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Research Article

AN INSIGHT INTO MN (II) CHEMISTRY: A STUDY OF REACTION KINETICS UNDER ALKALINE CONDITIONS

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ABSTRACT

Transition metals have many industrial and research applications. Also, many biological systems have transition metal ions as cofactors. One of the most extensively studied transition metals is Manganese. Under acidic conditions Mn^{2+} state is very stable, however, under alkaline condition Mn^{2+} state is readily oxidized to Mn^{3+} state. In solution, Mn^{3+} state disproportionate to Mn^{2+} state and Mn^{4+} state. Results from this study show that oxidation of Mn^{2+} state to Mn^{3+} state can take place in the presence or absence of oxygen. Also, the oxidation of Mn^{2+} state to Mn^{3+} state is faster in the oxygen rich environment than in inert environment suggesting different reaction kinetics are involved. Finally, the chemistry of aqueous Mn^{2+} state under alkaline condition is presented.

Keywords: Disproportionate, Oxidation, Manganese, Ion and kinetics

INTRODUCTION

The Mn^{2+} ion is a d^5 system, which is the most stable oxidation state of manganese in solution, and many Mn^{2+} compounds are known such as manganese (II) sulfate, manganese (II) chloride and etc. The Mn^{+3}oxidation state is known in compounds such as manganese (III) acetate. Under basic conditions aqueous Mn^{2+} does not exist. Instead of that it was found as insoluble oxides of manganese[1]. The following mechanism involving Mn^{2+}, Mn^{3+} and Mn^{4+} under alkaline conditions in the presence of hydrogen peroxide has been proposed[2,3]:

$2Mn^{2+} + H_2O_2 \rightarrow 2Mn^{3+} + 2OH^-$

$4Mn^{2+} + O_2 + 2H_2O \rightarrow 4Mn^{3+} + 4OH^-$

$2Mn^{3+} + H_2O_2 + 2OH^- \rightarrow 4Mn^{3+} + 4OH^-$

$2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$

$Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^+$

$MnO_2 + H_2O_2 \rightarrow Mn^{2+} + 2OH^- + O_2$

At pH less than 10, manganese also forms colloidal Oxo-bridged complexes that may involve Mn^{2+}, Mn^{3+} or Mn^{4+} species[4,5]. The following reaction scheme accounts for the presence of colloidal manganese[6-8].

$Mn^{4+} + H_2O_2 \rightarrow Mn^{3+} + 2H^+ + O_2^-$

$Mn^{3+} + H_2O_2 \rightarrow Mn^{2+} + 2H^+ + O_2^-$

$Mn^{3+} + O_2^{-\cdot} \rightarrow Mn^{2+} + O_2$

$Mn^{2+} + Mn^{4+} \rightarrow 2Mn^{3+}$

Kao and Weibel[9] reported that the oxidation state of Mn^{2+} to Mn^{3+} is followed by disproportionate reaction to produce Mn^{2+} and MnO_2. Randle and Kuhn[10] demonstrated that reaction order is one for both oxidation of Mn^{2+} to Mn^{3+} and the reduction of Mn^{3+} to Mn^{2+} at the platinum electrode. The presence of intermediate species such as $Mn(OH)_4^{2-}$ and $Mn(OH)_3^-$ has been suggested by Kozawa and Yeager[11]. However, no direct evidence of these species has been observed in voltammogram. In order to understand how some biological systems with manganese as a cofactor work, there is need to evaluate the chemistry of manganese in aqueous solution. Due to many controversies in the chemistry of Mn^{2+} under alkaline conditions, the aim of this project is to clarify these controversies.

MATERIALS AND METHODS

The manganese sulfate, manganese (III) acetate and sodium hydroxide (1.0 mol/L) from Fisher Scientific (Nepean, ON, Canada) were used in the experiments without further purification. De-ionized and distilled water was used throughout the experiments. The experimental runs were carried out in 250 ml Erlenmeyer flasks, water and sodium hydroxide were mixed together and then manganese (II) sulfate was introduced. Samples were collected during the course of the reaction for the determination of Mn^{3+} concentration.

