac{\alpha_c n_\alpha F}{RT}\right)\ (E_p - E_o)\right] \qquad \ldots\ldots\ldots \quad 5.3$$

Thus the plot of ln i_p vs $E_p - E_o$ (or $E_{p/2} - E_o$) for different with scan rates would be a straight line with a slope equal to $\frac{-\alpha_c n_\alpha F}{RT}$ and an intercept proportional to $k_{s,h}$. This is an extremely convenient method of determining the kinetic parameters for this case, although the scan rates have to be varied over several orders of magnitude.

The values of $k_{s,h}$ calculated from $k^{o}_{f,h}$ obtained from the different techniques (Table 5.5) for the redox reactions of Pb^{++}, Co^{++}, Ni^{++}, Fe^{+++} and Cu^{++} ions in (Li, Na, K) NO_3 melt at 423 K are quoted in Table 5.6. In this Table are given the values calculated from equation 4.5 and equation 2.33 for cyclic voltammetry. The methods of calculating $k_{s,h}$ from sampled current voltammetry are described in Chapter 4. The chronopotentiometric values of $k_{s,h}$ were calculated from $k^{o}_{f,h}$ by using equation 4.5. For calculating $k_{s,h}$ from any of these equations the value of E_o, the formal thermodynamic potential of the system is required. This value must conform to the particular medium and the temperature of the system. The experimental evaluation of E_o under these conditions in a nitrate melt is extremely difficult and no values are available, in literature, for these systems except in aqueous medium. In the absence of these values, E_o has been approximated to $E_{\tau/4}$ in chronopotentiometric calculations and to $E_{\frac{1}{2}}$ in sampled current voltammetry. For cyclic voltammetric calculations, also, $E_{\tau/4}$ values (Table 5.7) have been utilised.

A reaction can be said to be reversible on the basis of the standard rate constant if the $k_{s,h}$ value is equal to or greater than 2×10^{-2} cm s^{-1}. On the contrary if the value is less than 1×10^{-5} cm s^{-1}, then, the reaction can be termed irreversible. The reactions having values

Table 5.5

Values of the Heterogeneous Electron Rate Constants at -0.000 V vs NHE, Unit Area and 1 M Concentrations of Various Ions in (Li, Na, K) NO_3 Eutectic at 423 ± 2 K

Technique	$k^o_{f,h}$ cm s^{-1} Ions				
	Pb^{++}	Co^{++}	Ni^{++}	Fe^{+++}	Cu^{++}
Chronopotentiometry	4.5×10^{-4}	1.0×10^{-12}	3.0×10^{-9}	8.5×10^{-4}	2.0×10^{-6}
Cyclic voltammetry	5.4×10^{-7}	5.3×10^{-8}	3.2×10^{-10}	1.3×10^{-10}	3.7×10^{-10}

Technique	log $k^o_{f,h}$ Ions				
	Pb^{++}	Co^{++}	Ni^{++}	Fe^{+++}	Cu^{++}
Chronopotentiometry	-3.35	-12.00	-8.52	-3.07	-5.70
Cyclic voltammetry	-6.27	-7.28	-9.50	-9.89	-9.43

of standard rate constants falling between 2×10^{-2} and 1×10^{-5} are classified as quasi - reversible reactions.

A perusal of Table 5.6 shows that the values of $k_{s,h}$ obtained from cyclic voltammetric data using equations 4.5 and 2.33 vary in several orders of magnitude. Actually the values obtained from equation 2.33 are suspect for the very reason which gives the limitation to the use of equation 5.3. The value of K was calculated using equation 2.32 where log γ is an important factor. The change in scan rates used in the present work is of the order of factor of 5 only while for the proper utilisation of equation 2.32 the scan rates have to be varied over several orders of magnitude. However, the values have been calculated and included in order to assess the effect of scan rates.

The rate constant values cited in Table 5.6 indicate that the reactions are all irreversible, the magnitude of irreversibility touching on the fringes of quasi - reversibility. Out of these five elements the transition metal group of Co^{++}, Ni^{++} and Fe^{+++} are well - known to give irreversible reactions even in aqueous solutions. Delahay and Mattax[64] have determined the value of log $k^{o}_{f,h}$ as -13.69 for Co^{++} in 0.1 M KCl medium. In our case this value is much higher, most probably due to the higher temperature of 423 K. However, it is not explainable why such a high value should be obtained when Delahay and Mattax have used a dropping mercury electrode.

Table 5.6

Values of Standard Electron Transfer Rate Constants $k_{s,h}$ of Various Ions in (Li, Na, K) NO_3 Eutectic at 423 $\pm$ 2 K

Technique	$k_{s,h}$ cm s^{-1} Ions				
	Pb^{++}	Co^{++}	Ni^{++}	Fe^{+++}	Cu^{++}
Chronopotentiometry	1.3×10^{-3}	1.5×10^{-2}	1.3×10^{-4}	1.3×10^{-3}	1.3×10^{-4}
Cyclic voltammetry	2.7×10^{-5}	2.9×10^{-3}	1.1×10^{-2}	5.6×10^{-5}	1.3×10^{-4}
	6.7×10^{-1}	2.9×10^{-2}	9.1×10^{-5}	9.4×10^{-1}	2.3×10^{-1}
Sampled current voltammetry	5.3×10^{-4}	2.2×10^{-3}	2.4×10^{-4}	1.5×10^{-3}	1.0×10^{-3}

