CHAPTER III

EXPERIMENTAL SECTION

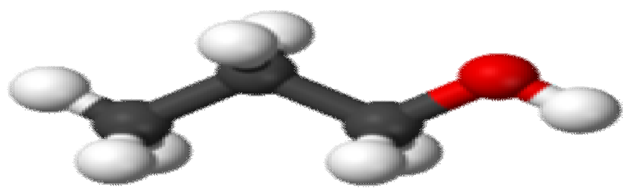
3.1. NAME, STRUCTURE, PHYSICAL PROPERTIES, PURIFICATION AND APPLICATIONS OF THE SOLVENTS AND SOLUTES USED IN THE RESEARCH WORK

3.1.1. SOLVENTS

The studied aqueous and non-aqueous solvents used in my research work are represented bellow

i. Propanol:

Propanol or 1-Propanol is a primary alcohol with the formula $CH_3CH_2CH_2OH$. It is formed naturally in small amounts during many fermentation processes. This colourless liquid is known as propan-1-ol, 1-propyl alcohol, n-propyl alcohol and n-propanol. It is isomeric with isopropanol (2-propanol, isopropyl alcohol).



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

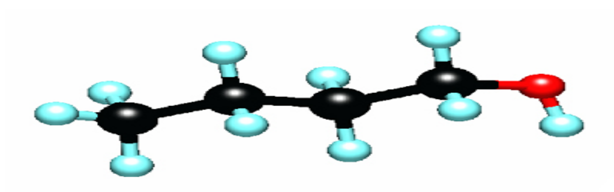
Purification: It was dried by adding drying agent $CaSO_4$ followed by filtration and then distilled [1].

Appearance:	**Colourless liquid**
Molecular Formula:	C_3H_8O
Molecular Weight:	**60.10 g/mol**
Boiling Point:	**300-371 K**
Melting Point:	**147 K**
Dielectric Constant:	**20.1 at 298.15 K**

Application: n-Propanol is used as a solvent for waxes, vegetable oils, resins, cellulose esters, and ethers. It is found in inks, brake fluids and polishing compounds and has been used as a degreasing agent, an antiseptic, and a chemical intermediate. More recently, it is being used as a hand disinfectant by health care workers.

ii. Butanol:

Butanol is a primary alcohol with a 4-carbon structure with the chemical formula C_4H_9OH. It's isomers include isobutanol, 2-butanol and tertiary Butanol. Butanol is one of the group of "fusel alcohols" (from the German for "bad liquor"), which have more than two carbon atoms and have significant solubility in water.



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

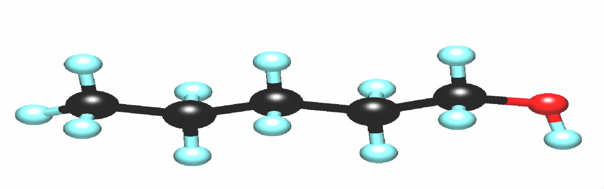
***Purification*:** It was dried by adding drying agent $CaSO_4$ followed by filtration and then distilled [1].

Appearance:	Colourless, refractive liquid
Molecular Formula:	$C_4H_{10}O$
Molecular Weight:	74.12 g/mol
Boiling Point:	390.8 K
Melting Point:	183.3 K
Dielectric Constant:	17.64 at 298.15 K

Application: n-Butanol is used as a solvent for waxes, vegetable oils, resins, cellulose esters, and ethers. It is found in inks, brake fluids and polishing compounds and has been used as a degreasing agent, an antiseptic, and a chemical intermediate. More recently, it is being used as a hand disinfectant by health care workers.

iii. Pentanol:

Pentanol is a primary alcohol with a 5-carbon structure with the chemical formula $C_5H_{12}O$.It is a colourless liquid with an unpleasant aroma. To reduce the use of fossile fuels, research is underway to discover cost-effective methods of utilizing fermentation to produce Bio-Pentanol.



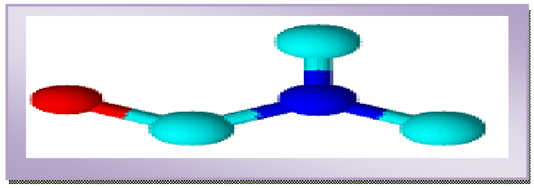
Source: S.D Fine Chemicals Ltd. Mumbai, India

Purification: It was dried by adding drying agent $CaSO_4$ followed by filtration and then distilled [1].

Appearance:	**Colourless liquid**
Molecular Formula:	**$C_5H_{12}O$**
Molecular Weight:	**88.15 g/mol**
Boiling Point:	**410 K**
Melting Point:	**195 K**
Dielectric Constant:	**13.9 at 298.15 K**

Application: n-Pentanol can be used as a solvent for coating CDs and DVDs and replacement of gasoline.

iv. N, N- dimethylformamide



N, N-dimethylformamide is an organic compound with the formula $(CH_3)_2NC(O)H$. Commonly abbreviated as DMF (though this acronym is sometimes used for dimethylfuran), this colorless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine. Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as $S_N2$reactions.

