

# CHAPTER-III

## EXPERIMENTAL SECTION

### III. 1 NAME, STRUCTURE, PHYSICAL AND CHEMICAL PROPERTIES, PURIFICATION AND APPLICATIONS OF THE CHEMICALS USED IN THE RESEARCH WORK

#### III.1.1 SOLVENTS

The details of the aqueous and non-aqueous solvents used in the research work are given below:

**Water (H<sub>2</sub>O):**



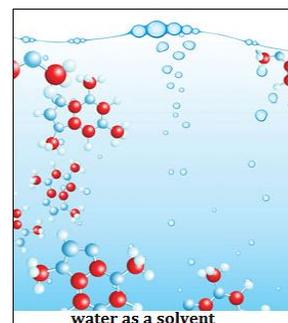
Water is an omnipresent chemical substance is composed of hydrogen and oxygen and is essential for all known forms of life. In typical usage, water refers only to its liquid form or state, but the substance also exists as solid state, ice, and a gaseous state, water vapour or steam. Water is a good solvent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

<b>WATER</b>	
<i>Appearance</i>	:Liquid
<i>Molecular Formula</i>	:H <sub>2</sub> O
<i>Molecular Weight</i>	:18.02 g·mol <sup>-1</sup>
<i>Density</i>	:0.99713 g·cm <sup>3</sup>
<i>Viscosity</i>	:0.891 mP·s
<i>Refractive Index</i>	:1.3333
<i>Ultrasonic Speed</i>	:1500.0 m·s <sup>-1</sup>
<i>Dielectric Constant</i>	:78.35 at 298.15K

**Source:** Distilled water, distilled from fractional distillation method in Lab.

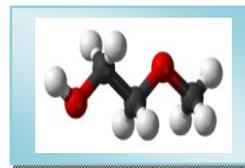
**Purification:** Water was first deionised and then distilled in an all glass distilling set along with alkaline  $\text{KMnO}_4$  solution to remove any organic matter therein. The doubly distilled water was finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from  $\text{CO}_2$  and other impurities. The triply distilled water had specific conductance less than  $1 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ .

**Application:** Water is widely used in chemical reactions as a solvent or reactant and less commonly as a solute or catalyst. In inorganic reactions, water is a common solvent, dissolving many ionic compounds. Supercritical water has recently been a topic of research. Oxygen saturated supercritical water combusts organic



pollutants efficiently. It is also use in various industries. It is a superb solvent, generally taken as the universal solvent, due to the marked polarity of the water molecule and its tendency to form hydrogen bonds with other molecules. Life on earth totally depends on water. Not only a high percentage of living things, both plants and animals are found in water, all life on earth is thought to have arisen from water and the bodies of all living organisms are composed largely of water. About 70 to 90 percent of all organic matter is water. The chemical reactions in all plants and animals that support life take place in a water medium. Water not only provides the medium to make these life sustaining reactions possible, but water itself is often an important reactant or product of these reactions. In short, the chemistry of life is water chemistry.

**2-Methoxyethanol or Methyl cellosolve (MC):**



2-Methoxyethanol, or methyl cellosolve, is an organic compound with formula  $C_3H_8O_2$  that is used mainly as a solvent. It is a clear, colorless liquid with an ether-like odor. 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.

<b>2-Methoxyethanol</b>	
<i>Appearance</i>	: Colourless Liquid
<i>Molecular Formula</i>	: $C_3H_8O_2$
<i>Molecular Weight</i>	: $76.09 \text{ g}\cdot\text{mol}^{-1}$
<i>Density</i>	: $0.965 \text{ g}\cdot\text{cm}^{-3}$
<i>Viscosity</i>	: $1.5414 \text{ mP}\cdot\text{s}$
<i>Refractive Index</i>	: 1.4002
<i>Ultrasonic Speed</i>	: $1327.0 \text{ m}\cdot\text{s}^{-1}$
<i>Dielectric Constant</i>	: 15.4 at 298.15 K

**Source:** Merck, India.

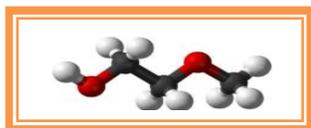
**Purification:** 2-Methoxyethanol, or methyl cellosolve (MC) obtained from Merck, India was used after further purification. It was distilled from  $P_2O_5$  and then from  $CaH_2$  in an all-glass distillation apparatus.<sup>[III.1]</sup> The middle fraction was collected. About 99% purified acetonitrile with specific conductivity  $0.8 - 1.0 \times 10^{-8} \text{ S cm}^{-3}$  was obtained. The purity of the liquid was checked by measuring its density and viscosity which were in good agreement with the literature values<sup>[III.1, III.2]</sup> as shown in Table IV.1.

**Application:** 2-Methoxyethanol is used as a solvent for many different purposes such as varnishes, dyes, and resins. It is also used as an additive in airplane deicing solutions. In organometallic chemistry it is commonly used for the synthesis of Vaska's complex and related compounds such as rutheniumhydridechlorocarbonyl tris(triphenyl)phosphine. During these reactions the alcohol acts as a source of hydride and carbon monoxide.

2-Methoxyethanol is toxic to the bone marrow and testicles. Workers exposed to high levels are at risk for granulocytopenia, macrocytic anemia, oligospermia, and azoospermia.

The methoxyethanol is converted by alcohol dehydrogenase into methoxyacetic acid which is the substance which causes the harmful effects. Both ethanol and acetate have a protecting effect. The methoxyacetate can enter the Krebs cycle where it forms methoxycitrate.

**Acetonitrile (ACN):**



Acetonitrile is the colourless liquid and of the simplest organic nitrile. It is produced mainly as a byproduct of acrylonitrile manufacture.

**Source:** Merck, India.

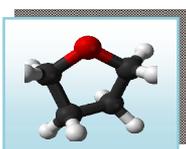
**Purification:** Acetonitrile (ACN) obtained from Merck, India was used after further purification. It was distilled from  $P_2O_5$  and then from  $CaH_2$  in an all-glass distillation apparatus.<sup>[III.1]</sup> The middle fraction was collected. About 99% purified acetonitrile with specific conductivity  $0.8 - 1.0 \times 10^{-8} \text{ S cm}^{-3}$  was obtained. The purity of the liquid was checked by measuring its density and viscosity which were in good agreement with the literature values<sup>[III.1, III.2]</sup> as shown in Table IV.1.

**Application:** It is widely used in battery applications because of its relatively high dielectric constant and ability to dissolve electrolytes. For similar reasons it is a popular

<b>Acetonitrile</b>	
<i>Appearance</i>	: Colourless Liquid
<i>Molecular Formula</i>	: $CH_3CN$
<i>Molecular Weight</i>	: $41.05 \text{ g}\cdot\text{mol}^{-1}$
<i>Density</i>	: $0.786 \text{ g}\cdot\text{cm}^3$
<i>Viscosity</i>	: $0.346 \text{ mP}\cdot\text{s}$
<i>Refractive Index</i>	: 1.3441
<i>Ultrasonic Speed</i>	: $1282.6 \text{ m}\cdot\text{s}^{-1}$
<i>Dielectric Constant</i>	: 35.95 at 298.15 K

solvent in cyclic voltammetry. Its low viscosity and low chemical reactivity make it a popular choice for liquid chromatography. Acetonitrile plays a significant role as the dominant solvent used in the manufacture of DNA oligonucleotides from monomers. Industrially, it is used as a solvent in the purification of butadiene and in the manufacture of pharmaceuticals and photographic film. Acetonitrile is a common two-carbon building block in organic synthesis as in the production of pesticides to perfumes.

**Tetrahydrofuran (THF):**



**Tetrahydrofuran (THF)** is an organic compound with the formula  $(\text{CH}_2)_4\text{O}$ . The compound is classified as heterocyclic compound, specifically a cyclic ether. It is a colorless, water-miscible organic liquid with low viscosity. THF has an odor similar to acetone. It is mainly used as a precursor to polymers. Being polar and having a wide liquid range, THF is a versatile solvent.

<b>Tetrahydrofuran</b>	
	
<i>Appearance</i>	: Colourless Liquid
<i>Molecular Formula</i>	: $\text{C}_4\text{H}_8\text{O}$
<i>Molecular Weight</i>	: $72.11 \text{ g}\cdot\text{mol}^{-1}$
<i>Density</i>	: $0.88074 \text{ g}\cdot\text{cm}^{-3}$
<i>Viscosity</i>	: $0.48 \text{ mP}\cdot\text{s}$
<i>Refractive Index</i>	: 1.4072
<i>Ultrasonic Speed</i>	: $1279.0 \text{ m}\cdot\text{s}^{-1}$
<i>Dielectric Constant</i>	: 7.58 at 298.15 K

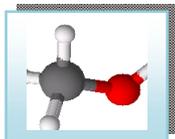
**Source:** Merck, Indian.

**Purification:** Tetrahydrofuran (THF), Merck, Indian was kept several days over potassium hydroxide (KOH), refluxed for 24 h and distilled over lithium aluminium hydride ( $\text{LiAlH}_4$ ) described earlier.<sup>[ III.3]</sup> The purified solvent had a boiling point of 339 K and a specific conductance of  $0.81 \times 10^{-6} \text{ S cm}^{-3}$ . The density and viscosity of the purified solvent

were in good agreement with the literature data<sup>[III.4, III.5]</sup> as shown in Table IV.1. The purity of the solvent was  $\geq 98.9\%$ .

