CHAPTER 2

PREPARATION OF MANGANESE (III) IN AQUEOUS HYDROFLOURIC ACID, AQUEOUS SULPHURIC ACID AND AQUEOUS ACETIC ACID MEDIA, THEIR CHARACTERIZATION AND STABILITIES
2.1 Introduction:

In this chapter a detailed procedure for the preparation of manganese(III) in aqueous hydrofluoric acid, aqueous sulphuric acid and in aqueous acetic acid media by chemical and electrolytic method is discussed. Manganese(III) species formed are identified and characterized by the uv-visible spectra. Stability of standard solution of Mn(III) at various concentrations of H$_2$SO$_4$, HOAc, Mn(II) and in the presence of anions like ClO$_4^-$, HSO$_4^-$ and complexing agents, CH$_3$COO $^-$, P$_2$O$_7^{4-}$, F $^-$ and Cl $^-$, is studied. Formal redox potential, $E_0^\' $ of Mn(III)- Mn(II) couple at different chemical environments is determined.

EXPERIMENTAL:

2.2 Preparation of Manganese(III) in Aqueous Hydrofluoric acid, Aqueous Sulphuric acid and in Aqueous Acetic acid Media:

2.2.1 Preparation of potassium trifluoro(oxalato)manganate(III) complex:

Potassium trifluoro(oxalato)manganate(III) was prepared according to procedure described by Bhattacharjee et al $^1$, by the reaction of manganese(III) oxide with 40% hydrogen fluoride and potassium oxalate in the ratio of 1.0/4-5/1.0 below 20$^\circ$C. Deep pink microcrystalline potassium trifluoro(oxalato)manganate(III) was isolated by the addition of ethanol. The solution was filtered, washed thrice with ethanol, and the solid was kept in a vacuum desiccator. The dry solid was stored at room temperature in a sealed polythene bottle.

Manganese (III) oxide was prepared by literature method $^2$ as follows:

2.2 g of manganese (II) sulphate was dissolved in 350 cm$^3$ water. It was treated with 34 cm$^3$ of 3% H$_2$O$_2$ solution with constant stirring by using magnetic stirrer. Then 50 cm$^3$ of 0.2M ammonia solution was added and brought to boil immediately to evolve excess of oxygen for 4 minutes. Then the solid was filtered, washed with hot water and dried below 100$^\circ$C.
2.2.2 Preparation of manganese(III) sulphate:

Both chemical and electrolytic methods are available for the preparation of manganese(III) sulphate, standard manganese(III) sulphate can be prepared by the oxidation of a hot solution of manganese(II) sulphate by potassium permanganate solution in aqueous sulphuric acid medium. When prepared by this chemical method, there is the problem of manganese dioxide precipitating out. After removal of precipitated manganese dioxide by filtration, the resulting solution would be too weak to be used for most of the purposes. Therefore, electrogeneration on Mn(III) from Mn(II) has been carried out in aqueous sulphuric acid medium. Some of the electrode materials which have been used are platinum, lead, glassy carbon and gold. Preparation of manganese(III) sulphate in the form of a paste, a highly concentrated form for the organic preparation work by electrolytic method, employing antimonial lead electrodes, have been reported previously. The procedure is suitably modified in the present study. The source on manganese (II) is, Glaxo, a special quality (SQ) sample of MnSO₄. 4H₂O. All other chemicals used are of analytical grade.

Electrolytic Cell:

A 500 cm³ beaker with a suitable lid carrying two holes with provisions to hold electrodes is used as a electrolytic cell (Fig.2.1). The anode of the generator circuit is a spectroscopically pure 1% antimony-lead alloy strip of rectangular shape with a dimension 3.0 X 8.0 cms. A narrow lead strip of dimension 0.3 X 8.0 cm is used as cathode. The ratio of anode to cathode area is maintained at 10:1 for higher current efficiency. A small percentage of antimony not only increases the stability of the electrode towards dissolution but also enhances its conductivity characteristics. The two electrodes are separated from each other by a distance of 2.0 cm. the anode to be used is first cleaned with dilute nitric acid and later by means of a wire brush so as to have a bright and polished surface.

