CHAPTER III

EXPERIMENTAL SECTION

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

3.1.1. SOLVENTS

The information of the aqueous and non-aqueous solvents used in the research work are specified below:

Water (H_20)

Water is the basis of life as life arose from water. Water is an universal chemical substance is maid up of hydrogen and oxygen and is crucial for all well-known forms of life. In distinctive treatment, water refers only to its liquid form or state, but the matter also exists as solid state or gaseous state e.g ice and steam respectively. Water is a high-quality solvent and is frequently referred to as the Universal Solvent.

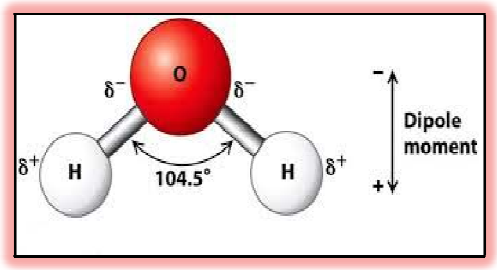


Figure1. Water molecule

State	Liquid
Molecular Formu	H_20
Molecular Weight	18.02 $g{\cdot}mol^{-1}$
Density	0.99713 $g{\cdot}cm^3$
Viscosity	0.891 $mP{\cdot}s$
Refractive Index	1.3333
Dielectric Constant	78.35 at 298.15K

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

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} $S \cdot cm^{-1}$.

Figure2. Water in two states: liquid (including the clouds, which are examples of aerosols), and solid (ice).

Application: Water is extensively used in chemical reactions as a solvent or reactant and less usually as a solute or catalyst. In inorganic reactions, water is a ordinary solvent, dissolving many ionic compounds. Supercritical water has newly been a impotant topic of research work. Oxygen saturated supercritical water combusts organic pollutants powerfully. It with no trouble forms hydrogen bond with other molecules and has appropriate polarity to freeze a numerous number of molecules and hence, it is said the universal solvent. Water is the most important constituent of life in the earth. Not only a elevated percentage of living substances , both plants and animals are set up in water, all forms of life on earth is consideration to have arisen from water and the biochemic bodies of all living organisms are composed mainly of water. About 70 to 92 percent of all organic matter is

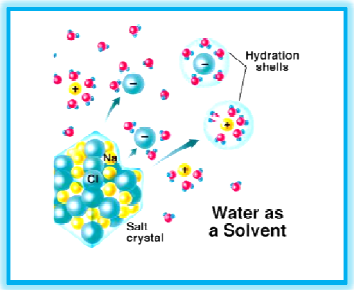


Figure 3. Water as solvent

water. The biochemical reactions in all plants and animals that sustain life take place occur in water medium. Water not only gives the medium to create these life satisfying reactions plausible, but water itself is often an essential reactant or product of all these reactions. In short, Biochemistry i.e. the 'Chemistry of life' is nothing but the " chemistry of water" in living bodies.

Ethyl Alcohol (CH_3CH_2OH)

Ethanol, also known as alcohol, ethyl alcohol, grain alcohol, and drinking alcohol, is a chemical compound, a simple alcohol with the chemical formula C_2H_5OH. Formula of ethanol can be also written as $CH_3–CH_2–OH$ or $C_2H_5–OH$ (an ethyl group linked to a hydroxyl group), and is often abbreviated as EtOH. Ethanol is a volatile, inflammable, pale liquid with a slight typical odor.

Source: Merck, India.

Purification: It was passed through Linde Å molecular sieves and then distilled[1]

Ethanol	
Appearance	Colourless Liquid
Molecular Formula	C_2H_6O
Molecular Weight	46.07 $g{\cdot}mol^{-1}$
Density (30^0C)	0.8029 $g{\cdot}cm^3$
Viscosity	0.948mP·s (303.15K)
Refractive Index	1.361(298.15 K)
Dielectric Constant	: 24.3 (298.15 K)

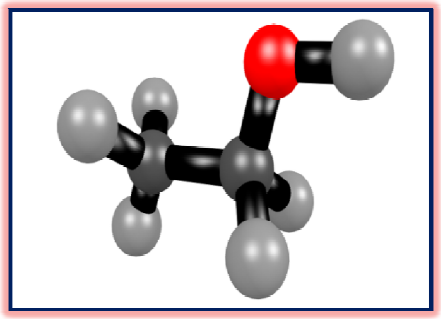


Figure 5. Ethanol

Application: Ethanol is naturally produced by the fermentation of sugars by yeasts or via petrochemical processes, and is most commonly consumed as a popular recreational drug. It also has medical applications as an antiseptic and disinfectant. The compound is widely used as a chemical solvent, either for scientific chemical testing or in synthesis of other organic compounds, and is a vital substance used across many different kinds of manufacturing industries. Ethanol is also used as a clean-burning fuel source.

Methyl Alcohol (CH_3OH):

Methanol or Carbinol is a simplest primary alcohol with the chemical formula CH_3OH. It is formed obviously in small amounts throughout many fermentation processes in addition to catalytic process. This is colorless, flammable and highly toxic liquids with distinct odor.

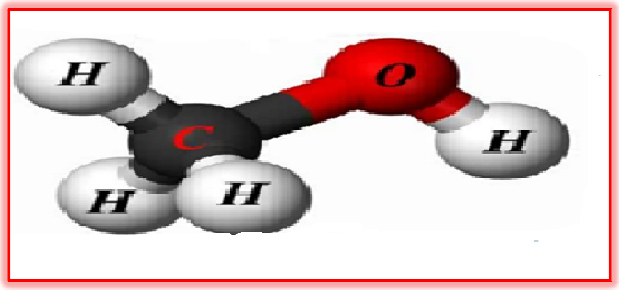


Figure 6. Methanol

***Source*:** Sigma Aldrich, Germany

***Purification*:** It was dried by passing molecular sieve and then distilled by appropriate method [4].

Appearance:	**Colourless liquid**
Molecular Formula:	**CH_4O**
Molecular Weight:	**32.04 g/mol**
Boiling Point:	**337-378 K**
Melting Point:	**175 K**
Dielectric Constant:	**32.70 at 293.15 K**

Application: It is used as solvent, fuel and producing biodiesel. About 40% methanol transformed to methanol and from which different products are obtained like, plastics, plywood, textile and paint industries. Methanol is also applied as a enegy carrier.