**Application:** The main application of THF is as an industrial solvent for PVC and in varnishes. It is an aprotic solvent with a moderately polar solvent and can dissolve a wide range of non-polar and polar chemical compounds. THF is a popular solvent in the laboratory when a moderately higher-boiling ethereal solvent is required and its water miscibility is not an issue. Hence, like diethyl ether, THF can be used in hydroboration reactions to synthesize primary alcohols, and as a solvent for organometallic compounds such as organolithium and Grignard reagents. THF is often used in polymer science as dissolve polymers prior to determining their molecular mass using gel permeation chromatography, to PVC as well and thus it is the main ingredient in PVC adhesives. It can be used to liquefy old PVC cement, and is often used industrially to degrease metal parts. THF is also used as a component in mobile phases for reversed-phase liquid chromatography.

**Methanol (MeOH):**

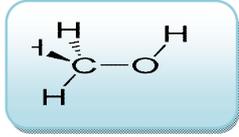


Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is the simplest alcohol, and is a light, volatile, colourless, flammable, liquid with a distinctive odour that is very similar to but slightly sweeter than ethanol (drinking alcohol).

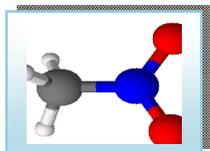
**Source:** Merck, India.

**Purification:** It was passed through Linde Å molecular sieves and then distilled.<sup>[III.6]</sup>

**Application:** The largest use of methyl alcohol by far is in making other chemicals. About 40% of methanol is converted to formaldehyde, and from there into products as diverse as plastics, plywood, paints, explosives, and permanent press textiles. Methanol is a traditional denaturant for ethanol, thus giving the term methylated spirit. Methanol is also used as a solvent, and as an antifreeze in pipelines. In some waste water treatment plants, a small amount of methanol is added to waste water to provide a food source of carbon for the denitrifying bacteria, which converts nitrates to nitrogen to reduce the denitrification of sensitive aquifers. Methanol is used on a limited basis to fuel internal combustion engines. Methanol is also useful as an energy carrier. It is easier to store than hydrogen, burns cleaner than fossil fuels, and is biodegradable.

<b>Methanol</b>	
	
<i>Appearance</i>	: Colourless Liquid
<i>Molecular Formula</i>	: CH <sub>4</sub> O
<i>Molecular Weight</i>	: 32.04 g·mol <sup>-1</sup>
<i>Density</i>	: 0.7866 g·cm <sup>3</sup>
<i>Viscosity</i>	: 0.5445 mP·s
<i>Refractive Index</i>	: 1.3284
<i>Ultrasonic Speed</i>	: 1103.0 m·s <sup>-1</sup>
<i>Dielectric Constant</i>	: 32.6 at 298.15 K

**Nitromethane (NM):**

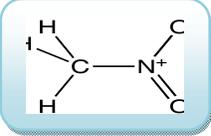


Nitromethane is one of the simplest organic nitro compounds. It is a slightly viscous, highly polar liquid.

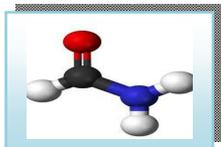
**Source:** S.D. Fine Chemicals Ltd., Mumbai, India.

**Purification:** It is dried with  $\text{CaSO}_4$  and then distilled.<sup>[111,6]</sup>

**Application:** The principle use of nitromethane is as a stabilizer for chlorinated solvents, which are used in dry cleaning, semiconductor processing, and degreasing. It is also used most effectively as a solvent or dissolving agent for acrylate monomers, such as cyanoacrylates. In more specialized organic synthesis, nitromethane serves as a Michael donor, adding to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds via 1,4-addition in the Michael reaction. Its acidity allows it to undergo deprotonation, enabling condensation reactions analogous to those of carbonyl compounds.

<b>Nitromethane</b>	
	
<i>Appearance</i>	: Colourless Liquid
<i>Molecular Formula</i>	: $\text{CH}_3\text{NO}_2$
<i>Molecular Weight</i>	: $61.04 \text{ g}\cdot\text{mol}^{-1}$
<i>Density</i>	: $1.13045 \text{ g}\cdot\text{cm}^3$
<i>Viscosity</i>	: $0.614 \text{ mP}\cdot\text{s}$
<i>Refractive Index</i>	: 1.3260
<i>Ultrasonic Speed</i>	: $1317.0 \text{ m}\cdot\text{s}^{-1}$
<i>Dielectric Constant</i>	: 35.87 at 298.15 K

**Formamide (F):**



**Formamide**, also known as **methanamide**, is an amide derived from formic acid. It is a clear liquid which is miscible with water and has an ammonia like odor. It is chemical feedstock for the manufacture of sulfa drugs, other pharmaceuticals, herbicides, pesticides and the manufacture of hydrocyanic acid.

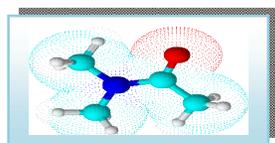
**Source:** Sigma Adrich, Germany

**Purification:** The Spectrographic grade formamide used as procured, without further purification. The purity of the solvent is 99.5%.

**Application:** It has been used as a softener for paper and fiber. It is a solvent for many ionic compounds. It has also been used as a solvent for resins and plasticizers. Formamide will begin to partially decompose into carbon monoxide and ammonia at 180°C. When heated strongly, formamide decomposes to hydrogen cyanide (HCN) and water vapor. It is also a constituent of cryoprotectant vitrification mixtures used for cryopreservation of tissues and organs. Formamide is also used as an RNA stabiliser in gel electrophoresis by deionizing RNA. In capillary electrophoresis, it is used for stabilizing (single) strands of denatured DNA. Another use is to add it in sol-gel solutions in order to avoid cracking during sintering. Formamide, in its pure state, has been used as an alternative solvent for the electrostatic self-assembly of polymer nano-films. It is used to

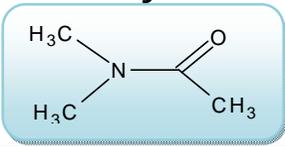
<b>Formamide</b>	
<i>Appearance</i>	: Colourless Liquid
<i>Molecular Formula</i>	: HCONH <sub>2</sub>
<i>Molecular Weight</i>	: 45.04 g·mol <sup>-1</sup>
<i>Density</i>	: 1.13300 g·cm <sup>-3</sup>
<i>Viscosity</i>	: 3.304 mP·s
<i>Refractive Index</i>	: 1.4475
<i>Ultrasonic Speed</i>	: 1626.3 m·s <sup>-1</sup>
<i>Dielectric Constant</i>	: 109.5 at 298.15 K

prepare primary amines directly from ketones via their N-formyl derivatives, using the Leuckart reaction.



***N,N-Dimethylacetamide (DMA):***

N,N-Dimethylacetamide is the organic compound with the formula  $(\text{CH}_3)_2\text{NCOCH}_3$ . This colorless, water-miscible, high boiling liquid is commonly used as a polar solvent in organic synthesis. DMA, as it often abbreviated, is miscible with most other solvents, although it is poorly soluble in aliphatic hydrocarbons.

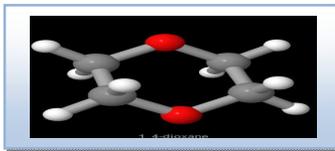
<b><i>N,N-Dimethylacetamide</i></b>	
	
<i>Appearance</i>	:Colourless Liquid
<i>Molecular Formula</i>	: $(\text{CH}_3)_2\text{NCOCH}_3$
<i>Molecular Weight</i>	: $87.12 \text{ g}\cdot\text{mol}^{-1}$
<i>Density</i>	: $0.93680 \text{ g}\cdot\text{cm}^{-3}$
<i>Viscosity</i>	: $0.871 \text{ mP}\cdot\text{s}$
<i>Refractive Index</i>	: 1.4384
<i>Ultrasonic Speed</i>	: $1458.5 \text{ m}\cdot\text{s}^{-1}$
<i>Dielectric Constant</i>	:37.78 at 298.15 K

**Source:** Thomas Baker, India

**Purification:** It was dried by passing through molecular sieves.<sup>[III.6]</sup>

**Application:** DMA is useful solvent for reactions involving strong bases such as sodium hydroxide. Dimethylacetamide is commonly used as a solvent for fibers (e.g., polyacrylonitrile, spandex) or in the adhesive industry.<sup>[III.11]</sup> It is also employed in the production of pharmaceuticals and plasticizers as a reaction medium.

**1,4 Dioxane (1,4 DO):**



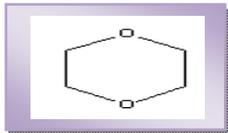
1,4-Dioxane, often simply called dioxane because the 1,2 and 1,3 isomers of dioxane are rare, is a heterocyclic organic compound. It is a colorless liquid with a faint sweet odor similar to that of diethyl ether. It is classified as an ether. Dioxane is used mainly as a stabilizer for the solvent trichloroethane. It is an occasionally used solvent for a variety of practical applications as well as in the laboratory.