Technique	log $k_{s,h}$ Ions				
	Pb^{++}	Co^{++}	Ni^{++}	Fe^{+++}	Cu^{++}
Chronopotentiometry	-2.88	-1.82	-3.89	-2.86	-3.89
Cyclic voltammetry	-4.56	-2.54	-1.96	-4.25	-3.89
	-0.82	-1.54	-4.04	-0.03	-0.64
Sampled current voltammetry	-3.28	-2.66	-3.62	-2.82	-3.00

The limits mentioned in this section for the magnitude of the standard heterogeneous electron transfer rate constants $\left[k_{s,h} \gg 2 \times 10^{-2},\ k_{s,h} < 1 \times 10^{-5}\ \text{and}\ 1 \times 10^{-5} < k_{s,h} \gg 2 \times 10^{-2}\ \text{cm s}^{-1} \right.$ for reversible, irreversible and quasi-irreversible reactions$\left.\right]$ refer to a temperature of 298 K. No attempt has been made, in the present work, to theoretically calculate the $k_{s,h}$ value at the higher temperature of 423 K, but a direct conversion could give values of $k_{s,h} \gg 3 \times 10^{-2}$, $k_{s,h} < 1.4 \times 10^{-5}$ and $1.4 \times 10^{-5} < k_{s,h} \gg 3 \times 10^{-2}$ cm s^{-1}, values not very much differing in magnitude to the values at 298 K.

5.5 QUARTER-WAVE AND HALF-WAVE POTENTIALS

In chronopotentiometry the values of the quarter-wave potentials are as important and fundamental as the half-wave potentials in polarography. In cyclic voltammetry it is the peak potential value that is important while in sampled current voltammetry it is again the half-wave potential. However, all these values become important when thermodynamic conditions prevail and not kinetic considerations. As has been discussed earlier in the present work mostly kinetic conditions prevail. In spite of this the values of the quarter-wave and half-wave potentials obtained from chronopotentiometric and sampled current voltammetric data are listed in Table 5.7. This data was utilised for the calculation of the standard electron transfer rate constants. The peak potential values are not given in this Table, as they are a function of the scan rates and are thus of no thermodynamic importance.

Table 5.7

Values of Quarter - wave Potentials and Half - wave Potentials of various Ions in (Li, Na, K) NO_3 Eutectic at 423 ± 2 K

Chronopotentiometry

Ion	$E_{\tau/4}$ V vs Ag/Ag^+
Pb^{++}	-0.340 (f) -0.050 (r)
Co^{++}	-0.490 (f) -0.050 (r)
Ni^{++}	-0.650 (f) +0.270 (r)
Fe^{+++}	-0.425 (f) +0.400 (r)
Cu^{++}	-0.703 (f)

Sampled current voltammetry

Ion	$E_{\frac{1}{2}}$ V vs Ag/Ag^+
Pb^{++}	-0.535
Co^{++}	-0.475
Ni^{++}	-0.585
Fe^{+++}	-0.415
Cu^{++}	-0.350 (First wave) -0.650 (Second wave)

5.6 REVIEW OF THE RESULTS

In these pages is given a comparison and discussion of the results obtained in the present work, as related to the work done earlier using linear sweep voltammetry and mostly the mercury electrode as the indicator electrode. Emphasis has been given to the work of Miles[47] who, as recently as 1987 has attempted to prove the absence of electrodeposition of Pb^{o} in the mechanism of the electrode reactions. Even though some work using the technique of chronopotentiometry have been done using the mercury electrode, little or practically no tangible results have been obtained by these workers. As already stated earlier most of the work was done using Pb^{++} ion. While some work on Co^{++} has been mentioned, mostly using the d.m.e and polarographic methods, even these methods have drawn a blank in the case of Fe^{+++} and Cu^{++} ions. This is the first time that sampled current voltammetry and chronoamperometry have been used for the study of the redox reactions of these metal ions in nitrate melt.

In a recent investigation Miles[47] conducted voltammetric studies of Pb^{++} and Cd^{++} ions in a $(Na-K)NO_3$ melt and suggested that the cathodic deposition of the metals does not occur. He, however, obtained a new cathodic wave produced by the addition of the metal to the melt due to irreversible reduction of the nitrato complex, i.e.,

$$PbO\,(NO_2)^{+} + 2e \longrightarrow PbO + NO_2^{-} \qquad 5.4$$

In contrast to the metal deposition reactions there is no oxidation state change for the metal ion since only the nitrate ligand is reduced. In the following pages a comparison of the results obtained by us with those obtained by Miles is given with a little commentary on the work of Inman[50] who has obtained results in agreement with the present values, in spite of the fact that the melts used in the three different papers are not exactly the same.

Miles employed a scan rate of 0.05 V s^{-1} for the 0.02 M $Pb(NO_3)_2$ in molten $(Na + K)NO_3$ melt at 523 K using both Pt and Hg electrodes. The electrode areas used were 0.17 cm^2 for Pt and approximately 0.2 cm^2 for Hg. The background currents obtained by him were quite significant for Hg electrode. However, for Pt the background current remained less than 0.5 mA (50 µA) through out the sweep range shown. For both the electrodes he got two cathodic peaks in contrast to the single one reported in this work. For the Pt electrodes the new cathodic peaks at -0.74 and -1.16 V are nearly equal in intensity in contrast to the results for the Hg electrode where the peak at -0.98 V was very much larger than the peak at -0.63 V. There were no reversible anodic peaks that can be attributed to the oxidation of any deposited metal. For the Pt electrode new anodic peaks appear at potentials positive to the Ag/Ag^+ reference that have been explained in terms of equation 5.4 by the oxidation of the NO_2^- ions[147] and lead oxide.

$$NO_2^- \longrightarrow NO_2\uparrow + e \qquad 5.5$$

$$PbO \longrightarrow Pb^{++} + \tfrac{1}{2}\,O_2 + 2\,e \qquad 5.6$$

or by the oxidation of PbO to higher oxides[148].