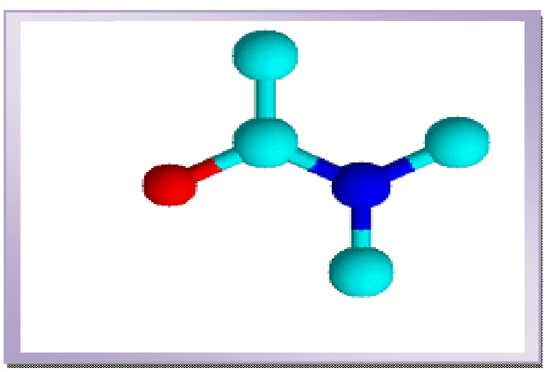
Appearance:	**Liquid**
Molecular Formula:	**C_3H_7NO**
Molecular Weight:	**73.09 g/mol**
Boiling Point:	**212.7 K**
Melting Point:	**425-427 K**
Dielectric Constant:	**36.71 at 298.15 K**

Source: Merck, India

Purification: It was dried by passing through Linde 4Å molecular sieves and then distilled [1].

Application: The primary use of dimethylformamide is as a solvent with low evaporation rate. DMF is used in the production of acrylic fibers and plastics. It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings [2]. It is used as a reagent in the Bouveault aldehyde synthesis and in the Vilsmeier-Haack reaction, another useful method of forming aldehydes. It is also a common catalyst used in the synthesis of acyl halides, in particular the synthesis of acyl chlorides from carboxylic acids using oxalyl or thionyl chloride [3]. DMF penetrates most plastics and makes them swell. This property makes it very suitable for solid phase peptide synthesis. It also frequently occurs as a component of paint strippers for this purpose. DMF is very effective at separating and suspending carbon nanotubes, and is recommended by the NIST for use in near infrared spectroscopy of such. DMF can be utilized as a standard in proton NMR allowing for a quantitative determination of an unknown chemical. DMF is used as a solvent to recover olefins such as 1,3-butadiene via extractive distillation. It is also used in the manufacturing of solvent dyes as an important raw material. It is consumed during reaction. Pure acetylene gas cannot be compressed and stored without the danger of explosion. Industrial acetylene gas is, therefore, dissolved in dimethylformamide and stored in metal cylinders or bottles. The casing is also filled with agamassan, which renders it safe to transport and use.

v. N, N- dimethylacetamide



N,N-dimethylacetamide is the organic compound with the formula $CH_3C(O)N(CH_3)_2$. 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.

Appearance:	Liquid
Molecular Formula:	C_4H_9NO
Molecular Weight:	87.12 g/mol

Boiling Point:	**253 K**
Melting Point:	**438.2 K**
Dielectric Constant:	**37.78 at 298.15 K**

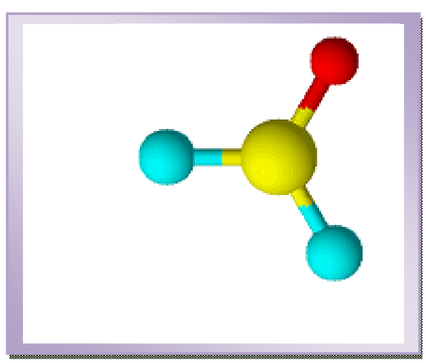
Source: Merck, India

Purification: It was dried by passing through molecular sieves [1].

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 [4]. It is also employed in the production of pharmaceuticals and plasticizers as a reaction medium.

vi. Dimethyl sulphoxide

Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$. This colorless liquid is an important polar aprotic solvent that dissolves both polar and non-polar compounds and is miscible in a wide range of organic solvents as well as water. It penetrates the skin very readily, giving it the unusual property for many individuals of being secreted onto the surface of the tongue after contact with the skin and causing a garlic-like taste in the mouth.



Although it has some niche medicinal uses it also has significant known side effects. It has been promoted as a fake cure for cancer and other conditions.

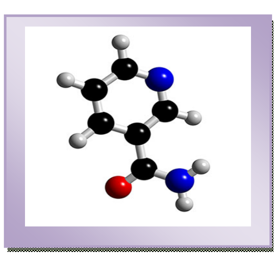
Source: Merck, India

Purification: It was dried by passing through Linde 4Å molecular sieves.

Appearance:	Liquid
Molecular Formula:	C_2H_6SO
Molecular Weight:	78.13 g/mol
Boiling Point:	292 K
Melting Point:	462 K
Dielectric Constant:	46.70 at 298.15 K

Application: DMSO is frequently used as a solvent for chemical reactions involving salts, most notably Finkelstein reactions and other nucleophilic substitutions. It is also extensively used as an extractant in biochemistry and cell biology. Because of its ability to dissolve many kinds of compounds, DMSO plays a role in sample management and high-throughput screening operations in drug design. DMSO is used in PCR to inhibit secondary structures in the DNA template or the DNA primers. It is added to the PCR mix before reacting, where it interferes with the self-complementarity of the DNA, minimizing interfering reactions. In medicine, DMSO is predominantly used as a topical analgesic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory, and an antioxidant [5]. Because DMSO increases the rate of absorption of some compounds through organic tissues, including skin, it can be used as a drug delivery system. It is frequently compounded with antifungal medications, enabling them to penetrate not just skin but also toe and fingernails. It is also used as veterinary medicines.

vii. Nicotinic acid



Nicotinic acid is an organic compound with the formula $C_6H_5NO_2$. Its appearance is white, translucent crystal powder, and it is soluble in water. Nicotinic acid is commonly known as vitamin B_3.

