CHAPTER -III

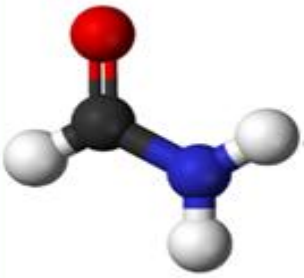
EXPERIMENTAL SECTION

3.1. NAME, STRUCTURE, PHYSICAL PROPERTIES, PURIFICATION AND APPLICATION OF THE USED SOLVENTS AND SOLUTES.

3.1.1. Solvents

Formamide:

It is also known as methanamide, is an amide with a chemical formula CH_3NO, derived from formic acid. It is a clear liquid being miscible with water and has an ammonia-like odour. It is hygroscopic in nature. It is used as a solvent for many ionic compounds.



Appearance: Colourless, oily liquid

M.F. CH_3NO

M.W. 45.04 $g.mol^{-1}$

M.P. 275 K

B.P. 483 K

D.C. 111.0

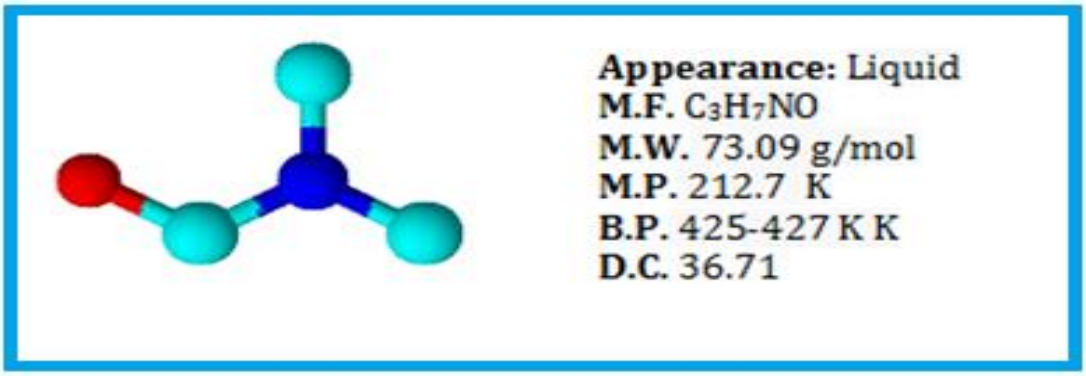
Source: S.D. Fine Chemicals Ltd. Mumbai, India.

Purification: It was dried by the passage through a column of 3A molecular sieves followed by the deionization with a mixed-bed-ion-exchange resin loaded with H^+ and $HCONH^-$ ions [1].

Application: Formamide is the chemical feedstock for the manufacture of sulfa drugs, other pharmaceuticals, pesticides and herbicides. It 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. It is also importantly used as a solvent for resins and plasticizers [2] and the electrostatic self-assembly of polymer nano-films [3].

N, N, Dimethylformamide:

N, N, Dimethylformamide is commonly abbreviated as DMF. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point with the molecular formula C_3H_7NO. This colourless liquid is miscible with water and the majority of organic liquids. Pure dimethylformamide is odourless 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. It facilitates those reactions involving polar mechanisms, such as S_N2 reactions.



Source: Thomas Baker, India

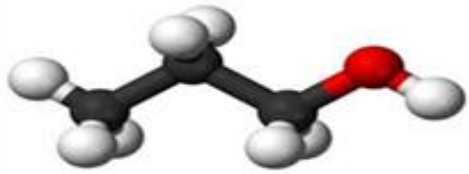
Purification: It was dried by passing through Linde 4Å molecular sieves and then distilled [1].

Application: DMF is used in the production of acrylic fibers and plastics. The primary use of dimethylformamide is as a solvent with low evaporation rate. 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 [4]. 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. 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. 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.

n-Propanol:

Propanol, technically known as 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 colorless liquid is also known as propan-1-ol, 1-propyl alcohol, n-propyl alcohol, and n-propanol. It is isomeric with isopropanol (2-propanol, isopropyl alcohol).



Appearance: Colourless liquid

M.F. C_3H_8O

M.W. 60.10 $g.mol^{-1}$

M.P. 147 K

B.P. 300-371 K

D.C. 20.1 at 25^0C

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

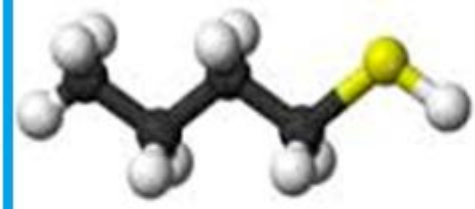
Purification: It was dried by adding drying agent $CaSO_4$ followed by filtration and then distillation [1].

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.

n-Butanol:

n-Butanol or n-butyl alcohol is a primary alcohol with a 4-carbon structure with the chemical formula C_4H_9OH. Its isomers include isobutanol, 2-butanol, and tert-

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. n-Butanol occurs naturally as a minor product of the fermentation of sugars and other carbohydrates [5] and is present in many foods and beverages.



