



STUDY OF INOSITOL IN ACIDIC MEDIUM

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Abstract: Redox reactions are commonly carried out by many types of oxidants. They are classified as an anionic deelectronator or cationic deelectronator according to their nature. Oxygenated ions like dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and permanganate (MnO_4^-), etc. Are anionic ones whereas cerium (IV), Hg(II) and Cu (II), etc. are cationic. The nature of an deelectronator plays an important role on the stages of oxidation as well as on the nature of final oxidation product.

The course of the reaction is also influenced by the nature of oxidant. The powerful oxidant, Ce(IV) behaves as 1-equivalent reagent. The Ce(IV)- Ce(III) couple is 1.6 volts, when the standard potentials of the titrated and titrant systems are close together. However, the change in potential at the equivalence point is not marked to any appreciable extent and satisfactory potentiometric titrations in such cases are therefore are not possible. Hence the essential condition for a satisfactory potentiometric redox titration is that the two redox systems involved should differ appreciably in their formal potential values (the recorded e.m.f. values). The greater the difference the larger will be the inflexion and more precisely can the end-point be determined. Nitric acid has been selected as a medium of the reaction in this case. Its concentration was 1.0(N), 1.5 and 2.0(N). The electrode used was a bright platinum wire.

Key words:

Inositol, oxidant, cation, oxidation, titration, Cerium(IV)

INTRODUCTION:

Inositol (hexahydroxy cyclohexane) is an important component of B-complex. It is widely distributed in plants and animal kingdom It is synthesized in the kidneys. It is also present in the muscles and organs of the animals. It is thus a growth promoting factor which possess in antialopecia (anti-baldness) property. Its chloro derivative has also been found to be powerful insecticide. The physiological importance and the structural aspect both have attracted attention to explore some properties and reactions of inositol. This study may thus provide a clue for understanding the oxidative metabolism of inositol

within a living being. Previous workers have published reports regarding the mechanistic studies of some lower alicyclic alcohols with a kinetic approach only. Higher alcohols in this class have remained little revealed till today. It is for these reasons, that mechanistic studies in some oxidations of inositol by Ce(IV) with an equilibrium approach has been planned. Cerium(IV) is a suitable oxidant for investigating the path of oxidation of organic compounds. It has been reported that most of the reactions involve direct oxidation of organic compound by cerium(IV) and as such the investigation of the mechanism of oxidation would be rather easier. Mechanistic studies with an equilibrium approach shall help in knowing the intermediate stages of oxidation as well as the nature of intermediates in a way to give a sound basis of mechanism. Potentiometry is a suitable and precise electrometric technique for investigating the mechanism of such oxidation. In the present project, potentiometric studies of meso-inositol has been carried out using platinum wire electrode under selected conditions of storage and temperature in aqueous acidic media. H₂SO₄, HCl and HNO₃ acids has been used in a narrow range of concentrations to avoid any complication. Direct oxidation of meso-inositol in aqueous medium has been done to know the final oxidation product and to fix up the stoichiometric proportions of redox systems.

Experimental methodology:

Redox reactions are commonly carried out by many types of oxidants. They are classified as an anionic de-electronator or cationic deelectronator according to their nature. Table (I to III) along with the potentiometric curves (Figs. 01 to 14) have shown a number of potentiometric inflexions arising from the changes in the potential of the various redox systems which were created by delivering different volumes of 0.05(M) ammonium ceric sulphate to a fixed volume (6.0ml) of 0.0125(M) meso-inositol solution in an inert atmosphere of carbon dioxide. The potentiometric inflexions of different kinds have been indicated at the foot note of each table. The conditions imposed were storage hours (varying from a few hours to several hours at room temperature and heating of redox systems between 60° – 70° C from three hours to six hours).

By looking in to the data (table I to III), of potentials recorded 1.0(N), 1.5(N) and 2.0(N) HNO₃ concentrations under various conditions of storage hours and the extent of heating. It appears that the decrease in potential in HNO₃ with increasing acid concentration can be attributed to complexation of Ce with NO₃⁻ (nitrate anion). Under the mild conditions of the experiments by imposing short storage hours (twenty four hours to forty eight hours), the required number of inflexions (except inflexions corresponding to 1e and 2e) have not emerged on volume – e.m.f. profiles (Figs. 1, 2 & 6). However, there are some representative curves (Figs. 3, 4, 7, 9, 12 & 13) which stand in favour of step-wise oxidation of inositol up to saccharic acid stage.

On the basis of over all potentiometric investigations in various HNO₃ concentrations, it may be said that single electron-transfer mechanism is involved in the oxidation of inositol by (NH₄)₄Ce(SO₄)₄ (ammonium ceric sulphate), in a narrow range of acid concentrations under selected conditions of experiments like storage hours and effect of temperature.