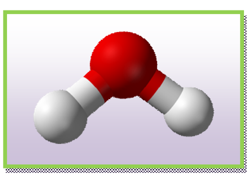
Source: S.D. Fine Chemicals LtD., Mumbai, India

Purification: Used as purchased

Appearance:	White, translucent crystal
Molecular Formula:	$C_6H_5NO_2$
Molecular Weight:	123.11 g/mol
Melting Point:	237^0C

Application: Nicotinic acid (3-pyridine carboxylic acid), also known as niacin or pellagra-preventing factor, is an important compound which play a crucial role in various physiological effects, biosynthesis, metabolic reactions, and several drug preparations.

viii. Water



Water is a 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 vapor 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 × 10-6 $S.cm^{-1}$ [1].

Appearance:	Liquid
Molecular Formula:	H_2O
Molecular Weight:	18.02 g/mol
Boiling Point:	100 ^0C
Melting Point:	0^0C
Dielectric Constant:	78.35 at 298.15 K

Application: Water is also a good solvent due to its polarity. The solvent properties of water are vital in biology, because many biochemical reactions take place only within aqueous solutions (e.g., reactions in the cytoplasm and blood). In addition, water is used to transport biological molecules. The most important use of water in agriculture is for irrigation. Water fit for human consumption is called drinking water. 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. In organic reactions, it is not usually used as a reaction solvent, because it does not dissolve the reactants well and is amphoteric (acidic *and* basic) and nucleophilic. Nevertheless, these properties are sometimes desirable. Also, acceleration of Diels-Alder reactions by water has been observed. Supercritical water has recently been a topic of research.

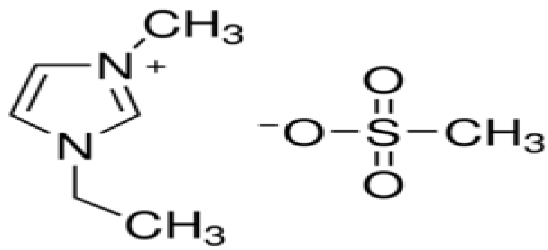
3.1.2. SOLUTES (Electrolytes and Non-Electrolytes)

The details of the electrolytes like ionic liquids and the non-electrolytes like amino acids, vitamins and β-cyclodextrin have been described below.

Ionic liquids:

i. 1-ethyl-3-methylimidazolium methanesulfonate [emim]CH_3SO_3

1-ethyl-3-methylimidazolium methanesulfonate is the imidazolium based ionic liquid, of molecular formula $C_7H_{14}N_2O_3S$, containing methyl, ethyl group with two active nitrogen atoms in the imidazole or five member ring, exist as a molten liquid phase with the melting point ≥ *33*^oC. .



Source: Sigma Aldrich, Germany

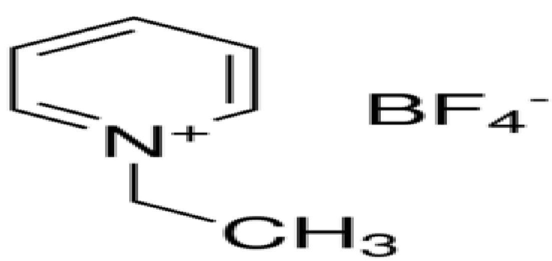
Purification: Used as purchased. The purity of the chemical is >99.0%

Appearance:	**Crystalline**
Molecular Formula:	$C_7H_{14}N_2O_3S$
Molecular Weight:	**206.26 g/mol**
Melting Point:	33^0C

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

ii. ***1-ethylpyridinium tetrafluoroborate***

1-ethylpyridinium tetrafluoroborate is the pyridinium based ionic liquid, of molecular formula $C_7H_{10}BF_4N$, containing ethyl group with one active nitrogen atom in the pyridinium or six member ring, exist as a fine crystal.



Source: Sigma Aldrich, Germany

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

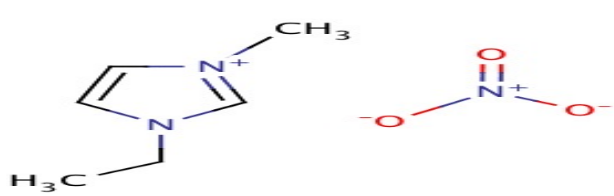
iii.

Appearance:	**Fine crystals with lumps**
Molecular Formula:	**$C_7H_{10}BF_4N$**
Molecular Weight:	**194.97 g/mol**

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

iv. 1-ethyl-3-methylimidazolium nitrate [EMIm]NO_3

1-ethyl-3-methylimidazolium nitrate is the imidazolium based ionic liquid, of molecular formula $C_6H_{11}N_3O_3$, containing methyl, ethyl group with two active nitrogen atoms in the imidazole or five member ring, exist as a molten liquid phase with the melting point ≥ 40^{o}C.



Source: Sigma Aldrich, Germany

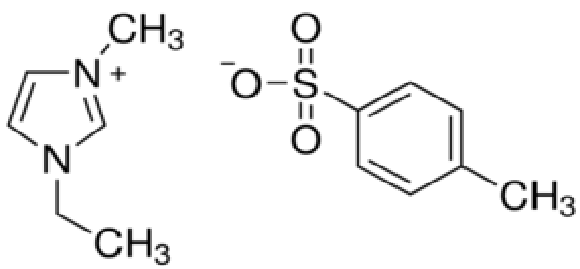
Purification: Used as purchased. The purity of the chemical is >98.0%

Appearance:	**Beige Crystalline**
Molecular Formula:	**$C_6H_{11}N_3O_3$**
Molecular Weight:	**173.17 g/mol**
Melting Point:	**313.15 K**

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

v. 1-ethyl-3-methylimidazolium tosylate [EMIm]OTs

1-ethyl-3-methylimidazolium tosylate is also the imidazolium based ionic liquid, of molecular formula $C_{13}H_{18}N_2O_3S$, containing methyl, ethyl group with two active nitrogen atoms in the imidazole or five member ring, exist as a molten liquid phase with the melting point ≥ 25-30^{o}C.