The work of Miles is more or less qualitative and the only quantitative data given by him are (1) the amounts of deposited metals viz., Pb and Cd on the Hg cathode by exhaustive electrolysis and (2) the peak current densities measured on a Pt electrode at 0.050 and 0.100 $V\,s^{-1}$ for various concentrations of $Pb(NO_3)_2$ ranging from 2×10^{-4} to 2×10^{-1} M in $(K-Na)NO_3$ melt at 523 K. In these experiments he performed exhaustive electrolysis of 0.10 M $Pb(NO_3)_2$ and 0.12 M $Cd(NO_3)_2$ in molten $NaNO_3$-KNO_3 followed by AAS analysis of the mercury cathode. In the first case he has tabulated the AAS results obtained by him on Hg cathodes for $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in the melt at 523 K. The data for the constant current electrolysis runs like below: I = 30 mA, time t = 2 hrs., mercury cathode = 56.9 g., area = 7 cm^2, $NaNO_3$ = 15.08 g, KNO_3 = 17.93 g, $Pb(NO_3)_2$ = 1.10 g. Temp. 523 K. For analysis 23 g of the Hg cathode used in the electrolysis was leached with 15 ml of 0.5 M HNO_3 for 12 days. The AAS analysis was for the acid solution used to extract any Pb metal.

The data for the constant potential electrolysis : $E = -0.700$ V vs Ag^{+}/Ag and then $E = -1.000$ V near the end of experiment, area = 7 cm^2, Hg cathode = 80.41 g, $NaNO_3$ = 15.08 g, KNO_3 = 17.93 g, $Cd(NO_3)_2$ = 0.92 g. The AAS analysis was for 0.5 g of the mercury cathode dissolved in conc. HNO_3.

The above experiments yielded results in which only 0.06% of the amount of lead (63.70 ppm) and 0.24% of the amount of cadmium were deposited on the mercury cathode. Miles has emphazized that this experiment has conclusively proved that no electrodeposition of metallic lead and cadmium has taken place in the cyclic voltammetric experiments. However, some salient points have to be taken into consideration in this context. Miles could have demonstrated by the same type of experiments that silver metal is deposited on the mercury cathode. If this were done, it could have revealed the effectiveness of the results. Further his experiments should have been supplemented with experiments using the platinum electrode. In fact the Pt electrode would have been a more suitable electrode for this deposition than the Hg cathode. At these high temperatures the metals are known to be soluble in the melt, itself and after deposition the amalgam would have decomposed and released the metals into the melt again taking the metals into solution. The probability of such a reaction is much more with a mercury cathode than with a platinum cathode. In fact the melts, from which alkali metals are deposited and prepared, are known to dissolve significant amounts of metals, thereby decreasing the current efficiency. In a fast electrolysis like cyclic voltammetry the kinetics may not be favourable for such a reaction. Thus, perhaps, it may not be told equivocally that the electrodeposition of the metals does not take place.

In his cyclic voltammetric experiments Miles has given the peak currents obtained againsst concentration at a scan rate of $0.05\,V\,s^{-1}$. The peak currents are very high of the order of several milliamps. Reproduced in these pages is the data of the peak current densities obtained by him together with the peak currents calculated. Table 5.8 lists these quantities while Table 5.9 shows the values of $i_p/\nu^{\frac{1}{2}}$, i_p/C and $i_p/C\,\nu^{\frac{1}{2}}$ calculated from the work of Miles. As can be seen from this Table $i_p/C\,\nu^{\frac{1}{2}}$ is not showing constancy as expected for a quasi or completely irreversible process. Actually the values are tailing off as the concentration increases. This may be due to the fact that the peak currents obtained are much larger than those measured in cyclic voltammetry ordinarily.

Cyclic voltammograms of lead and silver on the platinum microelectrode at a very fast scan rate of $1000\,V\,s^{-1}$ were also conducted by him to reveal the existence of reactive intermediates. Miles found that the redox reactions of both the metals irreversible even at this fast scan rate. ΔE_p was

Table 5.8

Peak Current Densities and Peak Currents Measured on Pb ($A = 0.14\ cm^2$) at $0.050\ V\ s^{-1}$ and $0.100\ V\ s^{-1}$ for Various Concentrations of Pb $(NO_3)_2$ in Molten (Na, K) NO_3 at 523 K *

$Pb(NO_3)_2$ M	i_p at $0.050\ V\ s^{-1}$ $\mu A\ cm^{-2}$	i_p μA	i_p at $0.100\ V\ s^{-1}$ $\mu A\ cm^{-2}$	i_p μA
2×10^{-4}	70	9.6	110	15.4
2×10^{-3}	640	89.6	860	120.4
2×10^{-2}	5600	784.0	8000	1120.0
2×10^{-1}	34300	4802.0	50700	7098.0

* For the first cathodic peak corrected for the background current densities (Ref. 47)

Table 5.9

Relationship between Peak Currents, Concentrations and Voltage Sweep Rates (Refer Table 5.8)

