The preparation and standardization of 0.1 *N* potassium permanganate solution

Introduction

Potassium permanganate ($KMnO_4$, m. wt. =158.0) is a dark purple or brownish black powder or dark purple or almost black crystals. It is soluble in cold water and freely soluble in boiling water. It is a strong oxidizing agent. It decomposes on contact with certain organic substances.

Due to its oxidizing abilities it has disinfectant and deodorizing properties. It is also astringent. Though bactericidal *in vitro* its clinical value as a bactericide is minimized by its rapid reduction in the presence of body fluids. It is widely used as a standard (volumetric) oxidizing solution because of its intense colour which serves as an indicator in titrations besides its low cost.

Aim of the experiment

One liter of 0.1 *N* potassium permanganate solution is to be prepared.

Chemical principle

Standardization of potassium permanganate against sodium oxalate (as the primary standard) follows oxidation- reduction reaction in which potassium permanganate is the oxidizing agent where as sodium oxalate is the reducing agent. The titration is carried out in acid medium.

$$\mathbf{5C_2O_4^{2-} + 2MnO_4^{1-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2}$$

Procedure

1. Preparation of 1000 ml of 0.1 *N* $KMnO_4$ solution.
   Weigh out approximately the appropriate amount of potassium permanganate (3.2 g, *why?*) using a watch-glass. Transfer into a 250- mL beaker containing water and stir thoroughly breaking up the crystals with a glass rod, to effect solution. Allow to stand for at least 2 days. Filter the solution through a small plug of glass-wool supported in a funnel, in to a one- liter volumetric flask,

leaving the undissolved residues in the beaker. Add more water to the beaker and repeat the process several times until all the potassium permanganate has dissolved. Make the solution up to the graduation mark by addition of water, and shake well to ensure thorough mixing. Store in a dark clean closed- container.

2. Standardization

   Accurately weigh 0.2 g of anhydrous sodium oxalate (mol. wt. 134) previously dried to 110 °C and dissolve it in 100 mL of water, add 7 mL of sulphuric acid and heat to about 70 °C. Then slowly add the permanganate solution from the burette with constant shaking. The first few drops result in a pink colour persisting for about 20 seconds. Wait until the colour disappears and then continue the titration in the usual manner. The end point is reached when a faint pink colour persists for about 30 seconds upon shaking the flask. Note that the temperature of the medium should not be less than 60°C throughout the titration. Record the volume of $KMnO_4$ solution used and calculate the normality using the following equation:

$$N \times V = \frac{wt.}{eq.wt.} \times 1000$$

where *N* is the normality of $KMnO_4$ solution to be calculated

V is the volume of $KMnO_4$ solution used (in mL)

wt. is the weight of sodium oxalate (in g)

eq. wt. is the equivalent weight of sodium oxalate (67, *why?*)

Discussion

Aqueous solutions of potassium permanganate are not entirely stable because of water oxidation:

$$\mathbf{4KMnO_4 + 2H_2O \longrightarrow 4MnO_{2\,(S)} + 3O_{2\,(g)} + 4KOH}$$

However, permanganate solutions, when properly prepared, are reasonably stable because the decomposition reaction is slow. It is catalyzed by light, heat, acids, bases, manganese (II), and manganese dioxide.

Moderately stable solutions of permanganate ion can be prepared if the effects of these catalysts, particularly manganese dioxide, are minimized. Manganese dioxide is a contaminant in even the best grade of solid potassium permanganate. Furthermore, this compound forms in freshly prepared solutions of the reagent as a consequence of the reaction of permanganate ion with organic matter present in the water used to prepare the solution. Removal of manganese dioxide by filtration before standardization markedly improves the stability of standard permanganate solutions. Before filtration, the reagent solution is allowed to stand for about 24 hours or is heated for a brief period to hasten oxidation of the organic species generally present in small amounts in distilled and deionized water. Paper cannot be used for filtering because permanganate ion reacts with it to form additional manganese dioxide.

Sufficient sulphuric acid is added during standardization because potassium permanganate oxidation ability is better in acidic media and to keep hydrogen ion concentration constant thorough out the standardization process.

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

Keeping the temperature near to 70 °C throughout the standardization process is important because the oxidation of sodium oxalate is rapid enough at such temperature. Formation of a brown colour during the titration is caused by insufficient acid, applying too high temperature, or the use of a dirty flask.

Standardized permanganate solutions should be stored in the dark. Filtration and restandardization are required if any solid is detected in the solution or on the walls of the storage bottle. In any event, restandardization every 1 or 2 weeks is a good precautionary measure.

Home work

Give the reason for the disappearance of the end point pink colour after a short period of time; confirm your explanation with a chemical equation.