2-Methoxyethanol:

2-Methoxy ethanol or methyl cellosolve, is an organic compound with formula $C_3H_8O_2$ and mostly used as a solvent. It is a colorless clear liquid with a characteristics ether-like odor. It is a glycol ethers category solvent and for

which extraordinary for ability to dissolve a variety of different types of chemical compounds.

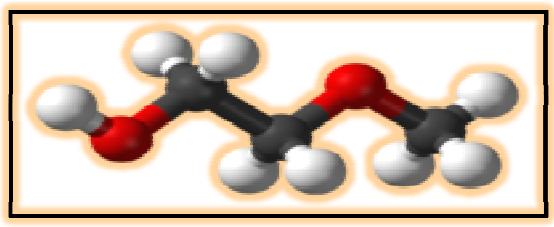


Figure 7. 2-Methoxyethanol

***Source*:** Sigma Aldrich, Germany

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

Appearance:	**Colourless, refractive liquid**
Molecular Formula:	**$C_3H_8O_2$**
Molecular Weight:	**76.09 g/mol**
Boiling Point:	**397-398 K**
Melting Point:	**188 K**
Dielectric Constant:	**17.38 at 293.15 K**

Application: 2-Methoxyethanol is used as a solvent for many practical 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 ruthenium (II) complexes.

2-Ethoxyethanol

2-Ethoxy ethanol or ethyl cellosolves is a clear colorless compound. It is prepared by the reaction of ethylene oxide with ethanol. It is a common solvent widely used commercial and industrial applications.

Figure 8. 2-Ethoxyethanol

***Source*:** Sigma Aldrich, Germany

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

Appearance:	**Colourless liquid**
Molecular Formula:	**$C_4H_{10}O_2$**
Molecular Weight:	**90.12 g/mol**
Boiling Point:	**408 K**
Melting Point:	**203 K**
Dielectric Constant:	**14.25 at 293.15 K**

Application: It dissolves chemically diverse compounds as it contains glycol ether linkage. Also, it dissolves some organic substances like, oils, resins, grease, waxes, nitrocellulose, and lacquers.

2-Propoxyethanol ($C_5H_{12}O_2$)

This is colorless, odorless oily liquid with formula $C_5H_{12}O_2$. It can act as bases. They form salts with strong acids and various complexes with Lewis acidic substances. It has propyl linkage with ethereal oxygen. Ethers may react violently with strong oxidizing substances. Many reactions, which typically involve the cleavage of the C-O bond, ethers are comparatively inert.

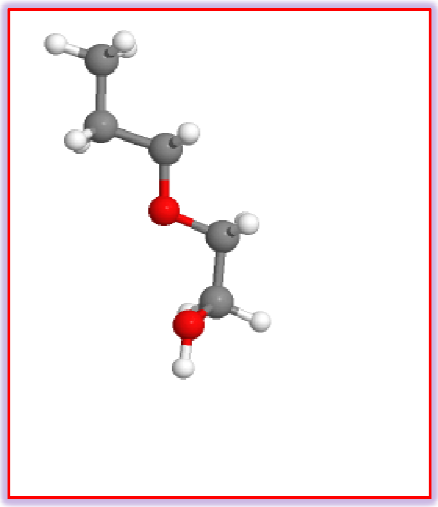


Figure 9(a). 3D image of 2-Propoxyethanol

Appearance	Liquid
Molecular Formula:	$C_5H_{12}O_2$
Molecular Weight:	**104.15 g/mol**
Boiling Point:	**423-425 K**
Melting Point:	**198 K**
Dielectric Constant:	**11.76 at 293.15 K**

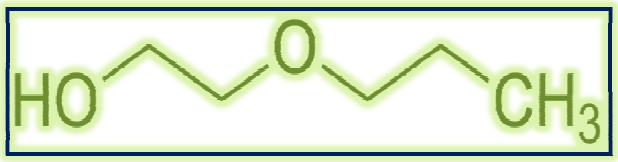


Figure 9(b). 2-Propoxyethanol

***Source*:** Sigma Aldrich, Germany

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

Application: Like other cellosolves, propoxy ethanol also dissolve some organic materials e.g., oils, resins, grease, waxes, nitrocellulose etc.

3.1.2. Ionic Liquids

1,3 - dimethylimidazolium methyl sulfate

1,3-dimethylimidazolium methyl sulfate is a imidazolium based ionic liquid, of molecular formula $C_6H_{12}N_2O_4S$, 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°C.

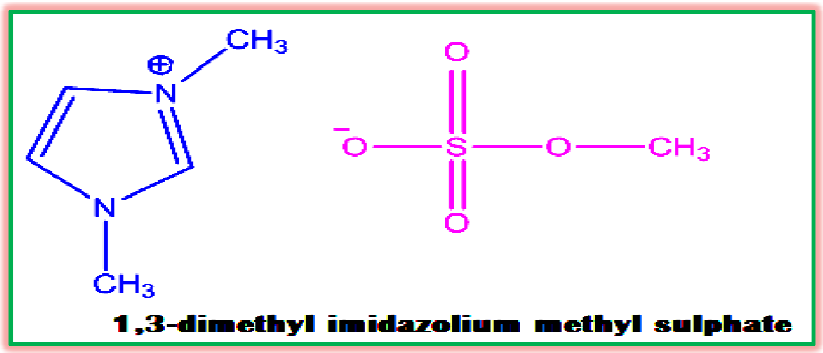


Figure 10. 1, 3 - dimethylimidazolium methyl sulfate

Source: Sigma Aldrich, Germany

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

Appearance:	**Solidified mass (off white)**
Molecular Formula:	**$C_6H_{12}N_2O_4S$**
Molecular Weight:	**208.24 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) and so forth. In the modern technology, industry, and also in academic research field, the vast application is frequently increases.

1-butyl-4-methylpyridinium hexafluorophosphate

1-butyl-4-methylpyridinium hexafluorophosphate is a pyridinium based ionic liquid, of molecular formula $C_{10}H_{16}F_6NP$, containing methyl, and butyl group with an active nitrogen atom. It exists in solid form.