$Pb(NO_3)_2$ M	Scan rate $V\,s^{-1}$	$i_p/\nu^{\frac{1}{2}}$ $\mu A\,V^{-\frac{1}{2}}\,s^{\frac{1}{2}}$	$i_p/C \times 10^{-4}$ $\mu A\,M^{-1}$	$i_p/C\nu^{\frac{1}{2}} \times 10^{-4}$ $\mu A\,M^{-1}\,V^{-\frac{1}{2}}\,s^{\frac{1}{2}}$
2×10^{-4}	0.05	43.0	4.8	21.5
2×10^{-3}	0.05	400.7	4.5	20.0
2×10^{-2}	0.05	3506.0	3.9	17.0
2×10^{-1}	0.05	21475.2	2.4	10.7
2×10^{-4}	0.10	48.7	7.7	24.4
2×10^{-3}	0.10	380.7	6.0	19.0
2×10^{-2}	0.10	3541.8	5.6	17.8
2×10^{-1}	0.10	22445.8	3.6	11.2

equal to 0.52 V for the Ag^{+}/Ag reaction at 1000 V s^{-1} compared with E_p equal to 0.14 V for this reaction at the much lower sweep rate of 0.200 V s^{-1}. The cathodic and anodic peaks resulting from the reduction of the $(PbO\,NO_2)^{+}$ complex gave $\triangle E_p$= 0.84 at 1000 V s^{-1}. Studies at other various sweep rates suggested that the difference in the wave form for the electrode reactions involving Ag^{+} and Pb^{++} ions become less distinct at the faster sweep rates and multiple oxidation or reduction peaks tend to emerge into a single peak. The study gave no suggestion of intermediates.

Even at the slow scan rates of 0.05 V and 0.10 V s^{-1} Miles obtained two cathodic peaks at -0.67 V and -1.12 V for 2.0×10^{-3} M $Pb(NO_3)_2$. As the concentration was increased it was noticed that there was a shift in the peak potentials towards less negative values. He could also witness gas evolution charging the second peak that resulted in the irregular fluctuations in the shape of the peak. This gassing, according to him, resulted from the further reduction of the nitrato complex to NO, N_2O or N_2. The formation of a film or the Pt electrode could be seen during the first cathodic peak, but quickly reforms. During the positive going sweep gas evolution occurs near 0.5 V as the film cracks and gradually falls away into the solution.

The above observations are not confirmed in the present work. In the place of the two cathodic peaks we could observe only one peak; no gassing or peeling off of the oxide layer could be noticed. In fact no anodic waves were observed revealing a completely irreversible reaction in direct contrast to the results obtained in cyclic voltammetry using a hanging mercury electrode[149]. This study has indicated a reversible reaction leading to an anodic wave with characteristics conforming to the diagnostic criteria of a reversible reaction in cyclic voltammetry.

The recent cyclic voltammetric studies by Inman[50] report three important factors in obtaining evidence for the electrodeposition of Pb and Cd in equimolar $NaNO_3 - KNO_3$ melt at 533 K. They are (1) the use of the mercury electrode (2) the use of high sweep rates and (3) the low concentrations of solute. In the present work the concentrations were low and the sweep rates small. The use of the platinum electrode in the place of the mercury electrode could change the whole picture and Inman[50], too, in conformity with the results in the present work, did not observe, when Pt indicators were used, anodic waves.

A possible explanation of Inman's[50] results can be given by the equations

$$(PbONO_2)^+ + 2e \longrightarrow PbO + NO_2^- \qquad 5.4$$

$$PbO + 3NO_3^- \rightleftharpoons Pb^{++} + 3NO_2 + 2O_2^- \qquad 5.7$$

$$O_2^- \rightleftharpoons O_2 + e^- \qquad 5.8$$

Other reactions involving the oxidation of the oxide or peroxide ions could also be postulated, but the reported $E = -0.765\,V$ for equation 5.8 involving the superoxide ion gives the best agreement with the observed potential[150-152,34]. High concentration of Pb^{++} would restrict the formation of O_2^- when slow sweep rates would allow the O_2^- ions to diffuse away from the electrode surface before it can react. The more negative E_p^c for Hg over the Pt may favour the adsorption and reaction of O_2^- at the mercury interface[45]. This reversible O_2/O_2^- couple is not readily apparent on Pt electrodes, but it has been readily apparent on the Pt electrodes. It has been previously observed at low current densities[34]. Despite occasional aberrations[153,154] equilibria and electrode reactions involving peroxide and superoxide ions in $NaNO_3 - KNO_3$ melts are well established[155-159]. However, it is to be stressed here that the formation of peroxide and superoxide ions should be excluded in the present case. The presence of acidic cations with high polarising power such as Li^+, Pb^{++} and Cd^{++} would favour the formation of insoluble oxides rather than peroxide and superoxide ions[148,25]. In the present work use has been made of a ternary eutectic containing Li^+. And further the present work has been done in the electrostability region of the melt in order to avoid electrolytic decomposition of the electrolyte itself. Emphasis has been given to the electrolytic redox reactions of the metals and not to the electrolyte.

Inman and Bockris[44] and Swofford and Holifield[160] have observed two steps in the reduction of Pb at higher concentrations on the Hg electrode. The two groups used different methods and differ both in the results and interpretation of the results. $E_{p/2}$ of $-0.30\,V$ obtained in the work for the main process (reduction of soluble Pb(II)) is in reasonable agreement with $E_{\tau/4}$, very nearly equal to $-0.38\,V$ of Inman and Bockris[44] for a simple reversible process at 518 K, $E_{\frac{1}{2}} = E_{p/2} - 0.024\,V$[76].

