CHAPTER III

Experimental Section

3.1. Name, Structure, Physical Properties, Purification and Application of the used Solvents and Solutes

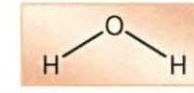
3.1.1. Solvents

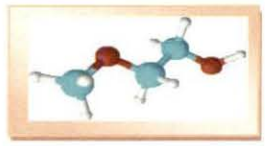
Water: 

Water is an ubiquitous chemical substance that is composed of hydrogen and oxygen and is essential for all known forms of life. In typical usage, water refers only to its liquid form or state, but the substance also has a solid state, ice, and a gaseous state, water vapour or steam. Water is a good solvent and is often referred to as the universal solvent.

Source: Distilled water.

Purification: Water was first deionised and then distilled in an all glass distilling set along with alkaline $KMnO_4$ solution to remove any organic matter therein. The doubly distilled water was finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO_2 and other impurities. The triply distilled water had specific conductance less than $1 \times 10\text{-}6$ $S.cm^{-1}$ [1].

WATER	
	
Appearance:	**Liquid**
Molecular Formula:	**H_20**
Molecular Weight:	**18.02g/mol**
Boiling Point:	**100 ^{0}C**
Melting Point:	**0 ^{0}C**
Dielectric Constant:	**78.35at 25^{0}C**

2-Methoxyethanol: 

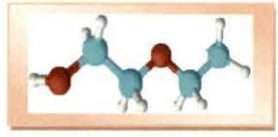
2-Methoxyethanol, or methyl cellosolve, is an organic compound that is used mainly as a solvent. It is a clear, colourless liquid with an ether-like odour. It is in a class of solvents known as glycol ethers which are notable for their ability to dissolve a variety of different types of chemical compounds and for their miscibility with water and other solvents.

Source: S.D. Fine Chemicals Ltd., Mumbai, India.

Purification: Peroxides were removed by refluxing with stannous chloride. It was then dried with silica gel crystals, with a final distillation with sodium[2].

2-Methoxyethanol

Appearance:	**Liquid**
Molecular Formula:	**$C_3H_8O_2$**
Molecular Weight:	**76.1g/mol**
Boiling Point:	**124^{0}C**
Melting Point:	**-85^{0}C**
Dielectric Constant:	**17.65 at25^{0}C**

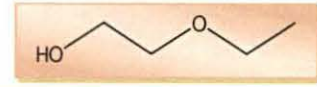
2-Ethoxy ethanol: 

2-Ethoxyethanol, also known by the trademark cellosolve or ethyl cellosolve, is a clear, colourless, nearly odourless liquid that is miscible with water, ethanol, diethyl ether, acetone, and ethyl acetate.

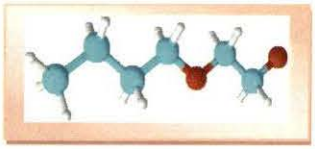
Source: S.D. Fine Chemicals Ltd., Mumbai, India.

Purification: It was dried with $CaSO_4$, filtered and fractionally distilled. Peroxides were removed by refluxing with anhydrous $SnCl_2$[3].

2-Ethoxy ethanol



Appearance:	**Liquid**
Molecular Formula:	**$C_4H_{10}O_2$**
Molecular Weight:	**90.121g/mol**
Boiling Point:	**135^{0}C**
Melting Point:	**-70^{0}C**
Dielectric Constant:	**13.94 at25^{0}C**

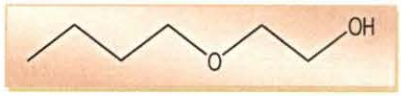
2-Butoxyethanol: 

It is a colorless liquid with a sweet, ether-like odour. It is butyl ether of ethylene glycol, but should not be confused with the simple glycol as it is glycol ether.

Source: S.D. Fine Chemicals Ltd., Mumbai, India.

Purification: It was dried with anhydrous K_2CO_3 and $CaSO_4$, filtered and distilled. Peroxides were removed by refluxing with anhydrous $SnCl_2$[3].

2-Butoxy ethanol



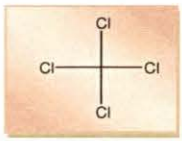
Appearance:	**Liquid**
Molecular Formula:	**$C_6H_{14}O_2$**
Molecular Weight:	**118.17g/mol**
Boiling Point:	**171 ^{0}C**
Melting Point:	**-77^{0}C**
Dielectric Constant:	**9.87 at25^{0}C**

Carbon tetrachloride: 

Carbon tetrachloride, also known by many other names (notably, **carbon tet** in the cleaning industry, and as a Halon or Freon in HVAC) is the organic compound with the formula CCl_4. In the carbon tetrachloride molecule, four chlorine atoms are positioned symmetrically as corners in a tetrahedral configuration joined to a central carbon atom by single covalent bonds. Because of this symmetrical geometry, CCl_4 is non-polar.

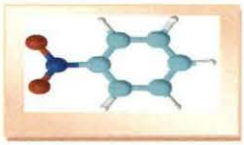
Source: Merck, India.

Carbon tetrachloride



Appearance:	**Liquid**
Molecular Formula:	**CCl_4**
Molecular Weight:	**153.83g/mol**
Boiling Point:	**77^{0}C**
Melting Point :	**-23^{0}C**
Dielectric Constant:	**2.2 at 20^{0}C**

Purification: It was dried with $CaCl_2$ and distilled over P_2O_5[2].

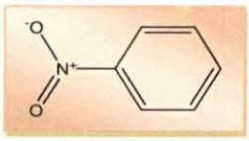
Nitrobenzene: 

Nitrobenzene is a colorless to pale yellow oily liquid with an odour resembling that of bitter almonds or "shoe polish." It represents a fire hazard, with a flash point (closed cup method) of 88 °C and an explosive limit (lower) of 1.8% by volume in air. Nitrobenzene can undergo degradation by both photolysis and microbial biodegradation.

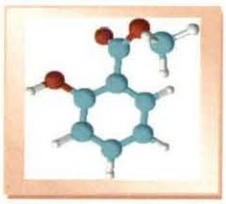
Source: Merck, India

Purification: It was purified by fraction distillation. Impure nitrobenzene was taken in a round bottomed flask fitted with a condenser and heated in a water bath maintained at 207-210^{0}C. Nitrobenzene was obtained as yellow vapours which was cooled by condenser and collected back[2].

Nitrobenzene



Appearance:	**Liquid**
Molecular Formula:	**$C_6H_5NO_2$**
Molecular Weight:	**123.06 g/mol**
Boiling Point:	**210.9^{0}C**
Dielectric Constant:	**34.8 at 25^{0}C**

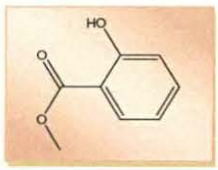
Methyl Salicylate: 

Methyl salicylate (oil of wintergreen or wintergreen oil) is a natural product of many species of plants. Some of the plants which produce it are called wintergreens, hence the common name. It is easily soluble in alcohol, acetic acid, soluble in ether, chloroform, slightly soluble in water.