Source: Sigma Aldrich, Germany

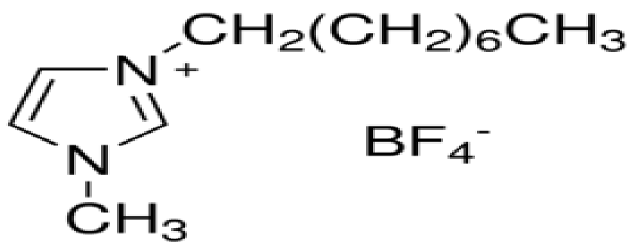
Purification: Used as purchased. The purity of the chemical is >98.0%

Appearance:	**Beige Crystalline**
Molecular Formula:	$C_6H_{11}N_3O_3$
Molecular Weight:	**173.17 g/mol**
Melting Point:	**313.15 K**

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 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.

vi. 1-methyl-3-octylimidazolium tetrafluoroborate

1-methyl-3-octylimidazolium tetrafluoroborate is also the imidazolium based ionic liquid, of molecular formula $C_{12}H_{23}BF_4N_2$, containing methyl, octyl group with two active nitrogen atoms in the imidazole or five member ring, exist as a molten liquid phase.



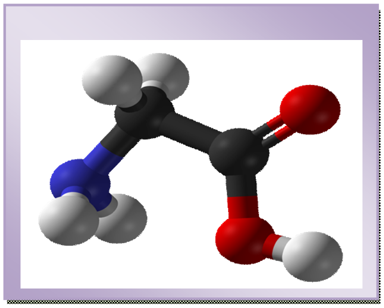
Source: Sigma Aldrich, Germany

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

Appearance:	**Liquid**
Molecular Formula:	**$C_{12}H_{23}BF_4N_2$**
Molecular Weight:	**282.13 g/mol**
Melting Point:	**313.15 K**

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 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.

vii. Glycine



Glycine is an organic compound with the formula $C_2H_5NO_2$.With only a hydrogen atom as the side chain, glycine is the smallest of the 20 amino acids commonly found in proteins. Glycine is a colorless, sweet-tasting crystalline solid. It is unique among the proteinogenic amino acids and it is not chiral. It can fit into hydrophilic and hydrophobic environments, due to its single hydrogen atom side chain.

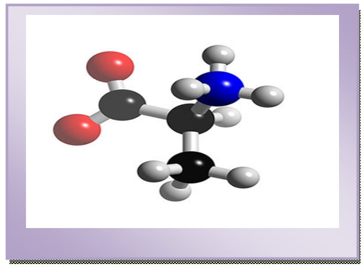
Appearance:	**White powder**
Molecular Formula:	$C_2H_5NO_2$
Molecular Weight:	**75.07 g/mol**
Melting Point:	233^0C

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

Purification: Used as purchased

Application: The principal function of glycine is as a precursor to proteins. It is also a building block to numerous natural products. Glycine is an inhibitory neurotransmitter in the central nervous system, especially in the spinal cord, brainstem and retina. Glycine serves as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries.

viii. L-alanine



Alanine is a α-amino acid with the chemical formula $C_3H_7NO_2$. The L-isomer is one of the 22 proteinogenic amino acids, i.e., the building blocks of proteins. It is classified as a non-polar amino acid. Alanine is a non-essential amino acid, meaning it can be manufactured by the human body, and does not need to be obtained directly through the diet.

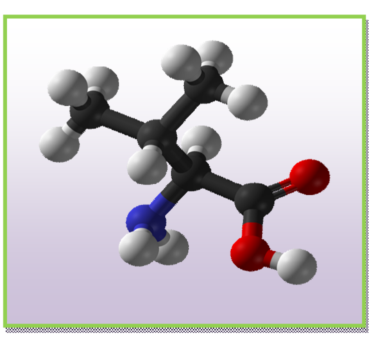
Appearance:	White powder
Molecular Formula:	**$C_3H_7NO_2$**
Molecular Weight:	**89.09 g/mol**
Melting Point:	**258^0C**

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

Purification: Used as purchased

Application: Alanine is used for low blood sugar (hypoglycemia), diarrhea-relateddehydration, liver disease, enlarged prostate (benign prostatic hypertrophy, BPH),fatigue, stress, and certain inherited disorders including glycogen storage disease and urea cycle disorders.

ix. L-vaine



L-valine is a α-amino acid with the chemical formula $C_5H_{11}NO_2$. The L-valine is one of the 22 proteinogenic amino acids, i.e., the building blocks of proteins. It is one of the most important amino acid.

