4.1 Preparation of Electrolyte Solutions

Potassium ferrocyanide, potassium ferricyanide, sodium thiosulphate, sodium chromate, potassium dichromate and potassium pyrophosphate from Merck were kept over anhydrous calcium chloride in desiccator. Dextrose, Fructose, Sorbitol and Mannitol from HIMEDIA were used as such to prepare different compositions (e.g. 5, 10 and 15 wt%) of the mixed solvents.

Different compositions of the mixed solvents were prepared by using conductivity water (sp. cond. ~10^{-6} \text{ Scm}^{-1}). Solutions of potassium ferrocyanide, potassium ferricyanide, sodium thiosulphate, sodium chromate, potassium dichromate and potassium pyrophosphate were prepared on molal basis by dissolving known weights of the salts in required weights of the corresponding solvents, and the concentration on molal scale was converted to molar scale by means of the relation, using the density values of mixed solvents[88,89, 89a] at the experimental temperatures.

\[ c = m d (1 + 0.001m M_2)^{-1} \]

Where 
- \( c \) = concentration in molarity
- \( m \) = concentration in molality
- \( d \) = density
- \( M_2 \) = Molecular mass of the solute

4.2 Chemicals and reagents used

4.2.1 Potassium Ferricyanide

Chemical Name: Potassium Hexacyanoferrate (III)

Molecular Mass: 329 g/mol

Properties: Soluble in water, Acid and slightly soluble in alcohol
Application: Used in blue print drawing, in photography and as an oxidizing agent.

**Fig. 4.1** Structure of potassium ferricyanide

### 4.2.2. Potassium Ferrocyanide

Chemical Name: Potassium Hexacyanoferrate (II)  
Molecular Mass: 368 g/mol  
Properties: Soluble in water, insoluble in alcohol and ether.  
Application: used in the production of wine and citric acid, used in the purification of tin and the separation of copper from molybdenum ores.

**Fig. 4.2** Structure of potassium ferrocyanide

### 4.2.3. Sodium Thiosulphate

Chemical Name: Sodium thiosulfate  
Molecular Mass: 158 g/mol  
Properties: Soluble in water, insoluble in alcohol.  
Application: used in Iodometric titrations, photographic processing, Gold extractions and antidote for cyanide poisoning.
4.2.4. Sodium Chromate

Chemical Name: Sodium chromate
Molecular Mass: 162 g/mol
Properties: Soluble in water, slightly in alcohol.
Application: It has wide applications in petroleum, textile, and pharmaceutical industries.

4.2.5. Potassium Dichromate

Chemical Name: Potassium dichromate (VI)
Molecular Mass: 294 g/mol
Properties: Soluble in water, insoluble in alcohol.
Application: used to prepare "chromic acid" for cleaning glassware and etching materials, photography and in photographic screen printing and for Wood treatment.
4.2.6. Potassium pyrophosphate

Chemical Name: Tetra potassium pyrophosphate

Molecular weight: 330 g/mol

Properties: It is a white powder, soluble in water but insoluble in alcohol, and the aqueous solution is alkaline.

Application: It is applied as emulsifier, tissue modifier, chelating agent, etc.

4.3 Details of Solvents used

Different aquo-organic solvent systems, such as water + dextrose, water + fructose, water + sorbitol, and water + mannitol have been used in the present investigation to study the ion-association and solvation of potassium ferrocyanide, potassium ferricyanide, sodium thiosulphate, sodium chromate, potassium dichromate and potassium pyrophosphate at different temperatures.
4.3.1. Water + 5, 10 and 15 Wt % of D-glucose (Dextrose)

Chemical Name: Glucose
Molecular weight: 180 g/mol
Properties: Soluble in water and acetic acid.
Application: Used as analyte in Blood sugar Test, Source of Instant Energy, Major content of ORS-Electral Powder.

![Fig. 4.7 Structure of D-glucose](image)

4.3.2. Water + 5, 10 and 15 wt% of D-fructose

Chemical Name: Fructose
Molecular weight: 180 g/mol
Properties: Soluble in water.
Application: For taste enhancement and palatability, it is added to foods and drinks.