Source: Merck, India

Purification: It was diluted with diethyl ether and then washed with saturated sodium bicarbonate to remove any free

Methyl Salicylate



Appearance:	**Colourless Oily Liquid**
Molecular Formula:	**$C_8H_8O_3$**
Molecular Weight:	**152.15 g/mol**
Boiling Point:	**222^{0}C**
Dielectric Constant:	**6.8 at 25^{0}C**

acid that may be present. Finally it was washed with brine, dried with magnesium sulphate, filtered, evaporated and then distilled.

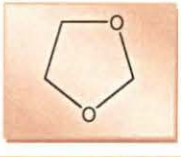
1,3-Dioxolane: 

Dioxolane or 1,3-dioxolane is an heterocyclic acetal. It is an analogue of tetrahydrofuran with an additional ring oxygen atom and an analogue of the 6 membered ring 1,3-dioxane. No unusual toxic effects have been associated with the use of 1,3-dioxolane. The product is not explosive, not spontaneously flammable and has no disagreeable odor. Dioxolanes are a group of organic compounds sharing the dioxolane ring structure.

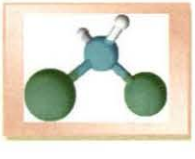
Source: Sigma Aldrich, India.

Purification: It was heated under reflux with PbO_2 for 2 hrs, then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled[1,2]. The solvent obtained after purification had a boiling point of 348 K / 760 mm, a density of 1057.1kg.m^{-3} and a coefficient of viscosity of 0.531mPa.s at 298.15 K.

1,3-Dioxolane



Appearance:	**Liquid**
Molecular Formula:	**$C_3H_6O_2$**
Molecular Weight:	**74.08 g/mol**
Boiling Point:	**75^{0}C**
Melting Point:	**-95^{0}C**
Dielectric Constant:	**7.34 at 25^{0}C**

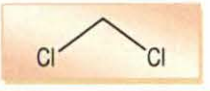
Dichloromethane: 

It is a colorless organic compound with a moderately sweet aroma. Although it is not miscible with water, it is miscible with many organic solvents

Source: Sisco Research Laboratories Pvt. Ltd., Mumbai, India.

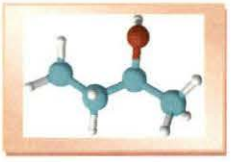
Purification: It was shaken with conc. H_2SO_4 or Aq. $KMnO_4$, then washed with water, Satd. Aq. $NaHCO_3$, again with water, dried with K_2CO_3 and distilled from CaH_2 or $CaSO_4$[3].

Dichloromethane



Appearance:	**Liquid**
Molecular Formula:	**CH_2Cl_2**
Molecular Weight:	**84.93 g/mol**
Boiling Point:	**39.8°C**
Melting Point:	**-97.3°C**
Dielectric Constant:	**8.93 at 25°C**

2-Butanol:

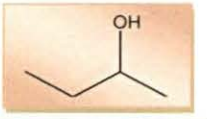


2-Butanol, or sec-butanol, is a colorless liquid that is completely miscible with polar organic solvent such as ethers and other alcohols. It is produced on a large scale, primarily as a precursor to the industrial solvent methyl ethyl ketone. 2-Butanol is chiral and thus can be obtained as either of two stereoisomers designated as (R)-(−)-2-butanol and (S)-(+)-2-butanol. It is normally found as an equal mixture of the two stereoisomers — a racemic mixture.

Source: Merck, India.

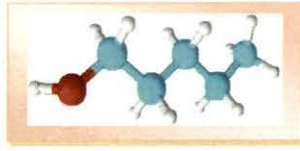
Purification: It was dried with K_2CO_3 or $CaSO_4$, followed by filtration and fractional distillation refluxing with CaO, distillation, then refluxing with Mg and redistillation; and refluxing with, then distillation with CaH_2[2].

2-Butanol



Appearance:	**Liquid**
Molecular Formula:	**$C_4H_{10}O$**
Molecular Weight:	**74.122 g/mol**
Boiling Point:	**99°C**
Melting Point:	**-115°C**
Dielectric Constant:	**15.8 at 25°C**

n-Amyl alcohol:



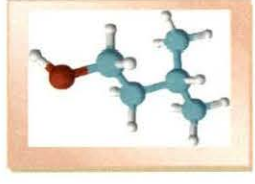
It is an alcohol with five carbon atoms. It is a colorless liquid with an unpleasant aroma. Commercial amyl alcohols are colourless liquids, slightly soluble in water, and having a characteristic penetrating odour.

Source: Merck, India.

Purification: It was dried with anhydrous K_2CO_3 and distilled. The middle fractions for both the liquids were collected and kept free from humidity with 3 Å molecular sieves[4].

n-Amyl alcohol	
	
Appearance:	**Liquid**
Molecular Formula:	**$C_5H_{12}O$**
Molecular Weight:	**88.15 g/mol**
Boiling Point:	**194.12°C**
Melting Point:	**-78.85°C**
Dielectric Constant:	**13.9at 25°C**

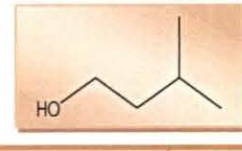
Iso amyl alcohol:



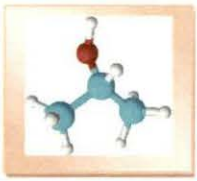
Isoamyl Alcohol is a colorless liquid with pungent taste and disagreeable aroma. It is soluble in alcohol and ether but slightly soluble in water.

Source: Merck, India.

Purification: It was dried with anhydrous K_2CO_3 and distilled. The middle fractions for both the liquids were collected and kept free from humidity with 3 Å molecular sieves[4].

Iso amyl alcohol	
	
Appearance:	**Liquid**
Molecular Formula:	**$C_5H_{12}O$**
Molecular Weight:	**88.15 g/mol**
Boiling Point:	**132°C**
Melting Point:	**-117°C**
Dielectric Constant:	**15.1 at 25°C**

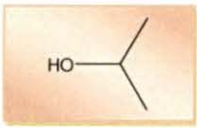
2-Propanol:



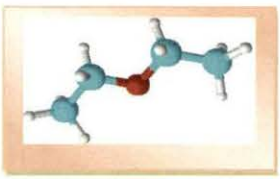
2-Propanol: Isopropyl alcohol (2-propanol or the abbreviation IPA) is a common name for a chemical compound with the molecular formula C_3H_8O. It is a colorless, flammable chemical compound with a strong odour.

Source: Merck, India.

Purification: It was dried with anhydrous $CaSO_4$ and distilled. After distillation were stored over activated 4 Å molecular sieves to reduce their water content before use[2].