The reaction runs in a 500 ml gas washing bottle with a side inlet and fitted disc at the bottom, with nitrogen or oxygen flowing through the solution continuously. The reactions starts immediately as the nitrogen or oxygen purge were applied, and the experiment runs were conducted. The Mn^{3+} was measured by following a method used by other workers[12]. Sodium gluconate was added to the sample, resulting in the formation of colored complexes, which were then monitored by UV-Vis spectrophotometer. The intensity of the color is correlated to the Mn^{3+} ion concentration.

A UV spectrophotometer (model Milton Roy 1001 plus), interfaced to µ-Quant software, which runs on IBM PC was used. The cuvette width was 1 cm. The Mn^{3+} ion complexes have maximum absorbance at 235 nm and 450 nm. A wavelength of 450 nm was chosen in this study. Runs under vacuum were performed with the vacuum pump connected to Erlenmeyer flask with side outlet. The system was kept under vacuum throughout the experimental runs. Samples were taken periodically from the system and the UV-Vis absorbance measured. All the glassware and other containers used in this experiment were soaked with a mixture of H_2O_2/H_2SO_4 and then rinsed three times with de-ionized distilled waters.

RESULTS AND DISCUSSION

When a solution of Mn^{2+} is added to an alkaline solution, the initially colorless solution turns brown. The formation of a brownish solution is a clear indication of the presence of Mn^{3+}, either in the form $MnO(OH)$ or $Mn(OH)_3$[1]. In alkaline media, sodium gluconate ($NaGH_4$) stabilizes Mn^{2+}, Mn^{3+} and Mn^{4+} oxidation states. Reaction of dinuclear Mn^{2+}-gluconate with O_2 is first order with respect to each reactant, yielding the Mn^{3+} species and H_2O_2. Further oxidation of the dinuclear Mn^{3+} complex gives Mn^{4+} complex and peroxide ion. All these reactions can be summarized as follows[12]:

$Mn^{2+} + 2GH_4^- \rightarrow [Mn^{2+}(GH_3)2]^{2-} + 2H_2O$

$2[Mn^{2+}(GH_3)_2]^{2-} + 2H_2O \rightarrow [Mn^{2+}{}_2(GH_3)_4(H_2O)_2]^{4-}$

$Mn^{2+}{}_2(GH_3)_4(HO)_2]^{4-} + O_2 \rightarrow [Mn^{3+}{}_2(GH_3)_4(HO)_2]^{4-} + H_2O_2$

On standing $[Mn^{3+}{}_2(GH_3)_4(HO)_2]^{4-}$ is very slowly oxidized to $[Mn^{4+}{}_2(GH_3)_4O_2(HO)_2]^{4-}$ by O_2:

$[Mn^{3+}{}_2(GH_3)_4(HO)_2]^{4-} + O_2 + 3OH^- \rightarrow Mn^{4+}{}_2(GH_3)_4O_2(HO)_2]^{6-} + HO_2^- + H_2O$

It is known that the complex ion $Mn^{4+}{}_2(GH_3)_4O_2(HO)_2]^{6-}$ gives a cherry-red color while $Mn^{3+}{}_2(GH_3)_4(HO)_2]^{4-}$ gives a brown color. Figure 1 presents the development of Mn^{3+} concentration as a function of wavelength at constant sodium hydroxide concentration. The Mn^{2+} concentrations used were 3 ppm, 6 ppm, 9 ppm and 12 ppm. As expected, there was an increase in absorbance with an increase in the Mn^{2+} concentration. This is because increasing the concentration of Mn^{2+} results in an increase in Mn^{3+} concentration as indicated by the following equations:

$2Mn^{2+} + 4OH^- \rightarrow 2Mn(OH)_2$

$4\ Mn(OH)_2 + O_2 \rightarrow 4MnOOH + 2H_2O$

$4\ Mn(OH)_2 + 4H_2O \rightarrow 4Mn^{3+} + 12OH^-$

$4\ Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn^{3+} + 12OH^-$

The last two equations explain why increasing Mn^{2+} concentration results in an increase in Mn^{3+} concentration. Also, it is possible that the manganese (II) hydroxide can give various oxo species of manganese as indicated by the following reactions:

$2Mn(OH)_2 \rightarrow 2MnOOH + H_2O$

$3Mn^{2+} + 9OH^- \rightarrow 3Mn(OH)_3$

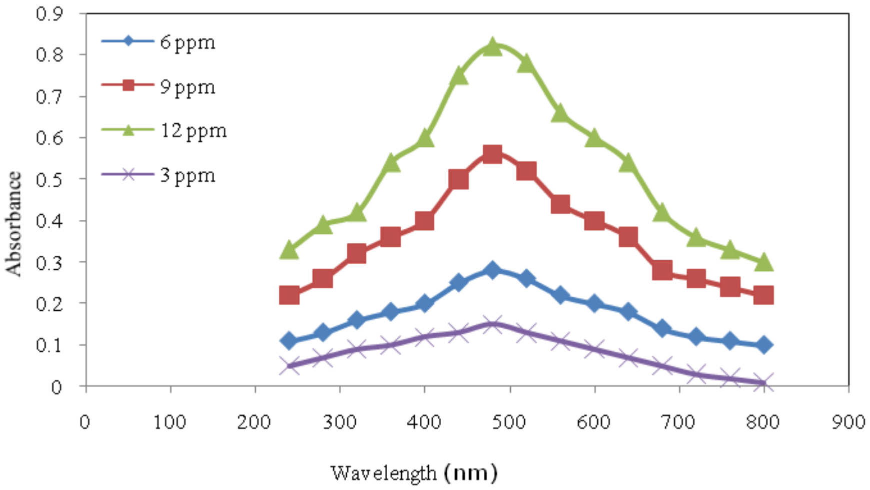

Fig. 1: Development of Mn^{3+} at various wavelengths (NaOH, 1.0 µmol/µL, 25°C)

We then held the concentration of Mn^{2+} constant and studied the development of Mn^{3+} at various concentrations of sodium hydroxide and the results are presented in Figure 2. There is an increase in Mn^{3+} absorbance with increase in sodium hydroxide concentration from 0.5 µmol/µL to 5 µmol/µL. Further increase in the sodium hydroxide concentration results in decrease in Mn^{3+} concentration and results in the drop in absorbance. This observation is not unusual because addition of excess sodium hydroxide to $Mn(OH)_3$ results in the formation of soluble manganese complex[1]:

$3Mn^{2+} + 9OH^- \rightarrow 3Mn(OH)_3$

$Mn(OH)_3 + OH^- \rightarrow Mn(OH)_4^-$

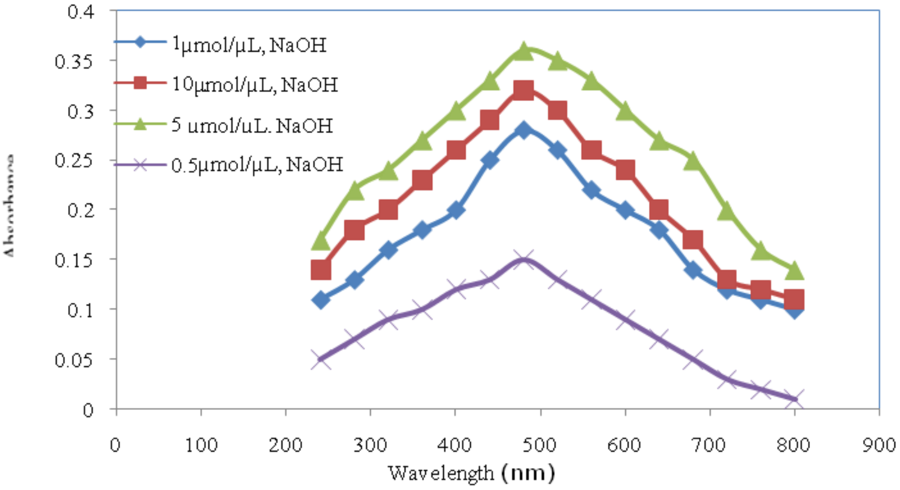

Fig. 2: Development of Mn^{3+} concentration at various wavelengths (3 ppm Mn^{2+}, 25°C)

The formation of soluble $Mn(OH)_4^-$ results in a decrease in the absorbance.

Previous workers had indicated that oxidation of Mn^{2+} to Mn^{3+} can only take place in the presence of O_2. We then studied the effect of N_2 purge on the development of Mn^{3+} and the results are presented in Figure 3. The concentration of Mn^{2+} was 6 ppm and 12 ppm, and the concentration of sodium hydroxide was maintained at 1µmol/µL. The concentration of Mn^{3+} without N_2 purge was found to be higher than with N_2 purge at the two Mn^{2+} concentrations studied. This confirms that O_2 is involved in the oxidation of Mn^{2+} to Mn^{3+}. Also, this observation proves that Mn^{2+} can be oxidized to Mn^{3+} in the absence of O_2.

We then studied the effect of O_2 purge instead of N_2 purge on the development of Mn^{3+} and the results are presented in Figure 4. It is clear from the two concentrations of Mn^{2+} used that with O_2 purge there is more development of Mn^{3+} than without. This further supports the fact that oxidation of Mn^{2+} to Mn^{3+} can take place with O_2. Also, the more Mn^{3+} formed results into faster disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+}.

Furthermore we studied the development of Mn^{3+} at Mn^{2+} concentrations 6 ppm and 9 ppm with and without O_2 purge as a function of time and the results are presented in Figure 5. It is clear that with O_2 purge the rate of development of Mn^{3+} is enhanced and this is because O_2 rich environment results in the following equations being shifted further to the right:

$$4\,Mn(OH)_2 + O_2 \rightarrow 4MnOOH + 2H_2O$$

$$4\,Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn^{3+} + 12OH$$

This observation confirms that oxidation of Mn^{2+} to Mn^{3+} follows different kinetics when O_2 is present as opposed to when it is absent.

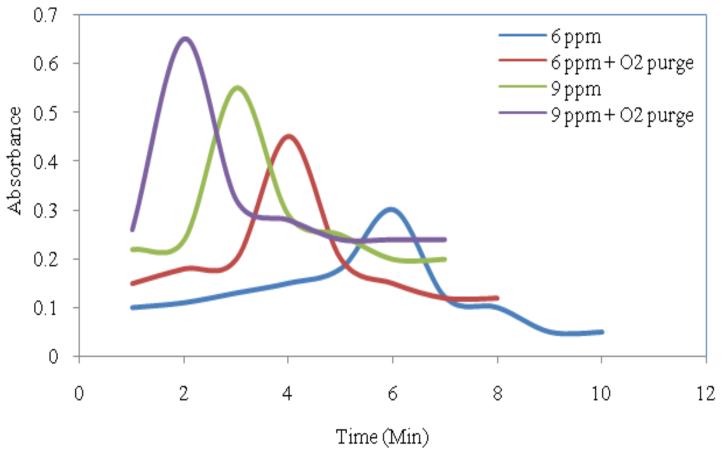

Fig. 5: The development of Mn^{3+} with time with and without O_2 purge (Mn^{2+} concentarions, 6 ppm and 9 ppm)

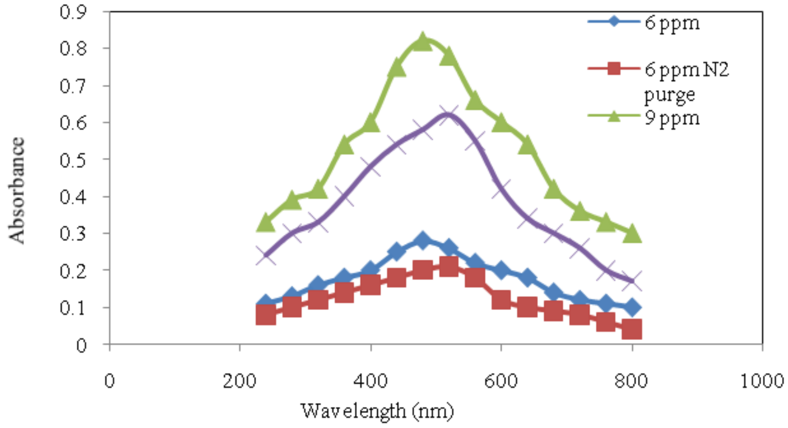

Fig. 3: Absorbance as a function of wavelength with and without N_2 purge (NaOH, 1.0 µmol/µL, 25°C)