1-butyl-4-methylpyridinium hexafluorophosphate	
Appearance:	**Solid**
Molecular Formula:	**$C_{10}H_{16}F_6NP$**
Molecular Weight:	**$295.20 g \cdot mol^{-1}$**
Melting point:	**318.15 K**

Figure 11. ***1-butyl-4-methylpyridinium hexafluorophosphate***

Source: Sigma Aldrich, Germany

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

Application:

1-butyl-4-methylpyridinium hexafluorophosphateis used as solvents for Polymer Chemistry. The ionic liquid is good examples of neoteric solvents, new types of solvents,or older materials that are finding new applications as solvents, which is envi nisms, 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 andsolar cells) and so forth. In the modern technology, industry, and also in academic researchfield, the vast application is frequently increases.ronmentally 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 electricallyconductive liquids as electrochemical device in the field of electrochemistry (batteries andsolar cells) and so forth. In the modern technology, industry, and also in academic researchfield, the vast application is frequently increases.

3.1.3. Uric Acid

The molecular structure of uric acid is the combination of carbon, nitrogen, oxygen and hydrogen with the formula $C_5H_4N_4O_3$. It is sparingly soluble in water.

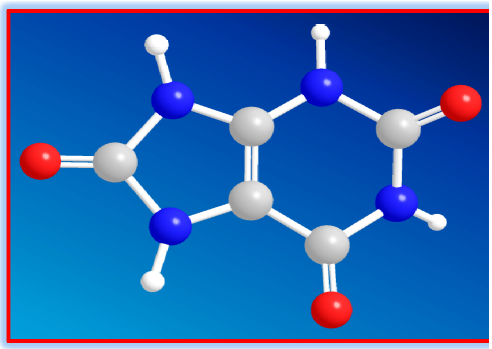


Figure 12(a). 3D Structure of Uric Acid

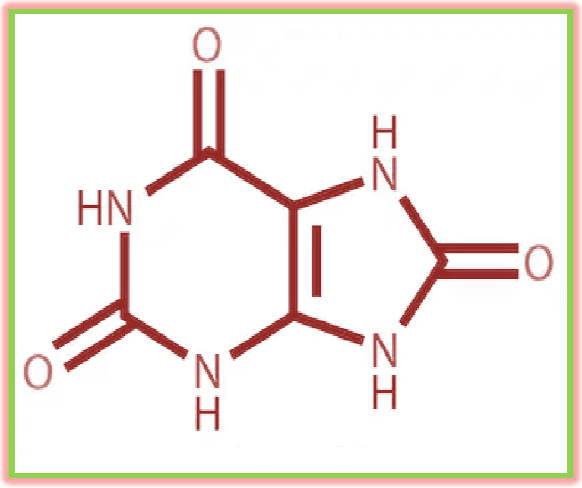


Figure 12(b). Uric Acid

Appearance	**White crystals**
Molecular Formula	**$C_5H_4N_4O_3$**
Molecular Weight	**168.11 g·mol^{-1}**
Melting point	**573.15 K**

Source: Sigma Aldrich, Germany

Purification: Used as purchased without further purification. The purity of the chemical is >99.0%

Application : Uric Acid forms ions and salts known as urates and acid urates, such as ammonium acid urate. Uric acid is produced by the metabolic break of purine nucleotides, and is found normally in urine. High blood concentrations of uric acid can lead to gout and are associated with other medical conditions including diabetes and the formation of ammonium acid urate kidney stones.

3.1.4.Drug Molecules

3.1.4.1.Nortiptyline hydrochloride

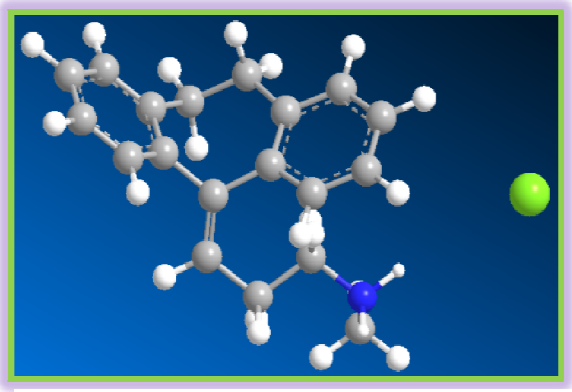


Figure13(a). 3D Structureof Nortiptyline hydrochloride

The drug molecule Nortriptyline [3-(10, 11-dihydro-5H-dibenzo [a,d] cyclohepten-5-ylidene)-*N*-methyl-1-propanamine] hydrochloride (NTPH) belongs to the class of medicines known as tricyclic antidepressant (TCAs). Depression is fetching one of the most imperilling diseases disturbing human health and quality of living [14-18]. Compared to the other TACs drug molecules, NTPH shows various advantag

Appearance :	White Powder
Molar mass:	263.384 g/mol
Molecular Formula:	$C_{19}H_{21}N$

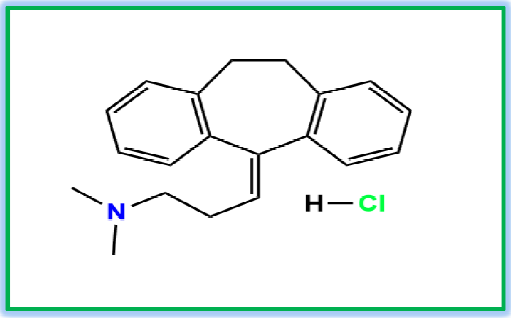


Figure 13(b), Nortiptyline hydrochloride

Source and purity of samples:

The above mentioned drug is purchased from Sigma-Aldrich, Germany. The mass fraction purity of drug and ether were ≥0.99.

Application : The antidepressant effects of TCA are thought to be due to an overall increase in serotonergic neurotransmission and in depressed individuals, NTPH exerts a positive effect on mood. TCAs can block histamine-H1 receptors, α1-adrenergic receptors which accounts for their sedative, hypotensive effects respectively. NTPH exerts less sedative side effects compared to the tertiary amine TCAs. NTHCL has also neuro protective effects and it is used as key models of chronic neuro-degeneration. It expanded as strong inhibitor of mitochondrial permeability transition (MPT) in both isolated [19] and brain. MPT results due to openings of protein pores that are formed in the inner membrane of

mitochondria and allow free diffusion of molecules having molecular weight less than 1500 resulting mitochondrial swelling and cell death [20]. NTPH can also inhibit the release of cytochrome C and capsize activation in tissue. As, 15-C-5s are secure and friendly for human health and considered as safe drug carrier in human body [21], so, formulating inclusion complex of NTPH with 15-C-5s could potentially introduce a new prospect and hope in drug delivery systems and also in research field[22]. Nortriptyline hydrochloride (nortriptyline hydrochloride capsules) is indicated for the relief of symptoms of depression. Endogenous depressions are more likely to be alleviated than are other depressive states.