The electrolyte is a 0.2 mol dm⁻³ solution of manganese(II) sulphate in 5.0 mol dm⁻³ H₂SO₄. Direct current is passed from a electronically stabilised d.c. power supply unit. Electrolysis is carried out at a cell voltage of 6V and at an anodic current density of 2 mA cm⁻² while the solution is stirred with a magnetic stirrer. The electrolysis is
continued until the concentration of Mn(III) reaches 0.05 mol dm$^{-3}$. Further electrolysis results in a turbid suspension of sparingly soluble manganese(III) sulphate. The clean cherry red coloured solution contains an excess but known concentration of manganese(II), to suppress the disproportionation reaction. The solution is prepared daily, although it appear to be stable for atleast for one month, at $[H^+]$ 5.0 mol dm$^{-3}$. To ascertain that the presence of lead ions in solution (from the dissolution of lead electrodes) is minimal, a blank electrolysis is carried out under identical conditions in 5.0 mol dm$^{-3}$ sulphuric acid but without manganese(II). The resulting solution is tested for lead ions in Pye Unicam Model PU 9000/21 atomic absorption spectrophotometer located at Chemical Laboratory, Mangalore Chemicals and Fertilisers Ltd., Mangalore. The lead ions present are found to be 2.0 ppm, well within the tolerance limit.

2.2.3 Preparation of manganese(III) acetate:

Both electrolytic and chemical methods are available for the oxidation of manganese(II) acetate to manganese(III) acetate. Electrogeneration of Mn(III) in non-aqueous conditions has been described by Pastor et al. In the present work, the current generation efficiency for the production of manganese(III) acetate in aqueous acetic acid is verified and the generated oxidant is used for the kinetic and potentiometric investigations. The electrolysis is carried out in an undivided cell with a platinum foil anode of generation area, 4 cm$^2$. The cathode of generation circuit is a thin platinum spiral of effective area, less than 0.2 cm$^2$. The electrolyte is 0.05 mol dm$^{-3}$ solution of manganese(II) acetate in aqueous acetic acid (90%V/V), also containing 0.5 mol dm$^{-3}$ sodium acetate. Sodium acetate not only enhances the conductivity of the electrolyte solution but also helps by increasing the solubility of manganese(III) acetate due to the formation of acetato complex, $\text{Mn(OAc)}_4^{-}$. When the oxidation is over, an aliquot is removed for estimation of the manganese(III) acetate formed. The solution is prepared daily although it appears to be stable for atleast 2-3 days in 90% glacial acetic acid.

A modified procedure has been recently reported for the oxidation of manganese(II) acetate to manganese(III) acetate. In a 250 cm$^3$ four necked round bottomed flask fitted with a stirrer, condenser and a thermometer, 4.0g of Mn(OAc)$_2$·4H$_2$O dissolved in 25 cm$^3$ of glacial acetic acid is heated to 383 K powdered
potassium permanganate (0.6g) is added in small portions through the condenser over a
20 minute period. Its temperature is maintained at 383K. The reaction mixture is heated
for an additional 20 minutes cooled, poured into water (6.0 cm³) and left to crystallise
over night. The solid is filtered off, washed with ether and dried. The yield is 1.5g (82%)
which is assayed by iodometric titration.

2.3 Estimation of manganese(III):

Standard titrimetric procedures of estimation of manganese(III) are available. In
this work we have made use of the iodometric method. An aliquot portion of
manganese(III) solution is quickly added to an acidified solution containing excess of KI
and the liberated iodine is titrated against sodium thiosulphate to the starch end point.
The results of these estimations are counter checked by sampling manganese(III) solution
into a solution containing excess of Fe(II), with standard solution of Ce(IV) or Cr(VI)
using barium diphenylamine sulphonate as indicator.

2.4 Spectrophotometric Investigation:

Absorption spectra of Mn(III) solution is recorded in HITACHI 220/SHIMADZU 1600/BECKMAN DU6/uv/vis spectrophotometer with one cm quartz cells. Under the experimental conditions, absorption maximum for the prepared potassium trifluoro(oxalato)manganate(III) shows two peaks at 440 nm and 505 nm (Fig. 2.2) i.e.,
the bands corresponding to transitions $^5\text{B}_{1g} \rightarrow ^5\text{B}_{2g}$ and $^5\text{B}_{1g} \rightarrow ^5\text{E}_{1g}$ respectively. Absorption maximum for the electrolytically generated manganese(III) sulphate at $[\text{H}_2\text{SO}_4] = 1.5 - 6.0$ mol dm$^{-3}$ always containing excess but known Mn(II) concentration shows that Beer’s law is obeyed at wavelength 490 nm in the concentration range $5.0\times10^{-4} - 1.0\times10^{-2}$ mol dm$^{-3}$ (Fig.2.3). Manganese (III) acetate shows absorption maximum of 450 nm. Electronic absorption spectra of the freshly prepared manganese
(III) acetate at different acetic acid and sodium acetate concentration are recorded.
(Fig. 2.4).
2.5 Stability of Manganese(III) in Aqueous Hydrofluoric acid, in Aqueous Sulphuric acid and in Aqueous Acetic acid Media:

2.5.1 Stability of potassium trifluoro(oxalato)manganate(III) solution:

Potassium trifluoro(oxalato)manganate(III) in the dry state, appears to be stable indefinitely, but aqueous solution of potassium trifluoro(oxalato)manganate(III) is quite unstable. The solution of trifluoro(oxalato)manganate(III) undergoes decomposition to Mn(II) stage at all temperature. While the decomposition is as much as 63% in 1.0 H₂SO₄, immediately on dissolution, the rate is lower in HCl and HF medium. Maintaining lower temperature increases the stability of the Mn(III) species. The percentage decomposition of the complex in different media at different temperatures are studied and the results are presented in figure 2.5 and 2.6. As a minimum concentration of acid is needed to prevent hydrolysis of the complex, 0.15 ml of 40% HF was added to approximately 0.005 M solution of the complex maintained at 5°C. At this temperature the pH of the solution was found to be 4.5. The concentration of Mn(III) in solution was found out by adding to the aliquot excess of 5% KI solution and quickly titrating the liberated iodine against standard sodium thiosulphate solution using starch as indicator.

2.5.2 Stability of manganese(III) sulphate:

Various attempts have been made to improve the stability of manganese(III) in solution. Manganese(III) solution is relatively more stable in sulphuric acid medium compared to other media like perchlorate or acetate.

The H₂SO₄ concentration is varied between 1.0 to 3.5 mol dm⁻³ and the optimum value of H₂SO₄ concentration and [Mn(III)] / [Mn(II)] ratio for the solution to be stable at least for 24 hours is found out. The concentration of Mn(III) in solution is found out by adding to the aliquot, excess of KI solution and quickly titrating the liberated iodine against sodium thiosulphate using starch indicator.

The change in the concentration and the absorbance with time is monitored for 48 hours. Whenever black particles of MnO₂ appear due to disproportionation reaction, the solution is filtered and the concentration and absorbance of the clear filtrate is noted. At lower concentration of sulphuric acid, manganese(III) deteriorates at a faster rate, but its
stability can be increased by adding higher amounts of manganese(II). Cations like Zn$^{2+}$, Ni$^{2+}$, Cd$^{2+}$ and anions like HSO$_4^-$, P$_2$O$_7^{4-}$, Cl$^-$, F$^-$ do not alter the stability.

There is a need for a suitable solvent medium to study the redox process involving manganese(III) sulphate in partial aqueous conditions. Common solvents used in such cases are methanol, ethanol, isopropyl alcohol, isobutyl alcohol, dimethyl sulphoxide, dimethyl formamide, dioxane and acetic acid. With the sole exception of acetic acid, manganese(III) sulphate reacts with all other solvents oxidatively. Therefore glacial acetic acid is used as solvent to study the systems under partial aqueous conditions.

Manganese(III) sulphate (0.001 - 0.01 mol dm$^{-3}$) in H$_2$SO$_4$-HOAc mixture of overall concentration 2.5 mol dm$^{-3}$ and 90-60% V/V respectively is prepared and the concentration of Mn(III) in the solution is monitored both iodometrically and spectrophotometrically. Because of lower solubility of Mn(II) sulphate in aqueous acetic acid, its concentration should be kept as low as possible. Consequently manganese(III) concentration should also be lowered. The investigation show that manganese(III) concentration less than 0.002 mol dm$^{-3}$ with associated manganese(II) concentration 0.02 mol dm$^{-3}$ is stable in aqueous sulphuric acid - acetic acid mixture for over 48 hours (Table 2.1 and 2.2).

2.5.3 Stability of manganese(III) acetate:

It is observed that 0.01 mol dm$^{-3}$ solution of manganese(III) acetate is stable in acetic acid water medium containing acetic acid above 75% (V/V) for about 48 hours, thereafter disproportionation slowly sets in and black particles of Mn(IV) are formed. The acetic acid concentrations are varied in the range 40-90 % (V/V) and the extent of disproportionation is noted. Acetic acid being a strong donor solvent, higher percentage (V/V) of acetic acid enhances the stability of Mn(III). At lower percentage of acetic acid, manganese(III) deteriorates at a faster rate but, its stability can be increased by adding higher amount of manganese(II) acetate. The details relating to the stability studies are shown in the table 2.3.
2.6 Redox Potential of Mn(III)-Mn(II) Couple in Aqueous Hydrofluoric acid, in Aqueous Sulphuric acid and in Aqueous Acetic acid Media and Cyclic Voltammetric Analysis:

The formal redox potential of Mn(III) – Mn(II) couple is a measure of the oxidising power of the oxidant and it generally decrease on complexation. A known concentration of Mn(III) solution was taken in beaker and the emf of the system was measured using a combination of platinum calomel electrode assembly and the concentration of Mn(III) was estimated iodometrically with standard sodium thiosulphate. The temperature of the solution was maintained at 5±2°C. As the complex undergoes decomposition with time, the concentrations of Mn(III) after fixed intervals of time were measured and hence the concentration of Mn(II) were computed.