In 1.0(N) HNO₃ concentration there are two representative curves which

reflects most of the required inflexions during oxidation of inositol (Figs. 3&4), only a few inflexions are missed in the above curves. In stead some anomalous inflexions at 11.4ml and 12.0ml have appeared. After imposing small storage hours, ranging from twenty four to forty eight, only the earlier stages of oxidation of inositol have been captured at 1.5ml and 3.0ml (Figs. 1&2). The inflexions at 1.5 ml is moderate in nature and and it corresponds to the formation of a free radical intermediate ($C_6H_{11}O_6$). This may be said first electron abstraction stage. Simultaneously, the second electron transfer stage can also be seen in the form of a weak inflexion at 3.0 ml. This is because of the fact that the formation of 2,3,4,5,6 hydroxy- 1- one has ensued. After heating the reaction mixtures between (60° - 70°), for a couple of hours (three to six hours), followed by a post-storage of twenty four to seventy two hours. The inflexions gain prominence invariably (fig 3 and 4). At the same time, the final inflexion, corresponding to 6e stage, has also appeared in a prominent way. Saccharic acid which is the final oxidation product of inositol, is held responsible for this. On increasing the concentration of nitric acid 1.5(N), the oxidation of inositol has been found to proceed in in a subtitle manner, without any complication. As a result of which the nature of inflexion obtained, are mostly conventional and well marked. There are two representative curves which have denoted most of the required inflexions corresponding to a number of stages of oxidation of inositol by ammonium ceric sulphate (Figs.7&9). These curves were obtained after imposing the pre-storage of 24 hours at room temperature (18 - 19° C), followed by three and six hours heating (60 - 70° C) along with a post-storage of twenty four hours to seventy two hours (Figs.7&9). The inflexions corresponding the formation of free radical intermediates at 1.5ml, 4.5ml and 7.5ml are also seen in the potential composition graphs, only under selected conditions of the experiments (Figs.7&9). There is a remarkable observation in this case that the natures of such inflexions are conventional instead of unconventional. A very prominent inflexion at 6.0 ml, corresponding to the fourth stage of oxidation of inositol has been observed after heating the reaction mixtures (60 - 70° C) for a couple of hours, followed by a post storage of twenty four to forty eight hours at room temperature 18 - 19° C (Figs.7&8). The formation of a stable intermediate like 3,4,5,6 hydroxy-1:2 dione may be attributed for the inflexion standing at 6.0ml which is the correct stoichiometric point. The formation of saccharic acid at the final stage or oxidation of inositol has also been supported by the emergence of a very prominent inflexion at 9.0ml, after imposing drastic conditions like heating between (60 - 70° C) followed by a long storage of seventy two hours at room temperature (18 - 19° C). This involve C_1 - C_2 bond fission in the molecule of inositol.

In 2.0(N) HNO_3 concentration , although some prominent inflexions corresponding to the stages of 1e, 2e, 3e, 4e, 5e and 6e are Obtainable (Figs. 10,11,12 &13), but are not seen at each condition of the experiments, like in position of small storage hours, heating as well as short and moderate post-storage hours. The missing of inflexions in this acid concentration may be explained by the observation that ceric nitrate equilibria are complicated by dimerisation, hydrolysis and association with cerium (III). This would provide an added complexity in cerium (IV) oxidation where appreciable quantity of cerium(IV) are formed. The inflexions corresponding to 1e, 2e, and 3e are marked only after giving a storage of 24 hours at 19° c (Fig. 10). The inflexions corresponding 1e and 3e are prominent and conventional where as the inflexion corresponding to 2e that is at 3.0 ml is, weak in nature. On the other hand inflexions