**Source:** Thomas Baker, India

**Purification:** It was dried by passing through molecular sieves.<sup>[111.6]</sup>

**Application:** 1,4 dioxane (1,4 DO) is miscible with water and in fact is hygroscopic. This water miscibility is a favorable property for some industrial applications. Dioxane is a versatile aprotic solvent. The oxygen atom is lewis base, so

it is able to solvate many inorganic compounds. Because of its lower toxicity, it is substituted for tetrahydrofuran (THF) in some processes. However, it has a higher boiling point (101 °C versus 66 °C for THF), which is important when reactions are to be conducted at a higher temperature. Besides 1,4 Dioxane is used in cosmetic industries and for environmental protection

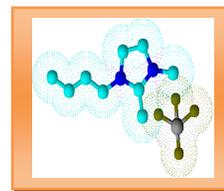
<b>1,4 Dioxane</b>	
	
<i>Appearance</i>	: Colourless Liquid
<i>Molecular Formula</i>	: $C_4H_8O_2$
<i>Molecular Weight</i>	: $88.11 \text{ g}\cdot\text{mol}^{-1}$
<i>Density</i>	: $1.033 \text{ g}\cdot\text{cm}^3$
<i>Viscosity</i>	: $1.37 \text{ mP}\cdot\text{s}$
<i>Refractive Index</i>	: 1.4224
<i>Ultrasonic Speed</i>	: $1343.90 \text{ m}\cdot\text{s}^{-1}$
<i>Dielectric Constant</i>	: 2.25 at 298.15 K

### III.1.2 ELECTROLYTES AND NON-ELECTROLYTES

The electrolytes ionic liquids, and non-electrolytes amino acids, respectively, and other chemicals than these two categories that are used in the research work have been describing follow:

#### III.1.2.1 Ionic Liquids

##### 1-Butyl 2,3 dimethyl imidazolium tetrafluoroborate [bmmim][BF<sub>4</sub>]:

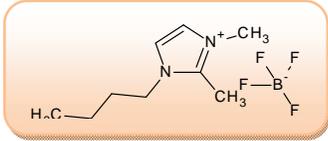


1-Butyl 2,3 dimethyl imidazolium tetrafluoroborate is the imidazolium based ionic liquid, containing bulky alkyl (n-butyl) and two methyl groups of molecular formula [C<sub>9</sub>H<sub>17</sub>N<sub>2</sub>BF<sub>4</sub>], exists as a molten solid phase (white crystalline) with the melting point 96-99°C.

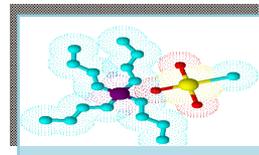
**Source:** Sigma Aldrich, Germany

**Purification:** Used as purchased. The purity of the chemical is >99.0%

**Application:** 1-Butyl-2,3 dimethylimidazolium tetrafluoroborate ([bmmim]BF<sub>4</sub>) was found to be an excellent solvent to realize a lipase recycling system using vinyl acetate as acyl donor. No accumulation of an acetaldehyde oligomer was observed in solvent system and it was possible to use the lipase repeatedly 10 times while still maintaining perfect enantioselectivity and high reactivity.

<b>[bmmim][BF<sub>4</sub>]</b>	
	
<i>Appearance</i>	: White Crystalline
<i>Molecular Formula</i>	: C <sub>9</sub> H <sub>17</sub> N <sub>2</sub> BF <sub>4</sub>
<i>Molecular Weight</i>	: 240.05 g·mol <sup>-1</sup>
<i>Melting Point</i>	: 369-372 K
<i>Relative Density</i>	: No data available
<i>Ionic radii</i>	: 1.5191 (Å) of bmmim <sup>+</sup> 2.78 (Å) of BF <sub>4</sub> <sup>-</sup>

**Tetrabutylphosphonium methanesulfonate [Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>]:**



Tetrabutylphosphonium methanesulfonate is the also phosphonium based ionic liquid, containing bulky alkyl (n-butyl) group of molecular formula [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>], exists as a molten solid phase (white crystalline) with the melting point 96-99°C.

**Source:** Sigma Aldrich, Germany

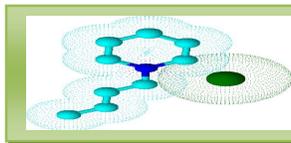
**Purification:** Used as purchased. The purity of the chemical is >99.0%

**Application:** Tetrabutylphosphonium methanesulfonate is perhaps used as same as tetrabutylphosphonium tetrafluoro-borate as electrolytes in electrochemical windows when control of electrode potentials is required source. The ionic liquid may be used in organic synthesis

and bio-catalysis, dye sensitized-cells, batteries, electrochemical application and phase transfer catalyst, etc

<b>[Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>]</b>	
<i>Appearance</i>	:White Crystalline
<i>Molecular Formula</i>	:C <sub>17</sub> H <sub>39</sub> PSO <sub>3</sub>
<i>Molecular Weight</i>	:354.53 g·mol <sup>-1</sup>
<i>Melting Point</i>	:369-372 K
<i>Relative Density</i>	:No data available
<i>Ionic radii</i>	:4.42 (Å) of Bu <sub>4</sub> P <sup>+</sup> 2.83(Å) of CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>

**1-Butyl pyridinium Bromide([bupy]Br):**

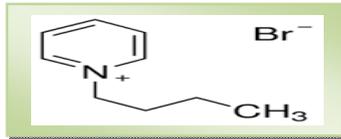


1-butyl pyridinium bromide is the pyridinium based ionic liquid, of molecular formula  $C_9H_{14}NBr$ , containing butyl group on active nitrogen atoms in the pyridinium or six member ring, exist as a molten liquid phase with the melting point  $\geq 40^\circ C$ .

**Source:** Sigma Aldrich, Germany

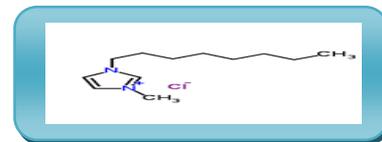
**Purification:** Used as purchased. The purity of the chemical is  $>98.0\%$

**Application:** The ionic liquid are good examples of neoteric solvents, new types of solvents, or older materials that are finding new applications as solvents, which is environmentally friendly (or eco-friendly) because they are less hazardous for human body as well as less toxic for living organisms, used as recyclable solvents for organic reactions and separation processes, lubricating fluids, heat transfer fluids for processing biomass

<b>[(bupy)Br]</b>	
	
<i>Appearance</i>	: Beige Crystalline
<i>Molecular Formula</i>	: $C_9H_{14}NBr$
<i>Molecular Weight</i>	: $216.12 \text{ g}\cdot\text{mol}^{-1}$
<i>Melting Point</i>	: $\geq 313.15 \text{ K}$
<i>Relative Density</i>	: $1.2134 \text{ g}\cdot\text{cm}^{-3}$ at $298.15 \text{ K}$
<i>Ionic radii</i>	: $1.68(\text{\AA})$ of $[\text{bupy}]^+$ $1.92(\text{\AA})$ of $Br^-$

and electrically conductive liquids as electrochemical device in the field of electrochemistry (batteries and solar cells).

**1-methyl-3-octyl imidazolium chloride [(mocim)Cl]:**



1-methyl-3-octyl imidazolium chloride is the also imidazolium based ionic liquid, of molecular formula  $C_{12}H_{23}N_2Cl$ , containing methyl and bulky octyl groups with two active nitrogen atoms in the imidazole or five member ring, exists as a molten liquid phase with the melting point  $< 4^{\circ}C$ .

**Source:** Sigma Aldrich, Germany

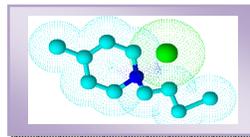
**Purification:** Used as purchased. The purity of

the chemical is  $>95.0\%$

**Application:** The ionic liquid are new types of solvents, or older materials that are finding new applications as solvents, which is environmentally friendly (or eco-friendly) because they are less hazardous for human body as well as less toxic for living organisms, used as recyclable solvents for organic reactions and separation processes, lubricating fluids, heat transfer fluids for processing biomass and electrically conductive liquids as electrochemical device in the field of electrochemistry (batteries and solar cells) and so forth.

<b>[(mocim)Cl]</b>	
<i>Appearance</i>	: Odourless liquid
<i>Molecular Formula</i>	: $C_{12}H_{23}N_2Cl$
<i>Molecular Weight</i>	: $230.78 \text{ g}\cdot\text{mol}^{-1}$
<i>Melting Point</i>	: $273.15 \text{ K}$
<i>Relative Density</i>	: $1.247 \text{ g}\cdot\text{cm}^{-3}$
<i>Ionic radii</i>	: $1.33 \text{ (\AA)}$ of $[\text{mocim}]^+$ $1.81 \text{ (\AA)}$ of $Cl^-$

***N*-butyl-4-methyl pyridinium chloride ([C<sub>4</sub>mpy]Cl):**

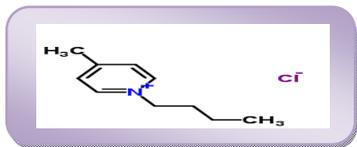


N-butyl-4-methyl pyridinium chloride is the pyridinium based ionic liquid, of molecular formula C<sub>10</sub>H<sub>16</sub>NCl, containing butyl group on the active nitrogen atom in the pyridinium ring and methyl group on forth position of the ring, exist as a molten liquid phase with the melting point ≥ 25-30°C.