Appearance: Colourless, refractive liquid

M.F. $C_4H_{10}O$

M.W. 74.12 $g.mol^{-1}$

M.P. 183.3K

B.P. 390.8K

D.C. 17.64

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

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

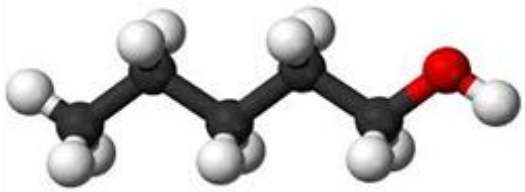
Application: n-Butanol is used as a solvent for waxes, vegetable oils, resins, cellulose esters, and ethers. It is used in inks, brake fluids and polishing compounds and has been utilized as a degreasing agent, an antiseptic and a chemical intermediate. More recently, it is being used as a hand disinfectant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

n-Pentanol:

1-Pentanol (or n-pentanol), is an alcohol with five carbon atoms with the molecular formula $C_5H_{12}O$. 1-Pentanol is a colorless liquid with an unpleasant aroma. To reduce the use of fossil 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 distillation [1].



Appearance: Colourless liquid

M.F. $C_5H_{12}O$

M.W. 74.12 $g.mol^{-1}$

M.P. 195 K

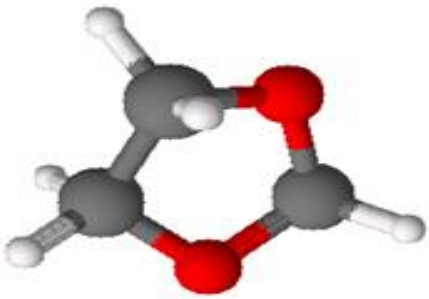
B.P. 410 K

D.C. 13.9

Application: Pentanol can be used as a solvent for coating CDs and DVDs. Another use is a replacement for gasoline.

1,3-Dioxolane

Dioxolane or 1,3-dioxolane is a heterocyclic acetal belonging to the group of organic compounds sharing the dioxolane ring structure. No unusual toxic effects have been associated with the use of 1,3-dioxolane. It is not explosive, not spontaneously flammable and has no disagreeable odour.



Appearance: Liquid.

M.F. $C_3H_6O_2$

M.W. 74.08 $g.mol^{-1}$

M.P. 178 K

B.P. 348 K

D.C. 7.34 at 298.15 K

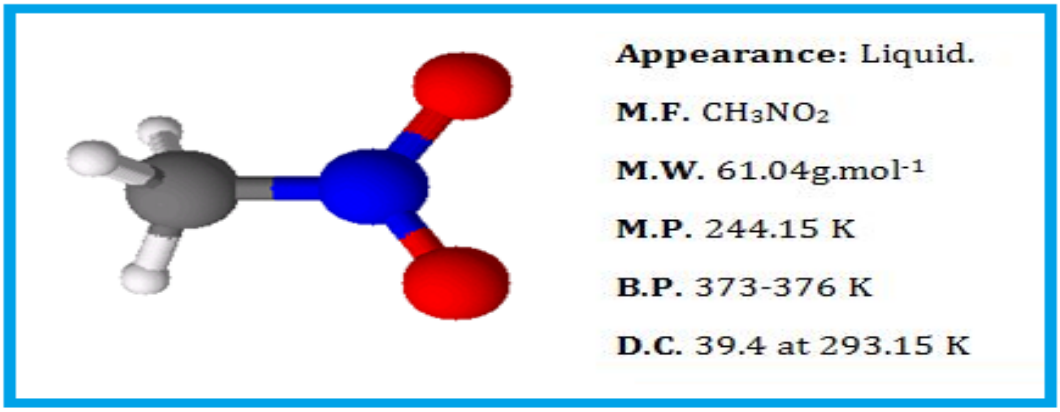
Source: S.D. Fine Chemicals, India.

Purification: It is dried with KOH and then distilled from sodium [1].

Application: It is a very crucial as the lithium battery electrolyte solvent component. This is also important in pharmaceutical manufacturing. It is used as a replacement for many chlorinated solvents, as a copolymerization agent with trioxane and formaldehyde for manufacturing polyacetal resins, paint stripper, glue stabilizer, water solubilizing agent for pesticides, herbicides and wood preservatives.

Nitromethane

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 $CaSO_4$ followed by distillation [1].

Application: The chief use of nitromethane is as a stabilizer for chlorinated solvents, which are used in dry cleaning, semiconductor processing, and degreasing. It is also used 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 α,β-unsaturated carbonyl compounds via 1,4-addition in the Michael reaction. Its acidicity allows it to undergo deprotonation, enabling condensation reactions analogous to those of carbonyl compounds.

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.

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

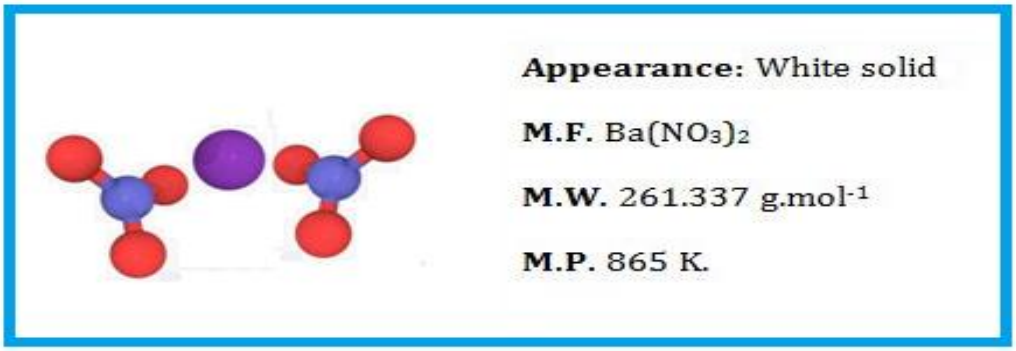
Purification: It was dried by passing through Linde 4Å molecular sieves[1].