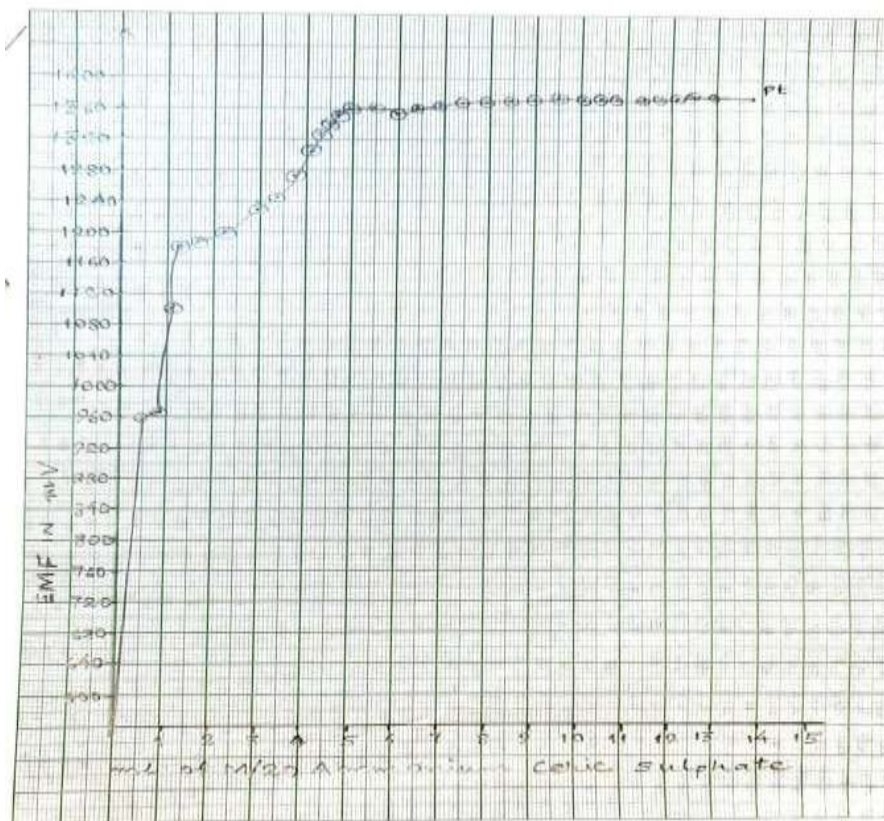


Figure: 1

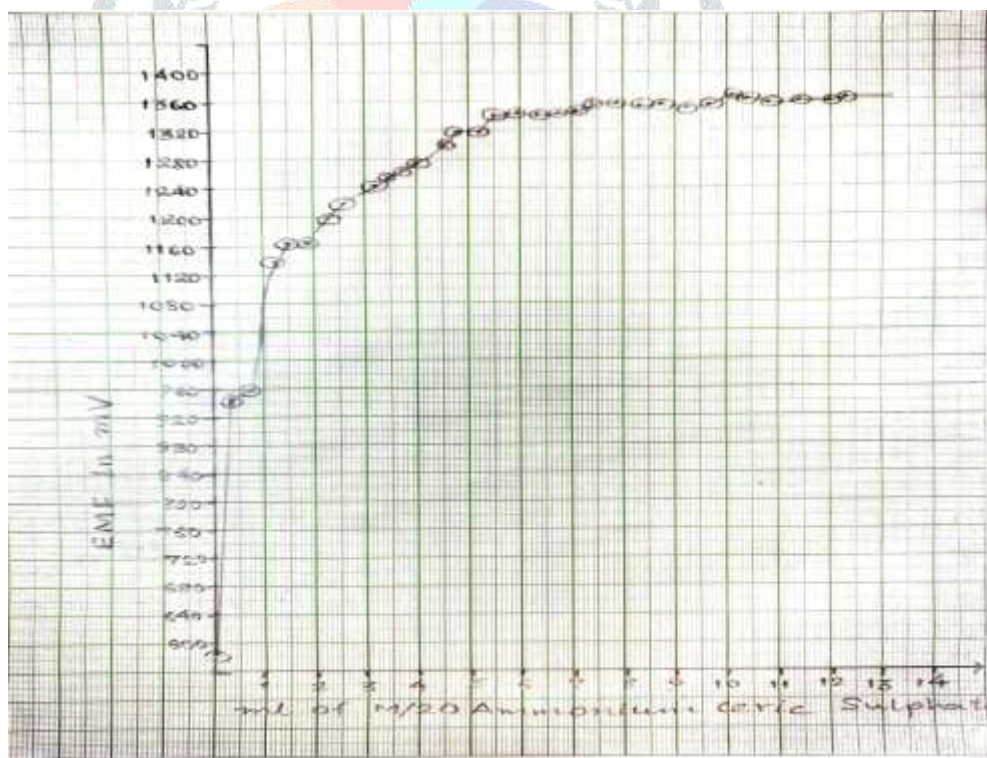


Figure - 2

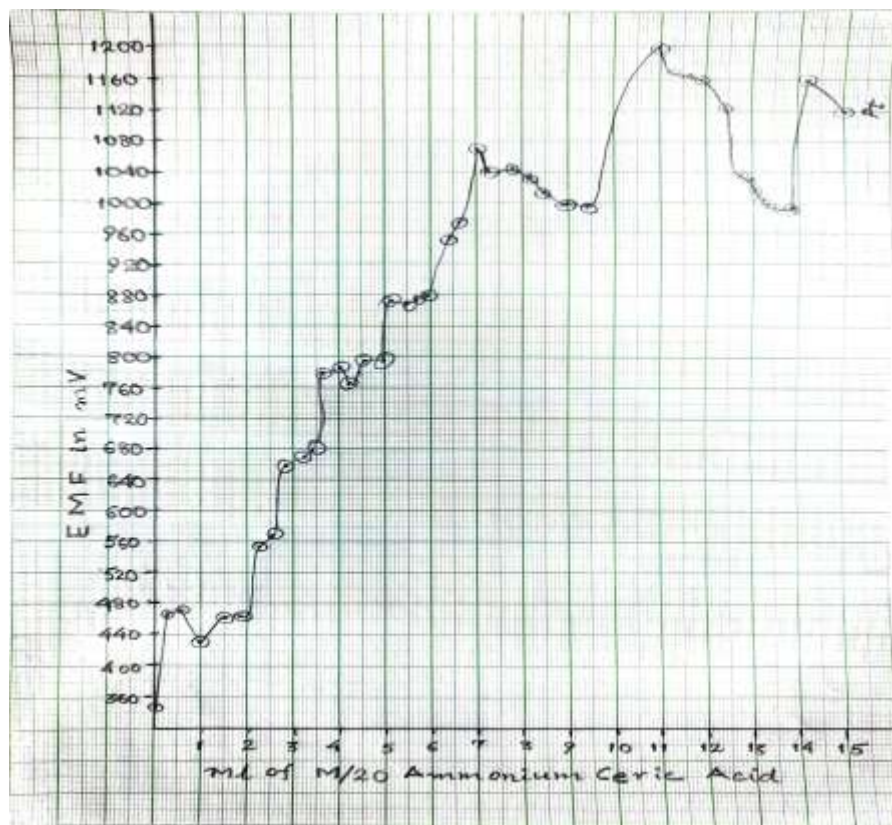


Figure - 3.