Appearance:	White powder
Molecular Formula:	$C_5H_{11}NO_2$
Molecular Weight:	117.15 g/mol
Melting Point:	298^0C

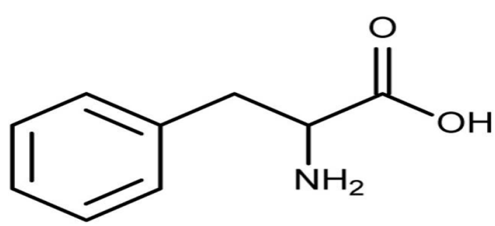
Source: Loba Chemie, India

Purification: Used as purchased

Application: Valine is needed to keep the body in balance for greater muscle growth and recovery. When it comes to muscle building and energy, valine is perhaps best known for its effects as a balancing agent of our bodies' nitrogen content. Valine has been shown to aid in correcting deficiencies created by drug addictions and as a supplemental treatment for those addictions.

x. Phenyl alanine

Phenyl alanine is a α-amino acid with the chemical formula $C_6H_5CH_2CH(NH_2)COOH$. It can be viewed as a benzyl group substituted for the methyl group of alanine, or a phenyl group in place of a terminal hydrogen of alanine. It is one of the most important amino acid.



Source: Sigma-Aldrich, India

Purification: Used as purchased

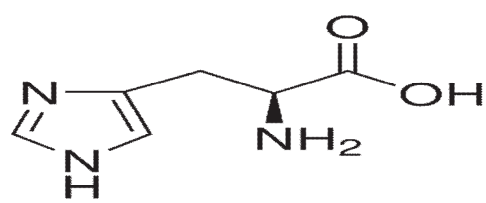
Appearance:	White powder
Molecular Formula:	$C_9H_{11}NO_2$
Molecular Weight:	165.19 g/mol

Melting Point:	**273-276^0C**

Application: Phenylalanine is a precursor for tyrosine; the monoamine neurotransmitters dopamine,norepinephrine (noradrenaline),and epinephrine (adr enaline); and the skin pigment melanin. Phenylalanine is found naturally in the breast milk of mammals. It is used in the manufacture of food and drink products and sold as a nutritional supplement for its reputed analgesic and antidepressant effects. It is a direct precursor to the neuro modulator phenethylamine, a commonly used dietary supplement.

xi. Histidine

Histidine is a α-amino acid with the chemical formula $C_6H_9N_3O_2$. It contains an α-amino group(which is in the protonated $-NH_3^+$ form under biological conditions), a carboxylic acid group (which is in the deprotonated $-COO^-$ form under biological conditions), and a side chain imidazole, classifying it as a positively charged (at physiological pH),aromatic amino acid. Initially thought essential only for infants, longer-term studies have shown it is essential for adults also.



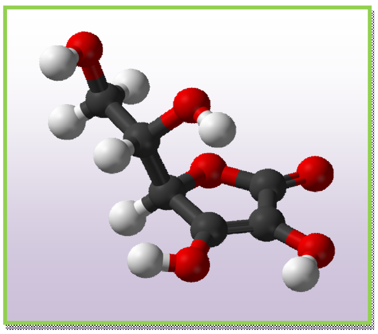
Source: Sigma-Aldrich, India

Purification: Used as purchased

Appearance:	**Solid**
Molecular Formula:	**$C_6H_9N_3O_2$**
Molecular Weight:	**155.15 g/mol**
Melting Point:	**282^0C**

Application: Histidine is used in the biosynthesis of protein. It is also a precursor to histamine, a vital inflammatory agent in immune responsessis Histidine is also important in haemoglobin in helices E and F. Histidine assists in stabilising oxyhaemoglobin and destabilising CO-bound haemoglobin.

xii. Ascorbic acid



Ascorbic acid ($C_6H_8O_6$) is a naturally occurring organic compound with antioxidant properties. Its appearance is white powder, and it is soluble in water. Ascorbic acid is commonly known as vitamin-C. The name is derived from α- (meaning "no") and scorbutus (scurvy), the disease caused by a deficiency of vitamin-C.

Appearance:	**White powder**
Molecular Formula:	$C_6H_8O_6$
Molecular Weight:	**176.12 g/mol**
Melting Point:	**190^0C**

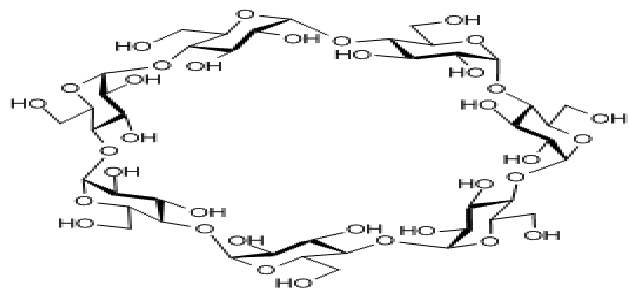
Source: S.D. Fine Chemicals LtD., Mumbai, India

Purification: Used as purchased

Application: Ascorbic acid and its sodium, potassium, and calcium salts are commonly used as antioxidant food additives. Ascorbic acid is easily oxidized and so is used as a reductant in photographic developer solutions (among others) and as a preservative. In fluorescence microscopy and related fluorescence-based techniques, ascorbic acid can be used as an antioxidant to increase fluorescent signal and chemically retard dye photo bleaching.

xiii. Beta 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 β-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%.

Appearance:	**Crystalline Powder**
Molecular Formula:	$C_{42}H_{70}O_{35}$
Molecular Weight:	**1134.98 g/mol**
Melting Point:	**563.15-573.15 K**
Boiling Point	**1814.33 K**
Relative Density	**1.44 g.cm3 at 200 C**

Application: β-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. 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, β-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.