The Nemst equation of the $E (V \text{ vs SCE})$ indicates equilibrium potential referring to the position the dynamic equilibrium between oxidised and reduced forms which is established at the platinum electrode surface coupled to a calomel electrode and can be represented as,

$$E (V \text{ vs SCE}) = E_o' + 2.303 \frac{RT}{nF} \log \frac{[\text{Mn(III)}]}{[\text{Mn(II)}]}$$

where $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 278 \text{ K}$, $n = 1$ and $F = 96,500 \text{ C mol}^{-1}$.

The equilibrium redox potential is attained slowly by taking 20-30 minutes in aqueous hydrofluoric acid and aqueous HOAc, but rapidly in aqueous H$_2$SO$_4$.

Plot of $E(V \text{ vs SCE})$ against log $[\text{Mn(III)}]/[\text{Mn(II)}]$ gives a straight line with intercept equal to $[E_o' - E_{calomel}]$ (Table 2.4 and Fig. 2.7). Taking $E_{cal}$ for standard KCl at 278 K as 0.2548V$^{10}$, the formal redox potential of Mn(III) - Mn(II) couple, $E_o'$ can be found out. The redox potential of trifluoro(oxalato)manganate(III) was found 1.071 V.

Different but known amounts of Mn(III) is anodically generated in measured volume of the anolyte in aqueous H$_2$SO$_4$ or aqueous HOAc and the electrode potential is measured each time plot of $E (V \text{ vs SCE})$ against log $[\text{Mn(III)}]/[\text{Mn(II)}]$ gives a straight line with intercept equal to $[E_o' - E_{calomel}]$. Taking $E_{calomel}$ for saturated KCl at 298 K as 0.241 V, the formal redox potential of Mn(III) - Mn(II) couple, $E_o'$, can be found out.
The measurements are made at various concentrations or percentages of H$_2$SO$_4$ or HOAc and in presence of anions HSO$_4^-$, ClO$_4^-$ and complexing agents CH$_3$COO$^-$, P$_2$O$_7^{5-}$, F$^-$ and Cl$^-$. The formal redox potential in the changed environment are computed (Table 2.5 and 2.6 and Figs. 2.8 and 2.9).

The redox systems used in this study are subjected to cyclic voltammetric (CV) investigations to substantiate the mechanistic schemes.

2.7 Results And Discussion :

2.7.1 Trifluoro(oxalato)manganate(III) in hydrofluoric acid :

Manganese(III) oxalate system which is quite unstable$^{11}$, can be stabilized in presence of fluoride ions$^{10}$. Though in the solid state trifluoro(oxalato)manganate(III) is quite stable, but in solution it in 0.3 mol dm$^{-3}$ HF was found to be reasonably stable at 5°C and used as an oxidant. The standard electrode potential of 1.07V of the system in HF media indicates that the trifluoro(oxalato)manganate(III) should be a reasonably good oxidizing agent.

The compound trifluoro(oxalato)manganate(III) is most stable than tris(oxalato)manganate(III). The electronic spectra of trifluoro(oxalato)manganate(III) in solution containing small amount of 40% HF was recorded, it shows two peaks at 505 nm and 440 nm i.e., the bands corresponding to transition $^5$B$_{1g}$ $\rightarrow$ $^5$B$_{2g}$ and $^5$B$_{1g}$ $\rightarrow$ $^5$E$_{1g}$ respectively. This suggests an appreciable splitting of the $^5$E$_{1g}$ ground stage of Mn$^{3+}$ in [MnF$_3$(C$_2$O$_4$)]$^{2-}$ as a consequence of Jahn–Teller effects. The infra red spectra of the compound are similar and show characteristic absorptions for the coordinated C$_2$O$_4^{2-}$ and F$^-$ groups. The pH of the solution at 5°C was found to be 4.5. The decrease in the oxidation power of trifluoro(oxalato)manganate(III) or manganese(III) acetate is manifested in the lowering of its redox potential values to 1.07 or 1.11 V respectively compared with 1.51V of manganese(III) sulphate. Mn$^{3+}_{(aq)}$ and Mn(OAc)$_3$ can be employed only in aqueous sulphuric acid and aqueous acetic acid respectively, of very high concentrations. Trifluoro(oxalato)manganate(III) has a very convenient working range and as such exhibits wide variation in its redox behavior in respect of stoichiometry, selectivity and overall mechanism of related reactions.
2.7.2 Manganese(III) sulphate in aqueous sulphuric acid:

Manganese(III) is readily formed on electrolysis of Mn (II) in the electrolytic cell. The optimum condition for the practical use of electrogeneration of manganese(III) sulphate from lead electrodes include H$_2$SO$_4$ of 2.5-5.0 mol dm$^{-3}$, cell voltage of 6.0V and anodic current density of 1-4 mA cm$^{-2}$ and relatively high concentration of manganese(II) (0.02 mol dm$^{-3}$). The direct reduction of Mn$^{3+}$ to Mn$^{2+}$ at the cathode is found to be negligible especially when the ratio of anode area to cathode area is sufficiently high.