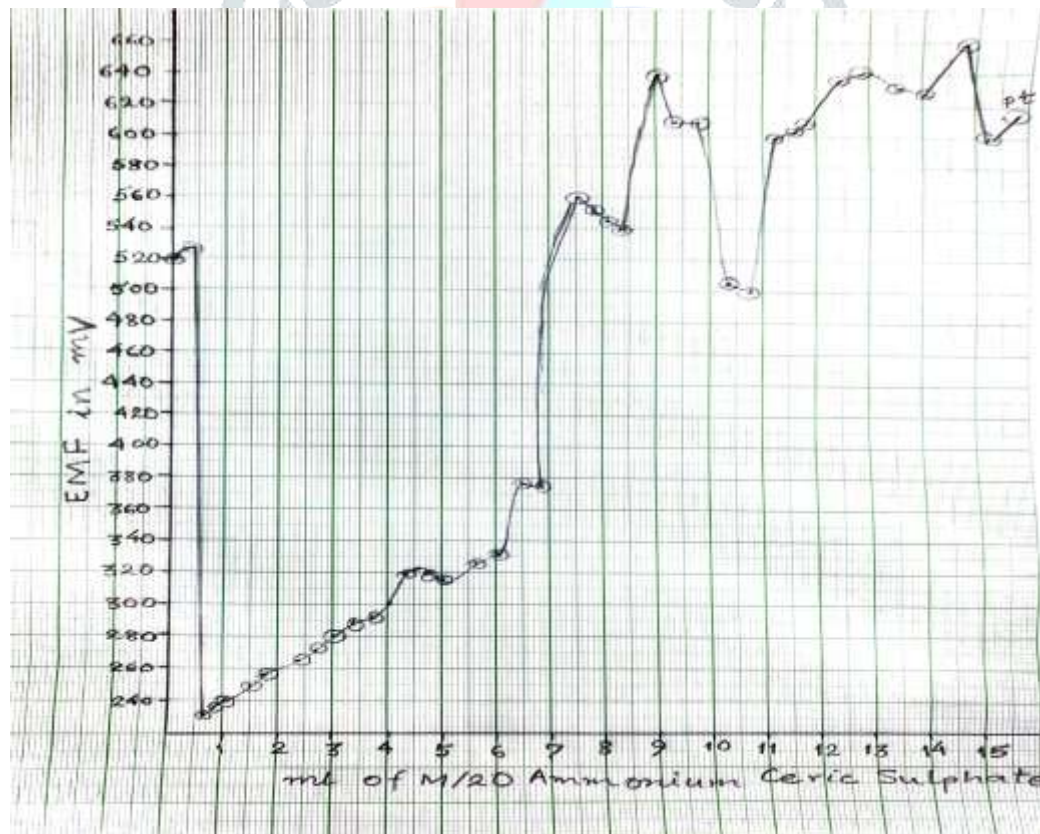


Figure - 4

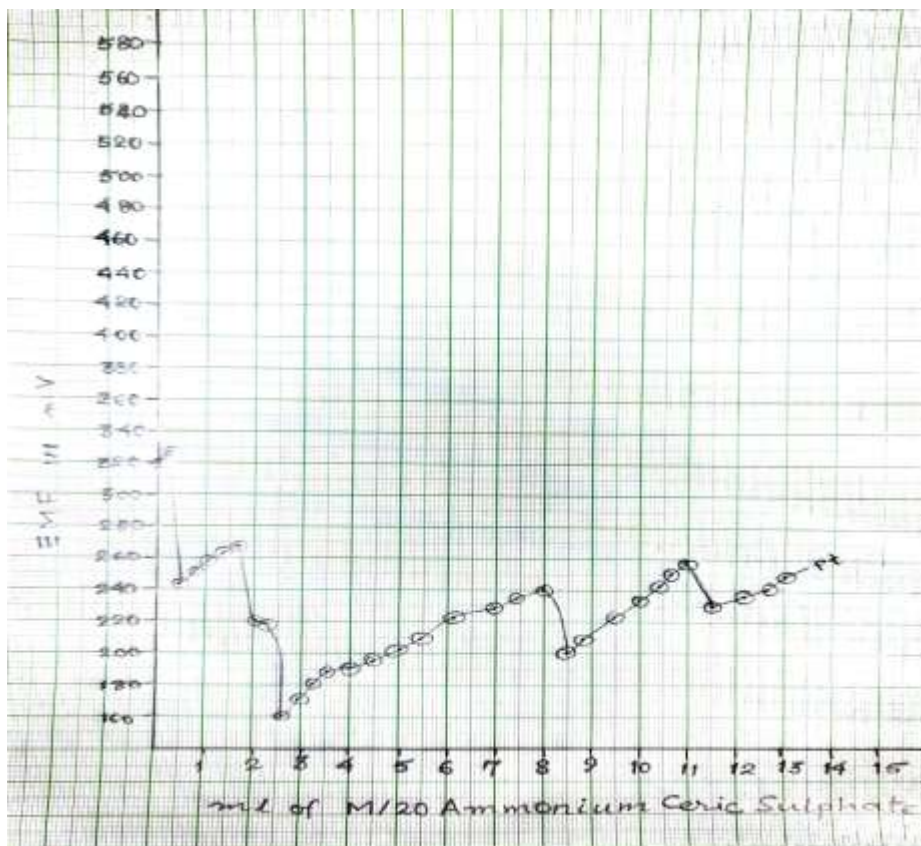


Figure - 5

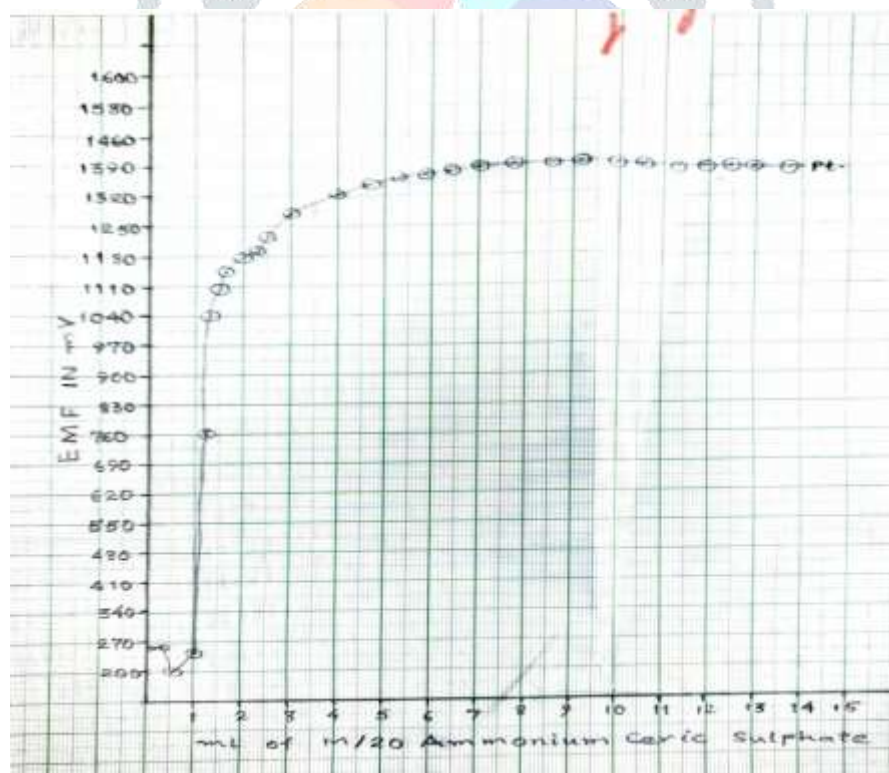


Figure - 6

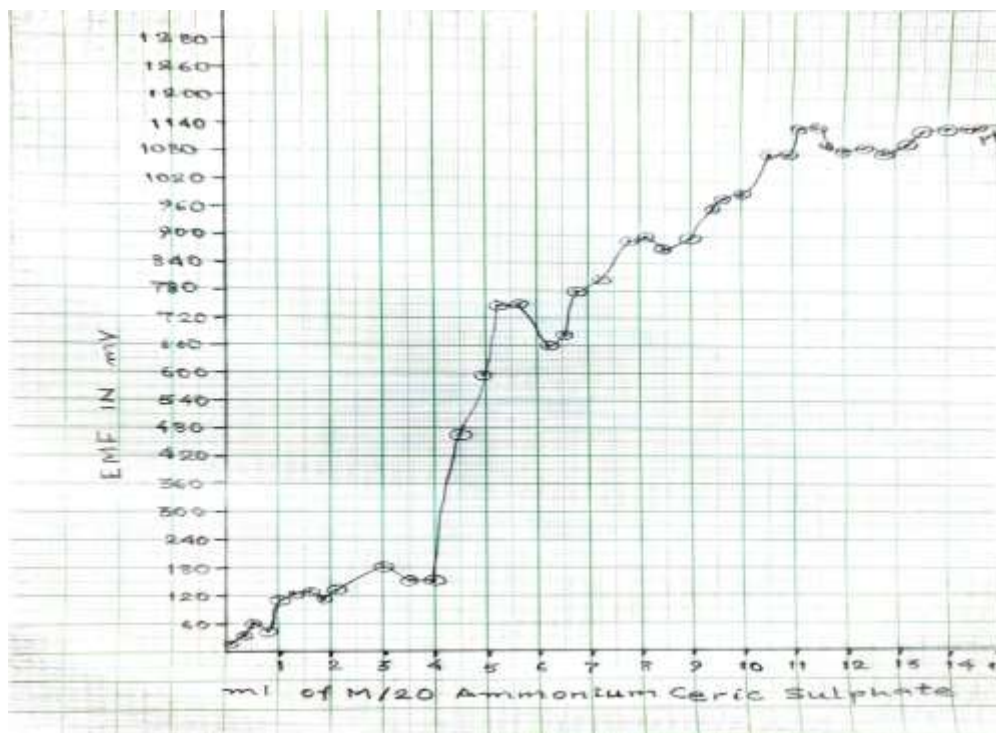


Figure -7

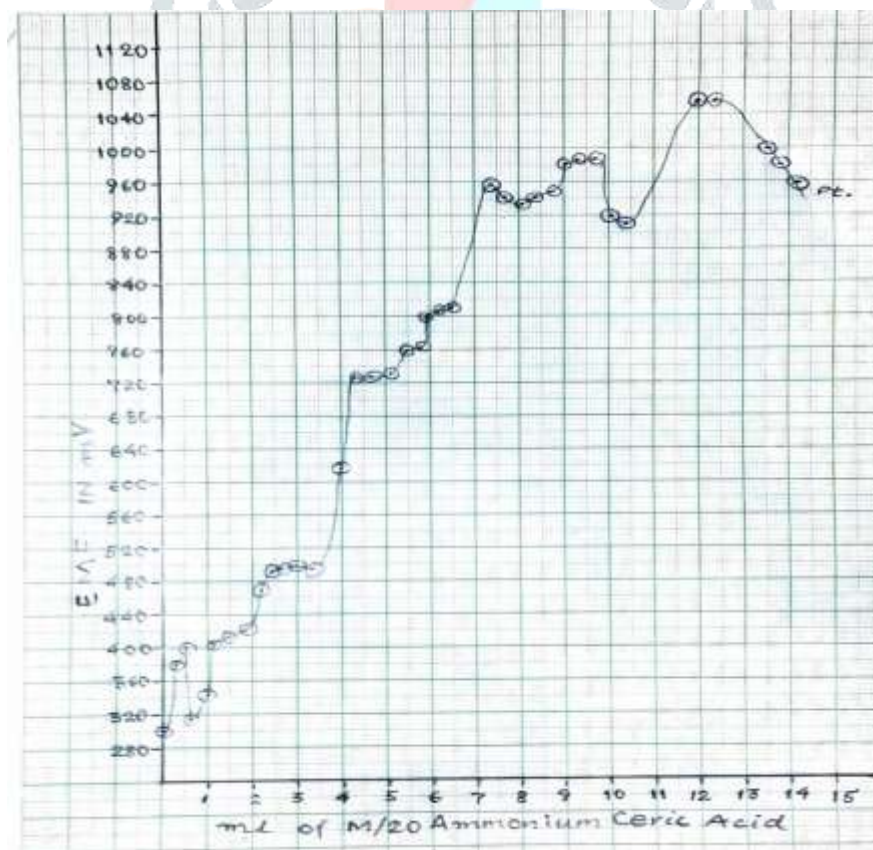