3.2. EXPERIMENTAL METHODS

3.2.1. PREPARATION OF SOLUTIONS

A sock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The uncertainty of molarity of different salt solutions was evaluated to be ± 0.0003 mol·dm^{-3}.

3.2.2. PREPARATION OF SOLVENT MIXTURES

The research work has been carried out with binary or ternary solvent systems with acrylonitrile, tetrahydrofuran, methanol, ethylene glycol, 1,3-dioxolane etc. as primary solvents with some polar, weakly polar and non-polar solvents as well as with some electrolytes (ionic liquids & other electroluytes) and non-electrolytes (amino acids and other solutes).

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.

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

Binary Solutions:
1-ethyl-3-methylimidazolium methanesulfonate + n-Propanol
1-ethyl-3-methylimidazolium methanesulfonate + n-Butanol
1-ethyl-3-methylimidazolium methanesulfonate + n-Pentanol
1-ethyl-3-methylimidazolium nitrate + N,N dimethyl formamide
1-ethyl-3-methylimidazolium nitrate + N,N dimethyl acetamide
1-ethyl-3-methylimidazolium nitrate + Dimethyl sulphoxide
1-ethyl-3-methylimidazolium methanesulfonate + N,N dimethyl formamide
1-ethyl-3-methylimidazolium methanesulfonate + N,N dimethyl acetamide
1-ethyl-3-methylimidazolium methanesulfonate + Dimethyl sulphoxide
1-ethyl-3-methylimidazolium tosylate + N,N dimethyl formamide
1-ethyl-3-methylimidazolium tosylate + N,N dimethyl acetamide
1-ethyl-3-methylimidazolium tosylate + Dimethyl sulphoxide

Ternary Solutions:
Glycine + 0.001(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
L-Alanine + 0.001(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
L-Valine + 0.001(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
Nicotinic Acid + 0.001(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
Ascorbic Acid + 0.001(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
Nicotinic Acid + 0.003(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
Ascorbic Acid + 0.003(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
Nicotinic Acid + 0.005(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
Ascorbic Acid + 0.005(M) Aqueous mixture of 1-ethylpyridinium tetrafluoroborate
Phenyl alanine + 0.01(M) Aqueous mixture of Nicotinic Acid
Histidine + 0.01(M) Aqueous mixture of Nicotinic Acid
Phenyl alanine + 0.03(M) Aqueous mixture of Nicotinic Acid
Histidine + 0.03(M) Aqueous mixture of Nicotinic Acid
Phenyl alanine + 0.05(M) Aqueous mixture of Nicotinic Acid
Histidine + 0.05(M) Aqueous mixture of Nicotinic Acid
1-methyl-3-octylimidazolium tetrafluoroborate + 0.001(M) Aqueous mixture of β-Cyclodextrin
1-methyl-3-octylimidazolium tetrafluoroborate + 0.003(M) Aqueous mixture of β-Cyclodextrin

3.2.3. 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.

3.2.4. DENSITY MEASUREMENT

The density was measured with the help of Anton Paar density-meter (DMA 4500M) with a accuracy of 0.0005 g.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 τ can be measured with high resolution and stands in simple relation to the density ρ of the sample in the oscillator [7]:

$$\rho = A \cdot \tau^2 - B \qquad (1)$$

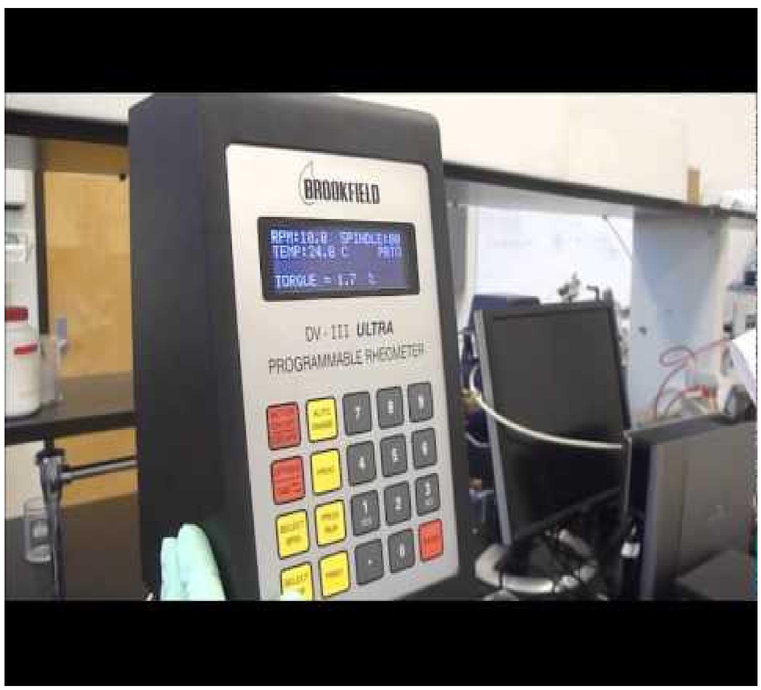
A and B are the respective instrument constants of each oscillator. Their values are determined by calibrating with two substances of the precisely known densities ρ_1 and ρ_2. Modern instruments calculate and store the constants A and B after the two calibration measurements, which are mostly performed with air and water. They employ suitable measures to compensate various 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 double-distilled water and dry air.