**Source:** Sigma Aldrich, Germany

**Purification:** Used as purchased. The purity of the chemical is >98.0%

**Application:** The ionic liquid are good examples of neoteric solvents, new types of solvents, or older materials that are finding new applications as solvents, which is environmentally friendly (or eco-friendly) because they are less hazardous for human body as well as less toxic for living organisms, used as recyclable solvents for organic

<b>[C<sub>4</sub>mpy]Cl</b>	
	
<i>Appearance</i>	:Crystalline
<i>Molecular Formula</i>	:C <sub>10</sub> H <sub>16</sub> NCl
<i>Molecular Weight</i>	:185.69 g·mol <sup>-1</sup>
<i>Melting Point</i>	: 298.15-303.15 K
<i>Relative Density</i>	:1.231 g·cm <sup>-3</sup>
<i>Ionic radii</i>	:1.03(Å) of [C <sub>4</sub> mpy] <sup>+</sup> 1.81 (Å) of Cl <sup>-</sup>

reactions and separation processes, lubricating fluids, heat transfer fluids for processing biomass and electrically conductive liquids as electrochemical device in the field of electrochemistry (batteries and solar cells) and so forth. In the modern technology, industry, and also in academic research field, the vast application is frequently increases.

### III.1.2.2 Electrolytes other than Ionic Liquids

#### Tetrabutylammonium tetrphenylborate

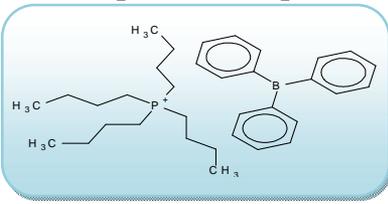
##### **[Bu<sub>4</sub>NBPh<sub>4</sub>]:**

Tetrabutylammonium tetrphenylborate is the most popular electrolyte, containing the approximately same ionic radii of cation (Bu<sub>4</sub>N<sup>+</sup>) and anion (Ph<sub>4</sub>B<sup>-</sup>) as well as same ionic conductance; for the reason the electrolyte commonly used as 'reference electrolyte' method.

**Source:** Sigma Aldrich, Germany

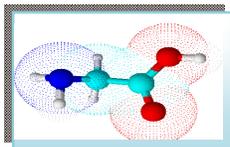
**Purification:** Used as purchased.

**Application:** It is widely used as supporting electrolytes in electrochemical measurements when control of electrode potentials is required.

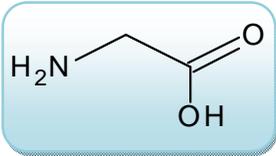
<b>[Bu<sub>4</sub>NBPh<sub>4</sub>]</b>	
	
<i>Appearance</i>	: White Powder
<i>Molecular Formula</i>	: C <sub>40</sub> H <sub>56</sub> BN
<i>Molecular Weight</i>	: 561.69 g·mol <sup>-1</sup>
<i>Melting Point</i>	: 506.15-510.15 K
<i>Relative Density</i>	: No data available
<i>Ionic radii</i>	: 5.00 (Å) of [Bu <sub>4</sub> N] <sup>+</sup> 5.33 (Å) of [BPh <sub>4</sub> ] <sup>-</sup>

### III.1.2.3 Amino Acids

#### Glycine (gly):



Glycine (abbreviated as Gly or G) is an organic compound with the formula  $\text{NH}_2\text{CH}_2\text{COOH}$ . Having a hydrogen substituent as its side-chain, glycine is the smallest of the 20 amino acids commonly found in proteins. Its codons are GGU, GGC, GGA, GGG of the genetic code. Glycine is a colourless, sweet-tasting crystalline solid. It is unique among the proteinogenic amino acids in that it is not chiral. It can fit into hydrophilic or hydrophobic environments, due to its minimal side chain of only one hydrogen atom.

<b>Glycine</b>	
	
<i>Appearance</i>	: <i>White Solid</i>
<i>Molecular Formula</i>	: $\text{C}_2\text{H}_5\text{NO}_2$
<i>Molecular Weight</i>	: $75.07 \text{ g}\cdot\text{mol}^{-1}$
<i>Melting Point</i>	: $506.15 \text{ K}$
<i>Relative Density</i>	: $1.607 \text{ g}\cdot\text{cm}^{-3}$
<i>pKa</i>	: $2.34$ (carboxyl); $9.6$ (amino)

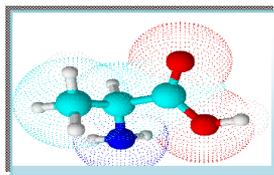
**Source:** Sigma Aldrich, Germany

**Purification:** Used as purchased without further purification. The purity is 99.99%.

**Application:** Pharmaceutical grade glycine is produced for or some pharmaceutical applications, as intravenous injections. Technical grade glycine is solid for use in industrial applications, e.g. as an agent in metal complexing and finishing. For humans, glycine is solid as a sweetener/taste enhancer. Certain food supplements and protein drinks containing glycine, for drug formulations it used to improve gastric absorption. Glycine serves as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. Many

miscellaneous products use glycine or its derivatives, such as the production of rubber sponge products, fertilizers, metal complexants.

**L-Alanine (Ala):**



Alanine (abbreviated as Ala or A) is an  $\alpha$ -amino acid with the chemical formula  $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ . The L-isomer is one of the 20 amino acids encoded by the genetic

code. Its codons are GCU, GCC, GCA, and GCG. It is

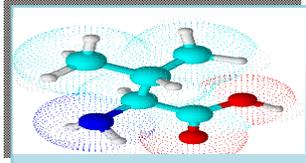
classified as a nonpolar amino acid. L-Alanine is second only to leucine in rate of occurrence, accounting for 7.8% of the primary structure in a sample of 1,150 proteins.<sup>[111.7]</sup>

D-Alanine occurs in bacterial cell walls and in some peptide antibiotics.

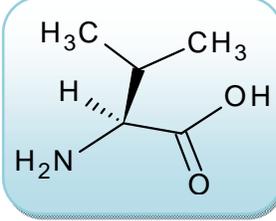
**Application:** alanine is used in dosimetric measurements in radiotherapy. Alanine plays a key role in glucose–alanine cycle between tissues and liver. In muscle and other tissues that degrade amino acids for fuel, amino groups are collected in the form of glutamate by transamination.

<b>Alanine</b>	
<i>Appearance</i>	: White Powder
<i>Molecular Formula</i>	: $\text{C}_3\text{H}_7\text{NO}_2$
<i>Molecular Weight</i>	: $89.09 \text{ g}\cdot\text{mol}^{-1}$
<i>Melting Point</i>	: 531.15 K
<i>Relative Density</i>	: $1.424 \text{ g}\cdot\text{cm}^{-3}$
<i>pKa</i>	: 2.35 (carboxyl); 9.69 (amino)

**L-Valine (Val):**



Valine is an  $\alpha$ -amino acid with the chemical formula  $\text{HO}_2\text{CCHCH}(\text{CH}_3)_2$ . L-valine is one of 20 proteinogenic amino acids. Its codons are GUU, GUC, GUA, and GUG. This essential amino acid is classified as nonpolar. Human dietary sources are any proteinaceous foods such as meats, dairy products, soy products, beans and legumes. Along with leucine and isoleucine, valine is a branched-chain amino acid. It is named after the plant valerian. In sickle-cell disease, valine substitutes for the hydrophilic amino acid glutamic acid in hemoglobin. Because valine is hydrophobic, the hemoglobin is prone to abnormal aggregation.

<b>L-Valine</b>	
	
<i>Appearance</i>	: <i>White Solid</i>
<i>Molecular Formula</i>	: $\text{C}_5\text{H}_{11}\text{NO}_2$
<i>Molecular Weight</i>	: $117.15 \text{ g}\cdot\text{mol}^{-1}$
<i>Melting Point</i>	: $506.15 \text{ K}$
<i>Relative Density</i>	: $1.316 \text{ g}\cdot\text{cm}^{-3}$
<i>pKa</i>	: $2.32 \text{ (carboxyl)}$ ; $9.62 \text{ (amino)}$

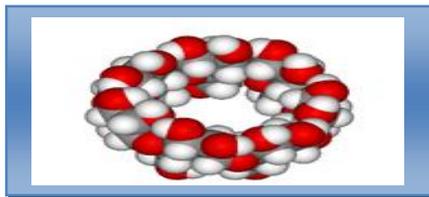
**Source:** Sigma Aldrich, Germany

**Purification:** Used as purchased without further purification. The purity is 99.99%.

**Application:** Valine is an essential amino acid; hence it must be ingested, usually as a component of proteins. It is used for some pharmaceutical applications, industrial applications, food supplements and protein drinks, give out as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, toiletries, production of rubber sponge products, fertilizers, metal complexants etc.

### III.1.2.4 Non-electrolytes other than amino acids

#### ***β-Cyclodextrin (β-CD):***



***β-Cyclodextrin*** is finely made from pure provision material-starch and translate enzyme, which is white powder and whose molecule structure is like a cylinder compounded from 7 glucose group with a key of 2-1.4. The function of  $\beta$ -Cyclodextrin depends on its cylinder molecule structure which can be easy to integrate other materials. That feature is applied widely in industry.