Figure -8

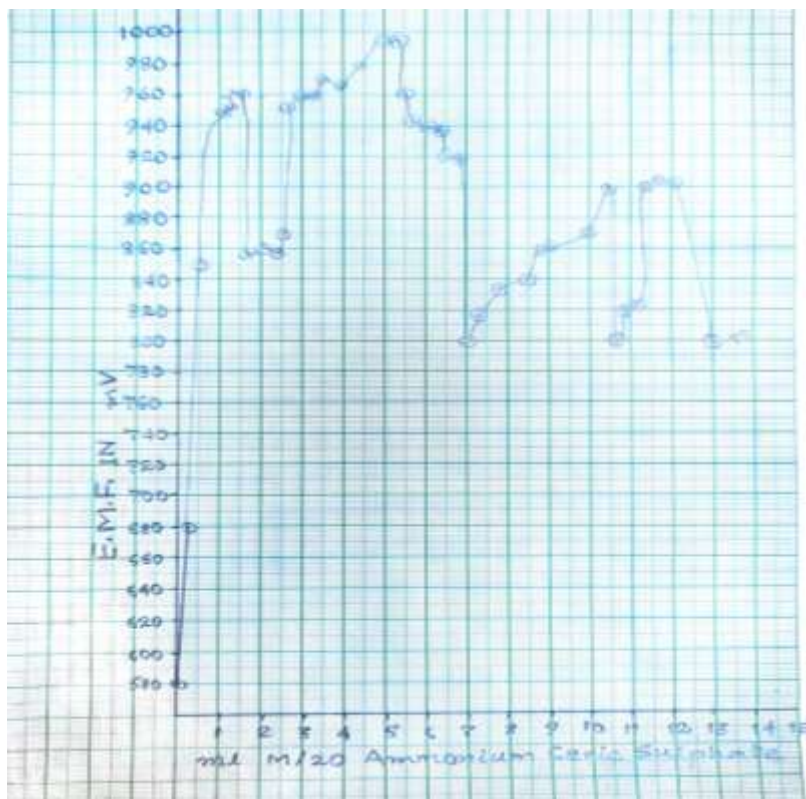


Figure -9

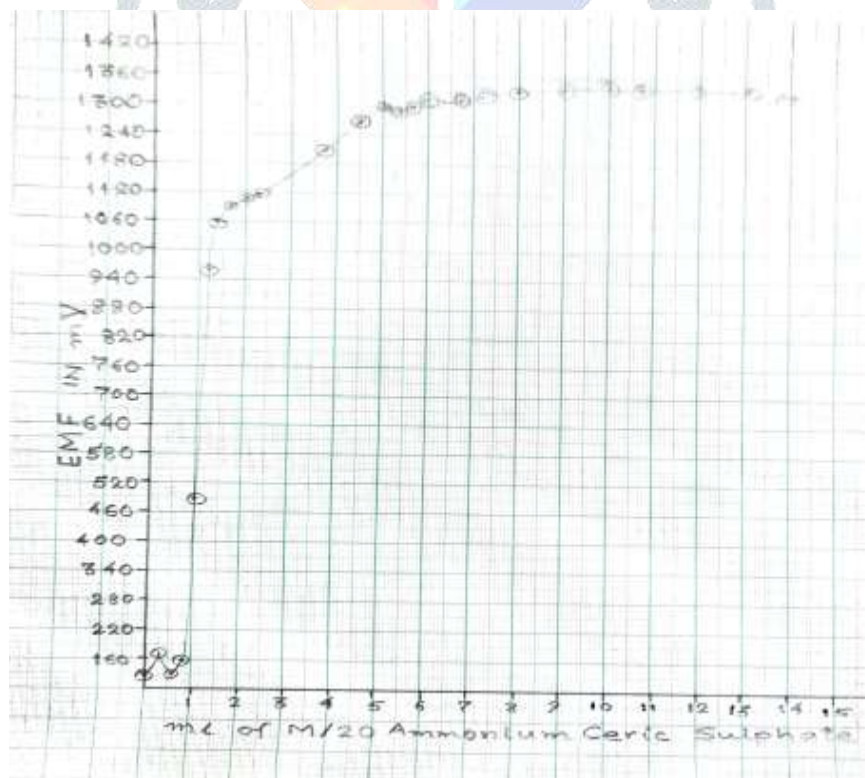


Figure -10