2-Propanol	
	
Appearance:	**Liquid**
Molecular Formula:	**C_3H_8O**
Molecular Weight:	**60.1 g/mol**
Boiling Point:	**82.5°C**
Melting Point:	**-89°C**
Dielectric Constant:	**19.92 at 25°C**

Diethyl ether:

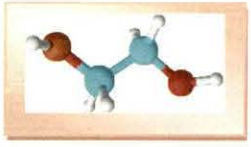


Diethyl ether, also known simply as ether, is the organic compound with the formula $(C_2H_5)_2O$. It is a colorless and highly flammable liquid with a low boiling point and a characteristic odor.

Source: Merck, India.

Purification: Diethyl ether (AR) was distilled and stored over sodium[5].

Diethyl ether	
	
Appearance:	**Liquid**
Molecular Formula:	**$(C_2H_5)_2O$**
Molecular Weight:	**74.12 g/mol**
Boiling Point:	**34.6°C**
Melting Point:	**-116.3°C**
Dielectric Constant:	**4.34 at 25°C**

Ethylene glycol: 

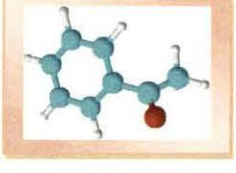
Ethylene glycol is a colorless, practically odorless, low-volatility, low-viscosity, hygroscopic liquid. It is completely miscible with water and many organic liquids. The hydroxyl groups on glycols undergo the usual alcohol chemistry, giving a wide variety of possible derivatives.

Source: Merck, India.

Purification: It was dried with anhydrous $CaSO_4$ and distilled under vacuum. The distillate was passed through linde type 4 Å molecular sieves[2].

Ethylene glycol

Appearance:	**Liquid**
Molecular Formula:	**$C_2H_6O_2$**
Molecular Weight:	**62.07 g/mol**
Boiling Point:	**197.3°C**
Melting Point:	**-12.9°C**
Dielectric Constant:	**40.97 at 25°C**

Acetophenone: 

Acetophenone, the simplest aromatic ketone, is a clear liquid or crystals; very slightly soluble in water.

Source: Merck, India.

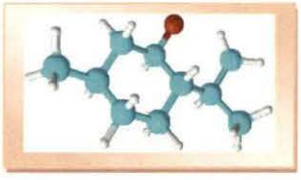
Purification: Dried by standing with anhydrous $CaSO_4$ for several days, followed by fractional distillation under reduced pressure[2].

Acetophenone

Appearance:	**Liquid**
Molecular Formula:	**$C_6H_5C(O)CH_3$**
Molecular Weight:	**120.1 g/mol**
Boiling Point:	**202°C**
Melting Point:	**-20°C**
Dielectric Constant:	**17.3 at 25°C**

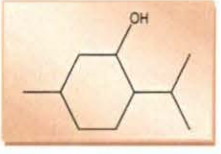
3.1.2. Solutes

Menthol:



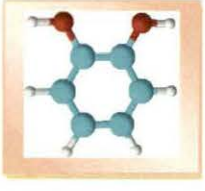
Menthol is an organic compound made synthetically or obtained from peppermint or other mint oils. It is a waxy, crystalline substance, clear or white in color, which is solid at room temperature and melts slightly above.

Menthol



Appearance:	**White or colourless crystalline solid**
Molecular Formula:	**$C_{10}H_{20}O$**
Molecular Weight:	**156.27 g/mol**
Melting Point:	**45°C**

Catechol:

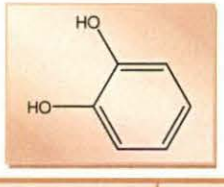


Catechol, formerly known as pyrocatechol, is 1, 2-dihydroxybenzene, an organic compound with the feathery white crystals which are very rapidly soluble in water. It is the ortho isomer of one of the three isomeric benzenediols.

Source: S.D. Fine Chemicals Ltd., Mumbai, India.

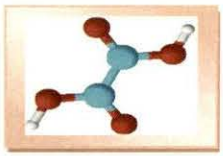
Purification: Commercial sample of catechol was purified by repeated crystallization from mixture of chloroform-methanol. The sample

Catechol



Appearance:	**White solid**
Molecular Formula:	**$C_6H_6O_2$**
Molecular Weight:	**110.11g/mol**
Melting Point:	**105°C**

was dissolved in chloroform in hot condition, filtered and to the filtrate dried & distilled methanol was added drop wise. Fine plate like crystal separated and recovered by rapid filtration & ready for use.

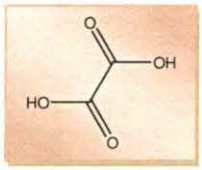
Oxalic acid: 

Oxalic Acid (also called Ethanedioic Acid) is a toxic organic compound belonging to the family of dicarboxylic acids. It occurs in the form of its metal salts (usually calcium or potassium) in many plants. It is commercially manufactured by heating sodium formate in the presence of an alkali catalyst to form sodium oxalate, which should be converted to free oxalic acid when treated with sulfuric acid. Oxalic acid is the only possible compound in which two carboxyl groups are joined directly; for this reason oxalic acid is one of the strongest acids in organic compounds.

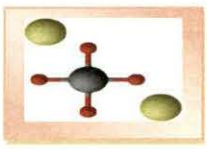
Source: Analytical Reagent Grade

Purification: Oxalic acid (of Analytical Reagent Grade) was used after drying over P_2O_5 in a desiccator for more than 24 hours.

Oxalic acid



Appearance:	**White Crystalline Solid**
Molecular Formula:	**$(COOH)_2,2H_2O$**
Molecular Weight:	**126.07 g/mol**
Melting Point:	**$(101\text{-}102)^0C$**

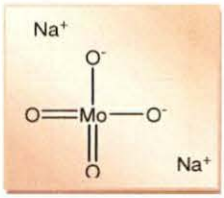
Sodium Molybdate: 

Sodium molybdate is useful as a source of molybdenum[6]. It is often found as the dehydrate $Na_2MoO_4{\cdot}2H_2O$. The molybdate (VI) anion is tetrahedral. Two sodium cations coordinate with every one anion[7].

Source: E. Merck, India

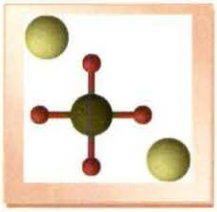
ırification: Sodium molybdate was ırified by re-crystallizing twice from ınductivity water and then dried in a ıcuum desiccator over P_2O_5 for 24 hours ːfore use.

Sodium Molybdate



Appearance:	**white crystalline solid**
Molecular Formula:	**$Na_2MoO_4,2H_2O$**
Molecular Weight:	**241.95 g/mol**
Melting Point:	**687°C**

ɔdium Tungstate:

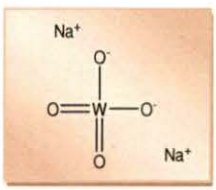


ɔdium tungstate, Na_2WO_4, a tungstate of sodium, is useful as a source of tungsten. It is ɾepared from tungsten ores used to anufacture tungsten by reducing it. It often found as the dihydrate, $a_2WO_4 \bullet 2H_2O$. This salt is soluble in ater and is a moderately strong ɨidizing agent,

ɔurce: E. Merck, India

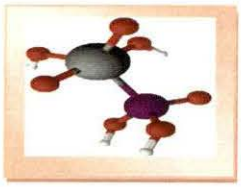
ɨrification: Sodium tungstate was ɨrified by re-crystallizing twice from ɔnductivity water and then dried in a ɨcuum desiccator over P_2O_5 for 24 ɔurs before use.