**Source:** Sigma Aldrich, Germany

**Purification:** Used as parched. The purity is 99.98%.

**Application:**  $\beta$ -Cyclodextrin is a new stuff which can be widely applied in production of medicine and food. It can be applied widely in production of medicine, food and cosmetics, whose function is improved stability, solubility and good smelled. In the production of medicine, it can strengthen the stability of medicine without being oxidized and resolving. On the other hand, it can improve the solubility. And the effect on living of medicine, lower the toxic and side-effect of medicine and cover the strange and bad smell. In the production of food, it can mainly cover strange and bad smell of food, improve the stability of perfume and condiment and keep food dry or wet at will.  $\beta$ -

<b><i>β-Cyclodextrin</i></b>	
<i>Appearance</i>	:Crystalline Powder
<i>Molecular Formula</i>	$C_{42}H_{70}O_{35}$
<i>Molecular Weight</i>	:1134.98 $g \cdot mol^{-1}$
<i>Melting Point</i>	:563.15-573.15 K
<i>Boiling Point</i>	:1814.33 K
<i>Relative Density</i>	:1.44 $g \cdot cm^{-3}$ at 20°C
<i>Refractive Index</i>	:1.59 ( $n_D^{20}$ )

CD with a cavity diameter of 6.4-7.5 Å, is the most interest because its cavity size allows for the best special fit for many common guest moieties. For this reason,  $\beta$ -cyclodextrin is most commonly used as a complexing agent in hormones, vitamins, and many compounds frequently used in tissue and cell culture applications. This capability has also been of assistance for different applications in medicines, cosmetics, food technology, pharmaceutical, and chemical industries as well as in agriculture and environmental engineering as an encapsulating agent to protect sensitive molecules in hostile environment.

## **III. 2 EXPERIMENTAL METHODS**

### ***III.2.1 PREPARATION OF SOLUTIONS***

A stock solution for each salt was prepared by mass (digital electronic analytical balance, Mettler Toledo, AG 285, Switzerland), and the working solutions were obtained by mass dilution of the stock solution. The uncertainty of concentration (molarity or molality) of different working solutions was evaluated to be  $\pm 0.0002$ .

### ***III.2.2. PREPARATION OF MULTICOMPONENT LIQUID MIXTURES***

The binary and multicomponent liquid mixtures can be prepared by any one of the methods discussed below:

- (a) Mole fraction**
- (b) Weight fraction**

**(c) Volume fraction**

**(a) Mole fraction:** The mole fraction ( $x_i$ ) of the multicomponent liquid mixtures can be prepared using the following relation:

$$x_i = \frac{(w_i / M_i)}{\sum_{i=1}^n (w_i / M_i)}$$

where  $w_i$  and  $M_i$  are weight and molecular weight of  $i^{\text{th}}$  component, respectively.

The values of  $i$  depends on the number of components involved in the formation of a mixture.

**(b) Weight fraction:** The mole fraction ( $w_i$ ) of the multicomponent liquid mixtures can be prepared using the following relation:

$$w_i = \frac{(x_i / M_i)}{\sum_{i=1}^n (x_i M_i)}$$

**(c) Volume fraction:** The volume fraction ( $\phi_i$ ) of the multicomponent liquid mixtures can be prepared by following employing three methods:

**i. Using volume:** The volume fraction ( $\phi_i$ ) of the multicomponent liquid mixtures can be prepared by following relation

$$\phi_i = \frac{V_i}{\sum_{i=1}^n V_i}$$

where  $V_i$  is the volume of pure liquid  $i$ .

**ii. Using molar volume:** The volume fraction ( $\phi_i$ ) of the multicomponent liquid mixtures can be prepared by following relation

$$\phi_i^l = \frac{x_i V_{mi}}{\sum_{i=1}^n (x_i V_{mi})}$$

where  $V_{mi}$  is the molar volume of pure liquid  $i$ .

**iii. Using excess volume:** The volume fraction ( $\phi_i^{ex}$ ) of the multicomponent liquid mixtures can be prepared by following relation

$$\phi_i^{ex} = \frac{x_i V_i}{\sum_{i=1}^n (x_i V_i) + V^E}$$

where  $V^E$  is the excess volume of the liquid mixture.

### **III.2.3. PREPARATION OF SOLVENT MIXTURES (MIXED SOLVENTS)**

The research work has been carried out with binary or ternary solvent systems with water, methyl cellosolve, tetrahydrofuran, methanol, N,N-dimethylacetamide, 1,4-dioxane, nitromethane, formamide, acetonitrile etc. as primary solvents with some electrolytes (ionic liquids & other electrolytes) and non-electrolytes (amino acids and other solutes).

Experimental Section

<b>Binary Solutions:</b>
<i>1-butyl 2,3-dimethylimidazolium tetrafluoroborate + Methyl cellosolve</i>
<i>1-butyl 2,3-dimethylimidazolium tetrafluoroborate + N,N-dimethyl acetamide</i>
<i>1-butyl 2,3-dimethylimidazolium tetrafluoroborate + Tetrahydrofuran</i>
<i>1-Butylpyridinium bromide + 1,4 Dioxane</i>
<i>1-Butylpyridinium bromide + Tetrahydrofuran</i>
<i>1-Butylpyridinium bromide + Acetonitrile</i>
<i>Tetrabutylphosphonium methanesulfonate + Water</i>
<i>Tetrabutylphosphonium methanesulfonate + Acetonitrile</i>
<i>Tetrabutylphosphonium methanesulfonate + Methanol</i>
<i>Tetrabutylphosphonium methanesulfonate + Nitromethane</i>
<i>Tetrabutylphosphonium methanesulfonate + Formamide</i>

For the preparation of solvent mixture, pure components were taken separately in glass stoppered bottles and thermostated at the desired temperature for sufficient time. When the thermal equilibrium was ensured, the required volumes of each component were transferred in a different bottle which was already cleaned and dried thoroughly. Conversion of required mass of the respective solvents to volume was accomplished by using experimental densities of the solvents at experimental temperature. It was then stoppered and the mixed contents were shaken well before use. While preparing different solvent mixtures care was taken to ensure that the same procedure was adopted throughout the entire work. The physical properties of different pure and mixed solvents have been presented in the respective chapters.

Experimental Section

The following different binary and ternary solutions have been prepared and used for my research studies.

<b><i>Ternary Solutions:</i></b>
<i>w<sub>1</sub>=0.001 mass fraction of aqueous 1-butylpyridinium bromide mixtures + Glycine</i>
<i>w<sub>1</sub>=0.003 mass fraction of aqueous 1-butylpyridinium bromide mixtures + Glycine</i>
<i>w<sub>1</sub>=0.005 mass fraction of aqueous 1-butylpyridinium bromide mixtures + Glycine</i>
<i>w<sub>1</sub>=0.001 mass fraction of aqueous 1-butylpyridinium bromide mixtures + L-Alanine</i>
<i>w<sub>1</sub>=0.003 mass fraction of aqueous 1-butylpyridinium bromide mixtures + L-Alanine</i>
<i>w<sub>1</sub>=0.005 mass fraction of aqueous 1-butylpyridinium bromide mixtures + L-Alanine</i>
<i>w<sub>1</sub>=0.001 mass fraction of aqueous 1-butylpyridinium bromide mixtures + L-Valine</i>
<i>w<sub>1</sub>=0.003 mass fraction of aqueous 1-butylpyridinium bromide mixtures + L-Valine</i>
<i>w<sub>1</sub>=0.005 mass fraction of aqueous 1-butylpyridinium bromide mixtures + L-Valine</i>
<i>w<sub>1</sub>=0.001 mass fraction of aqueous <math>\beta</math>-cyclodextrin mixtures + 1-methyl-3-octylimidazolium chloride</i>
<i>w<sub>1</sub>=0.003 mass fraction of aqueous <math>\beta</math>-cyclodextrin mixtures + 1-methyl-3-octylimidazolium chloride</i>
<i>w<sub>1</sub>=0.005 mass fraction of aqueous <math>\beta</math>-cyclodextrin mixtures + 1-methyl-3-octylimidazolium chloride</i>
<i>w<sub>1</sub>=0.001 mass fraction of aqueous <math>\beta</math>-cyclodextrin mixtures + N-butyl-4-methylpyridinium chloride</i>
<i>w<sub>1</sub>=0.003 mass fraction of aqueous <math>\beta</math>-cyclodextrin mixtures + N-butyl-4-methylpyridinium chloride</i>
<i>w<sub>1</sub>=0.005 mass fraction of aqueous <math>\beta</math>-cyclodextrin mixtures + N-butyl-4-methylpyridinium chloride</i>

### III.2.4 MEASUREMENTS OF EXPERIMENTAL PROPERTIES

#### III.2.4.1 MASS MEASUREMENT

Mass measurements were made on digital electronic analytical balance (Mettler Toledo, AG 285, Switzerland).

It can measure mass to a very high precision and accuracy. The weighing pan of a high precision (0.0001g) is 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.

#### **Instrument Specification:**

<i>Readability</i>	: 0.1 mg/ 0.01mg
<i>Maximum capacity</i>	: 210 g/81g/41g
<i>Taring range</i>	: 0 . . . 210 g
<i>Repeatability</i>	: 0.1 mg/ 0.05 mg
<i>Linearity</i>	: ±0.2 mg/±0.1 mg
<i>Stabilization time</i>	: 3 s/ 15 s
<i>Adjustment with external weights</i>	:200 g
<i>Sensitivity</i>	: ±0.003%
<i>Display</i>	: LCD
<i>Interface</i>	: LocalCAN universal interface

Experimental Section

<i>Weighing</i>	<i>: <math>\Phi</math> 85 mm, stainless steel</i>
<i>Effective height above pan</i>	<i>: 240 mm</i>
<i>Dimensions(w/d/h)</i>	<i>: 205×330×310 mm</i>
<i>Net wt/with packaging</i>	<i>: 4.9 kg/7.25 kg</i>

**III.2.4.2 CONDUCTIVITY MEASUREMENT**

Conductivity measurement was done using Systronics Conductivity TDS meter-308.