Pb - Pt alloys are readily attacked by HNO_3 solutions[161] and stripping experiments at slow scan rates indicate that the oxidation of the reduction products in both the systems is appreciable. The values of n or $\alpha_c n_\alpha$ from the plots of E vs $\log \frac{i_p - i}{i_p}$ or $\log (i_p - i)$[162] were found to be less than unity. In the present work, the voltammograms were too drawn out, indicating that the reduction may be inhibited by the oxide film on the electrode. If the inhibiting oxide film is formed during the voltammogram it is to be expected that the function $i_p/\nu^{\frac{1}{2}}$ will increase with ν and then become constant, indicating that at faster scan rates the oxidation of the reduction product by the nitrate ions has little effect on the cathodic process. The alternative explanation of a slow irreversible charge transfer is the most likely, since the charge transfer process involving metal ions in molten salts are invariably rapid[163].

According to Mamantov[43] the reduction of Pb^{++} ions in $NaNO_3 - KNO_3$ melt using the technique of linear sweep voltammetry may involve

A. the reaction $Pb^{++} + 2\,NO_3^- \longrightarrow PbO_{(s)} + 2\,NO_2 + \frac{1}{2}O_2$[164]

B. alloy formation with Pt[161] and

C. the oxidation of the reduction product (metal or alloy) by the nitrate solvent. According to him reaction A is apparently not very important. He assumes that the linear dependence of the peak cathodic currents with $\nu^{\frac{1}{2}}$ and formal concentration went to show that the reduction is directly as a result of the Pb^{++} ions in the melt. On the other hand the oxide may be formed on the electrode, following the oxidation of the reduction product by the nitrate solvent. The oxide layer can result in " blocking " of the main electrode[165,166]; it can also serve as oxide ions and may be oxidised at anodic potentials.

At fast scan rates it was possible for Mamantov to observe the reduction of NO_2 in agreement with Topol et al[167]. The origin of the concentration dependent prewave in the reduction of Pb^{++} is not known, although voltammetric experiments have shown that the prewave is a function of the initial potential of the working electrode. In his reported experiments Mamantov applied an anodic potential of + 0.5 V (vs. Ag/Ag^+ reference electrode) to the working electrode after each voltammogram for the reduction of Pb^{++}. In some experiments another wave near -0.9 V was observed for the reduction of Pb^{++}. This wave was small compared to the main wave at -0.3 V and not reproducible and could be due to the reduction of PbO.

In a systematic study conducted earlier in our laboratory, Sawant[149] has investigated the redox system of Pb^{++} ion in five eutectics, viz., ($NaNO_3$ + NH_4NO_3), ($Co(NH_2)_2$ + KNO_3), (Li, Na, K) NO_3, ($Co(NH_2)_2$ + NaCl) and ($Co(NH_2)_2$ + NaCl + $NaNO_3$) using the cyclic voltammetric technique and employing a hanging mercury drop electrode (HMDE). The temperatures were different with each eutectic and ranged between 390 to 475 K. He has claimed perfectly reversible cathodic and anodic waves for Pb^{++} ions at scan rates of 0.010 V s^{-1} and 0.02 V s^{-1}. $\left|I_p^c - I_{p/2}^c\right|$, $\left|I_p^a - I_{p/2}^a\right|$, ΔE_p, $\frac{i_p}{i_a}$ etc. were found to correspond to a full thermodynamic reversibility of this reaction, both oxidation and reduction. The formal redox potentials of Pb^{++} ion in these eutectics are given in Table 5.10. Sawant has arrived at conclusion, on the basis of his data, that metal deposition is definitely taking place in these reactions as the nitrato complex redox reaction is not supposed to show any reversibility. This is in perfect agreement with the work of Inman[44] in (Na, K) NO_3 melt which has been mentioned earlier.

Sawant has further extended this work to anodic stripping voltammetry and has shown that the already mentioned

Table 5.10

Formal Redox Potentials of Pb^{++} in Various Eutectics by Cyclic Voltammetry on a HMDE

Eutectic	Temperature K	Formal Redox Potential E_o V vs. SCE
$NaNO_3 + NH_4NO_3$	403	-0.535
$CO(NH_2)_2 + KNO_3$	391	-0.418
(Li, Na, K) NO_3	403	-0.501
$CO(NH_2)_2 + NaCl$	393	-0.180
$CO(NH_2)_2 + NaCl + NaNO_3$	359	-0.234

eutectics can be successfully used as electrochemical solvents for the determination of Pb^{++} ions by this technique. He does not claim any higher sensitivity or more advantage for this method. The conditions for his experiments in anodic stripping voltammetry could be summarised as follows: Working electrode HMDE, concentration 3 - 10 $\mu g\ cc^{-1}$ of Pb^{++}, sweep rate 11 $mV\ s^{-1}$, electrolysis at -0.600 V, area of the drop 0.014 cm^2, time of electrolysis 30 s, stirring speed 800 r p m and a rest time 30 s. He claimed that all these five eutectics could serve the purpose of solvent in this determination. On the basis of his study the deposited substance can be successfully stripped out of the electrode and so could be only metal. The reversibility of the cyclic voltammetric reaction together with the success of the anodic stripping voltammetry in five such eutectics unequivocally points out metal deposition as a final reaction in the electrostability region studied by Sawant. Of course, his results are valid only for the mercury electrode and he has not mentioned anything about platinum electrodes, where, whether metal deposition is taking place or not, it is a matter of doubt.