Application: In medicine, DMSO is predominantly used as a topical analgesic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory, and an antioxidant [6]. 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. 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.

3.1.2. Solutes

Barium Nitrate:

Barium nitrate with chemical formula $Ba(NO_3)_2$ is a salt composed of barium and the nitrate ion. Barium nitrate exists as a white solid at room temperature. It is soluble in water, and like other soluble barium compounds, is toxic.



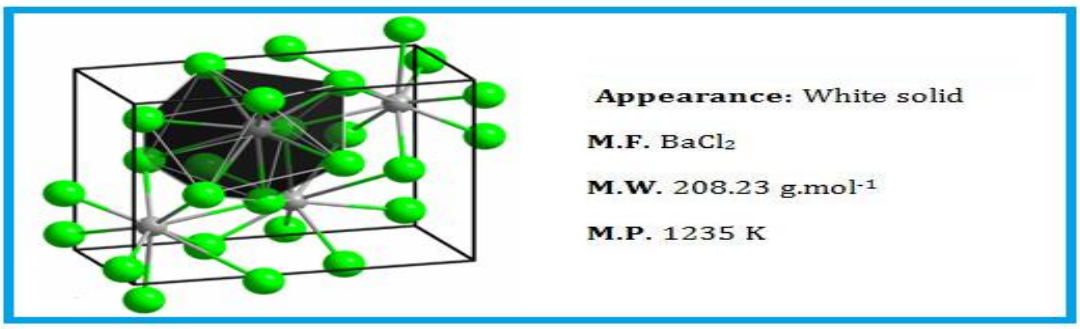
Source: Sigma Aldrich, Germany.

Purification: A method of preparing purified barium nitrate includes precipitating barium nitrate crystals from a solution including barium ions, and washing the barium nitrate crystals with an aqueous solution including at least 10 wt % nitric acid.

Application: Barium nitrate finds wide application in the laboratory. Barium nitrate is used to produce a 'green fire' and green signal flares, pyrotechnic devices and tracer bullets. It also has uses in the vacuum tube industry. Barium Nitrate is use to manufacture other barium compounds.However, its toxicity limits its applicability.

Barium Chloride:

Barium chloride is the inorganic compound with the formula $BaCl_2$. It is one of the most common water-soluble salts of barium. Like other barium salts, it is toxic and imparts a yellow-green coloration to a flame. It is also hygroscopic.

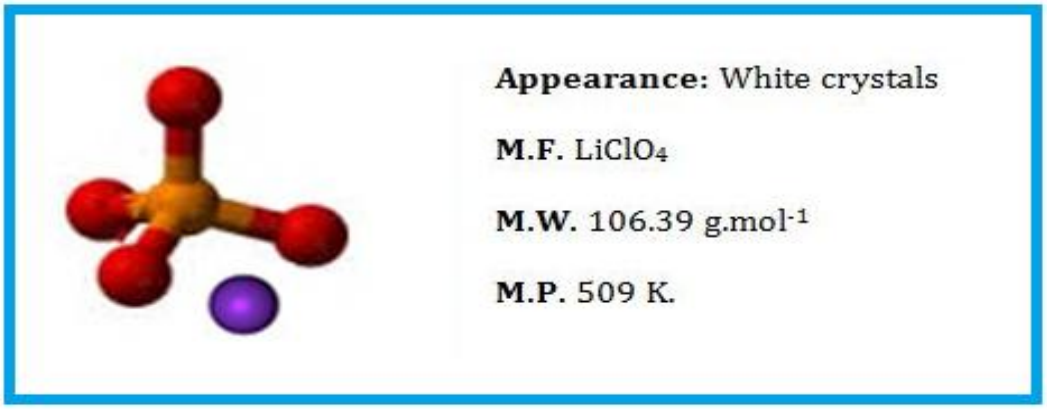


Source: Sigma Aldrich, Germany.

Purification: Recrystalised from aqueous Ethanol solution followed by drying under vacuum at 348 K and it was stored over P_2O_5 in a desiccator.

Application: As an inexpensive, soluble salt of barium, barium chloride finds wide application in the laboratory. It is commonly used as a test for sulfate ion. In industry, barium chloride is mainly used in the purification of brine solution in caustic chlorine plants and also in the manufacture of heat treatment salts, case hardening of steel, in the manufacture of pigments, and in the manufacture of other barium salts. $BaCl_2$ is also used in fireworks to give a bright green color. However, its toxicity limits its applicability.

Lithium Perchlorate: Lithium perchlorate is the inorganic compound with the chemical formula $LiClO_4$. It is a white crystalline solid being highly soluble in water and in alcohol.



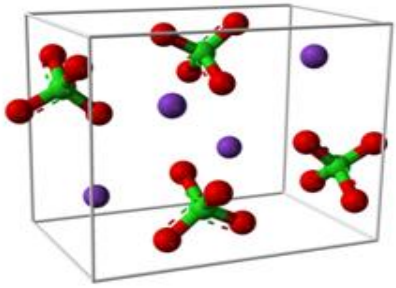
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: Lithium perchlorate is used as an electrolyte in lithium-ion batteries. Lithium perchlorate is chosen over alternative electrolytes such as lithium hexafluorophosphate or lithium tetrafluoroborate when its superior electrical impedance, conductivity, hygroscopicity, and anodic stability properties are of importance to the specific application. One of the most promising potential applications of lithium perchlorate is in the manufacture of chemical sources of energy (i.e. fuel cells) for electric cars [7].

Sodium Perchlorate:

Sodium perchlorate is the most soluble common perchlorate salt with the chemical formula $NaClO_4$. It is a hygroscopic , white crystalline solid that is highly soluble in water and in alcohol. It usually comes as the monohydrate, which has a rhombic crystal system.



Appearance: White crystalline solid

M.F. $NaClO_4$

M.W. 122.44 $g.mol^{-1}$

M.P. 741 K

Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

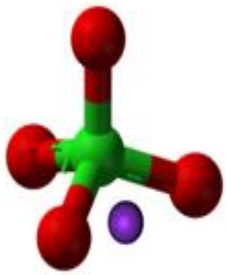
Application: Sodium perchlorate can be used to block iodine uptake before administration of iodinated contrast agents in patients with subclinical hyperthyroidism. $NaClO_4$ has a variety of uses in the laboratory, often as a nonreactive electrolyte. For example, it is used in standard DNA extraction and hybridization reactions in molecular biology.

Potassium Perchlorate:

Potassium perchlorate is the colorless, crystalline solid inorganic salt with the chemical formula $KClO_4$. Like other perchlorates, this salt is a strong oxidizer although it usually reacts very slowly with organic substances. $KClO_4$ has the lowest solubility among the alkali metal perchlorates.

Source: Sigma Aldrich, Germany.

Purification: Used as purchased.



Appearance: Colourless white crystalline powder

M.F. $KClO_4$

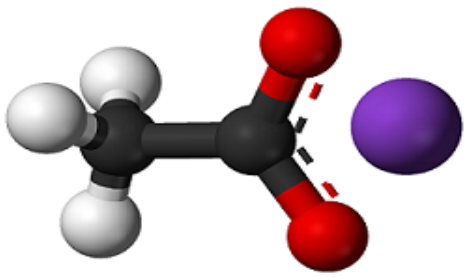
M.W. 138.55 $g.mol^{-1}$

M.P. 833 K.

Application: $KClO_4$ is a common oxidizer used in fireworks, ammunition percussion caps, explosive primers, and is used variously in propellants, flash compositions and sparklers. It has been used as a solid rocket propellant. $KClO_4$ can be used as an antithyroid agent used to treat hyperthyroidism, usually in combination with one other medication.

Potassium Acetate:

Potassium Acetate (CH_3COOK) is the potassium salt of acetic acid. It is the salt that is formed along with water as acetic acid and potassium hydroxide are neutralized together. It appears as white, deliquescent, crystalline powder.



Appearance: White, deliquescent, crystalline powder

M.F. CH_3COOK

M.W. 98.14 $g.mol^{-1}$

M.P. 565 K

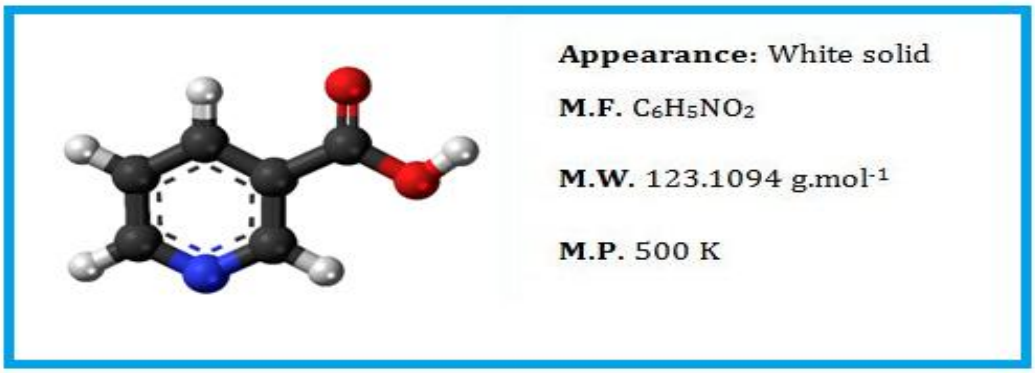
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: Potassium acetate is used as a catalyst in the production of polyurethanes [8]. Potassium acetate is also the extinguishing agent used in class-K fire extinguishers because of its ability to cool and form a crust over burning oils.It is used as a food additive as a preservative and acidity regulator. In medicine, potassium acetate is used as part of replacement protocols in the treatment of diabetic ketoacidosis because of its ability to break down into bicarbonate and help neutralize the acidotic state. In molecular biology, potassium acetate is used to precipitate dodecyl sulfate (DS) and DS-bound proteins, allowing the removal of proteins from DNA. It is also used as a salt for the ethanol precipitation of DNA.

Nicotinic Acid:

Nicotinic acid is a B vitamin (vitamin B3) with the chemical formula $C_6H_5NO_2$. It appears as white translucent crystals. This is a water-soluble solid is a derivative of pyridine, with a carboxyl group (COOH) at the 3-position. It occurs naturally in plants and animals. It is also added to many foods as a vitamin supplement. It is also present in many multiple vitamins and nutritional supplements. It cannot be directly converted to nicotinamide, but both compounds are precursors of the coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) in vivo. [9]



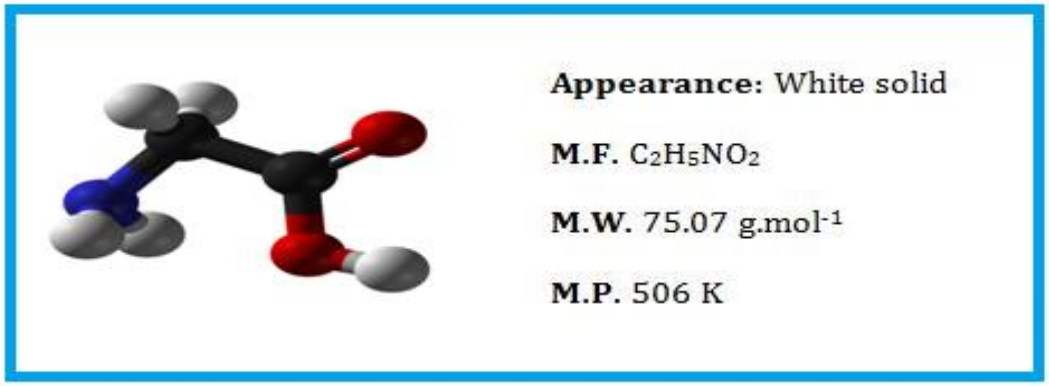
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: As a treatment, higher amounts of nicotinic acid can improve cholesterol levels and lower cardiovascular risks. It is alternatively known as 'Niacin'. It can boost levels of good HDL cholesterol and lower triglycerides as well or better than some prescription drugs. Niacin also modestly lower the bad LDL cholesterol. It is very often prescribed in combination with statins for cholesterol control, such as Crestor, Lescol or Lipitor. Chronic niacin deficiency leads to a disease called pellagra.

Glycine:

Glycine is an important organic amino acid with the formula NH_2CH_2COOH. Having a hydrogen substituent in its side-chain, glycine is the smallest of the 20 amino acids commonly found in proteins and indeed is the smallest possible. Glycine is a colourless, sweet-tasting crystalline solid. It is non-chiral in nature. It can fit into hydrophilic or hydrophobic environments, due to its minimal side chain of only one hydrogen atom.



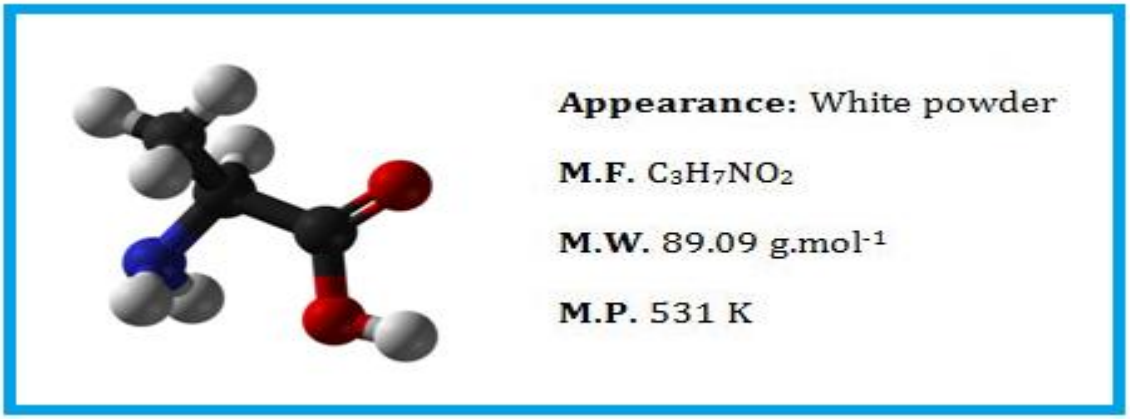
Source: S.D. Fine Chemicals Ltd. Mumbai, India.

Purification: Used as purchased.

Application: Glycine is used as an additive in pet food and animal feed. Certain food supplements and protein drinks contain glycine. Pharmaceutical grade glycine is used for intravenous injections. In industry technical grade glycine acts

as an agent in metal complexing and finishing. For humans, glycine is sold as a sweetener/taste enhancer. Certain drug formulations include glycine to improve gastric absorption of the drug. 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: Alanine is a non-polar α-amino acid with the chemical formula $CH_3CH(NH_2)COOH$. The L-isomer is one of the 20 amino acids encoded by the genetic code. 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.



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

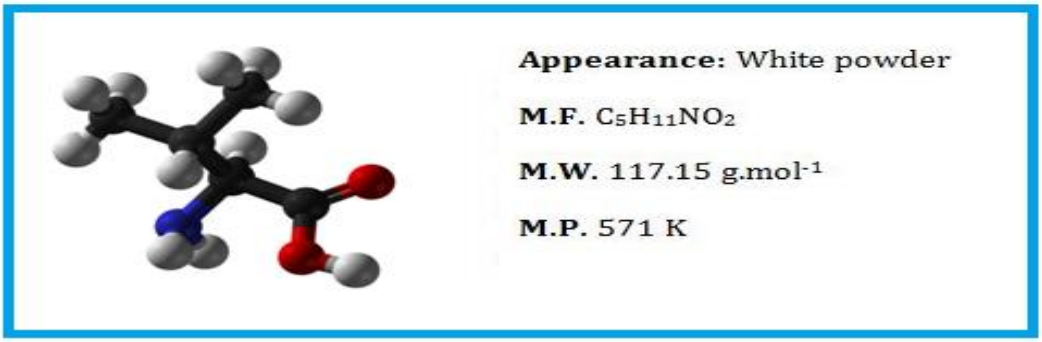
Purification: Used as purchased.