3.1.4.2.Allopurinol

Allopurinol(1H-Pyrazolo[3,4-d]pyrimidin-4-ol) is a drug used to treat gout which is caused by a build up of sodium urate crystal. Allpurinol is the most commonly used urate lowering therapy.

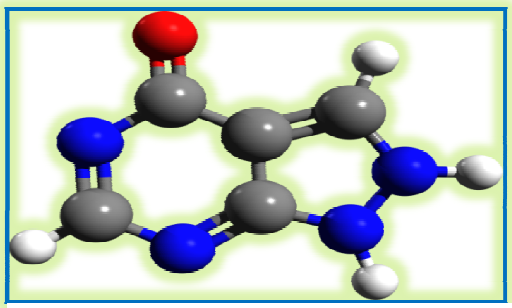


Figure 14(a).Ball & Stick Model of Allopurinol

Appearance :	White crystals or powder
Melting point :	>350 °C
Molecular Formula :	$C_5H_4N_4O$
Water solubility :	480 mg/L
Molecular Formula :	$C_5H_4N_4O$
Molecular Weight:	136.114 g/mol

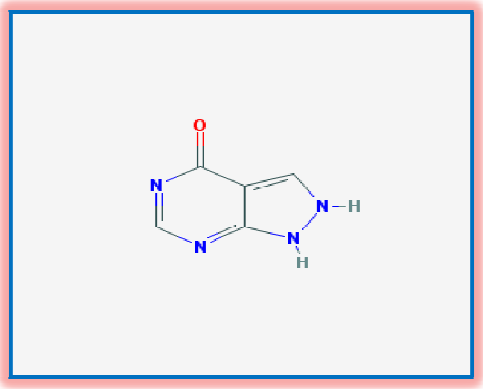


Figure14 (b). Allopurinol

Source and purity of materials:

Allopurinol was purchased from Sigma-Aldrich .The mass fractions purity of allopurinol was ≥0.99. The reagent was always placed in the desiccators over P_2O_5 to keep them in dry atmosphere. These chemicals were used as received without further purification. The provenance and purity of the chemical used has been depicted in table 1.

Source and purity of the chemicals (Table1)

Chemical name	Source	mass fraction purity	Purification Method
Allopurinol(Zyloric Tablet)	Sigma-Aldrich	≥0.99	Used as procured

Application : It has the benefits of once-daily dosing as well as effectiveness in patients with renal impairment. Allopurinol is rapidly metabolized to oxypurinol, which inhibits xanthine oxidase, thereby preventing the formation of uric acid. The drug is well tolerated by the majority of patients, and serious side effects are rare .

3.1.5. HOST MOLECULES

3.1.5.1.α-Cyclodextrin (α-CD)

α-Cyclodextrin is a cyclic oligosaccharide composed of 6 glucose groups. This is white amorphous solid with a cylinder like molecular structure.The structural arrangement makes it versatile in different fields. The properties are widely used in industry for various purposes.

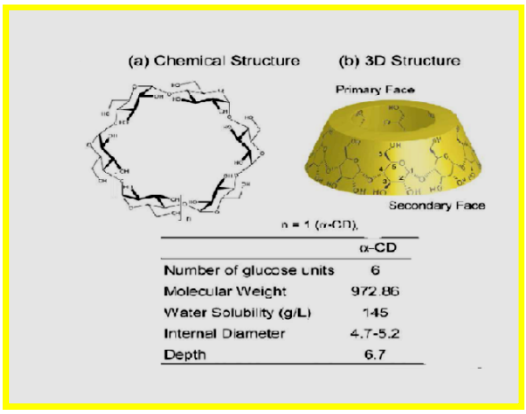


Figure 15(a). α-Cyclodextrin

Source: Sigma Aldrich, Germany.

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

Application: α-Cyclodextrin is a new substance with high solubility in water and which has wide application in medicinal chemistry, food processing industry. Moreover, it is extensively used in modification of cosmetics, food stuffs etc.; whose function is to improve stability, solubility and good smell. 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 food industry, it is used to cover strange and bad smell of food, improve the stability of perfume and the

condiment and keep food dry or wet at will. α-CD with a cavity diameter of 4.7-5.3Å, is of the good interest because it is easily available in market and its cavity size allows to encapsulate many common guest moieties like hormones, vitamins, and many compounds. 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.

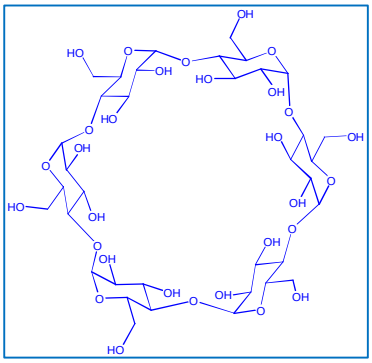


Figure 15(b). α-Cyclodextrin

α-Cyclodextrin

Appearance	**Crystalline Powder**
Molecular Formula	**$C_{42}H_{70}O_{35}$**
Molecular Weight	**1134.98 g·mol^{-1}**
Melting Point	**563.15-573.15 K**
Boiling Point	**1814.33 K**
Relative Density	**1.44 g·cm^{-3} at 20°C**
Refractive Index	**1.59 (n_D^{20})**

3.1.5.2. β-Cyclodextrin (β-CD)

β-Cyclodextrinis white amorphous solid compound composed of 7 glucose groups having a cylinder like molecular structure. The function of β-Cyclodextrin depends on its molecular structure which can be easy to integrate other materials. That feature is applied widely in industry

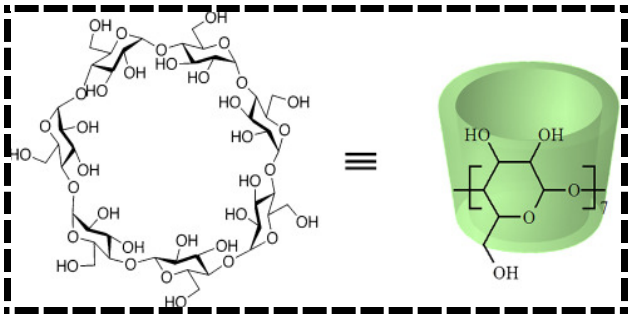


Figure 16(a). β-Cyclodextrin (β-CD)

Source: Sigma Aldrich, Germany.