Barker and Faircloth[10] have studied the reduction of Co^{++} in a (Li, Na, K) NO_3 melt by square wave polarography using a dropping mercury electrode. They obtained a well defined wave on the square wave polarogram, the half - wave potential being -0.730 V vs the Hg pool reference electrode. In sampled current voltammetry using a Pt stationary electrode, the present work reports a half-wave potential of -0.475 V vs. Ag/Ag^{+}. A comparison of the two values is not possible here due to the uncertainty of the value of the Hg pool reference electrode in the nitrate melt. Baker and Faircloth[10] found the reduction process to be less reversible than the corresponding nickel case, the conductance ratio at the peak of the wave having a value of 1.076. D. Inman et. al[6] have reported that half-wave potential of Co^{++} ion in the same nitrate melt and suggested that the $E_{\frac{1}{2}}$ values was relatively more negative in aqueous solutions. In contrast to the reduction of Ni^{++} and Co^{++} from aqueous solutions, the reduction of these metals in nitrate melt is less irreversible. This is in agreement with the results in the present work. Also it is to be expected that the reversibility should decrease on the change over of the working electrode from mercury to platinum.

Steinberg and Nachtrieb[46] observed only one wave for the reduction of Co^{++} ion in (Li, Na, K) NO_3 melt at 429 K using polarography and a dropping mercury electrode. They found that the $E_{\frac{1}{2}}$ values were dependent on the purity and dryness of the solute and the solvent melt. The limiting current and the shape of the reduction wave, for Co^{++} ions, added as partially dried $Co(NO_3)_2$, $6H_2O$ to a solvent melt which probably contained a considerable quantity of water as impurity, was well defined. The wave, obtained using pure, anhydrons $Co(NO_3)_2$ as solute in a well purified solvent melt was distorted at the foot of the wave and exhibited an ill defined limiting current region and a more negative $E_{\frac{1}{2}}$. The diffusion coefficient was lower at 0.8×10^{-6} $cm^2\ s^{-1}$ at 433 K.

Lowering and Oblath[24] studied the influence of water on the Ni(II) / Ni (Hg) electrode process in molten (Li, K) NO_3 melt at 415 K as a function of the water content, which was varied from 0 to 3.36 M, using the techniques of D.C, differential pulse and linear sweep polarography. Water contents above 1.8×10^{-1} M were introduced directly into the sealed cell via a neoprene septum and microlitic syringe. Henry's Law[168] was adopted for calculating the precise concentration of water dissolved in the melt. The D.C. polarographic $E_{\frac{1}{2}}$ varied from -0.560 V to -0.709 V when the water concentration was varied from 0 to 3.36 M and the i_p from 1.83 to 2.34 uA. With very small quantities of water added to the melt the D.C polarograms were initially shifted in the anodic direction and above 5×10^{-3} M this shift reverted back to the cathodic direction. This signifies the steady, stepwise formation of more stable aquo - complexes. At the same time the polarographic wave becomes progressively less reversible until at 3 M it more clearly resembles the wave obtained in aqueous media.

In the case of Fe^{+++} ion chronopotentiometric curves yielded both a forward wave and a reverse wave, with the $E_{\tau/4}$, quarter-wave potential values equal to -0.425 and + 0.400 V for the forward and reverse waves respectively. The $E_{1/2}$ value obtained from sampled current voltammetry was -0.415 V vs. Ag/Ag^{+}, which was within experimental errors of the quarter-wave potential for the forward reaction. This value is not far from the value of -0.5 V obtained by Barker and Faircloth[10] for the Fe^{+++}-nitrate complex in nitrate melt at 433 K. This work in more detail has been referred to afterwards. The $k_{s,h}$ values obtained by chronopotentiometric, cyclic voltammetric and sample current voltammetric techniques as cited in Table 5.6 indicated an irreversible reaction.

Barker and Faircloth[10] in a study on the reduction of $Fe(NO_3)_3$, $6\,H_2O$ in a nitrate melt gave no waves in the operable voltage range, even after the addition of potassium bisulphate. This was done because $KHSO_4$ acts as an acid competing for the FeO or Fe_2O_3 which may be formed during the reduction process. However, when citric acid was added, a wave was obtained with a half-wave potential about -0.5 V vs. the mercury pool electrode. This wave was, according to them, caused by a reversible reduction and corresponded in shape to a single electron transfer. It seemed likely therefore that a citrate complex was formed which was sufficiently stable to be polarographically detectable and this complex was reduced to the ferrous state. No sign of the further reduction of the ferrous iron to iron metal was seen. They carried out blank determinations with melts containing small amounts of added citric acid and showed that citric acid did not give any significant response .

As far as Cu^{++} was concerned in chronopotentiometry only one single forward and one single reverse wave have been reported in this work. Any other wave if it existed, was too ill - shaped to give any quantitative information and so has been ignored. In cyclic voltammetry we could get the same pattern, one cathodic and another anodic wave and the kinetic shape factor almost pointed out to a one electron reduction from Cu^{++} to Cu^{+} with practically no indication for the formation of CuO; this indication being confirmed with the constancy of $i_p/\gamma^{\frac{1}{2}}C$ for both the cathodic and anodic waves. However, in sampled current voltammetry we could obtain two well defined cathodic waves, the first wave being half of the second wave (Fig. 4.5.9). Cyclic voltammetric studies pointed out to irreversibility of the redox reaction, while sampled current voltammetry almost points out to a near quasi-reversible reaction. As has been pointed out earlier, various techniques could give different values of transfer coefficients and other things being constant different values of heterogeneous standard rate constants also can be obtained.