![Fig. 4.8 Structure of D-fructose](image)
4.3.3. Water + wt % of D-Sorbitol

Chemical Name: Sorbitol

Molecular weight: 182 g/mol

Properties: Soluble in water.

Application: used as sugar substitute(sweetener), used in mouth wash and tooth paste, cosmetics, solid rocket fuel, and as humectant in some cigarettes.

![Fig. 4.9 Structure of D-sorbitol](image)

4.3.4. Water + wt% of D-mannitol

Chemical Name: Mannitol

Molecular weight: 182

Properties: Soluble in water.

Application: Used to treat patients with oliguric renal failure, used as a sweetener for people with diabetes, and in chewing gums, used as cutting agent for heroin, and cocaine

![Fig. 4.10 Structure of D-mannitol](image)
4.4 **Hydrotropic Agents**

The role of hydrotropic agents is to make soluble the solute mainly in organic solvent systems. In the present investigation, we have just considered three hydrotropic agents namely sodium bromide, nicotinamide and sodium benzoate to see the effect on solvolysis phenomena in case of potassium ferricyanide case only in the presence of 5 wt% sorbitol.

### 4.4.1. Nicotinamide

**Chemical Name:** Pyridine-3-carboxamide

**Molecular weight:** 122 g/mol

**Properties:** Soluble in water.

**Application:** used as water soluble vitamin, used as a precursor in enzymatic oxidation-reduction reactions and posses anti-inflammatory properties towards the skin.

![Structure of Pyridine-3-carboxamide](image)

**Fig. 4.11 Structure of Pyridine-3-carboxamide**

### 4.4.2. Sodium Bromide (NaBr)

**Chemical Name:** Sodium Bromide

**Molecular weight:** 102.8 g/mol

**Properties:** Soluble in water.

**Application:** used as a hypnotic, anticonvulsant, and sedative in medicine.

![Structure of Sodium bromide](image)

**Fig. 4.12 Structure of Sodium bromide**
4.4.3. Sodium benzoate

Chemical Name: Sodium benzoate
Molecular weight: 144 g/mol
Properties: Soluble in water.
Application: It is mostly used as food preservative, also preservative in medicines and cosmetics, treatment for urea cycle disorders and possesses lots of pharmaceutical applications.

![Structure of Sodium Benzoate](image)

**Fig. 4.13 Structure of Sodium Benzoate**

4.5 Experimental Techniques used

Various experimental techniques, such as conductance, density, ultrasonic velocity and viscosity measurements have been used to evaluate different parameters that help to predict ion-ion, ion-solvent, and solvent-solvent interactions. The basic principles, preliminary descriptions, importance and method of use of different experimental techniques, along with the scope of the present investigation are furnished in the following sections.

4.5.1 Conductance measurements

Conductivity study is a powerful tool for measurement of mobility of ions or solutes in solution as well as detailed study of ion-solvent interactions. Conductivity meter principle is a digital representation of solution conductivity with conduction current capacity. The electrical conductivity of the water and the inorganic salt have a certain relationship, when their low concentration, conductivity increases with concentration, therefore, the index is used to speculate that the total concentration of ions in the water or salt content.
The conductance measurements were made by using a digital conductivity meter [89] (Systronics, Type 304) with a sensitivity of 0.1%. A dipping type conductivity cell with platinized platinum electrodes (cell constant 1 S cm\(^{-1}\)) was used. The conductance values of solutions of different concentrations (ranging from 1 \(\times\) 10\(^{-2}\) to 8 \(\times\) 10\(^{-2}\) M) of potassium ferrocyanide, potassium ferricyanide, sodium thiosulphate, sodium chromate, potassium dichromate and potassium pyrophosphate have been measured in the temperature range 298.15 K to 313.15 K with a precision of ± 0.05 K with solvent correction. The values of specific and molar conductances are expressed in S cm\(^{-1}\) and S cm\(^{-2}\) mol\(^{-1}\), respectively.

\[ \Lambda = 1000 \, \kappa / c \]

Where \( \kappa \) = specific conductance

\[ c = \text{concentration in mol/dm}^3 \]