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

Application: β-Cyclodextrin is a new stuff which can be widely applied in production of medicine and food. 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. β-CD with a cavity diameter of 6.4-7.5 Å, is the most interest because its cavity size allowsfor the best special fit for many common guest moieties. For this reason, β-cyclodextrin is widely used as host in the host-guest chemistry with various biologically active molecules such as hormones, vitamins, drug molecules and various compounds commonly 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.

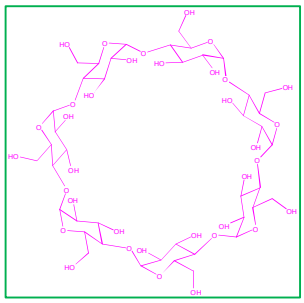


Figure 16(b). **β-Cyclodextrin**

β-Cyclodextrin

Appearance	**Crystalline Powder**
Molecular Formula	**$C_{42}H_{70}O_{35}$**
Molecular Weight	**1134.98 g·mol^{-1}**
Melting Point	**563.15-573.15 K**
Boiling Point	**1814.33 K**
Relative Density	**1.44 g·cm^{-3} at 20°C**
Refractive Index	**1.59 (n_D^{20})**

3.1.5. 3. Hydroxy propyl-β-Cyclodextrin (HP-β-CD)

HP-β-CYD is a 2-hydroxypropyl beta-cyclodextrin which is highly soluble derivative of beta-cyclodextrin. As (2-hydroxypropyl) beta-cyclodextrin (HP-β-CD) is always a mixture of isomers with various degrees and pattern of hydroxyl propylation, no wonder that the products of different manufacturers are often different.

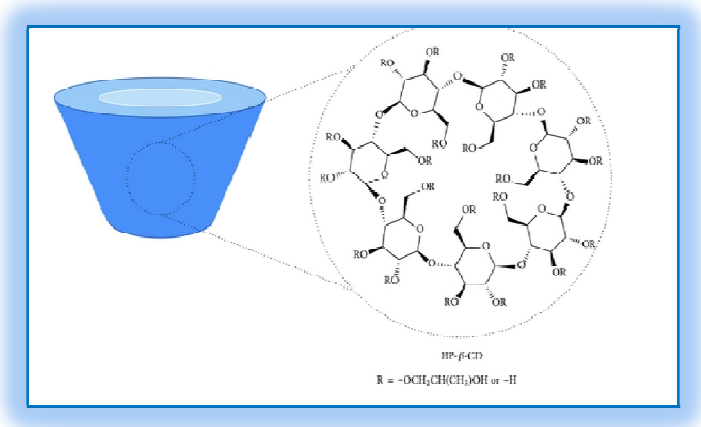


Figure 17(a).Hydroxy propyl-β-Cyclodextrin (HP-β-CD)

Since the discovery about 30 years ago (2-hydroxypropyl) beta-cyclodextrin(HP-β-CD), a highly soluble derivative of beta-cyclodextrin, has become an approved excipient of drug formulations included both in the United States and European Pharmacopoeias.

It is recommended to use as solubilizer and stabilizer for oral and parenteral formulations.

Appearance	White to slightly yellow powder
Molecular Formula	$C_{54}H_{102}O_{39}$
Molecular Weight	**1375.371** g/mol
Melting point	**551.15K**
Solubility (H_2O)	**14.5 mg/ mL (w/v) at 298.15K**

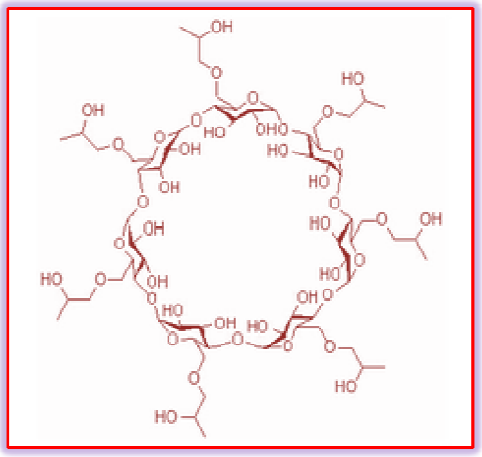


Figure17(b). HP-β-CD

Application : It has enhanced solubility and less toxicity. Recently, its pharmacological activity has been recognized in various diseases. The increasing applications require a closer look to the structure-activity relationship

Recently, the anticancer effect of HP-β-CYD has been discovered and proved in vivo in mouse model of leukemia

3.1.5.4.15-Crown-5

15-Crown-5 is a crown ether with the formula $(C_2H_4O)_5$. It is a cyclic pentamer of ethylene oxide that forms complex with various cations, including sodium and potassium, however, it is complementary to Na^+ and thus has a higher selectivity for Na^+ ions.

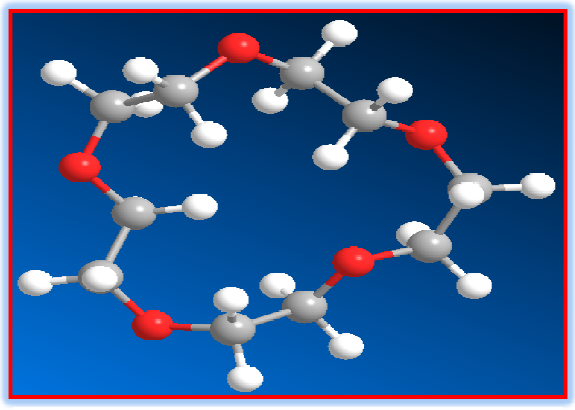


Figure 18(a): **Ball & stick representation of 15-C-5**

Application:

15-Crown-5 is a crown ether that is generally used as a ligand in coordination chemistry. It shows the ability to complexes with alkali metal ions. Crown ethers can be used in the laboratory as phase transfer catalysts.