Suffice it to say that we have not obtained any evidence of oxide formation within the conditions of our experiments.

Barker and Fairclothe[10] in a study of the redox reactions of several ions including Cu^{++} ions by square wave polarography could not get a proper wave. The wave that was obtained was partially observed by the mercury dissolution wave. Its half - wave potential was + 0.08 V vs the Hg pool reference electrode. However, a later reference[43] on the redox reaction of Cu^{++} ions in nitrate melt using platinum as the indicator electrode and an Ag/Ag^{+} as the reference electrode gave results, slightly contradictory to the present work.

In one of the few studies, or perhaps the only study of Cu^{++} ions in a nitrate melt (Na, K) NO_3 at 518 K Mamantov et, al[43] have observed linear dependence of the peak current (first wave) on concentration, within the concentration range of 0.05 to 40 millimolar $Cu(NO_3)_2$ or $CuCl_2$. In all they obtained three waves of which only one wave was found to be concentration dependent. Their experimental technique was linear sweep voltammetry and the sweep rates used were varied from 30 - 250 mV s^{-1}. A second wave at -0.2 V and a third wave at -0.5 V were observed; the first one for both $Cu(NO_3)_2$ and $CuCl_2$ while the third wave was observed only if $CuCl_2$ was used or upon the addition of KCl to the melt containing $Cu(NO_3)_2$. Both the 2nd and 3rd waves were much better refined at faster scan rates. One could assume that this behaviour is qualitatively similar to the case of multiple step charge transfer with catalytic regeneration of the reactant[169] suggesting that Cu^{++} may be regenerated by the reaction of Cu^{+} with NO_3^- ions. One could say that the decrease of $i_p/\gamma^{1/2}$ observed was in qualitative agreement with the theory[169]. The theory of the above mechanism is not directly applicable if partial precipitation of Cu^{++} and Cu^{+} takes place. This study thus cannot give any firm conclusions regarding the reduction of Cu^{++} in the nitrate medium unless additional chemical studies on both Cu^{++} and Cu^{+} in molten nitrates have been performed.

It has however to be borne in mind that Cu^{++} is a better oxide ion acceptor than either Cd^{++} or Pb^{++} [164]. Apparently the precipitation of CuO, more important at higher temperature[170], has in same cases[125,120], prevented the voltammetric studies of Cu^{++}. Voltammetry was made possible by either the addition of an acid ($KHSO_4$)[171] which competes successfully with Cu^{++} for the oxide ion or the use of $CuCl_2$ as a solute[125] indicating the formation of a chloro complex.

The present work conducted in a (Li, Na, K) NO_3 melt differs in two important aspects from the work of Gleb Mamantov[43] et. al. The temperature of 518 K used by the authors was significantly higher than the temperature of 423 K used in the present case. Secondly in the present work a

(Li, Na, K) NO_3 melt has been used while in the earlier work there was no Li NO_3 present. Li with its highly polarising nature could compete with any moisture present for replacement of coordinating molecules bearing the descrete complex $[Cu(NO_3)_3]^-$ ion for reduction. This could completely change the picture of the redox reaction.

5.7 CONCLUSIONS

In this concluding section a summary of the conclusions drawn are detailed together with the logic behind these. Suggestions for further work are also drawn out.

As far as the nitrate melt is concerned, numerous modes of coordination with metal ions have been found for the versatile NO_3^- bond[172-173]. In the present investigation the eutectic (Li, Na, K) NO_3 has been used and the theoretical calculation of Li NO_3 structure shows that the lowest energy is given by a planar bidentate species[174-175]. On the other hand hypersonic velocity measurements indicate that (Na, K) NO_3 melts contain associated species[176] such as ion pairs. Electrochemical studies in another investigation have shown that even an alkaline earth element like calcium exists as a nitrato - complex in a nitrate melt[40].

Considering the ions separately, the Pb^{++} ion is relatively large, exerts a weak field, is rarely adsorbed at most electrodes and being a non - transition element of low polarising power is only weakly solvated or complexed in most oxyanionated media. On the other hand consideration of diffusion[6] and spectroscopic[168,177,178] data indicates that the small, highly polarising Ni^{++} ions are complexed by nitrate ions in nitrate melts; these species are reduced at half-wave potentials close to the theoretical standard electrode potential[6,45,46] unlike the behaviour of hexaaquo-nickelate (II) complexes which predominate in aqueous environments[145]. Moreover coordinating aquo-ligands are not significantly displaced until the water content is reduced well beyond than in aqueous melts[179]. In nitrate melts Ni^{++} ions are thus substantially coordinated by didentate nitrate ions with ligand number of 3 or 4[168,177,178], probably in an octahedral complex. Spectrophotometric studies have shown that discrete complex ions exist in molten nitrates such as $[Ni(NO_3)_3]^-$ where the NO_3^- ions behave as bidentate ligands[177,168]. Electrochemical studies by other investigators suggest nitrato-complexes of Ni^{++}[6,180]. The aforesaid conclusions that Ni^{++} ions exist in a nitrate melt as discrete complex ions can be extended to all the transition metal ions under the present investigation, viz., Fe^{+++}, Co^{++} and Cu^{++}.