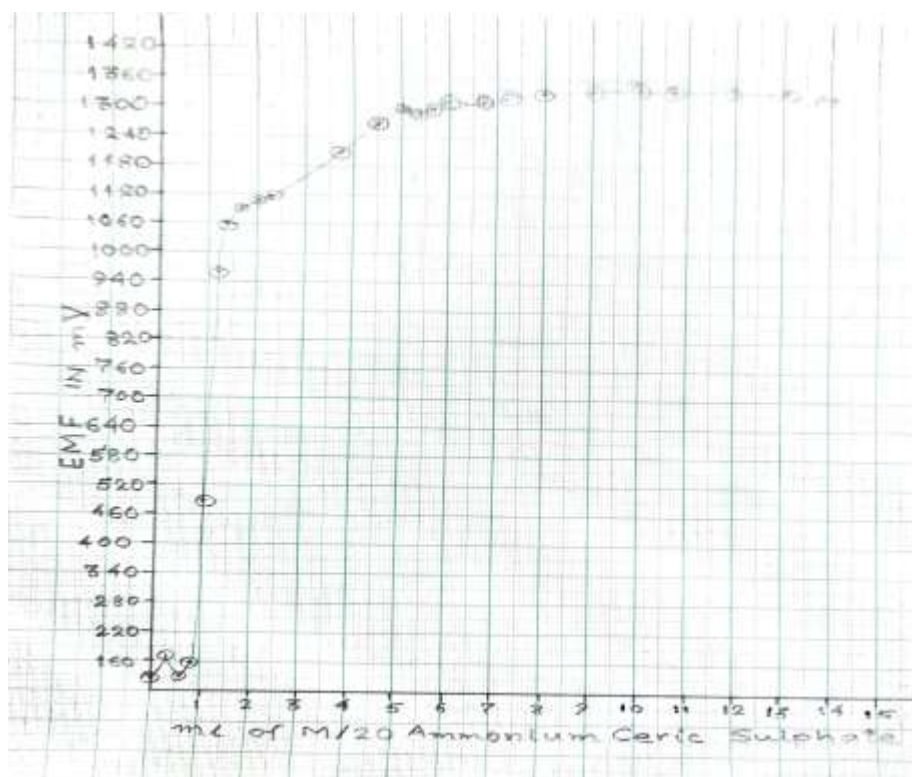


Figure -11

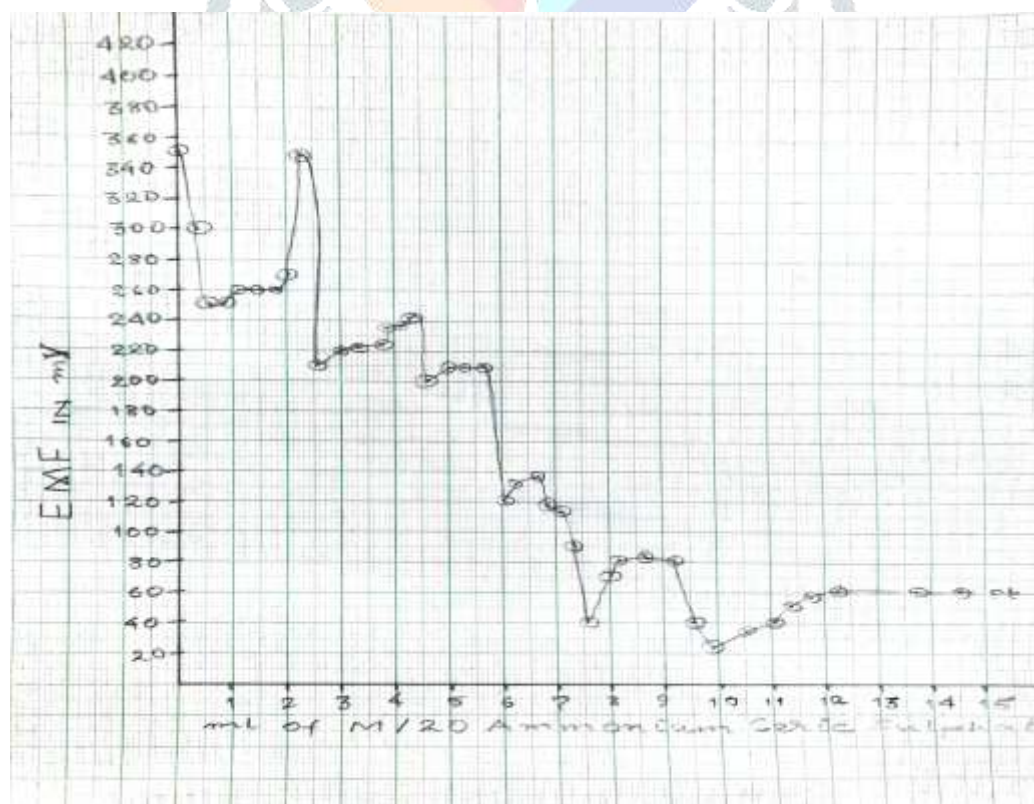


Figure -12

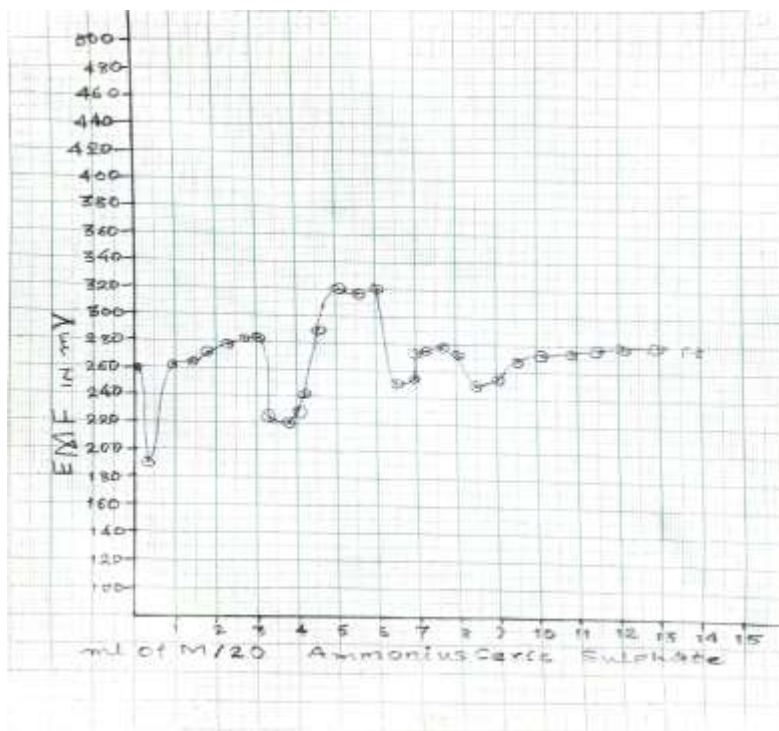


