Al-ISRAA University College
Pharmacy Department

Practical

Organic Pharmaceutical Chemistry

3rd Stage (2nd course)

Lab. 3

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2017-2018

The preparation and standardization of 0.1 N Sodium Thiosulphate solution

Aim of the experiment:

Preparation and Standardization of One Liter of 0.1 *N* Sodium Thiosulphate Solution.

Introduction:

Sodium Thiosulphate ($Na_2S_2O_3 . 5H_2O$, M. wt. =248.2) is a Transparent Colourless Crystals with Efflorescent Properties In Dry Air. It is very Soluble in Water.

Medically it is used as Injection in Treatment of Cyanide Poisoning. It is also used Topically as Antifungal.

Chemically it is a Moderately Strong Reducing Agent that has been Widely used to Determine Oxidizing Agents by an Indirect Procedure that Involves Iodine as an Intermediate.

Chemical principle:

If a Strong Oxidizing Agent is Treated, in Acidic Solution, with a Large Excess of Iodide Ion, the Latter Reacts as a Reducing Agent and the Oxidant will be Quantitatively Reduced. In such Cases, an Equivalent Amount of Iodine is Liberated, and is then Titrated with a Standard Solution of a Reducing Agent, which is usually Sodium Thiosulphate. This is an Indirect Iodometric Titration (also called *Iodometry*) which deals with the Titration of Iodine Liberated in Chemical Reactions.

Sodium Thiosulphate is Standardized Against a Weighed Amount of the Good Primary Standard Potassium Iodate which has a Purity of at Least 99.9%. However, Potassium Dichromate, Potassium Bromate, and Others can be used. Potassium Iodate (Strong Oxidizing Agent, KIO_3, M. wt. =214) Reacts with Potassium Iodide in Acidic Solution (*p*H Lower Than 7) to Liberate Iodine:

$$\underset{\text{iodate ion}}{IO_3^-} + \underset{\text{iodide ion}}{5I^-} + 6H^+ \longrightarrow \underset{\text{iodine}}{3I_2} + 3H_2O \qquad (1)$$

The Liberated Iodine (Insoluble) Reacts with the usually used Excess of Potassium Iodide to Result in the Tri-Iodide Ion which is Freely Water Soluble:

$$I_2 + I^- \longrightarrow \underset{\text{tri- iodide ion}}{I_3^-} \qquad (2)$$

The Tri-Iodide Ion Reacts with Thiosulphate Ion in the Titration Step causing it to be Oxidized into Tetrathionate Ion:

$$I_2 + \underset{\text{thiosulphate}}{2S_2O_3^{2-}} \longrightarrow 2I^- + \underset{\text{tetrathionate}}{S_4O_6^{2-}} \qquad (3)$$

Procedure:

A) Preparation of 1000ml 0.1N $Na_2S_2O_3$ Solution

1) Weight Accurately 25g of Sodium Thiosulphate.
2) Dissolve it in Boiled Distilled Water and make the Volume up to One Liter with Boiled Distilled Water .

Note : If the Solution is to be kept for more than a Few Days , Add 0.1g of Sodium Carbonate or Three Drops of Chloroform.

B) Standardization

1) Weight Accurately 1.5g of Pure Potassium Iodate.
2) Dissolve it in Boiled Distilled Water and make the Volume up to One Liter with Boiled Distilled Water.
3) Transfer Accurately 20 ml of this Primary Standard Solution into a Clean Stoppered Conical Flask.
4) Add 0.4g Potassium Iodide and 5ml of 1M Sulphuric Acid and Shakewell.
5) Titrate the Liberated Iodine (Brown Intense Colour) with the Prepared Sodium Thiosulphate Solution with Constant Shaking.
6) When the Colour of the Liquid has Become a Pale Yellow Dilute To about 200ml with D.W.
7) Add 2ml of Starch Solution, Continue the Titration Until the Colour Changes from Blue to Colourless.
8) Record the Volume of $Na_2S_2O_3$ Solution Used.

Calculations:

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

Where *N* is the Normality of $Na_2S_2O_3$ Solution to be Calculated

V is the Volume of $Na_2S_2O_3$ Solution Used (in mL)

wt. is the Weight of KIO_3 (in g) Present in 20 mL Sample (how much?)

eq. wt. is the Equivalent Weight of KIO_3 (35.66)

Notes for preparation:

❖ Why do we use Recently Boiled Distilled Water?