Sodium Tungstate



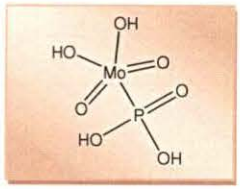
Appearance:	**Colorless or white crystalline powder**
Molecular Formula:	**$Na_2WO_4.2H_2O$**
Molecular Weight:	**329.86**
Melting Point:	**698 ° C**

Phosphomolybdic acid:

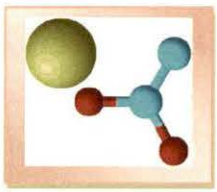


Phosphomolybdic acid, also known as dodeca molybdophosphoric acid or PMA is a component of Masson's trichrome stain. It is a yellow-green compound, freely soluble in water and polar organic solvents such as ethanol

Source: Thomas Baker, India

Phosphomolybdic acid	
	
Appearance:	**Solid yellow crystals**
Molecular Formula:	**$H_3Mo_{12}O_{40}P$**
Molecular Weight:	**1825.25 g/mol**
Melting Point:	**(78-90)^{0}C**

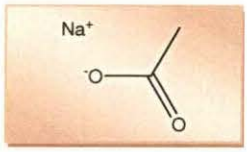
Sodium Acetate:



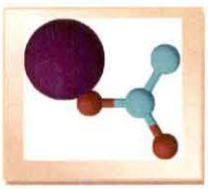
Sodium Acetate is a salt of a strong base and a weak acid providing the application to be used as buffers.

Source: Thomas Baker, India

Purification: It was crystallized from aqueous ethanol, as trihydrate. This material was converted to anhydrous salt by heating slowly in a porcelain dish, so that the salt melts again. After several minutes, the salt was allowed to solidify and cooled to a convenient temperature before being powdered and bottled.

Sodium Acetate	
	
Appearance:	**White Crystalline Solid**
Molecular Formula:	**CH_3COONa**
Molecular Weight:	**82.03 g/mol**
Melting Point:	**324 ^{0}C**

Potassium acetate:

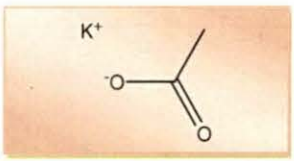


Potassium acetate, is the potassium salt of acetic acid.

Source: Thomas Baker, India

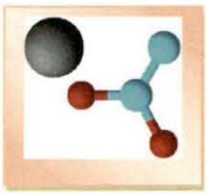
Purification: It was crystallized three times from water – ethanol (1:1) dried to constant weight in a oven and pumped dry under vacuum for 30hr at 100°C.

Potassium Acetate



Appearance:	**white crystalline solid**
Molecular Formula:	**CH_3CO_2K**
Molecular Weight:	**98.15 g/mol**
Melting Point:	**292 °C**

Lithium acetate:

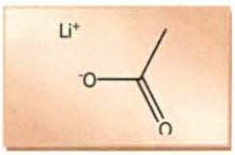


Lithium acetate: It is a salt of lithium and acetic acid

Source: Thomas Baker, India

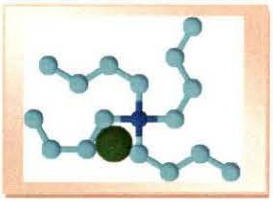
Purification: It was crystallized from ethanol (5ml/g) by partial evaporation.

Lithium Acetate



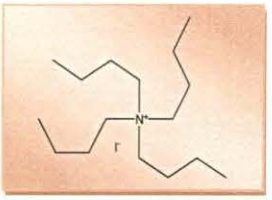
Appearance:	**white crystalline solid**
Molecular Formula:	**CH_3COOLi**
Molecular Weight:	**102.02 g/mol**
Melting Point:	**54-56 °C**

Quaternary ammonium iodide:



Quaternary ammonium compounds (R_4N^+) are any of a group of ammonium salts in which organic radicals have been substituted for all four hydrogens of the original ammonium cation. They have a central nitrogen atom which is joined to four organic radicals (for e.g. butyl group) and one acid radical (for e.g. iodide ion). The organic radicals (R) may be alkyl, aryl, or aralkyl, and the nitrogen can be part of a ring system. They are prepared by treatment of an amine with an alkylating agent. They show a variety of physical, chemical, and biological properties and most compounds are soluble in water and strong electrolytes. In addition to their tendency of locating at the interface of two phases (liquid–liquid or solid–liquid) to introduce continuity between the two different phase, they have properties of disrupting micro-organisms' cell processes.

Quaternary ammonium iodide



Appearance:	**White crystalline solid**
Molecular Formula:	**R_4NI**

Source: Sigma Aldrich, Germany

3.2. Experimental Methods and Instruments Used

Measurement of Density

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298.15 K with doubly distilled water and THF. The total uncertainty in density was estimated to be ±0.0001 g cm^{-3}.

The measurements were carried out in a thermostatic water bath (Science India, Kolkata) maintained with an accuracy of ± 0.01 K of the desired temperature. A 60W heating element and a toluene-mercury thermo-regulator were used to maintain the temperature of the experimental thermostat which was placed in a hot-cum-cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. [8-10]

Density meter(Anton Paar(DMA 4500 M) GmbH, Austria-Europe

In the digital density meter, the mechanic oscillation of the U-tube is e.g. electromagnetically transformed into an alternating voltage of the same frequency. The period τ can be measured with high resolution and stands in simple relation to the density ρ of the sample in the oscillator

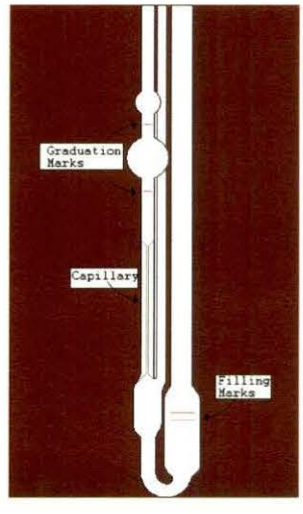
In the digital density meter, the mechanic oscillation of the U-tube is e.g. electromagnetically transformed into an alternating voltage of the same frequency. The period τ can be measured with high resolution and stands in simple relation to the density ρ of the sample in the oscillator.

$$\rho = A\tau^2 - B \tag{1}$$

A and B are the respective instrument constants of each oscillator. Their values are determined by calibrating with two substances of the precisely known densities ρ_1 and ρ_2. Modern instruments calculate and store the constants A and B after the two calibration measurements, which are mostly performed with air and water. They employ suitable measures to compensate various parasitic influences on the measuring result, e.g. the influence of the sample's viscosity and the non-linearity caused by the measuring instrument's finite mass.