Mn(III) system is oxidizing and is unstable with respect to the simplified disproportionation scheme$^{12}$.

\[
2 \text{Mn(III)} \rightarrow \text{Mn(IV)} + \text{Mn(II)} \quad \ldots (2.2)
\]

\[
2 \text{Mn(III)} + 2\mathrm{H}_2\mathrm{O} \rightarrow \text{MnO}_2 + \text{Mn(II)} + 4\mathrm{H}^+ \quad \ldots (2.3)
\]

According to Waters and Littler, the stabilising effect of sulphate ion is either due to its effect on the disproportionation equilibrium or on the hydrolysis of Mn (IV)$^{13}$. Formation of the complex, H$_2$[Mn(SO$_4$)$_4$] also contributes to the stability of the system$^5$.

It is observed that solutions containing [Mn(III)] 0.05 mol dm$^{-3}$ are unstable even in 5.0 mol dm$^{-3}$ H$_2$SO$_4$ giving rise to a precipitate of MnO$_2$ after standing for 24 hours as per the above scheme. At 5.0 mol dm$^{-3}$ a stock solution of 0.02 mol dm$^{-3}$ Mn(III) with associated Mn(II) of 0.18 mol dm$^{-3}$ is monitored for about a month, and it shows only 5% deterioration. At lower acid concentration, say 1.0 mol dm$^{-3}$ higher concentration of Mn(II) will make the system stable for over 48 hours (Table 2.1). The ideal working range for kinetic and analytical studies is 0.01 mol dm$^{-3}$ Mn(III) with 0.1 mol dm$^{-3}$ Mn(II) in overall H$_2$SO$_4$ concentration of 2.5 mol dm$^{-3}$. And on the partial aqueous condition, Mn(III) of 0.002 mol dm$^{-3}$ with associated Mn(II) of 0.02 mol dm$^{-3}$ in a medium of H$_2$SO$_4$ - HOOAc of concentration 2.5 mol dm$^{-3}$ and 20-60 % respectively is stable for over 48 hours (Table 2.2).

Identical species are produced either by electrolytic or by chemical oxidation of Mn(II). It has been established that manganese (III) sulphate in aqueous sulphuric acid contains Mn$^{3+}_{(aq)}$ and Mn(OH)$^{2+}_{(aq)}$ as reactive species$^{14}$. 

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The hydrolysis constant calculated was $K_h = 0.93 \pm 0.03$

The absorption spectra of both $\text{Mn}^{3+} \text{(aq)}$ and $\text{Mn(OH)}^{2+} \text{(aq)}$ have been reported to be similar in both visible and uv-region. Our observation of the electronic absorption spectra is consistent with the values reported. Kinetic studies have shown that $\text{Mn(OH)}^{2+} \text{(aq)}$ is more reactive. This is found to be due to the decrease in the rate of oxidation with increase in $\text{H}^+$ concentration. Formation of dihydroxo species, $\text{Mn(OH)}^{2+}$ produced by further hydrolysis of $\text{Mn(OH)}^{2+}$ is another possibility.

\[
\text{Mn(OH)}^{2+} + \text{H}_2\text{O} \longrightarrow \text{Mn(OH)}_2^+ + \text{H}^+ \quad \ldots (2.5)
\]

But fresh solution of manganese(III) sulphate is always prepared and used immediately after cessation of the electrolysis there by eliminating any reaction due to $\text{Mn(OH)}^{2+}$. Molar absorption coefficient, $\varepsilon$ ranges between 131-110 dm$^3$ mol$^{-1}$ cm$^{-1}$ at $[\text{H}^+]$, 1.20-2.50 mol dm$^{-3}$ (Fig 2.3). The high value of $\varepsilon$ has been attributed to the presence of hydrolyzed species $\text{Mn(OH)}^{2+}$. An absorption maximum at 490 nm for both the species has been ascribed to the $^5T_{2g} \rightarrow ^5E_g$ transition which is the only spin allowed transition in a spin free $d^4$ system with octahedral symmetry. It is further stated that the extinction coefficient of $\text{Mn(OH)}^{2+} \text{(aq)}$ in the visible region is greater than that of $\text{Mn}^{3+} \text{(aq)}$, perhaps because of greater 4p-3d mixing in the lower symmetry of $\text{Mn(OH)}^{2+} \text{(aq)}$. The peaks of $\text{Mn}^{3+} \text{(aq)}$ are some what broader than that for $\text{Mn(OH)}^{2+} \text{(aq)}$ because of the greater influence of Jahn-Teller effect in the octahedral aquo-ion.

