CHAPTER 1

Introduction
1.1. **An overview on cyclodextrin**

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The individual glucose units are held in a C-1 chair conformation and they are joined together by α-1,4glycosidic linkages to form a cyclic structure. The CDs are also known as Schardingerdextrins, cycloglucopyranoses, cycloamyloses, cycloglucans, and cyclomaltooligoses. The discovery and the first work on CDs are attributed to Villiers in 1891, who isolated them as degradation products of starch. In 1904, Schardinger was the first to describe their preparation and properties in details. In 1988, Clarke et al. published an interesting historical review on the discovery, the determination of the structure, the formation from starch, and the inclusion properties of CDs [1]. CDs having fewer than six ring glucose residues cannot be formed because of steric reasons and hence are unknown. Although CDs containing as many as twelve glucose units were identified, only the first three homologues were studied in details. The three smallest CDs, alpha-cyclodextrin (cyclohexaamylose, α-CD), beta-cyclodextrin (cycloheptaamylose, β-CD) and gamma-cyclodextrin (cyclooctaamylose, γ-CD), which consist of six, seven, and eight α-1,4 linked D(+)-glucopyranose units respectively, are well known and are available commercially. Higher homologues exist but they are difficult to prepare and purify on an industrial scale. Endo et al. reported the isolation, purification, and characterization of cyclomaltodecaose, cyclomaltoundecaose, and cyclomaltotridecaose containing ten, eleven, and thirteen glucopyranose units, respectively [2]. The structure and the molecular dimensions of α-, β-, and γ-CD are shown in Figure 1.1.
As a consequence of the C-1 conformation of glucopyranose units [3-5], all secondary hydroxyl groups are situated on one of the two edges of the toroidal ring of the CD molecule, while all primary hydroxyl groups are on the other side (Figure 1.1). The primary hydroxyl groups attached to C-6 of the glucose unit form a smaller opening. Thus, the CD molecule is shaped like a truncated cone with the secondary hydroxyl side more open than the primary hydroxyl side. While the primary hydroxyl groups can freely rotate to block the cavity partially, the secondary hydroxyl groups are held relatively rigidly. The interior of the cavity is lined by a ring of hydrogen atoms bonded to the C-5 atom, a ring of glycosidic oxygen atoms, and another ring of hydrogen atoms at position C-3. As a result, inside of the cavity is relatively hydrophobic (apolar cavity). The glycosidic oxygen bridges produce a high electron density (a Lewis character). Since all of the hydroxyl groups are on the outside of the molecule, the external faces are hydrophilic. The shape of the molecule is stabilized by hydrogen bonds between the secondary hydroxyl groups of adjacent D-glucopyranosyl residues. All these features enable CDs to form inclusion complexes with other molecules.

CDs are soluble in water, and the solubility increases with temperature. β-CD has the lowest solubility of all native CDs. The CD solubility decreases in the presence of
organic solvents. The $\alpha$- and $\beta$-CD are insoluble in solvents like methanol, ethanol, isopropanol, acetone, chloroform, and tetrahydrofuran. Dimethylformamide is a good solvent for $\alpha$- and $\beta$-CD. Another important feature of CDs is chairality which appears due to presence of D (+)-glucopyranose units. Each of the glucose units contains five chiral centres and two secondary hydroxyl groups at the entrance to the cavity that enable hydrogen bonding. Thus, a combination of the inclusion process and the chiral centers of the CD molecules provide the enantioselectivity.

### 1.1.1. Role of Cyclodextrin in separation of organics

The structure of CD gives rise to the remarkable ability to form inclusion complexes with inorganic [6-10], organic (benzene and phenol derivatives, amino acids, barbiturates, prostaglandins, pesticides, glycolipids, proteins, tryptophan) [11-19] and ionic compounds [6, 7], and also with polymers [20-27]. Encapsulation of a molecule changes its physicochemical properties with regard to hydrolysis, oxidation, photolysis, volatility, and solubility, and also its chemical reactivity. Native, derivatized, and modified CDs and their inclusion properties have several applications in different fields such as organic and polymer synthesis [6, 28-32], catalysis [33-36], pharmaceuticals [11, 37-40], biotechnology [41-44], foods [7, 45], supramolecular chemistry [46-48], and chromatography [9, 49-62]. In particular, the selective properties of CDs and their derivatives can be employed in all chromatographic techniques for the separation of structural, geometric, and optical isomers. They are used in HPLC [8-9, 49-51], TLC [7, 52], GC [8, 10, 53-55], affinity chromatography [56, 57], ion-exclusion chromatography [58], preparative chromatography [59], electrophoresis [60, 61] and micellarelectrokinetic chromatography [62]. They were
employed successfully as selective components in the mobile phase and as stationary phase. Selection of Cyclodextrin is based on unique characteristics of uniform macromolecular structure, molecular self-assembling etc [63]. Due to its ability to form host-guest complexes with organic components having appropriate diameters and physical interactions, it can also be used for host guest chemistry [64, 65].

Environmental aspects of aromatic organic solvents have become increasingly important in recent years [11]. Frequently encountered solvents of concern are methanol, ethanol, butanol, DMF, DMA, DMSO, BTX, acetone, acetic acid etc. The dilute aqueous/organic solution containing these solvents may be generated in reaction effluent, downstream processing and as waste stream. Recovery of solvent is needed for recycling and production of high quality solvent which is generally used in electronic industries (chip processing). The recovery of solvents using membranes is more prominent as large volume of liquid complex is separated.

Cyclodextrin-polysulfone (CD-PS) composite can be used as nanostructural material for membrane preparation and evaluation for solvent recovery in nanofiltration (NF) mode. CD is expected to provide good membrane morphology, however a very limited study is available in literature [66-69]. Hence, we have attempted to study the membrane formation capability of CD composite with polysulfone.