In the present investigation cathodic currents, whether by cyclic voltammetry, chronopotentiometry or sampled current voltammetry, are proportional to the amount of metal ion added.

This observation has been confirmed by other workers[6,11,26,44,43,46,50] using other techniques in the case of lead. This implies that the dominant equilibrium reaction in molten nitrates is

$$M(NO_3)_2 \rightleftharpoons M(NO_3)^+ + NO_3^-$$

where at least most of the added metal ions are present in the form of a nitrato complex. Further dissociation of the $M(NO_3)^+$ to form M^{++} should not be considered negligible and it is only reasonable to assume that the metal ions are diffusing to the electrode as $M(NO_3)^+$ and M^{++} in the nitrate melt on the application of potentials. Due to the higher electrical charge on the M^{++} ions they may be diffusing faster and getting deposited as the metal. This disequilibrium near the electrode surface may cause more of the nitrate complex to dissociate. It should be concluded that the deposited metal phase must be rapidly getting oxidised by the nitrate melt according to the reaction

$$M + NO_3^- \longrightarrow MO + NO_2^-$$

In some cases multiple cathodic peaks have been reported for Pb^{++} additions to (Na, K) NO_3 melt[47] and for other melts that contain at least two different cations[42,46]. The possible explanation is that association with melt cations gives complexes that vary in their energy states such as $(PbO\,NO_2, NaO\,NO_2)^+$, $(PbO\,NO_2, KO\,NO_2)^+$ and $(PbO\,NO_2, Li\,NO_2)^+$.

Separate reduction peaks for such complexes are not unexpected since the potentials required for the reduction of pure $NaNO_3$, KNO_3 and $LiNO_3$ melts can vary by as much as 0.5 V due to the electric field effects of the melt[25,181]. However, the nature of the electrode melt can also exert a significant effect on the relative size of the multiple peaks. This will be evident if the comparison is made for the relative peak sizes when platinum and mercury electrodes are used. The further reduction of the nitrato or nitrito complex to form NO, N_2O or N_2 could also produce a second cathodic peak. It can be shown by thermodynamic calculations that such reactions are possible at the potentials encountered for this peak in the presence of cations like Pb^{++}, Co^{++}, Ni^{++}, Fe^{+++} and Cu^{++}. However, in the present investigation no second cathodic peaks were encountered and hence no formation of complexes like $(MO\,NO_2, M'O\,NO_2)^+$, where M = Li, Na or K, M' = Pb, Co, Ni, Fe or Cu, is stipulated.

The possible reactions that can occur at the platinum electrode surface on application of a potential in a nitrate melt containing an electroreducible species can be summarised as follows : (a) $M^{++} + 2\,NO_3^- \longrightarrow MO + 2\,NO_2 + \frac{1}{2}\,O_2$

(b) $M^{++} + 2\,e^- \longrightarrow M^0$ and then alloy formation with Pt

(c) $M^{++} + 2\,e^- \longrightarrow M^0$ and $M + NO_3^- \longrightarrow MO + NO_2^-$

(d) $(MO\,NO_2)^+ + 2\,e^- \longrightarrow MO + NO_2^-$

The first reaction is not apparently probable and is not important. Alloy formation on a mercury surface cannot be ruled out, but on a platinum electrode seems improbable, though not impossible. As has been discussed earlier, experiments[149] in our laboratories, using the technique of anodic stripping voltammetry, have shown that metal deposition, at least in the case of lead, takes place in four eutectics, two pure nitrate solvents, another containing urea and nitrate and the fourth containing urea, nitrate and chloride. To a certain extent this substantiates the possibility of alloy formation with Pt, in the present case. Certain metals[182] like Co, Ni etc. are known to form intermetallic compounds even when they are deposited together on a mercury surface, i.e., instead of formation of individual alloys they prefer to react with each other to form intermetallic compounds. When such cases are known[183] it is not improbable that alloy formation with Pt will not take place. This could only be conformed by anodic stripping voltammetry using a platinum electrode on which any of these metal is deposited. The present discussion strongly points out to either (c) or (d), i.e., metal deposition followed by rapid oxidation of the deposited metal by the NO_3^- ion to form oxides or the reduction of the $(MO\ NO_2)^+$ ion to give the same final product. At this juncture it is difficult to say which is the more possible one but according to the present study the more probable reaction is (c). One of the primary reasons for this conjecture is the strict adherence in the present work to the electrostability region of the melt and the results obtained by the use of mercury electrode by earlier workers in the laboratory using nitrate eutectics. Further studies in this direction can only confirm this view. The present work was done using small concentrations of the electroactive solutes, slow scan rates in cyclic voltammetry, sampled current voltammetry, chronopotentiometry etc.

Evidently many complicated factors are involved in the redox reactions of transition metals in nitrate melts. Liquid rearrangement, homogeneous ligand exchange and an enhanced statistical probability of ligand substitution constitute additional features in the mechanism and are best studied, per se, by spectroscopy. It has to be remembered that polarisation forces between all the ions in the melt have to be considered. In any lithium - containing melt the highly polarising Li^{+} ion must be considered a competitor for any water molecules present. This competition may not be particularly effective compared to the field exerted by Ni^{++} or Cu^{++} ions, but any attempt to quantify this conjecture, whether or not the Born equation is invoked, seems hazardous at present. Suffice to say that a complete and quantitative treatment remains elusive and can be achieved by hyphenated methods, a combination of electrochemistry and spectroscopy.