Addition of sodium pyrophosphate, sodium fluoride and sodium chloride lowers the redox potential of $\text{Mn(III)}$-$\text{Mn(II)}$ couple (Table 2.5). This may be attributed to the displacement of coordinated $\text{SO}_4^{2-}$ ligand leading to the establishment of a new $\text{Mn(III)}$-$\text{Mn(II)}$ couple with $\text{P}_2\text{O}_7^{4-}$, $\text{F}^-$ or $\text{Cl}^-$ as ligands.
2.7.3 Manganese(III) acetate in aqueous acetic acid:

Although manganese(III) acetate prepared by the chemical method serves the purpose as analytical reagent, the associated Mn(II) concentration cannot be known exactly. That is the reason why electrochemical method is preferred. The first attempt to generate manganese(III) acetate electrochemically was made by Bawn et al. Lead electrodes cannot be used for this purpose, as the traces of lead dioxide formed dissolves in acetic acid to form lead(IV) acetate, which acts as an oxidizing agent and a satisfactory reproducibility in current efficiency cannot be achieved. However, platinum electrodes can be used with success.

The optimum condition for the practical use of electrogeneration from platinum electrodes include HOAc between 85-95% (V/V), current density of 1.5 mA cm$^{-2}$, Mn(II) concentration about 0.05 mol dm$^{-3}$ and the electrolyte, NaOAc of 0.5 mol dm$^{-3}$. The current efficiency achieved in the undivided cell is about 80%. Absorption spectra of manganese(III) acetate in aqueous HOAc shows a distinct absorption pattern. Below 60% HOAc(V/V) there will not be an absorption maximum. As the HOAc concentration is increased a shoulder appears in the region 410-460 nm and becomes more distinct at 100% HOAc (Fig. 2.4). In the presence of NaOAc, a distinct absorption peak appears around 450 nm. That phenomenon is attributed to the formation of acetato complex, Mn(OAc)$_4^{-}$ where water ligand is replaced by acetate ion.

From the table 2.6 it can be seen that the formal redox potential of the system under study decreases with increase in concentration of the supporting electrolyte, NaOAc. However in presence of different electrolytes like Cl$^{-}$, F$^{-}$, ClO$_4^{-}$ formal redox potential shows a slight increase in value. Variation in percentage HOAc(V/V) does not bring about any significant changes in the redox potential value. But the significant changes in formal redox potential values observed due to the added complexing agent or anions may be attributed to the changes in the co-ordination environment of the oxidising species. Comparison with the data of oxidation in sulphate medium shows that there is a large decrease in formal redox potential values when the system changes from sulphate to acetate media, i.e., 1.52V to 1.16V. Variation in the formal redox potential value due to the added complexing agents is relatively higher in case of manganese(III) sulphate in aqueous H$_2$SO$_4$ than in manganese(III) acetate in aqueous acetic acid (Tables 2.5 & 2.6).
The cyclic voltammogram of trifluoro(oxalato)manganate(III), manganese(III) sulphate and manganese(III) acetate were studied. The 2 mM trifluoro(oxalato)manganate(III) in 0.03 mol dm$^{-3}$ hydrofluoric acid at platinum electrode shows that Mn(III) reduced to Mn(II) at potential -800 mV (Fig. 2.10). The 2 mM manganese(III) sulphate in 1.2 mol dm$^{-3}$ sulphuric acid and 2 mM manganese(III) acetate in 0.2 mol dm$^{-3}$ acetic acid media at glassy carbon electrode shows that Mn(III) reduced to Mn(II) at potentials -900 mV and -1100 mV respectively (Figs. 2.11 and 2.12).
Table 2.1

Changes in concentration of 0.005 mol dm$^{-3}$ solution of manganese(III) sulphate at various concentrations of H$_2$SO$_4$ and Mn(II).

<table>
<thead>
<tr>
<th>[H$_2$SO$_4$] (mol dm$^{-3}$)</th>
<th>[Mn(II)] (mol dm$^{-3}$)</th>
<th>% Mn(III) found at time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>2.5</td>
<td>0.102</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.062</td>
<td>100</td>
</tr>
<tr>
<td>1.75</td>
<td>0.162</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.112</td>
<td>100</td>
</tr>
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<td></td>
<td>0.062</td>
<td>98.2</td>
</tr>
<tr>
<td>1.5</td>
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<td>100</td>
</tr>
<tr>
<td></td>
<td>0.112</td>
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</tr>
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<td>0.062</td>
<td>98.0</td>
</tr>
<tr>
<td>1.25</td>
<td>0.262</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.162</td>
<td>100</td>
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<tr>
<td></td>
<td>0.112</td>
<td>100</td>
</tr>
<tr>
<td>1.0</td>
<td>0.862</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.662</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.262</td>
<td>100</td>
</tr>
<tr>
<td>0.5</td>
<td>0.850</td>
<td>Solution become cloudy with 15 minutes</td>
</tr>
</tbody>
</table>

Ref. 26
Table 2.2

Changes in concentration of 0.002 mol dm$^{-3}$ solution of manganese(III) sulphate in varying [HOAc].