Appearance: Clear, colorless liquid

Chemical formula: $C_{10}H_{20}O_5$
Molar mass: 220.27 g·mol^{-1}

Boiling point: **366.15-369.15 K**
Refractive index (n_D) : 1.465

Flash point: 113 °C (235 °F; 386 K)
Density **:** 1.11 g/cm³

Source : Sigma-Aldrich, Germany

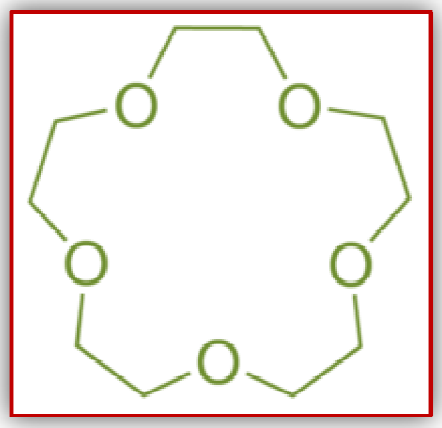


Figure 18(b).15-Crown-5

Purification: Used as purchased without further purification.The Purity is 98%

Application: ***15-Crown-5 is a crown ether that is generally used as a ligand in*** coordination chemistry. It shows the ability to complexes with alkali metal ions. Crown ethers can be used in the laboratory as phase transfer catalysts.

3.2. EXPERIMENTAL METHODS

3.2.1. PREPARATION OF SOLVENT MIXTURES

Solvent mixtures are prepared from pure components which were taken independently in glass stoppered bottles and thermo stated at the needed temperature for adequate time. When the thermal equilibrium was ensured, the requisite volumes of each component were transferred in a dissimilar bottle which was already cleaned and dried methodically. Translation of essential mass of the relevant solvents to volume was skilled by using experimental densities of the solvents at experimental temperature. It was then Stoppard and the mixed contents were shaken well before use. While preparing different solvent mixtures care was taken to ensure that the same process was adopted right through the whole work. The physical properties of diverse pure and mixed solvents have been offered in the relevant chapters.

3.2.2. PREPARATION OF SOLUTIONS

A stock solution for each salt was equipped (digital electronic analytical balance, Mettler Toledo, AG 285, Switzerland) by mass, and the functioning solutions

were obtained by mass dilution. The doubt of molarity of dissimilar salt solutions was evaluated to be ± 0.0003 mol·dm^{-3}.

3.2.3. PREPARATION OF MULTICOMPONENT LIQUID MIXTURES

The double and polycomponent liquid mixtures can be equipped by any one of the procedure discussed below:

(i) Mole fraction

(ii) Mass fraction

(iii) Volume fraction

(i) Mole fraction: The mole fraction (x_i) of the polycomponent liquid mixtures can be equipped 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 mass and molecular mass of i^{th} component, correspondingly. The values of i depends on the number of components implicated in the development of a mixture.

(ii) Mass fraction: The mole fraction (w_i) of the polycomponent liquid mixtures can be equipped using the following relation:

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

(iii) Volume fraction: The volume fraction (ϕ_i) of the poly component liquid mixtures can be equipped by following employing three methods:

a.Using volume: The volume fraction (ϕ_i) of the polycomponent 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$_i$.

b.Using molar volume: The volume fraction (ϕ_i^l) of the polycomponent liquid mixtures can be equipped 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$_i$.

c.Using excess volume: The volume fraction (ϕ_i^{ex}) of the polycomponent liquid mixtures can be equipped 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.

3.2.4. MEASUREMENTS OF EXPERIMENTAL PROPERTIES

3.2.4.1 MEASUREMENT OF MASS

Using digital electronic analytical balance Mettler Toledo, AG 285, Switzerland, mass in various cases were considered.

It can determine mass with a excessive precision and accuracy. The weighing pot is of elevated accuracy and precision (0.0001g) is kept inside a glass enclosed space with sliding doors to save from harm from dust and air currents.

Figure3. 2.1: Analytical balance Mettler Toledo, AG 285

3.2.4.2. WATER DISTILLER

Water from the natural sources is manually or automatically fed into steaming chamber of the distiller unit's. The steam arises from the steaming chamber is

passed through a built-in vent to condenser where the steam gets converted into water which then passes through and store into a container. Minerals and salts due to high boiling point remains in the boiling chamber as hard deposits or scale. The distilled water is then 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 contains a flask with heating elements embedded in glass and fused in spiral type coil internally of the bottom and tapered round glass, joins at the top double walled condenser with B-40/B-50ground glass joints, suitable to work on 220 volt 50 Hz AC supply.

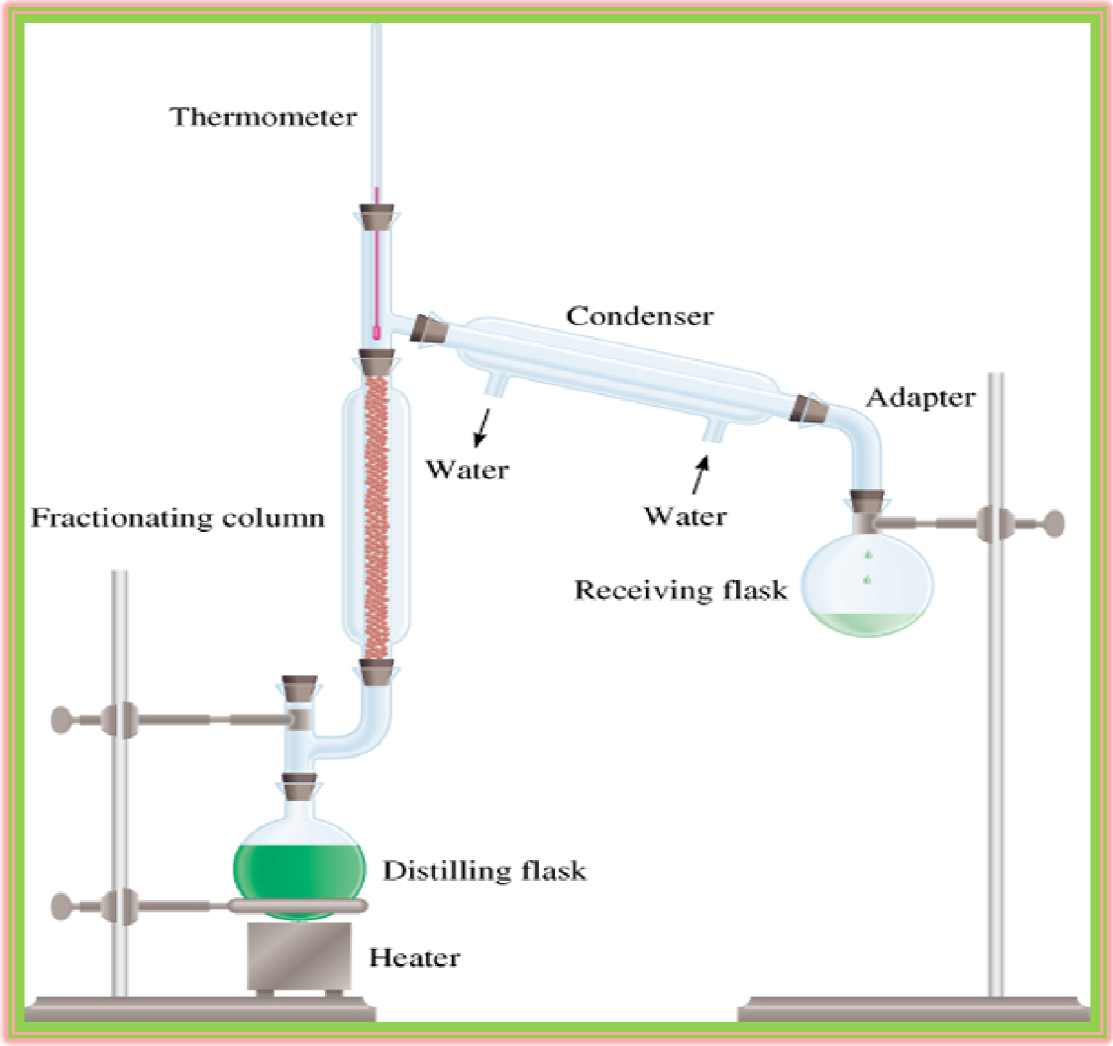


Figure 3.2.2: WATER DISTILLER

3.2.4.3. THERMOSTAT WATER BATH (Science India, Kolkata)

Temperature was controlled using thermostatic water bath and in which the experiments were also carried out. The temperature was maintained with an

accuracy of ± 0.01 K of the desired temperature. Brookfield TC-550 water bath was used for viscometric measurements and other experiments.

Features and Benefits of Brookfield TC-550 water bath

*Provides standalone operation - no tap water required

*Easy control of set-point

*Configured to measure viscosity directly in the bath - accommodates 600 mL beaker

*Programmable Controller version is designed to automate sample temperature control.

*Built-in circulator pumps to external devices.

Figure 3.2.3: THERMOSTAT WATER BATH

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.

3.2.4.4. DENSITY (ρ)

The density can be measured by Anton Paar (DMA 4500 M) GmbH, Austria-Europe, digital density mete , where the density (ρ) of the sample can be calculated by itself in the simple relation $\rho = A \cdot \tau^2 - B$ (III.1)

where A and B are the respective instrument constants,

and τ is the oscillating time period.

The density measurement was performed with the help of Anton Paar DMA 4500M digital density-meter with a precision of ±0.0005 g·cm^{-3}.

Figure 3.2.4: 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 τ can be measured with high resolution and stands in simple relation to the densityρ of the sample in the oscillator : $\rho = A \cdot \tau^2 - B$ (III.1)

A and B are the respective instrument constants of each oscillator. The values of A and B are determined by the calibration with the solutions of two different substances of 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 produce suitable values to balance various influences during the measurement,

Figure 3.2.5: Digital Refractometer (Mettler Toledo 30GS).

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.

3.2.4.5. REFRACTIVE INDEX MEASUREMENT

Refractive index can be measured 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.

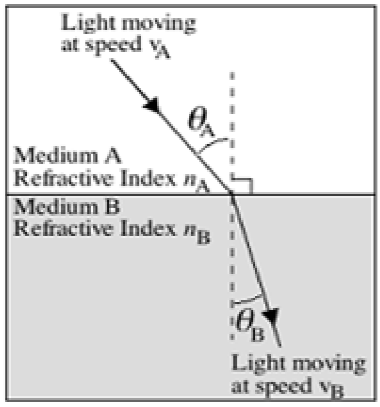
The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the index of refraction (aka refractive index or n_D) for the substance.

$$Refractive\ index\ of\ the\ substance\ (n_D) = \frac{Speed\ of\ light\ in\ a\ vacuum}{Speed\ of\ light\ in\ substance} \qquad \text{(III.2)}$$

$$\frac{V_A}{V_B} = \frac{\sin\theta_A}{\sin\theta_B} = \frac{n_B}{n_A} \qquad \text{(III.3)}$$

Hence, without measuring the speed of light in a sampleits index of refraction can easily be determined. It measures angle of refraction with refractionindex of the layer which isin contact with the solution of the sample andcalculates the refractive index precisely[8][9] Nearly all refractometers utilize this principle, but may differ in their optical design.

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



A light from its source is projected towards the illuminating prism with ground bottom surface that means roughened like a ground-glass joint so that each point on this surface can be regarded as producing light rays to betravelled in all directions. As in figure2 light propagating from point A to point B with largest angle of incidence (q_i) and consequently the largest possible angle of refraction (q_r) for a particular sample. Rest of the rays of light which go into the refracting prism withq_r and consequentlyget revealed to the left of point C. Thus, the detector positioned on the back side of the refracting prism would show a light region to the left and a dark region to the right.

3.2.4.6 CONDUCTIVITY MEASUREMENT

Conductivity measurement was done using Systronics Conductivity TDS meter-308. It can provide both automatic and manual temperature compensation.Systronic Conductivity-TDS meter 308 is a microprocessor based instrument used for measuring specific conductivity of the solution. It can provide both automatic and manual temperature compensation. Provision for storing the cell constant and 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 re calibrating the instrument even after switching it off.

Fig3.2.6:Systronic-308 Conductivity Bridge

The conductance measurements were carried out on this conductivity bridge of accuracy ±0.01%, using a dip-type immersion conductivity cell, CD-10 having a cell constant of approximately (0.1±0.001) cm^{-1}. Measurements were made in a thermostate water bath maintained at T = (298.15 ± 0.01) K. The cell was calibrated by the method proposed by Lind et al[4]and cell constant was measured based on 0.01 M aqueous KCl solution[5]. During the conductance measurements, cell constant was maintained within the range 1.10–1.12 cm^{-1}. The conductance data were reported at a frequency of 1 kHz with the accuracy of±0.3%. 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 stopadmittance of air into the cell during the addition of solvent or solution. 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[6].

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.