It can provide both automatic and manual temperature compensation.

<p>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.</p>	
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**Systronic-308 Conductivity Bridge**

The conductance measurements were carried out on this conductivity bridge of accuracy  $\pm 0.01\%$ , using a dip-type immersion conductivity cell, CD-10 having a cell constant of approximately  $(0.1 \pm 0.001) \text{ cm}^{-1}$ . Measurements were made in a thermostate water bath maintained at  $T = (298.15 \pm 0.01) \text{ K}$ . The cell was calibrated by the method proposed by Lind et al.<sup>[III.8]</sup> and cell constant was measured based on 0.01 M aqueous KCl solution.<sup>[III.9]</sup> During the conductance measurements, cell constant was maintained within the range  $1.10\text{--}1.12 \text{ cm}^{-1}$ . The conductance data were reported at a frequency of 1 kHz and the accuracy was  $\pm 0.3\%$ . The conductivity cell was sealed to the side of a 500 cm<sup>3</sup> 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  $\pm 0.01 \text{ K}$  by means of mercury in glass thermoregulator.<sup>[III.10]</sup>

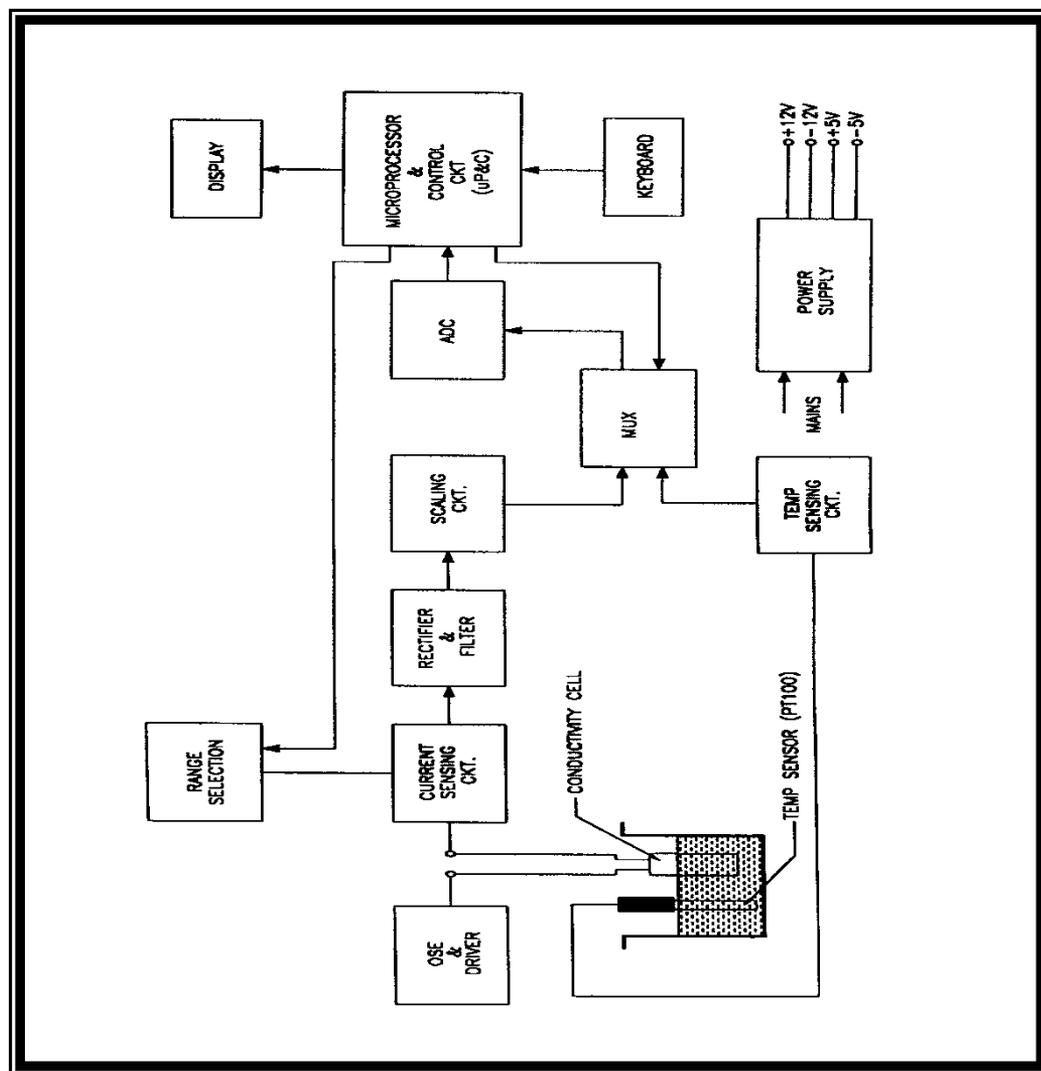
**Instrument Specifications:**

<i>Frequency</i>	<i>: 100 Hz or 1 KHz Automatic</i>
<i>Conductivity</i>	
<i>Range</i>	<i>: 0.1 <math>\mu\text{S}</math> to 100 mS. (6 decadic range)</i>
<i>Accuracy</i>	<i>: <math>\pm 1\%</math> of F.S. <math>\pm 1</math> digit</i>
<i>Resolution</i>	<i>: 0.001 <math>\mu\text{S}</math></i>
<i>TDS</i>	
<i>Range</i>	<i>: 0.1 ppm to 100 ppt. (6 decadic range)</i>

*Experimental Section*

<i>Accuracy</i>	<i>: ±1% of F.S. ±1 digit</i>
<i>Temperature</i>	
<i>Range</i>	<i>: 0°C to 100°C (Auto/Manual)</i>
<i>Accuracy</i>	<i>: ± 0.2 °C ±1 digit</i>
<i>Resolution</i>	<i>: 0.1 °C</i>
<i>Cell Constant</i>	<i>: Acceptable from 0.1 to 5.0</i>
<i>Auto Temp. Compensation</i>	<i>: 0°C to 100°C with PT 100 sensor</i>
<i>Manual Temp. Compensation</i>	<i>: 0°C to 60°C user selectable</i>
<i>Conductivity temp. Co-efficient</i>	<i>: 0.0% to 9.9% user selectable</i>
<i>Display</i>	<i>: 7 digits, 7 segment LEDs  (3 digits for TEMP/TEMPCO 4 digits for Conductivity/TDS)  With automatic decimal point selection</i>
<i>TDS-factor</i>	<i>: 0.00 to 9.99 user selectable</i>
<i>Printer Port</i>	<i>: Epson compatible 80 Column Dot Matrix</i>
<i>Power</i>	<i>: 230V AC, ±10%, 50 Hz</i>
<i>Dimensions</i>	<i>: 250(W)× 205(D)× 75(H)</i>
<i>Weight</i>	<i>: 1.25 Kg (Approx.)</i>
<i>Accessories</i>	<i>: i) Conductivity cell, cell constant 0.1  ii) Conductivity cell, cell constant 1.0  iii) Temp. Probe (PT-100 sensor)  iv) Stand &amp; Clamp</i>

Solutions were prepared by weight precise to  $\pm 0.02\%$ . The weights were taken on a Mettler electronic analytical balance (AG 285, Switzerland). The molarity being converted to molality 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

### III.2.4.3 DENSITY MEASUREMENT

The density measurement was performed with the help of Anton Paar DMA 4500M digital density-meter with a precision of  $\pm 0.0005 \text{ g}\cdot\text{cm}^{-3}$ .

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  $\tau$  can be measured with high resolution and stands in simple relation to the density  $\rho$  of the sample in the oscillator



**Anton Paar DMA 4500M digital density-meter**

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  $\tau$  can be measured with high resolution and stands in simple relation to the density  $\rho$  of the sample in the oscillator:

$$\rho = A \cdot \tau^2 - B \quad (\text{III.1})$$

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  $\rho_1$  and  $\rho_2$ . 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 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. The instrument was calibrated by triply-distilled water and dry air.

***Instrument Specification:***

<i>Density</i>	<i>: 0 to 1.5 g.cm<sup>-3</sup></i>
<i>Temperature</i>	<i>: 15°C to 25°C</i>
<i>Pressure</i>	<i>: 0 to 6 bar</i>
<i>Repeatability Standard Deviation</i>	
<i>Density</i>	<i>: 0.00001 g.cm<sup>-3</sup></i>
<i>Temperature</i>	<i>: 0.01 °C</i>
<i>Additional information</i>	
<i>Minimum sample volume</i>	<i>: approx. 2 ml</i>
<i>Dimensions (L×W×H)</i>	<i>: 400×225×231 mm</i>
<i>Weight</i>	<i>: approx. 15 kg</i>
<i>Automatic bubble detection</i>	<i>: yes</i>
<i>Interfaces</i>	<i>: 2×CAN</i>
<i>Power</i>	<i>: Supplied by the master instrument</i>

### III.2.4.4 VISCOSITY MEASUREMENT

**By Brookfield DV-III Ultra Programmable Rheometer:** The viscosities ( $\eta$ ) were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The viscosities were obtained using the following equation

$$\eta = (100 / RPM) \times TK \times \text{torque} \times SMC$$

where *RPM*, *TK* (0.09373) and *SMC* (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The instrument was calibrated against the standard viscosity samples supplied with the instrument, water and aqueous CaCl<sub>2</sub> solutions.<sup>[III.11]</sup> The temperature was maintained to within  $\pm 0.01^\circ\text{C}$  using Brookfield Digital TC-500 thermostat bath. The viscosities were measured with an accuracy of  $\pm 1\%$ . Each measurement reported herein is an average of triplicate reading with a precision of 0.3%.