$[\text{H}_2\text{SO}_4] = 2.5 \text{ mol dm}^{-3}$; $[\text{Mn(III)}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Mn (II)}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; Temperature = 298 ±2K.

<table>
<thead>
<tr>
<th>[HOAc] (%V/V)</th>
<th>% Manganese(III) found at time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>10.0</td>
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</tr>
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<td>60.0</td>
<td>100</td>
</tr>
<tr>
<td>70.0</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 2.3

Changes in concentration of 0.005 mol dm\(^{-3}\) solution of manganese(III) acetate at various concentration of acetic acid, manganese(III) acetate and sodium acetate.

Temperature = 298±2K.

<table>
<thead>
<tr>
<th>[HOAc] % (V/V)</th>
<th>[Mn(II)] (mol dm(^{-3}))</th>
<th>[NaOAc] (mol dm(^{-3}))</th>
<th>% of Mn (II) found at time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>80</td>
<td>0.045</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>70</td>
<td>0.045</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.145</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>60</td>
<td>0.045</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.095</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.145</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>50</td>
<td>0.045</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.145</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>0.045</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.065</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.145</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.245</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.545</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.545</td>
<td>0.5</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 2.4

Variation of cell EMF with Mn(III)-Mn(II) ratio.

Temperature: 278±2K; [Mn (III)] = 0.010025 mol dm$^{-3}$.

<table>
<thead>
<tr>
<th>Mn(III) (mol dm$^{-3}$)</th>
<th>Mn(II) (mol dm$^{-3}$)</th>
<th>Log{[Mn(III)]/[Mn(II)]}</th>
<th>E (mV vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00881</td>
<td>0.00122</td>
<td>0.8586</td>
<td>760</td>
</tr>
<tr>
<td>0.00852</td>
<td>0.00151</td>
<td>0.7515</td>
<td>779</td>
</tr>
<tr>
<td>0.00822</td>
<td>0.00180</td>
<td>0.6596</td>
<td>784</td>
</tr>
<tr>
<td>0.00793</td>
<td>0.00210</td>
<td>0.5770</td>
<td>786</td>
</tr>
<tr>
<td>0.00759</td>
<td>0.00244</td>
<td>0.4929</td>
<td>788</td>
</tr>
<tr>
<td>0.00715</td>
<td>0.00288</td>
<td>0.3949</td>
<td>797</td>
</tr>
<tr>
<td>0.00592</td>
<td>0.00410</td>
<td>0.1595</td>
<td>807</td>
</tr>
</tbody>
</table>

$E_0^1 = 1071$ mV
Table 2.5

Effect of complexing agent, $P_2O_7^{4-}$, $F^-$ and $Cl^-$ on the electrode potential of Mn(III)-Mn(II) Couple.
$[H_2SO_4] = 2.5\ \text{mol dm}^{-3}$ ; $[\text{Complexing agent}] = 0.1\ \text{mol dm}^{-3}$.

<table>
<thead>
<tr>
<th>$10^3 [\text{Mn(III)}]$ (mol dm$^{-3}$)</th>
<th>$10 [\text{Mn (II)}]$ (mol dm$^{-3}$)</th>
<th>E (mV vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>3.64</td>
<td>1080</td>
</tr>
<tr>
<td>4.0</td>
<td>3.36</td>
<td>1150</td>
</tr>
<tr>
<td>8.0</td>
<td>3.12</td>
<td>1165</td>
</tr>
<tr>
<td>10.0</td>
<td>0.90</td>
<td>1210</td>
</tr>
</tbody>
</table>

$E_0^{1}$ Mn(III) / Mn(II) (mV)   1520   1481   1441   1421

Ref. 27
Table 2.6

Effect of complexing agents, CH$_3$COO', Cl', F' and ClO$^-$ on the formal electrode potential of Mn(III)-Mn(II) couple.

Acetic acid = 80% (V/V); [Complexing agent] = 0.05 mol dm$^{-3}$; Temperature = 298±2K.