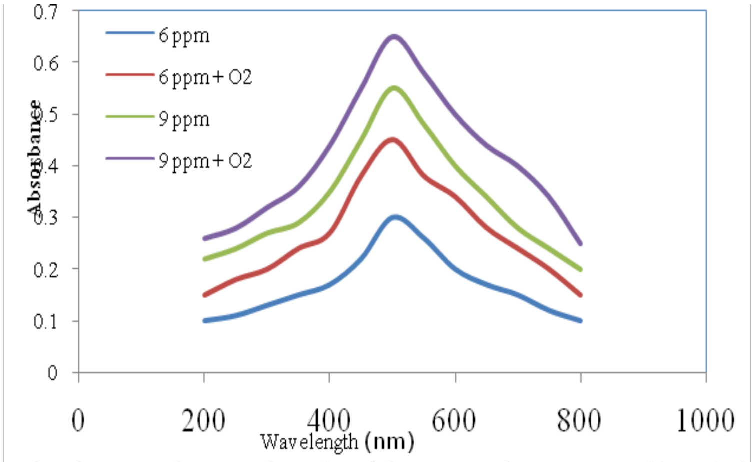

Fig. 4: Absorbance as a function of wavelength for O_2 purge (NaOH, 1.0 µmol/µL, 25°C)

We then studied the development of Mn^{3+} at normal conditions and under vacuum. It is clear that the development of Mn^{3+} is slower and the amount of Mn^{3+} formed is less. This was confirmed when the Mn^{2+} concentration was increased to 9 ppm. All these observations lead to the conclusion that the oxidation of Mn^{2+} to Mn^{3+} can still take place in absence of O_2.

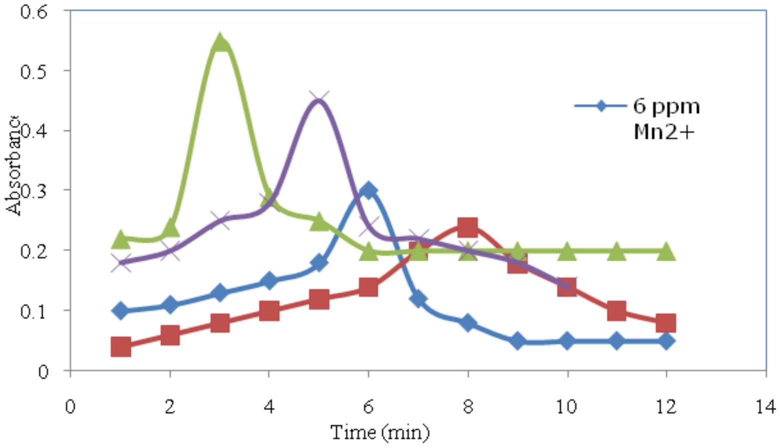

Fig. 6: Development of Mn^{3+} at various time interval at normal conditions

CONCLUSION

Manganese (II) is very unstable under alkaline medium. It is readily oxidized to Mn^{3+} in the presence of oxygen or absence of oxygen. Manganese (III) species is also very unstable, once formed it readily disproportionate into Mn^{2+} and Mn^{4+}. The Mn^{4+}, then undergoes hydrolysis to form MnO_2 which appears as a black precipitate. It has been demonstrated that removal of O_2 in Mn^{2+} system under alkaline media decreases the oxidation process of Mn^{2+} to Mn^{3+}, well as the disproportionation of Mn^{3+} to Mn^{4+} and Mn^{2+} species.

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