Application: L-alanine plays a decisive role as a building block of important proteins. Mostly synthesized by the muscle cells from lactic acid it is considered the most important nutrient for the amino acid metabolism in the blood together with L-Glutamine. Once synthesized L-alanine is absorbed via the liver and converted to a pyruvate. This compound is critical for the production of glucose and and hence blood sugar management. L-alanine supplements are therefore often used in cases of hypoglycaemia to prevent the organism from suffering low blood sugar or insuline shocks. They enable rapid energy delivery by stimulating the immediate release of glucose into the blood stream. Other important

functions of this amino acid are the support of the immune system and prevention of kidney stones. Alanine increases in durance and strengthens the immune system.

L-valine:

Valine is an essential α-amino acid with the chemical formula $HO_2CCH(NH_2)CH(CH_3)_2$. L-Valine is one of 20 proteinogenic amino acids. This essential amino acid is non-polar. 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.



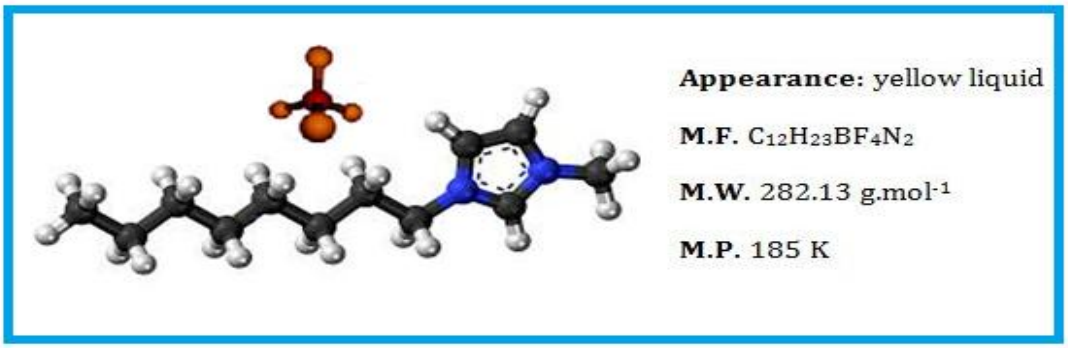
Source: S.D. Fine Chemicals Ltd. Mumbai, India.

Purification: Used as purchased.

Application: L-valine is a branched chain amino acid being very important for supplying energy to muscles. The branched chain amino acids enhance energy, increase endurance and aid in muscle tissue recovery and repair. Being a branched chain amino acid, L-valine is important for optimal growth in infants and children and nitrogen balance in adults. Branched chain preparations are used in sports nutrition and health foods.

1-Methyl-3-Octylimidazoliumtetrafluoroborate:

It is a 'Room temperature ionic liquid' (RTIL) based on the imidazolium cation with tetrafluoroborate as the anionic counterpart. It is highly polar, nonvolatile, nonflammable, stable in air or water and recyclable.



Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: 1-Methyl-3-octylimidazolium tetrafluoroborate is 'green' replacement for volatile organic solvents used in reactions involving inorganic and bio catalytic reactions. It is also utilized as electrically conductive liquids in electrochemistry. Moreover, It is vastly important in multiphase bioprocess operations, batteries, fuel cells.

Tetrabutylphosphonium Tetrafluoroborate:

It is a 'Room temperature ionic liquid' (RTIL) based on the phosphonium cation with tetrafluoroborate as the anionic counterpart. It is highly polar, nonvolatile, nonflammable, stable in air or water and recyclable. They are highly polar, nonvolatile, nonflammable, stable in air or water and recyclable.

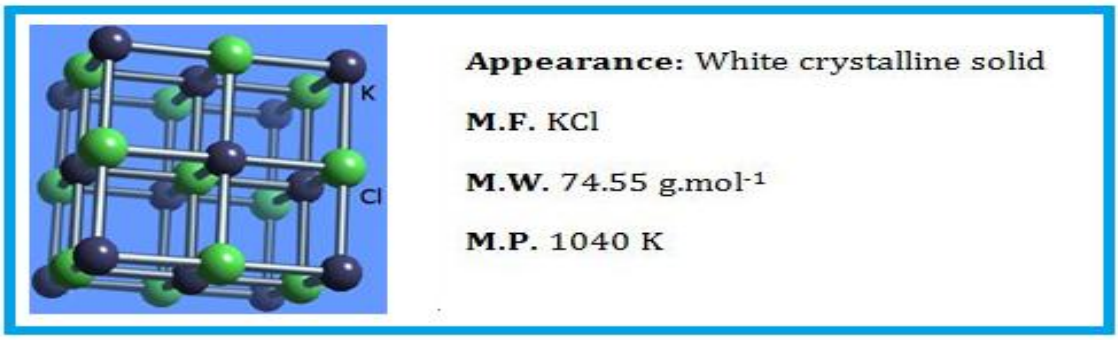
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: Tetrabutylphosphonium Tetrafluoroborate (Bu_4PBF_4) is 'green' replacement for volatile organic solvents used in reactions involving inorganic and bio catalytic reactions. It is also utilized as non-aqueous electrolyte in electrochemistry. It can be used to adjust the selectivity and enhance resolution of HPLC, High Performance Liquid Chromatography, the preferred technique used in explosive analysis. It is also used as heat-transfer fluids for processing biomass and as electrically
conductive liquids in electrochemistry (batteries and solar cells).

Potassium Chloride:

Under standard conditions in its pure state potassium chloride is odourless having white or colourless ,vitreous crystal appearance. The solid dissolves readily in water and its solutions have a salt-like taste.



Source: Sigma Aldrich, Germany.

Purification: It was purified by re-crystallizing twice from conductivity water and then dried in vacuum desiccator over P_2O_5 for 24 hours before use.

Application: The majority of the potassium chloride produced is used for making fertilizer, since the growth of many plants is limited by their potassium intake. As an important chemical feedstock, it is used for the manufacture of potassium hydroxide and potassium metal. It is also used in medicine, lethal injections, scientific applications, food processing, and as a sodium-free substitute for table salt for persons concerned about its health effects. It is sometimes used in water as a completion fluid in petroleum and natural gas operations, as well as being an alternative to sodium chloride in household water softener units.

Potassium Bromide:

Under standard conditions, potassium bromide is a white crystalline powder. It is freely soluble in water. In a dilute aqueous solution, potassium bromide tastes sweet, at higher concentrations it tastes bitter, and tastes salty when the concentration is even higher. These effects are mainly due to the properties of the potassium ion.

Source: Sigma Aldrich, Germany.

Purification: It was purified by re-crystallizing twice from conductivity water and then dried in vacuum desiccator over P_2O_5 for 24 hrs before use.

Application: KBr helps characterize liquid compounds using infrared spectroscopy. Infrared spectroscopy, like all types of spectroscopy, is a technique used to identify compounds and investigate sample compositions. Every molecule has a unique absorbance profile determined by passing a beam of infrared light through the sample. Potassium bromide is a salt used to make photographic papers and plates and for process engraving. Found in general purpose and print developing solutions, potassium bromide is a highly soluble alkaline accelerator in solutions for X-ray films, continuous tone films requiring higher than normal contrast, intensifier solutions recommended for increasing the printing density of thin negatives, cold and warm tone developer solutions and universal developers for projection and contact papers.

Potassium Iodide:

Potassium iodide is an inorganic compound with the chemical formula KI. It is less hygroscopic (absorbs water less readily) than sodium iodide, making it easier to work with. Potassium iodide occurs naturally in kelp.

Source: Sigma Aldrich, Germany.

Purification: It was purified by re-crystallizing twice from conductivity water and then dried in vacuum desiccator over P_2O_5 for 24 hrs before use.

Application: KI is used with silver nitrate to make silver iodide an important chemical in film photography. KI is a component in some disinfectants and hair treatment chemicals. KI is also used as a fluorescence quenching agent in biomedical research, an application that takes advantage of collisional quenching of fluorescent substances by the iodide ion. However, for several fluorophores addition of KI in μM-mM concentrations results in increase of fluorescence intensity, and iodide acts as fluorescence enhancer. Potassium iodide is a component in the electrolyte of dye sensitized solar cells (DSSC) along with iodine. Potassium iodine finds its most important applications in organic synthesis mainly in the preparation of aryl iodides in the Sandmeyer reaction, starting from aryl amines.

3.2. EXPERIMENTAL METHODS

3.2.1. Preparation of Solvent Mixtures

Pure components were taken separately in glass stoppered bottles and thermostated at the desired temperature for sufficient time. After the attainment

of thermal equilibrium, 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 from experimental densities of the solvents at experimental temperature. It was then stoppered and the mixed contents were shaken well before use. Same procedure was adopted throughout the entire work while preparing different solvent mixtures. The physical properties of different pure and mixed solvents have been given in the respective chapters.

3.2.2. Preparation Of Solutions

A stock 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 $mol \cdot dm^{-3}$.

3.2.3. Mass Measurement

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

Figure 1: 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 precision of 0.0005 g·cm^{-3}.

Figure 2: Anton Paar Density-Meter (DMA 4500M)

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

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

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. 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

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer,

Figure 3: Suspended Ubbelohde-type Viscometer

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

$$\gamma = k\,t - l/t \tag{2}$$

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

where, t is the time of flow, ρ is the density and k and l are the characteristic constants of the particular viscometer. The precision of the viscosity measurement was ± 0.003 %. In all cases, the experiments were performed in at least three replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation:

$$\eta_r = \eta / \eta_0 = \rho\, t / \rho_0\, t_0 \tag{4}$$

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

The viscosity was also measured with the help Brookfield DV-III Ultra Programmable Rheometer fitted to a Brookfield Digital Bath TC-500.

Figure 4: Brookfield DV-III Ultra Programmable Rheometer & Brookfield Digital Bath TC-500.

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.

Figure 5: Thermostatic Water Bath (Science India, Kolkata)

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.

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.