<table>
<thead>
<tr>
<th>$10^2$ [Mn(OAc)$_3$] (mol dm$^{-3}$)</th>
<th>$10^2$ [Mn(OAc)$_2$] (mol dm$^{-3}$)</th>
<th>E (mV vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>0.467</td>
<td>0.967</td>
<td>896</td>
</tr>
<tr>
<td>0.467</td>
<td>1.717</td>
<td>865</td>
</tr>
<tr>
<td>0.467</td>
<td>2.967</td>
<td>836</td>
</tr>
<tr>
<td>0.467</td>
<td>3.467</td>
<td>825</td>
</tr>
<tr>
<td>$E_0^{1}$ Mn(III) / Mn(II) (mV)</td>
<td>1157</td>
<td>1126</td>
</tr>
</tbody>
</table>
Fig. 2.1 Schematic representation of electrolysis cell
Fig. 2.2 Absorption spectrum of 0.001 mol dm$^{-3}$ trifluoro(oxalato)-manganate(III) in 0.03M HF.
Fig. 2.3 Absorption spectra of 0.004 mol dm$^{-3}$ manganese(III) in H$_2$SO$_4$. 
$[\text{H}^+]$ (mol dm$^{-3}$): 1.20(a); 1.62(b); 2.04(c); 2.50(d).
Fig. 2.4 Visible absorption spectra of manganese (III) acetate.

(a) 0.05 mol dm$^{-3}$ manganese(II) acetate, $5.0 \times 10^{-3}$ mol dm$^{-3}$ manganese(III) acetate in 100% HOAc.

(b) 0.05 mol dm$^{-3}$ manganese(II) acetate, $5.0 \times 10^{-3}$ mol dm$^{-3}$ manganese(III) acetate, 0.6 mol dm$^{-3}$ NaOAc in 80% (V/V) HOAc.

(c) 0.05 mol dm$^{-3}$ manganese(II) acetate, $5.0 \times 10^{-3}$ mol dm$^{-3}$ manganese(III) acetate, 0.6 mol dm$^{-3}$ NaOAc in 100% (V/V) HOAc.

(d) 0.05 mol dm$^{-3}$ manganese(II) acetate, $5.0 \times 10^{-3}$ mol dm$^{-3}$ manganese(III) acetate, 0.3 mol dm$^{-3}$ NaOAc in 100% (V/V) HOAc.

(e) 0.2 mol dm$^{-3}$ manganese(III) sulphate in the mixture $H_2SO_4 (2.5$ mol dm$^{-3}) + 50\% (V/V) HOAc$.

(f) 0.2 mol dm$^{-3}$ manganese(III) sulphate with 5.0 mol dm$^{-3}$ $H_2SO_4$. 

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Fig. 2.5 Percentage decomposition of $K_2[MnF_3(C_2O_4)] \cdot H_2O$ in 0.03 mol dm$^{-3}$ HF at different temperatures.
Fig. 2.6 Percentage decomposition of $\text{K}_2[\text{MnF}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$ in HCl, H$_2$SO$_4$ and HF medium at 5 ± 2°C.

a, 0.05 mol dm$^{-3}$ HCl;    b, 1.0 mol dm$^{-3}$;

x, 0.05 mol dm$^{-3}$ H$_2$SO$_4$;    y, 1.0 mol dm$^{-3}$ H$_2$SO$_4$;

z, 0.03 mol dm$^{-3}$ HF.
Fig. 2.7 Plot of $E$ (mV versus SCE) vs $\log \frac{[\text{Mn(III)}]}{[\text{Mn(II)}]}$ for trifluoro(oxalato)manganate(III) in HF medium; Temperature = $5 \pm 2^\circ$C.
Fig. 2.8 Plot of E(mV vs SCE) versus log \([Mn(III)] / [Mn(II)]\) for manganese(III) sulphate system.

Temperature = 298 ± 2K;
\([H_2SO_4] = 2.5\) mol dm\(^{-3}\);
Complexing agent (0.1 mol dm\(^{-3}\)):
- nil (a);
- HSO\(_4\) (b);
- \(P_2O_7^{4-}\) (c);
- F\(^-\) (d);
- Cl\(^-\) (e).
Fig. 2.9 Plot of $E$(mV vs SCE) versus log [Mn(III)/Mn(II)] for manganese(III)acetate system. Temperature = 298 + 2K; [HOAc] = 60% V/V; Complexing agent (0.05 mol dm$^{-3}$): Cl(a); ClO$_4^-$; nil (C); F(d); CH$_3$COO(e).
Fig. 2.10 Cyclic voltammogram of 2mM trifluoro(oxalato)manganate(III) in 0.03M hydrofluoric acid at platinum electrode. Sweep rate: 50mV/s
Fig. 2.11 Cyclic voltammogram of 2mM manganese(III) sulphate in 1.2 M sulphuric acid at glassy carbon electrode. Sweep rate: 50mV/s.
Fig. 2.12 Cyclic voltammogram of 2 mM manganese(III) acetate in 0.2M acetic acid medium at glassy carbon electrode. Sweep rate 50mV/s
2.8 References:


