Chapter 2

Preliminary Investigations Of Solvents Used In The Titrimetric Determination Of Sulphate

2.1 Introduction

Various indicators have been used for the titration of sulphate with barium perchlorate. These indicators include Thoron[85, 97-99, 101, 130, 132, 135-139] (end-point: change from yellow to pinkish orange colour), arsenazo III[85, 101, 140] (end-point :change from red to dark purple colour), sulphonazo III[102, 126, 141, 142](end-point: change from violet to blue-green colour) and dimethylsulphanazo III[102, 124, 141-145] (end-point: change from mauve-purple to azure-blue colour).

In the direct titrimetric determination of sulphate using Alizarin Red S as indicator, Fritz and Freeland[125] found that optimum concentration of alcohol used to enhance the end-point is 30-40% (v/v). The titration in 80% (v/v) iso-propanol using arsenazo III as indicator has been studied by Aldrich[135]. Budensinsky[85] discovered that 70%-80% (v/v) acetone medium appears to be the best titration medium when using chlorophosphonazo III as indicator. Acetone, 1-4-dioxane or dimethylformamide[146] also provide a good medium for titration with Alizarin Red S indicator.

Aqueous and water miscible organic solvents mixtures are often used to enhance the sharpness of the end point of the titration. This kind of titration mediums have hasten the precipitation of barium sulphate and reduced its solubility, and attained a rapid response of the indicator towards the initial excess of barium ions as soon as the titration equivalence is reached.

In this work, dimethylsulphanonazo III is chosen as the indicator based on the work of Budensinsky et al[85], as well as preliminary investigation done by Tioh[31]

on the choice of indicator. Sulphate (as standard sulphuric acid) in non-aqueous solvent of various composition was titrated with standard barium perchlorate solution using dimethysulphonazo III as indicator. The solvents used were methanol, ethanol, n-propanol and acetone because these solvents are easily available.

2.2 Procedure

5.00 cm^3 of standard sulphuric acid (0.025 $moldm^{-3}$) was pipetted into a conical flask. After adjusting to a desired composition of solvent mixture, two drops of dimethylsulphonazo III indicator was added. The solution was then titrated with standardised barium perchlorate solution. End-point: colour change from maure-purple to Azure-blue colour.

2.3 Results and Discussion

The result of the investigation is shown in Table 1.

Table 1: Relative Distinctness of End-point Using Different Solvent Composition

Solvent	Solvent Composition , % (v/v)*					
	10	25	40	50	60	70
Methanol	-	+	++	++	++	--
Ethanol	-	+	++	++	++	-
n-Propanol	-	+	+++	+++	++	++
Acetone	-	+	+++	+++	+++	++

Note: The number of +'s and –' s represents the physiological grades for distinct or indistinct end-point respectively.
* Represent volume of solvent : volume of water

The titration is basically a type of acid-base reaction. In dissolving ionic compound a solvent must have a high dielectric constant. This means it has high insulating properties to lower the attraction between oppositely charged ions once they are solvated. Only water and or other highly polar solvents are able to dissolve ionic compound appreciably.

Water is a superior solvent to ionic substances due to its polarity, high dielectric constant and the –OH group which can form hydrogen bonding. Water solvates both cations and anions: cations at its negative pole and anions through hydrogen bonding.

In aqueous medium, water keep on solvating both anions and cations, hence it is very hard for excess barium to reach the dimethylsulphonazo III indicator and resulted indistinct colour change of the indicator . This caused a great uncertainty in the determination of the end-point in sulphate-barium perchlorate titration. Hence, the end-point may be enhanced by increasing the dielectric constant of the medium so as to decrease some solvating power of water. This can be done by partially substituting water with less polar and lower dielectric constant solvent such as alcohol and ketone.

Among the four solvents system studied, it was learnt that an approximately 40-50% (v/v) non-aqueous solvent medium generally gave sufficiently distinct end-point.

Titration medium containing about 40-50% (v/v) of n-propanol or acetone seems to be the best solvent mixture for the sulphate-barium perchlorate titration with dimethylsulphonazo III as indicator. This is because the dielectric constant of n-

propanol and acetone are lower than methanol and ethanol, which produce better effect on reducing the solvating power of water.

Dielectric constant of theses solvent in descending order are :

Methanol > Ethanol > n-propnaol ~ acetone

However, at higher solvent concentration, slow equilibrium gave pre-mature end-point which faded on standing. This is very serious in the case of methanol and ethanol systems. Although the dielectric constant of methanol and ethanol are smaller than water, their molecular size is much more bigger. This caused great steric hindrance to the movement of other ions, especially at higher solvent concentration.

Steric hindrance to the movement of other ions also happened in water-n-propanol and water-acetone medium when their concentration is high. This was shown in the decreasing of the end-point distinctness. However, the end-point is still comparatively clear compared to aqueous-methanol and aqueous-propanol medium because they have lower value of dielectric constants.

A 50% (v/v) acetone medium seems to give more distinct end-point. As a result, a 50%(v/v) of acetone medium was used in subsequent studies of this work, whenever possible. In cases where acetone is not suitable, n-propanol was chosen as the alternative to acetone.