**Instrument Specifications:**

<i>Speed Range</i>	<i>: 0-250 RPM, 0.1 RPM increments</i>
<i>Viscosity Accuracy</i>	<i>: ±1.0% of full scale range for a specific spindle running at a specific speed.</i>
<i>Temperature sensing range</i>	<i>: -100°C to 300°C (-148°F to 572°F)</i>
<i>Temperature accuracy</i>	<i>: ±1.0°C from -100°C to 150°C ±2.0°C from +150°C to 300°C</i>
<i>Analog Torque Output</i>	<i>: 0 - 1 Volt DC (0 - 100% torque)</i>
<i>Analog Temperature Output</i>	<i>: 0 - 4 Volts DC (10mv / °C)</i>

**III.2.4.5 ULTRASONIC SPEED MEASUREMENT**

The ultrasonic speed was measured with an accuracy of 0.2% using single-crystal variable-path ultrasonic interferometer (Model M-81 Mittal Enterprises, New Delhi) operating at 4MHz which was calibrated with water, methanol and benzene at required temperature.

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  $\pm 0.01$  K by circulating thermostatic water around the cell by a circulating pump.



**Multifrequency Ultrasonic Interferometer**

**Instrument Specification:**

<i>High Frequency Generator</i>	<i>: Single and Multi-frequency</i>
<i>Model No.</i>	<i>: M-81 Mittal Enterprises</i>
<i>Measuring Cell</i>	<i>: Four cell (1, 2,3, &amp; 4 MHz)</i>
<i>Max. displacement of the reflector</i>	<i>: 20 mm</i>
<i>Required Quantity of liquid</i>	<i>: 10 c.c.</i>
<i>Least Count of micrometer</i>	<i>: 0.01mm/0.001 mm</i>
<i>Accuracy</i>	<i>: 0.2%</i>
<i>Shielded Cable Impedance</i>	<i>: 50 <math>\Omega</math></i>

### **Working Principle of Ultrasonic Interferometer**

The principle used in the measurement of the ultrasonic speed ( $u$ ) is based on the accurate determination of the wavelength ( $\lambda$ ) 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 ( $\lambda/2$ ) or integral multiples of it, anode current becomes maximum. From the knowledge of the wave length ( $\lambda$ ), the speed ( $u$ ) can be obtained by the relation.

$$\text{Ultrasonic speed } (u) = \text{Wave Length } (\lambda) \times \text{Frequency } (f) \quad (\text{III.2})$$

**Experimental set-up** - ultrasonic interferometer consists of the following parts,

- 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 ( $\lambda$ ) with the following relation.

$$d = n \times \lambda / 2 \quad (III.3)$$

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

$$\beta_s = 1 / (u^2 \cdot \rho) \quad (III.4)$$

where  $\rho$  is the density of the experimental liquid.

The following Figure 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  $\lambda/2$ ) and)
- (c) Electronic circuit diagram of the instrument

The Multifrequency Ultrasonic Interferometer

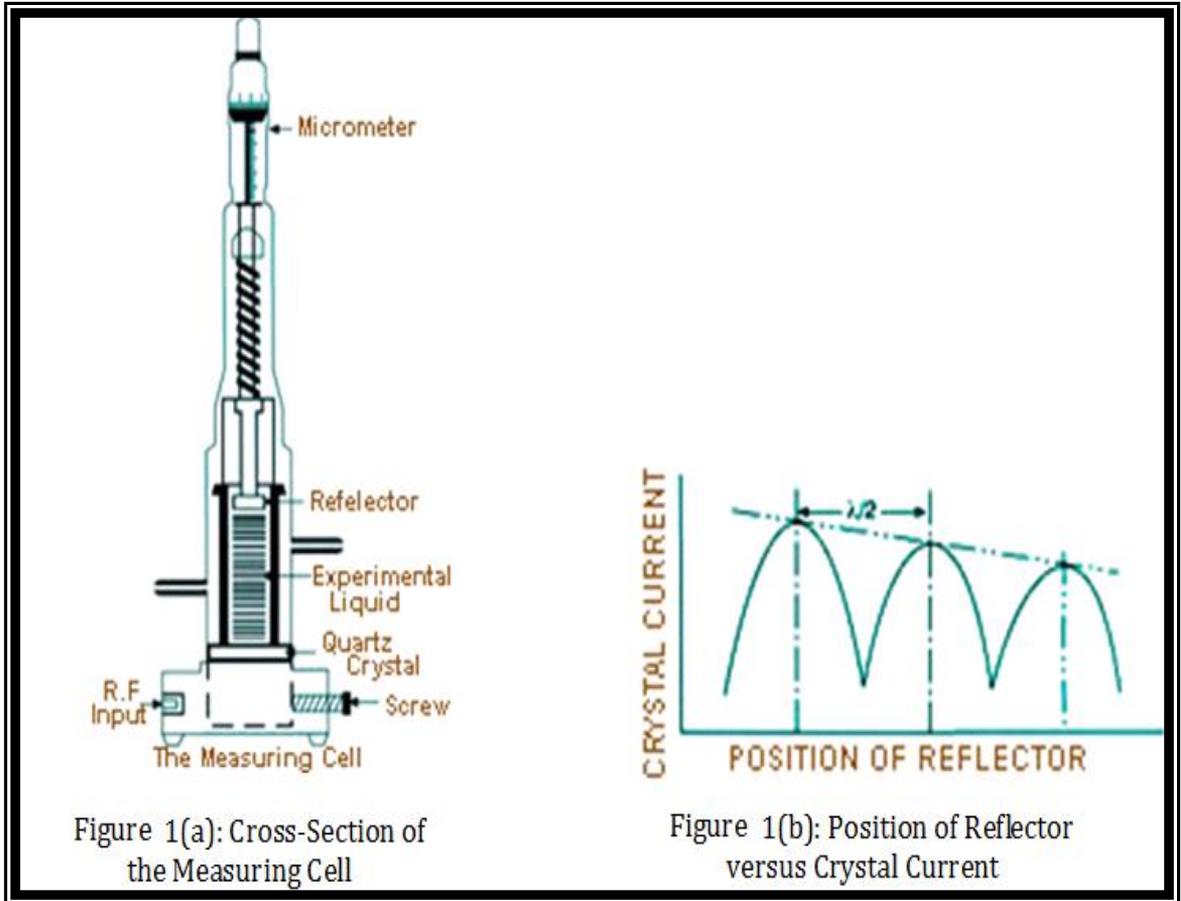


Figure 1(a): Cross-Section of the Measuring Cell

Figure 1(b): Position of Reflector versus Crystal Current



### III.2.4.6 REFRACTIVE INDEX MEASUREMENT

Refractive index was be measure with the help of Digital Refractometer (Mettler Toledo 30GS).

Calibration was performed by measuring refractive indices of double-distilled water, toluene, cyclohexane, and carbon tetrachloride defined temperature. The accuracy of the instrument is  $\pm 0.0005$ . 2-3 drops of the sample was put onto the measurement cell and the reading was taken. The refractive index of a sample depends on temperature. During measurement, refractometer determines the temperature and then corrects the refractive index to a temperature as desired by the user.



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#### **Specifications-Refracto 30GS- extended RI measuring range**

<i>Model</i>	: Refracto 30GS
<i>Measurement range</i>	: 1.32 -1.65
<i>Resolution</i>	: 0.0001
<i>Accuracy</i>	: +/- 0.0005
<i>Measurement range BRIX</i>	: 0 - 85 Brix%

*Experimental Section*

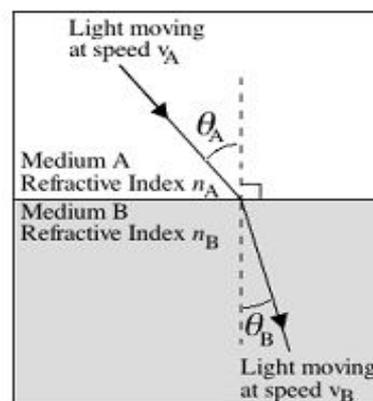
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<i>Resolution</i>	<i>: 0.1 Brix%</i>
<i>Accuracy</i>	<i>: +/- 0.2 Brix%</i>
<i>Temperature range</i>	<i>: 10 - 40°</i>
<i>Resolution of temperature</i>	<i>: 0.1°</i>
<i>display</i>	<i>: °C or °F</i>
<i>Trade Name</i>	<i>: 51324660</i>

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  $n_D$ ) for the substance.

$$\text{Refractive index of the substance } (n_D) = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in substance}} \quad (\text{III.5})$$

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 ( $\theta_A$ ) and refraction ( $\theta_B$ ) 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

$$\frac{v_A}{v_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (\text{III.6})$$

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.<sup>[III.12]</sup> Nearly all refractometers utilize this principle, but may differ in their optical design.

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.

#### **III.2.4.7 SURFACE TENSION MEASUREMENT**

Surface tension were measured by using Digital Tensiometer KRUSS K9 (Germany). The tensiometer is a precision instrument which will only perform reliably on a solid and vibration-free base. It places the same demands on its surroundings as a laboratory balance with a resolution of 0.1 mg. In addition surface tension measurements require a clean and dust-free atmosphere as atmospheric pollutants could directly falsify the results.