3.2.4.7. VISCOSITY MEASUREMENT

Brookfield DV-III Ultra Programmable Rheometer: 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

$$\eta = (100 / RPM) \times TK \times \text{torque} \times SMC \qquad (\text{III.4})$$

Where, *RPM*, *TK* (0.09373) and *SMC* (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively. The calibration of the instrument wasdone using the standard viscosity sample solutions supplied with the instrument, water and aqueous $CaCl_2$ solutions[7].The temperature was maintained to within ± 0.01°C using Brookfield Digital TC-500 thermostat bath. This instrument provides viscosity values with an accuracy of ± 1 %. Each measurement was reported as an average of three separate reading with a precision of 0.3 %.

Figure 3.2.7 : Brookfield DV-III Ultra Programmable Rheometer

3.2.4.8. SURFACE TENSION MEASUREMENT

Surface tension was 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.

Figure 3.2.8 : Digital Tensiometer KRUSS K9 (Germany)

3.2.4.9. FT-IR MEASUREMENT

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

Figure 3.2.9 : 8300 FTIR spectrometer (Shimadzu, Japan)

The intensity of light (I_0) passing through a blank is measured. The intensity is the number of photons per second. The blank solution is identical to the sample

solution only differing inthe case that it does not contain the substrate which 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 lightper second, which is the result of the flow of the photons per second (or intensity) and the energy per photon. The experimental data is used to calculate two quantities: the transmittance (*T*) and the absorbance (*A*).

$$T = \frac{I}{I_0}; \qquad A = -log_{10}\, T \tag{III.5}$$

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

3.2.4.10. UV-VIS SPECTRA MEASUREMENT

Compounds that absorb Ultraviolet and/or visible light have characteristic absorbance curves as a function of wavelength. Absorbance of altered wavelengths of light arises as the molecules travel to upper 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 from a specially designed mirror, the light beam travels through a narrow slit and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. A filter is used to remove unwanted higher orders of diffraction. There is a half mirror where half of the light is reflected and the other half passes through. Before the half mirror the light beam hits a second mirror to avoid the splitting. The spectra of the solvent is first recorded and saved to use it further as reference while recording the spectra of the sample.

Figure 3.2.10: The UV-VIS spectrophotometer

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 *bcI* or $dI/I = -kbc$ (where *k* is a proportionality constant, this makes *b*, *c* and *I* always positive. equation leads to Beer-Lambert's law [11]:

$$-\ln I/I_0 = kbc \qquad \text{(III.6)}$$

$$-\log I/I_0 = 2.303kbc \qquad \text{(III.7)}$$

$$\varepsilon = 2.303k \qquad \text{(III.8)}$$

$$A = -\log I/I_0 \qquad \text{(III.9)}$$

$$A = \varepsilon bc \qquad \text{(III.10)}$$

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.

3.2.4.11. NMR SPECTRA MEASUREMENT

As on the strength of the magnetic field the resolution is mainly dependent, the NMR spectrometers are designed with very strong, big and liquid helium-cooled superconducting magnet. Less expensive machines where permanent magnets are used are also available, which still give sufficient performance for certain application such as reaction monitoring and quick checking of samples but resolution is quite low.

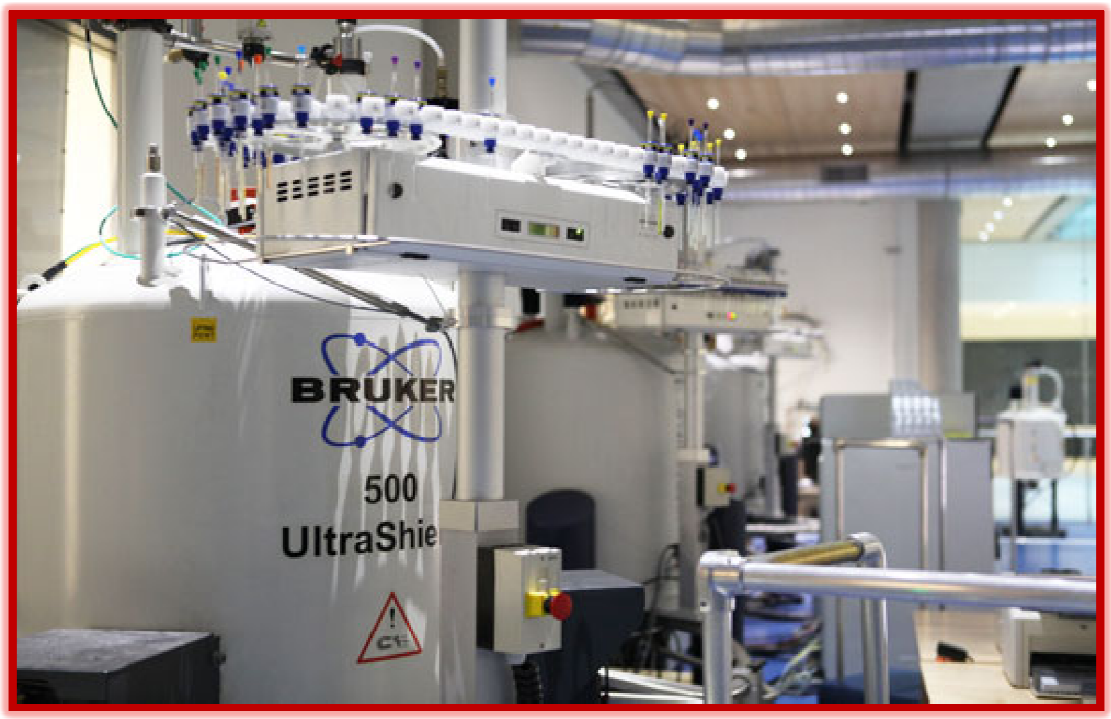


Figure 3.2.11 : Bruker AVANCE 500

The protons of the solvents, as most regular solvents are hydrocarbons, are NMR active. While recording the NMR spectra often known solvent residual proton peak was taken as the internal standard where applicable instead of

Adding tetramethylsilane NMR spectra were recorded in D2O unless otherwise stated. ^{1}H NMR spectra were recorded at 300 MHz and 400 MHz using Bruker

AVANCE 500 MHzand Bruker AVANCE 400 MHz instruments respectively at 298.15K. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard (D2O : δ 4.79 ppm). Data are reported as chemical shift[12][13].

3.3. REFERENCES

References of CHAPTER III are given in BIBLIOGRAPHY (Page No.288-289)