3.2.5. VISCOSITY MEASUREMENT

The viscosities (η) 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 $CaCl_2$ solutions.The temperature was maintained to within ± 0.01°C using Brookfield Digital TC-500 thermostat bath. The viscosities were measured with an accuracy of ± 1 %. Each measurement reported herein is an average of triplicate reading with a precision of 0.3 %.



3.2.6. TEMPERATURE CONTROLLER

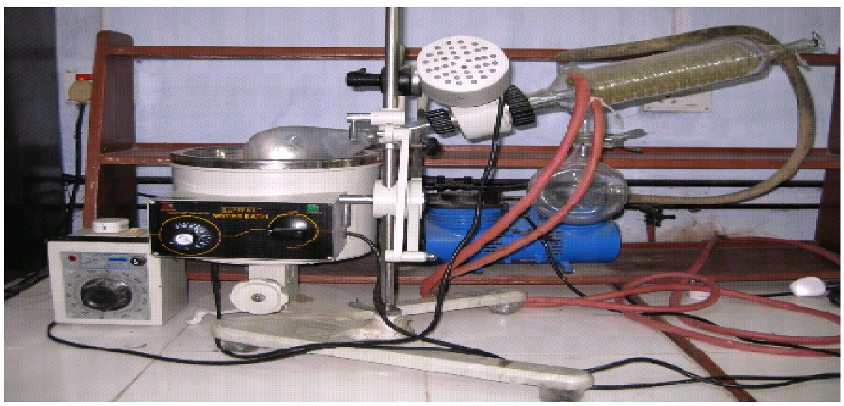
All the measurements were carried out in thermostatic water bath (Science India, Kolkata) maintained with an accuracy of ± 0.01 K of the desired temperature.

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 equipments 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.

Water Distiller (Borosil Glass Works Limited, India):

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.

Rotary Vacuum Flash Evaporator (Superfit, An ISO 9001:2000 Certified Company):



Rotary evaporation is most often and conveniently applied to separate "low boiling" solvents such as n-hexane or ethyl acetate from compounds which are solid at room temperature and pressure. 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.

3.2.7. 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.

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.

$$\text{Ultrasonic speed } (u) = \text{Wave Length } (\lambda) \times \text{Frequency } (f) \tag{5}$$

The ultrasonic interferometer consists of the following two parts, (i) the high frequency generator, and (ii) the measuring cell. 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:

$$K_S = 1 / (u^2 . \rho) \tag{7}$$

where ρ is the density of the experimental liquid.

Figure 1(a) shows the Multifrequency Ultrasonic Interferometer i.e. (i) Cross-section of the measuring cell, (ii) 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 (b) Electronic circuit diagram of the instrument)