1) To Destroy Sulfur Bacteria
2) To Expel CO2

$$Na_2S_2O_3 + 2H_2CO_3 \longrightarrow 2NaHCO_3 + H_2S_2O_3$$

$$H_2S_2O_3 \longrightarrow H_2SO_3 + S\Downarrow$$

thiosulfuric acid — sulfar

$$H_2SO_3 \longrightarrow SO_2 + H_2O$$

- ❖ Moreover, decomposition may also be caused by bacterial action (e.g. *Thiobacillus thioparus,* sulphur metabolizing bacteria), particularly if the solution has been standing for some time. Sun light may also affect stability. For these reasons, the following recommendations are made:

1) The solution should be prepared with recently boiled distilled water to expel out carbon dioxide and to provide sterile conditions.
2) Chloroform (3 drops) or mercuric iodide (traces) should be added to improve the stability of the solution and slow decomposition. Bacterial activity is least when the *p*H lies between 9 and 10. The addition of a small amount of sodium carbonate (0.1 g/L) is advantageous to ensure this correct *p*H. In general, sodium hydroxide and high concentration sodium carbonate (> 0.1 g/L) should be avoided since they tend to accelerate the decomposition.
3) Avoid exposure to light, as this tends to hasten the decomposition.

- ❖ Na_2CO_3 is added to the solution as preservative.

Chemical principle of standardization:

- Pot. Iodate is an Oxidizing Agent

$KIO_3 + 5KI + 6H^+ \longrightarrow 3I_2 + 3H_2O$

- The Liberated I_2 is Titrated Against Na2S2O3

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Sod. Tetrathionate

- This Indirect Procedure is Known as ***Iodometry***.

Notes for standardization:

1) We use Stoppered Flask to Prevent the Loss of I_2 .
2) KI is Added to Liberate I_2.
3) Excess KI is Added, Why?

   $I^- + I2 \longrightarrow I3^-$ Tri-Iodide Ion ***(Soluble form of iodine)***
4) The Standardization should be carried in Acidic Media and not in Alkaline Media:

   because Alkaline Media I_2 will React with OH^- to give:

   $I_2 + OH^- \longrightarrow HI + IO^-$ Hypoiodite Ion

   $3\ IO^- \longrightarrow IO_3^- + 2I^-$

   These Ions will Oxidize the Thiosulfate to:

   $IO^- + IO_3^- + S_2O_3^{-2} \longrightarrow SO_4^{-2}$

   Thiosulfate Sulfate

5) On the Other Hand in Higher Acidic Media the Excess KI will React with HCl to Give HI, HI will be Oxidized by Atmospheric O2 to I2:

$$KI + HCl \longrightarrow HI + KCl$$

Excess

$$HI \xrightarrow{\text{Atmospheric } O_2} I_2$$

Sod. Bicarbonate is Added to React with Formed HI:

$$NaHCO_3 + HI \longrightarrow NaI + H_2O + CO_2 \nearrow$$

6) Starch Ind. is Added at the End (when the Color of the Solution Change to Pale Yellow) or we can said the Ind. is Added when the Iodine Concentration is Low Because β-Amylase which the Soluble Form of Starch React :

$$\beta\text{-Amylase} + I_2 + I^- \longrightarrow \text{Blue Colour Complex}$$

the Color Change is Reversible, the Color Being Discharged (Change to Colorless) when Iodine is Reduced by $Na_2S_2O_3$.

This Reversibility is Reduced when the Iodine Conc. is High for this Reason Starch Ind. should be Added Until most of I_2 has Been Reduced by $Na_2S_2O_3$.

Notes For Calculations:

The Oxidation of Thiosulphate into Tetrathionate Involves the Loss of Two Electrons from Two Moles of Sodium Thiosulphate (Equation 3), *i. e.* One Electron from One Mole. Accordingly its Equivalent Weight is Equal to its Molecular Weight and that is why 25g are used to Prepare 1 L of 0.1 *N* Solution According to this Equation:

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

Equation 3 shows that Reduction of One Mole of Iodine happens by Gaining Two Electrons. Equations 1-3 show that for One Mole of Potassium Iodate three Moles of Iodine are Liberated and these should be Consumed Totally by Six Moles of Sodium Thiosulphate. Therefore, there is a Net of a Six Electrons - Transfer Involved in the Titration. That is why the Equivalent Weight of Potassium Iodate is One- Sixth the Molecular Weight (M.Wt./6).