Measurement of Viscosity

The kinematic viscosities were measured by means of a suspended-level Ubbelohde viscometer. The time of flow was measured with a stop watch. The viscometer was always kept in a vertical position in the water- bath. The viscometer needed no correction for kinetic energy.



The kinematic viscosity (γ) and the absolute viscosity (η) are given by the following equations:

$$\gamma = kt - 1/t \tag{2}$$

$$\eta = \gamma.\rho \tag{3}$$

where, t is the time of flow, ρ is the density and k and l are the characteristic constants of the particular viscometer. The precision of the viscosity measurement was ± 0.004 %. In all cases, the experiments were performed in at least three replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation:

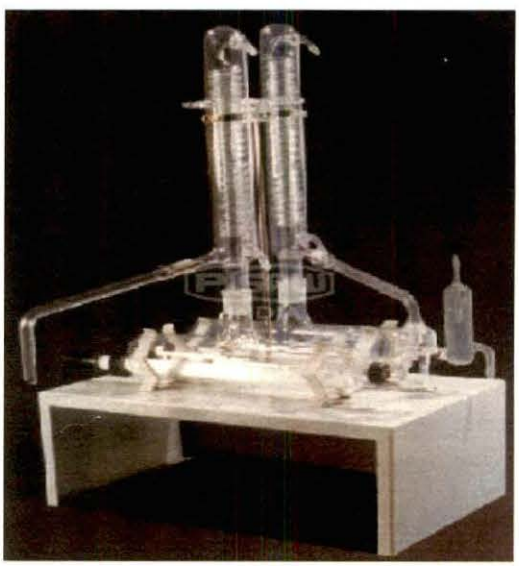
$$\eta_r = \eta / \eta_0 = \rho t / \rho_0 t_0 \qquad (4)$$

where η, η_0, ρ, ρ_0 and t, t_0 are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic water bath maintained with an accuracy of ± 0.01 K of the desired temperature.

Water Distiller

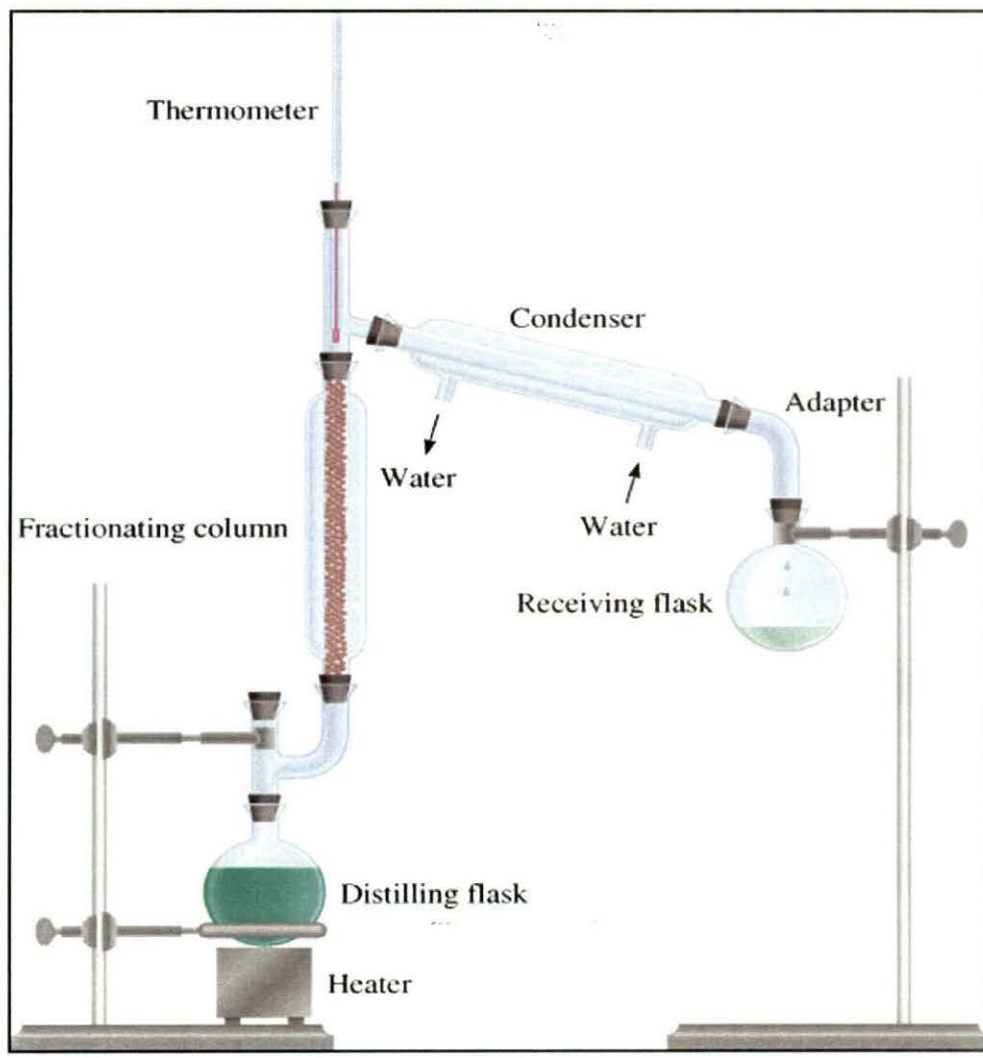
Water distillation units produce highly treated and disinfected water for laboratory usage. The distillation process removes minerals and microbiological contaminants and can reduce levels of chemical contaminants. A water distiller works by boiling water into water vapour, condensing it and then returning it to its liquid state. It is collected in a storage container.



Municipal or well water is manually or automatically fed into the distiller unit's boiling chamber. A heating element in the boiling chamber heats the water until it boils. The steam rises from the boiling chamber. Volatile contaminants (gases) are discharged

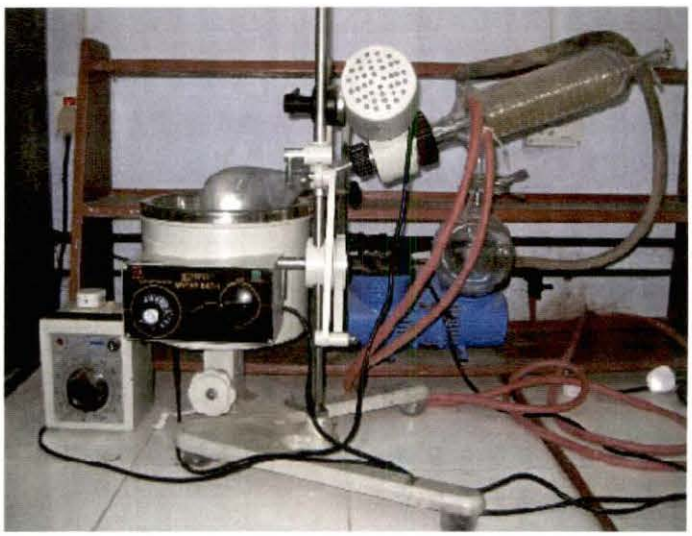
through a built-in vent. Minerals and salts are retained in the boiling chamber as hard deposits or scale. The steam enters a coiled tube (condenser), which is cooled by cool water. Water droplets form as condensation occurs. The distilled water is collected in a storage tank. If the unit is an automatic model, it is set to operate to fill the storage tank. The distillation apparatus consists of flask with heating elements embedded in glass and fused in spiral type coil internally of the bottom and tapered round glass, joints at the top double walled condenser with B-40/B-50 ground glass joints, suitable to work on 220 volts, 50 cycles AC supply.

Fractional Distillation Apparatus



Rotary Vacuum Flash Evaporator

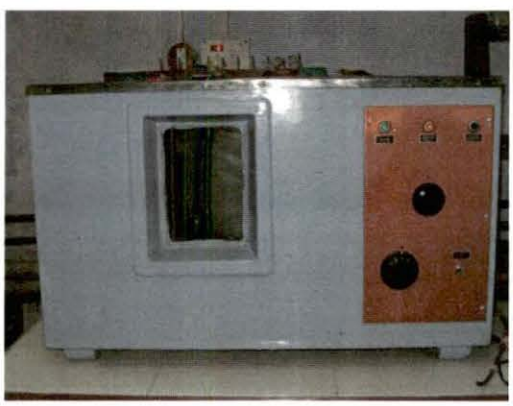
A rotary evaporator (or rotavap) is a device used in chemical laboratories for the efficient and gentle removal of solvents from samples by evaporation. When referenced in the chemistry research literature, description of the use of this technique and equipment may include the phrase "rotary evaporator", though use is often rather signaled by other language (e.g., "the sample was evaporated under reduced pressure").



Rotary evaporation is most often and conveniently applied to separate "low boiling" solvents such a n-hexane or ethyl acetate from compounds which are solid at room temperature and pressure [11]. However, careful application also allows removal of a solvent from a sample containing a liquid compound if there is minimal co-evaporation (azeotropic behavior), and a sufficient difference in boiling points at the chosen temperature and reduced pressure.

Thermostat Water Bath (Science India, Kolkata):

The measurements were carried out in thermostatic water bath maintained with an accuracy of ± 0.01 K of the desired temperature.



Laboratory water bath is a system in which a vessel containing the material to be heated is placed into or over the one containing water and to quickly heat it. These laboratory equipment supplies are available in different volumes and construction with both digital and analogue controls and greater temperature uniformity, durability, heat retention and recovery. The chambers of water bath lab products are manufactured using rugged, leak proof and highly resistant stainless steel and other lab supplies.

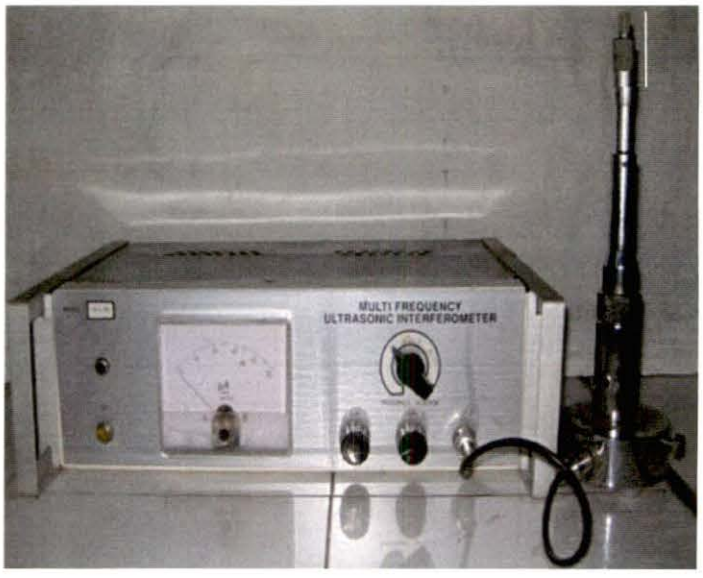
Digital Electronic Analytical Balance

The mass measurements accurate to ±0.01 mg were made on a digital electronic analytical balance (Mettler Toledo, AG 285, Switzerland). An analytical balance is used to measure mass to a very high degree of precision and accuracy. The weighing pan(s) of a high precision (.01 mg or better) analytical balance are inside a transparent enclosure with doors so that dust does not collect and so any air currents in the room do not affect the balance's operation.

The use of a vented balance safety enclosure, which has uniquely designed acrylic airfoils, allows a smooth turbulence-free airflow that prevents balance fluctuation and the weighing of mass down to 1 μg without fluctuations or loss of product. Also, the sample must be at room temperature to prevent natural convection from forming air currents inside the enclosure, affecting the weighing.

Ultrasonic Interferometer

Ultrasonic speeds were measured, with an accuracy of 0.2 %, using a single-crystal variable-path ultrasonic interferometer (Model M-81, Mittal Enterprise, New Delhi) operating at 4 MHz, which was calibrated with water, methanol and benzene at required temperature. The temperature stability was maintained within ± 0.01 K by circulating thermostatic water around the cell by a circulating pump.



Experimental set-up of Ultrasonic Interferometer

The principle used in the measurement of the ultrasonic speed (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum.

If the distance is now increased or decreased and the variation is exactly one half of wave length (λ /2) or integral multiples of it, anode current becomes maximum. From the knowledge of the wave length (λ), the speed (u) can be obtained by the relation.

$$Ultrasonic\ speed\,(u) = Wave\ Length(\lambda) \times Frequency(f) \qquad (5)$$

Experimental set-up

a. *One high frequency generator.*

b. *Measuring cell, 1, 2, 3 and 4 MHz.*

c. *Shielded cable*

The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The cell is filled with the experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal. The micrometer is slowly moved till the anode current on the meter on the high frequency generator shows a maximum. A number of maxima readings of anode current are passed and their number (n) is counted. The total distance (d) thus moved by the micrometer gives the value of the wavelength (λ) with the following relation:

$$d = n \times \lambda / 2 \tag{6}$$

Further, the velocity is determined from which the isentropic compressibility (K_S) is calculated by the following formula:

$$K_s = 1/\left(u^2 \rho\right) \tag{7}$$

where ρ is the density of the experimental liquid.

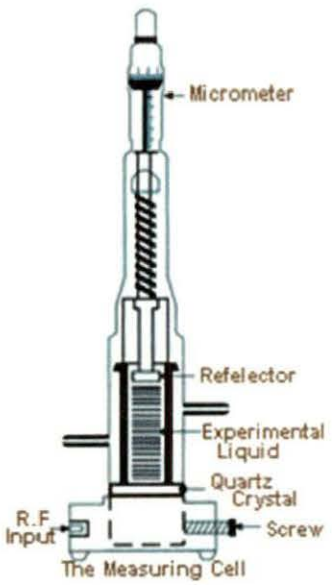


Fig.1(a): Cross-Section of the Measuring Cell

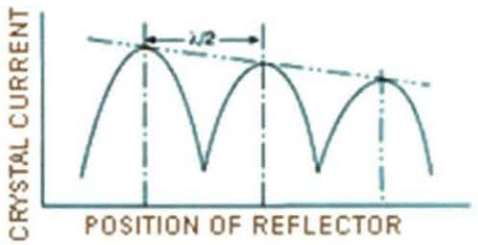
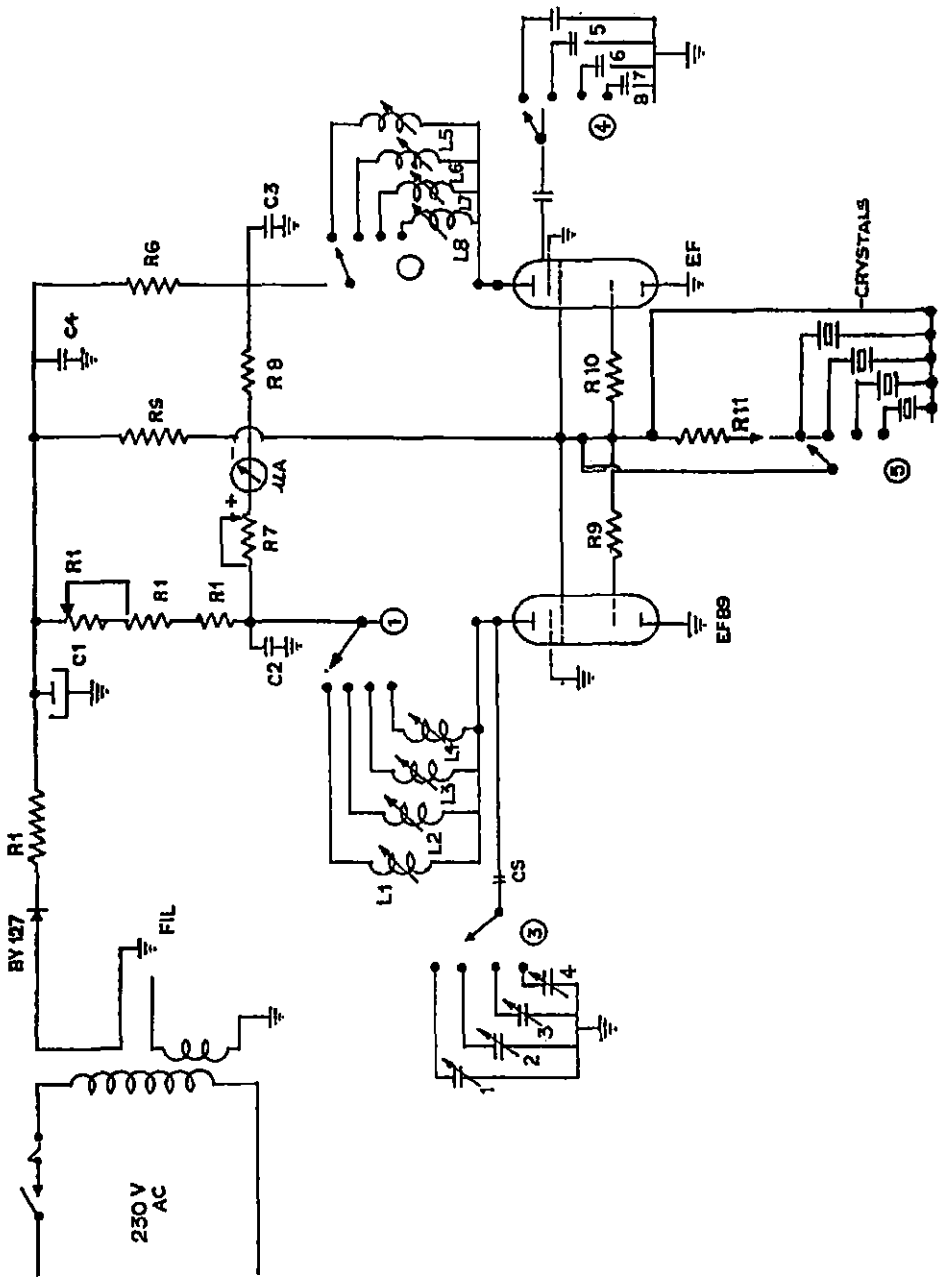


Fig.1(b): Position of Reflector versus Crystal Current

Figure 1 shows the Multifrequency Ultrasonic Interferometer i.e.

(a) Cross-section of the measuring cell, (b) Position of reflector vs. crystal current (Note : The extra peaks in between minima and maxima occurs due to a number of reasons, but these do not effect the value of $\lambda/2$).



Electronic Circuit Diagram of the Instrument

Conductivity Bridge

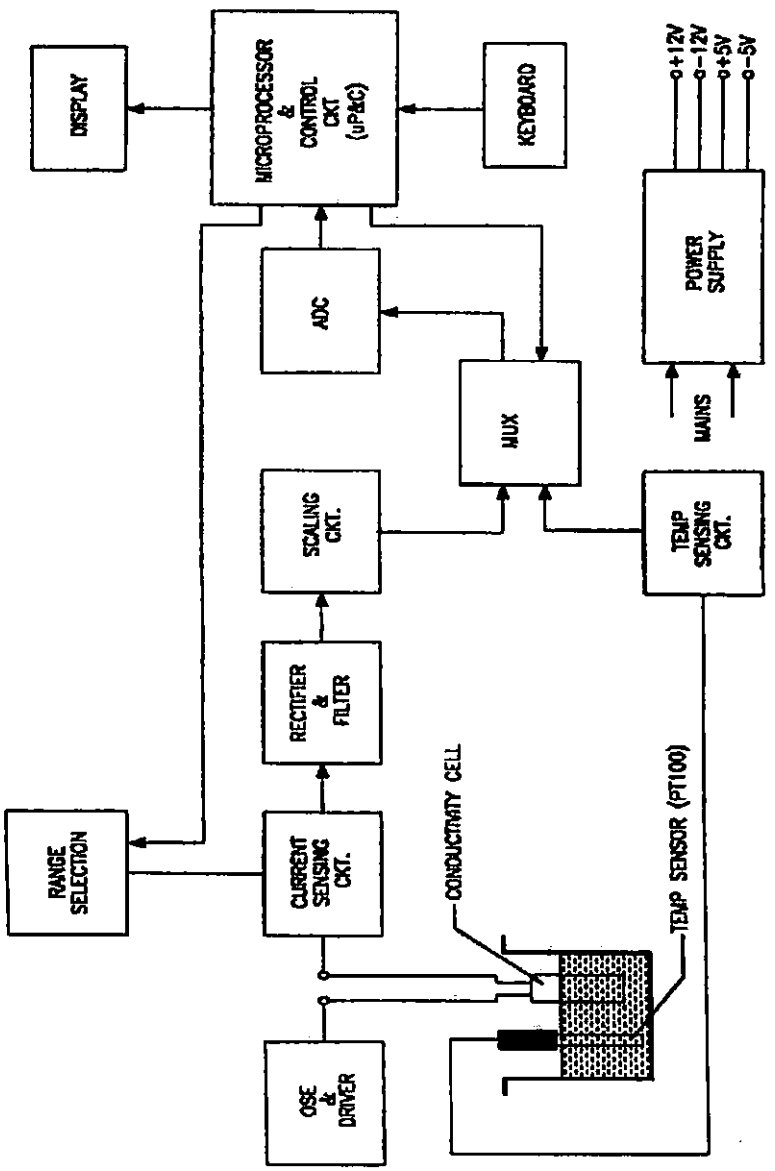
Systronics Conductivity-TDS meter 308 is a microprocessor based instrument used for measuring specific conductivity of solutions. It can provide both automatic and manual temperature compensation. The instrument shows the conductivity of the solution under test at the existing temperature or with temperature compensation. Provision for storing the cell constant and the calibrating solution type, is provided with the help of battery back-up. This data can be further used for measuring the conductivity of an unknown solution, without recalibrating the instrument even after switching it off.

The conductance measurements were carried out on this conductivity bridge using a dip-type immersion conductivity cell of cell constant 1.11cm^{-1}. The entire conductance data were reported at 1 KHz and was found to be ±0.3 % precise. The instrument was standardized using 0.1(M) KCl solution. The cell was calibrated by the method of Lind and co-workers[12]. The conductivity cell was sealed to the side of a 500 cm^3 conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen gas was passed to prevent admission of air into the cell when solvent or solution was added. The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of ± 0.01 K by means of mercury in glass thermoregulator[13].

Solutions were prepared by weight precise to ± 0.02 %. The weights were taken on a Mettler electronic analytical balance (AG 285, Switzerland). The molarities being converted to molalities as required. Several independent solutions were prepared and

runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvents at desired temperatures.

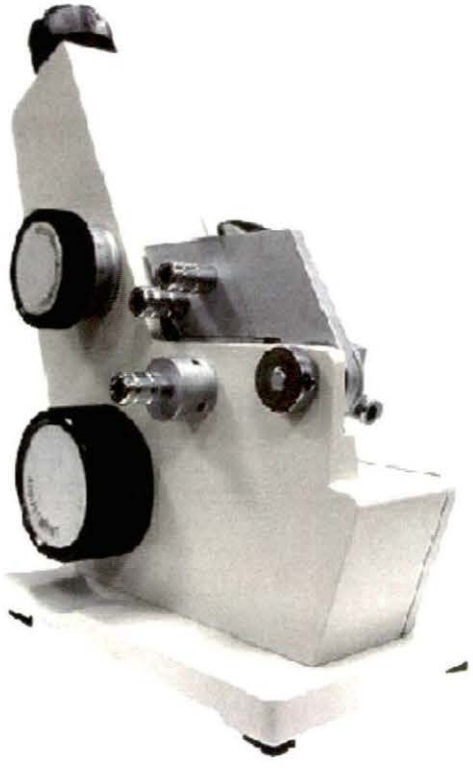
The following figure shows the Block diagram of the Systronics Conductivity-TDS meter 308.



Block Diagram of the Instrument

Abbe Refractometer (Cyberlab, MA01527,USA)

The refractive indices of pure liquids and their binary mixture were measured by using a thermostated Abbe refractometer. The values of refractive index were obtained using sodium D light. The uncertainty of refractive index measurements was within 0.0001. The thermostat temperature was constant to ±0.01 K. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostated water bath.



Calibration was performed by measuring the refractive indices of double-distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperature. The sample mixtures were directly injected into the prism assembly of the instrument using an airtight hypodermic syringe, and an average of four measurements was taken for each mixture.

The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the index of refraction (aka refractive index or n) for the substance.

$$\text{refractive index } (n) \text{ of substance} = \frac{\text{speed of light in a vacuum}}{\text{speed of light in substance}} \quad (8)$$

Whenever light changes speed as it crosses a boundary from one medium into another its direction of travel also changes, i.e., it is refracted (Figure 1). (In the special case of the light traveling perpendicular to the boundary there is no change in direction upon entering the new medium.) The relationship between light's speed in the two mediums (v_A and v_B), the angles of incidence (q_A) and refraction (q_B) and the refractive indexes of the two mediums (n_A and n_B) is shown below:

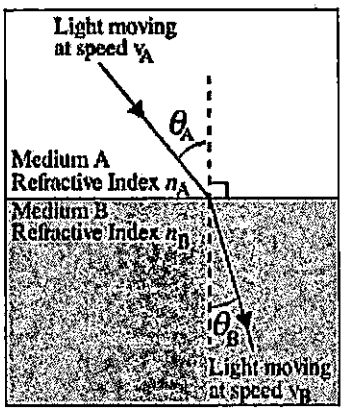


Figure 1. Light crossing from any transparent medium into another in which it has a different speed, is refracted, i.e., bent from its original path (except when the direction of travel is perpendicular to the boundary). In the case shown, the speed of light in medium A is greater than the speed of light in medium B

$$\frac{V_A}{V_B} = \frac{\sin\theta_A}{\sin\theta_B} = \frac{n_B}{n_A} \tag{9}$$

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is possible to determine the refractive index of the sample quite accurately[14]. Nearly all refractometers utilize this principle, but may differ in their optical design.

In the Abbe' refractometer the liquid sample is sandwiched into a thin layer between an illuminating prism and a refracting prism (Figure 2). The refracting prism is made of a glass with a high refractive index (e.g., 1.75) and the refractometer is designed to be used with samples having a refractive index smaller than that of the refracting prism.

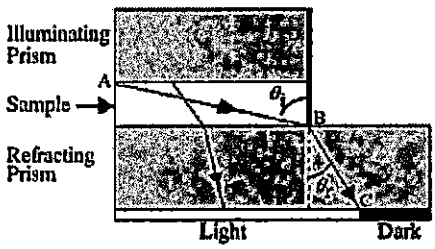


Figure 2. Cross section of part of the optical path of an Abbe refractometer. The sample thickness has been exaggerated for clarity.

A light source is projected through the illuminating prism, the bottom surface of which is ground (i.e., roughened like a ground-glass joint), so each point on this surface can be thought of as generating light rays traveling in all directions. Inspection of Figure 2 shows that light traveling from point A to point B will have the largest angle of incidence (q_i) and hence the largest possible angle of refraction (q_r) for that sample. All other rays of light entering the refracting prism will have smaller q_r and hence lie to the left of point C. Thus, a detector placed on the back side of the refracting prism would show a light region to the left and a dark region to the right.

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