#### **III.2.4.8 FTIR MEASUREMENT**

Infrared spectra were recorded in 8300 FTIR spectrometer (Shimadzu, Japan).

It measures the intensity of light passing through the blank and measures the intensity of light passing through the sample. It is useful to calculate the transmittance and the absorbance



The intensity of light ( $I_0$ ) passing through a blank is measured. The intensity is the number of photons per second. The blank is a solution that is identical to the sample solution except that the blank does not contain the solution that absorbs light. The intensity of light ( $I$ ) passing through the sample solution is measured. (In practice, instrument measures the power rather than the intensity of the light. The power is the energy per second, which is the product of the intensity (photons per second) and the energy per photon. The experimental data is used to calculate two quantities: the transmittance ( $T$ ) and the absorbance ( $A$ ).

$$T = \frac{I}{I_0}; \quad A = -\log_{10} T \quad (\text{III.7})$$

The transmittance is simply the fraction of light in the original beam that passes through the sample and reaches the detector.

### III.2.4.9 UV-VIS SPECTRA MEASUREMENT

Compounds that absorb Ultraviolet and/or visible light have characteristic absorbance curves as a function of wavelength. Absorbance of different wavelengths of light occurs as the molecules move to higher energy states.



The UV-VIS spectrophotometer uses two light sources, a deuterium ( $D_2$ ) lamp for ultraviolet light and a tungsten (W) lamp for visible light. After bouncing off a mirror, the light beam passes through a slit and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. At any specific orientation of the grating, only monochromatic (single wavelength) successfully passes through a slit. A filter is used to remove unwanted higher orders of diffraction. The light beam hits a second mirror before it gets split by a half mirror (half of the light is reflected, the other half passes through). One of the beams is allowed to pass through a reference cuvette (which contains the solvent only), the other passes through the sample cuvette. The intensities of the light beams are then measured at the end. Regarding this the Beer-Lambert law has been stated below.

### Beer-Lambert Law

The change in intensity of light ( $dI$ ) after passing through a sample should be proportional to the following:

- (i) Path length ( $b$ ), the longer the path, more photons should be absorbed
- (ii) Concentration ( $c$ ) of sample, more molecules absorbing means more photons absorbed
- (iii) Intensity of the incident light ( $I$ ), more photons means more opportunity for a molecule to see a photon. Thus,  $dI$  is proportional to  $b c I$  or  $dI/I = -kbc$  (where  $k$  is a proportionality constant, the negative sign is shown because this is a decrease in intensity of the light, this makes  $b$ ,  $c$  and  $I$  always positive. Integration of the above equation leads to Beer-Lambert's law :<sup>[III.13]</sup>

$$- \ln I/I_0 = kbc \quad \text{(III.8)}$$

$$- \log I/I_0 = 2.303kbc \quad \text{(III.9)}$$

$$\epsilon = 2.303k \quad \text{(III.10)}$$

$$A = - \log I/I_0 \quad \text{(III.11)}$$

$$A = \epsilon bc \quad \text{(III.12)}$$

$A$  is defined as absorbance and it is found to be directly proportional to the path length,  $b$  and the concentration of the sample,  $c$ . The extinction coefficient is characteristic of the substance under study and of course is a function of the wavelength.

#### III.2.4.10 NMR SPECTRA MEASUREMENT

NMR spectrometers are relatively expensive; universities usually have them, but they are less common in private companies. Modern NMR spectrometers have a very strong, large

and expensive liquid helium-cooled superconducting magnet, because resolution directly depends on magnetic field strength. Less expensive machines using permanent magnets and lower resolution are also available, which still give sufficient performance for certain application such as reaction monitoring and quick checking of samples.

The vast majority of nuclei in a solution would belong to the solvent, and most regular solvents are hydrocarbons and would contain NMR-reactive protons. Thus, deuterium (hydrogen-2) is substituted (99+%). The most used deuterated solvent is deuteriochloroform ( $\text{CDCl}_3$ ), although deuterium oxide ( $\text{D}_2\text{O}$ ) and deuterated DMSO ( $\text{DMSO-}d_6$ ) are used for hydrophilic analytes. NMR spectra are often calibrated against the known solvent residual proton peak instead of added tetramethylsilane.



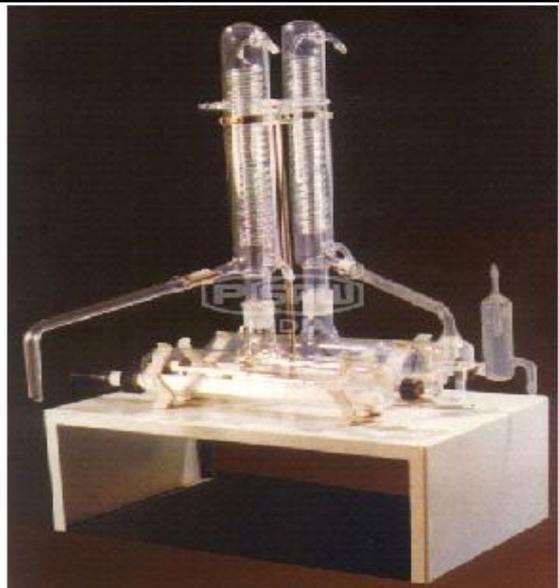
NMR spectra were recorded in  $\text{D}_2\text{O}$  unless otherwise stated.  $^1\text{H}$  NMR spectra were recorded at 400 MHz and 500 MHz using Bruker ADVANCE 500 MHz and Bruker ADVANCE 400 MHz instruments respectively at 298.15K. Signals are quoted as  $\delta$  values in ppm using residual

protonated solvent signals as internal standard ( $D_2O$  :  $\delta$  4.79 ppm). Data are reported as chemical shift.

### ***Other Instruments Used:***

#### ***III.2.4.11 WATER DISTILLER***

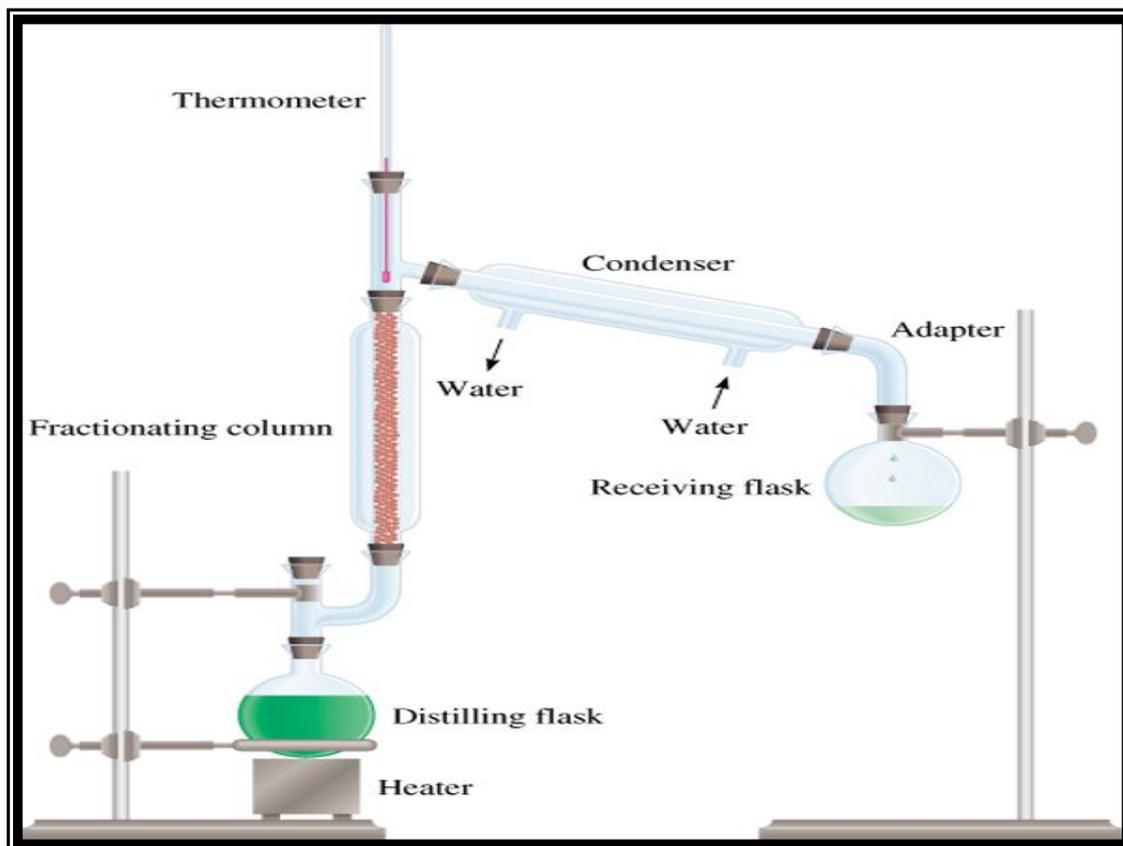
Water distillation units produce highly treated and disinfected water for laboratory usage. The distillation process removes minerals and microbiological contaminants and can reduce levels of chemical contaminants. A water distiller works by boiling water into water vapour, condensing it and then returning 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



#### III.2.4.12 THERMOSTAT WATER BATH (Science India, Kolkata):

The measurements were carried out in thermostatic water bath maintained with an accuracy of  $\pm 0.01$  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.