4.5.2 Density measurements

Density values of the pure solvent and the solutions were determined by using specific gravity bottle (25 ml) at different temperatures. At first, the specific gravity bottles were calibrated at different temperatures using conductivity water. The data for densities of the pure water were taken from the literature. At least 3 readings were taken and difference in any two readings would be within ±0.03%. By using the formula given below, the densities of the experimental solutions were calculated as follows,
\[ d_2 = \left( \frac{W_2}{W_1} \right) \times d_1 \]

where \( d_1 \) = density of water
\( d_2 \) = density of solution
\( W_1 \) = Weight of water
\( W_2 \) = Weight of solution

4.5.3 Ultrasonic velocity measurements

Measurement of sound velocity was carried out by interferometric method which provides continuous wave method of ultrasonic velocity measurements, highly suitable for measurements in liquids in MHz region.

4.5.3.1 Description of Ultrasonic Interferometer

The experiments were performed by employing a commercially available ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi) with a single crystal variable path[90]. The ultrasonic interferometer has two parts.

(a) High Frequency generator[88]

(b) The measuring Cell

(a) High Frequency generator:

It consists of an oscillator controlled by high frequency crystal. The oscillator is in the form of a modified pierce circuit which operates in the MHz region. The high frequency generator is designed to excite a quartz crystal called the transducer which is fixed at the bottom of the cell[88] to produce ultrasonic frequency in a experimental liquid taken in the measuring cell. The generator is provided with a micro ammeter to note the change in current. There are two controlling knobs in the generator. The knob marked ‘Adj’ is used to adjust the position of the needle on the ammeter. The knob marked ‘Gain’ is used to increase the sensitivity of the instrument for greater deflection. When the deflection in the micro ammeter is insufficient for any particular liquid, the generator provided with a timer can be adjusted or tuned to make the instrument effective.
(b) The Measuring Cell

It is made up of a double walled cell, connected to high frequency generator by a short co-axial cable, to hold the liquid for measurement. It consists of three parts: (i) metal base, (ii) container and (iii) reflector. A thermostatically regulated bath is connected to it to maintain required temperature of the liquid by means of water circulation through the doubly walled cell with an accuracy of ± 0.1 K. The reflector can be moved downward or upward by a micrometer screw system.

4.5.3.2 Principle of Ultrasonic Interferometer

The ultrasonic velocity (U) in the solution is determined from the wave length (λ) of the medium at known frequency (f) as follows,

Ultrasonic velocity = Wavelength x Frequency , U = λ x f
The accuracy in the velocity measurements is within ± 0.05%. The sound velocity was measured at a frequency of 2MHz.

4.5.4 Viscosity Measurements

Viscosity is the inherent property of a liquid which offers frictional resistance to its motion and provide indicative data on solute-solute and solute-solvent interactions.

In order to determine the viscosity of the experimental solution, Ostwald’s method was employed to find out the flow time of both the reference liquid, water and the experimental solution at the required temperature. From the density values of the reference liquid and solution, the viscosity of the experimental is determined as follows,

\[ \frac{\eta_1}{\eta_2} = \frac{d_1}{d_2} \frac{t_1}{t_2} \]  \hspace{1cm} (4.5.1)

where \( \eta_1 \) is the co-efficient of viscosity of water.

\( \eta_2 \) is the co-efficient of viscosity of solution

\( d_1 \) is the density of water

\( d_2 \) is the density of the solution

\( t_1 \) is the time of flow of water

\( t_2 \) is the time of flow of solution
The viscosity values of the solutions were measured by means of a calibrated Ostwald’s viscometer in a water thermostat [6] maintained at a required temperature controlled to ±0.05 K. A digital stop watch with an accuracy of 0.01s was used to note the flow time of the reference liquid and the experimental solution. The calculated viscosity values were accurate to within ± 0.3 x 10^{-3} c P. The concentrations of the multi-charged electrolyte solutions vary over a range of 0.01 to 0.1 M in all solvent systems studied at different temperatures. The viscosity values of water at the experimented temperatures [6] were obtained from the literature.