Figure 6: The Multifrequency Ultrasonic Interferometer

The principle used in the measurement of the ultrasonic speed (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum. If the distance is now increased or decreased and the variation is exactly one half of wave length ($\lambda/2$) or integral multiples of it, anode current becomes maximum. From the knowledge of the wave length (λ), the speed (u) can be obtained by the relation.

Ultrasonic speed (u) = Wave Length (λ) × Frequency (f) (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.

$$d = n \times \lambda/2 \qquad (6)$$

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

$$K_S = 1 / (u^2 . \rho) \qquad (7)$$

where ρ is the density of the experimental liquid.

Figure. 6 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 is as follows.

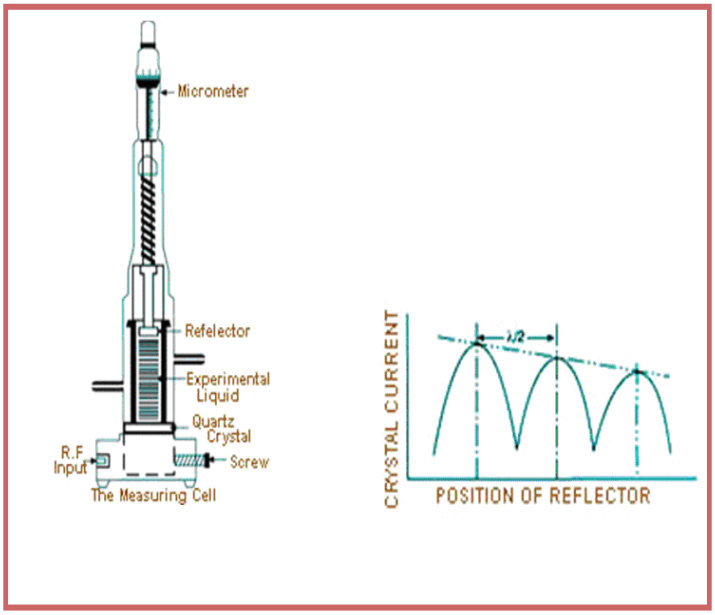


Figure 6(a): Cross section of the Measuring Cell and 6(b) Position of Reflector Versus Crystal Current

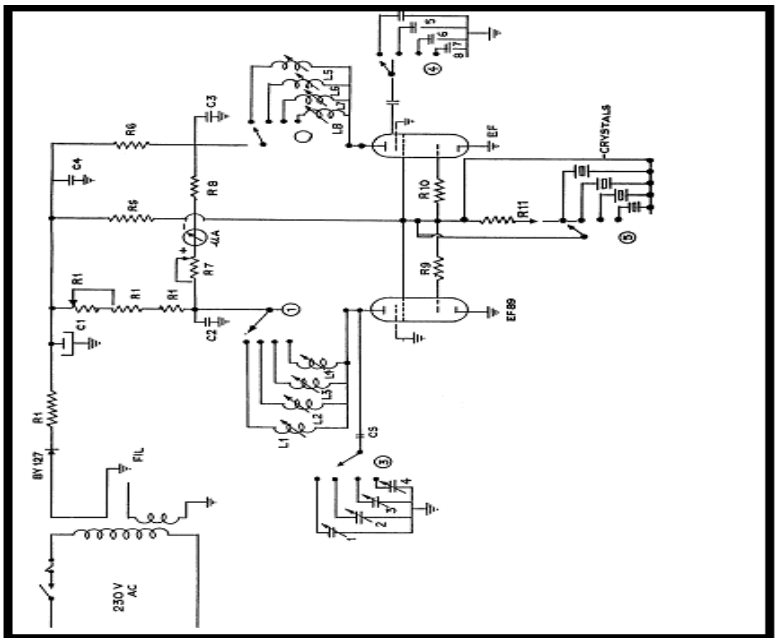


Figure 6(c): Electronic Circuit Diagram of the Instrument

3.2.8. Conductivity Measurement

Conductivity measurement was done using Systronics Conductivity TDS meter-308. It can provide both automatic and manual temperature compensation.

Figure 7: Systronics Conductivity TDS meter-308.

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 [10]. The conductivity cell was sealed to the side of a 500 cm^3 conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen gas was passed to prevent admission of air into the cell when solvent or solution was added. The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of ± 0.01 K by means of mercury in glass thermoregulator [11].

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.

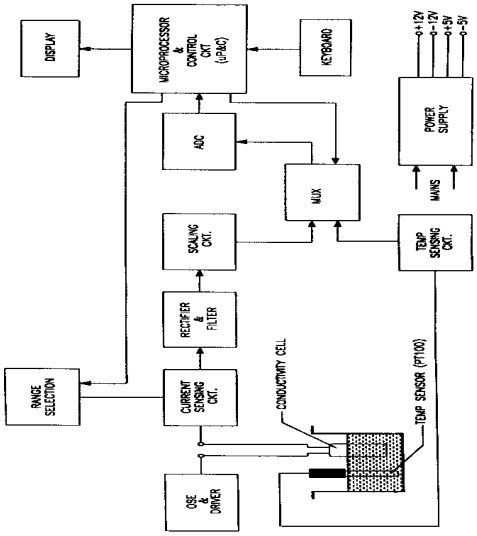


Figure 8: Block Diagram of Systronics Conductivity-TDS meter 308.

3.2.9. Refractive Index Measurement

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

Figure 9: 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.

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