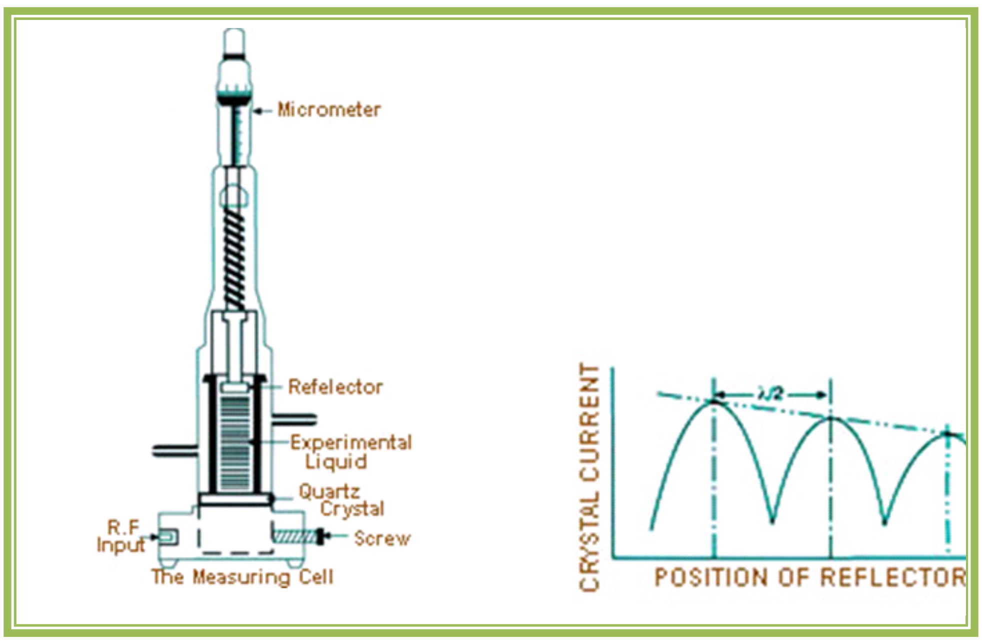


Figure **1(a): The Multifrequency Ultrasonic Interferometer**

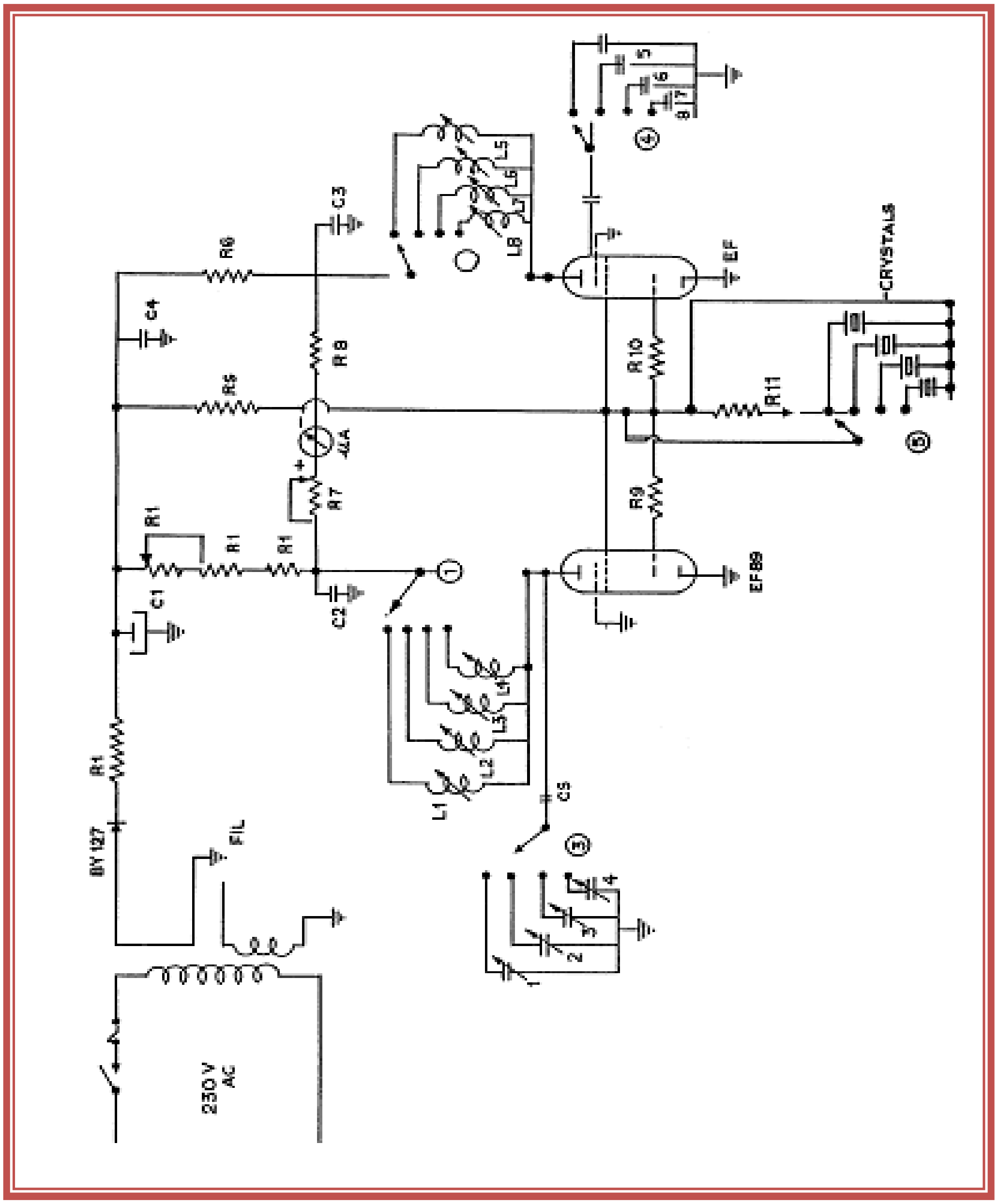


Figure 1(b): Electronic Circuit Diagram of the Instrument

3.2.8. CONDUCTIVITY MEASUREMENT

Systronics Conductivity TDS meter-308 is used for measuring specific Conductivity of electrolytic solutions. It can provide both automatic and manual temperature compensation.

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 [8]. 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 thermo regulator [9].

Several solutions were prepared by weight precise to ± 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.

3.2.9. REFRACTIVE INDEX MEASUREMENT

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

Calibration was performed by measuring the refractive indices of double-distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperature. The accuracy of the instrument is +/- 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.

3.2.10. FT-IR MEASUREMENT

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan)

with a resolution of ± 0.25 cm^{-1} in the region of 400-4000 cm^{-1} at room temperature (25 ^{0}C) with 49-54 % humidity. This KBr optics based instrument records data in different modes (KBr pellets, Nujol mull, non-aqueous solutions).

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).

$$T = \frac{I}{I_0} \quad , \qquad A = -\log_{10} T \tag{10}$$

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

3.2.11. SURFACE TENSION

The surface tension experiments were completed by platinum ring detachment method using a Tensiometer (K9, KRŰSS; Germany) at the experimental temperature. The precision of the measurement was within ±0.1 mN·m^{-1}. Temperature of the system has been preserved by circulating auto-thermostated water (within ± 0.01K) through a double-wall glass vessel holding the solution.

3.2.12. UV-VIS SPECTRA MEASUREMENT

Compounds that absorb Ultraviolet and/or visible light have characteristic absorbance curves 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 (D2) lamp for ultraviolet light and a tungsten (W) lamp for visible light. After bouncing of 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 beam 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 (dl) 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 bcI 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 :

$$-\ln I/I0 = kbc \quad \text{(III.8)}$$

$$-\log I/I0 = 2.303kbc \quad \text{(III.9)}$$

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

$$A = -\log I/I0 \quad \text{(III.11)}$$

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

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.