Figure -13

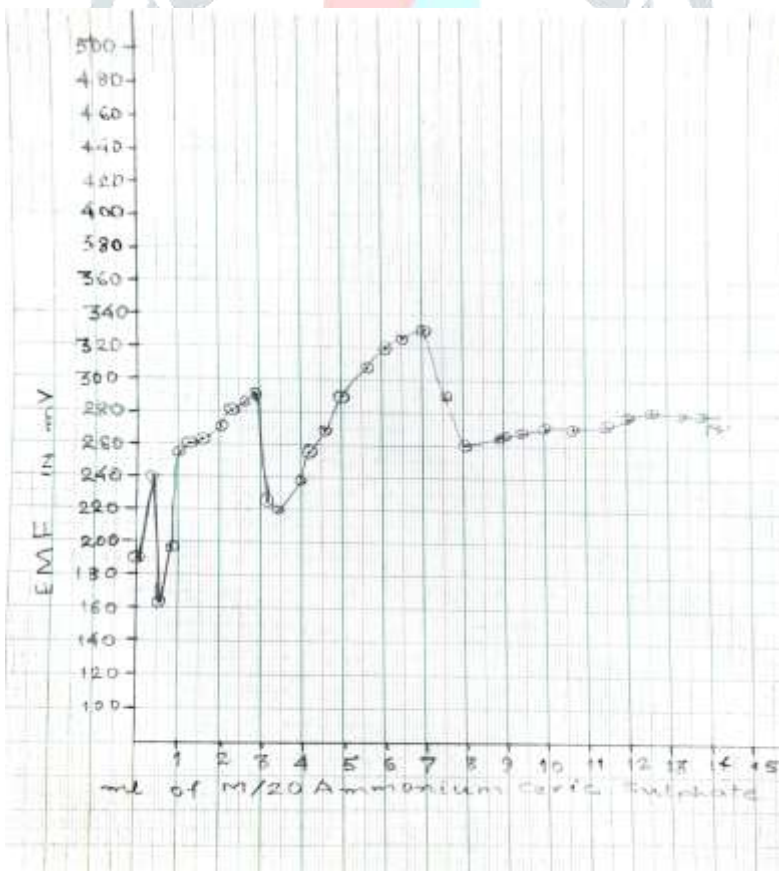


Figure -14

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