Membrane is a permeable selective barrier that restricts the motion of particles through it, and they differ in their applications and structures. They operate in different ways and their main objective is to separate one component from a mixture by allowing the component to permeate though it. It has the ability to transport one component more readily
than other components because of the differences in physical and/or chemical properties between the membrane and the permeating component. The membrane performance is controlled by two factors: membrane selectivity of the solute in the solution, and the flux of the solvent through the membrane. To gain the best separation results, the membrane must be thermally stable, must possess high selectivity toward the solutes, high permeability and chemical resistance. Membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, and may be either neutral or carry positive charge, negative charge or both charges. The separation process can be achieved because of difference in size, and also physical and chemical structures between the different components in the solution. Membrane separation process occurs at ambient temperature; as a result, if the solution is insensitive toward temperature, it can be treated without the constituents of being damaged or chemically altered. Membrane separation process is faster, more efficient and more economical than conventional separation techniques. The advantages of membrane separation process are as follows:

1. Separation occurs continuously.
2. Energy consumption is low.
3. Membrane process can be combined with other separation processes.
4. Separation can be carried under mild conditions.
5. Separation process can be up-scaled easily.
6. Membranes have different properties and can be adjusted.
7. No additives are required.

Only disadvantage of membrane is membrane fouling due to concentration polarization.
A membrane has the property of being selective towards molecules, where the molecules either can permeate through the membrane or be rejected by the membrane. The membrane selectivity is determined by the flux through the membrane and the membrane itself. Membrane separation technology involves different kinds of processes, which can be divided into the followings:

1. First generation of membrane process, which includes microfiltration, ultrafiltration, hyper-filtration, nanofiltration, reverse osmosis, electrodialysis and dialysis.
2. The second generation of membrane processes, which include gas separation, pervaporation, membrane distillation and separation by liquid membranes.

An example of a membrane process that would be a good choice to be considered is the nanofiltration membrane process, where it can be used in treating water such as removing organic and inorganic compounds, removing hardness, removing viruses and bacteria, pesticides and also removing taste and odours. Thus, with the ability to do what have been mentioned gives nanofiltration membrane more favour over conventional desalinating processes because they cannot perform such job in one stage and need additional processes to complete the needed task. In the case of treating brackish water, nanofiltration has the advantages of being selective towards ions types, operates at low applied pressure values and has a high permeate flux. Reverse osmosis is considered more efficient process because it has higher rejection rates than nanofiltration. Nonetheless, reverse osmosis requires higher applied pressure than nanofiltration which would result in higher operating costs. In addition, in some cases minerals have to be added to the treated
water by reverse osmosis, which again increases the operating cost. On the other hand, nanofiltration has lower rejection than reverse osmosis, where some compounds permeates through it and the resulting product would be as desired. Thus to make nanofiltration process more usable and efficient, in-depth understanding is necessary to understand its separation behaviour, so that it could be optimised and made more efficient to be used in real life.

Membrane process is a new approach that is being considered in treating brackish water because of its capability of being able to reject ions and its selectivity towards ions. Hence, the work would be more concerned with the first generation of membranes especially the nanofiltration membrane process. Nanofiltration membrane is a pressure-driven membrane with properties that lie between ultrafiltration and reverse osmosis. Since there are several uses for nanofiltration membrane, there is a need to try to understand its separation behaviour and to improve its separating mechanism, especially in the separation of organics.

Membrane science has become an emerging area of research and development in view of its importance for separation and extraction of various molecules advantageously [70, 71]. Membranes have gained an important position chemical technology and are used for a broad range of separation problems. The driving forces in the membrane are considered interdependent; for example, the concentration gradient across the membrane may not only cause mass flow but also build-up of a hydrostatic pressure difference, which is known as osmosis. Another example is that the gradient of a hydrostatic pressure may not only cause volume flow but also the formation of a concentration gradient, which is known
as reverse osmosis. In the membrane separation process, the important driving forces that lead to a significant flux are as follows:

1. **Hydrostatic pressure**: If the hydrodynamic permeability of the membrane is different for different solutes, the difference in the hydrostatic pressure between the two phases separated by a membrane can lead to a volume flux and separation of solutes.

2. **Concentration difference**: The difference in concentration between two phases separated by membrane can lead to the transport of solute and the separation of different types of solutes, when the diffusivity and concentration for the different solute types are different.

3. **Electrical potential**: The difference in electrical potential can cause the transport and separation of solute when the different charged particles show different mobility through the membrane.

The driving force can either be pressure difference ($\Delta P$), concentration difference ($\Delta C$), temperature difference ($\Delta T$) or electrical potential difference ($\Delta E$). The membrane processes can be classified according to their driving force as follows:

**Table 1.1: Membrane Processes.**

<table>
<thead>
<tr>
<th>$\Delta P$</th>
<th>$\Delta C$</th>
<th>$\Delta T$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>Gas separation</td>
<td>Pervaporation</td>
<td>Electrodialysis</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Vapour permeation</td>
<td>Membrane distillation</td>
<td>Electro-osmosis</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Dialysis</td>
<td>Thermo-osmosis</td>
<td>Membrane electrolysis</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Diffusion dialysis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.1.2. Membrane using pressure difference as a driving force

Pressure-driven membranes can be used to concentrate or purify a dilute solution. The membrane pore size and the pore size distribution are determined by the solute properties such as the solute molecule size and the solute chemical properties. The membranes that use the pressure as a driving force include microfiltration, ultrafiltration, nanofiltration and reverse osmosis (hyper filtration). The driving force in the pressure-driven process is the applied pressure, where the solvent permeates through the membrane and the solute in the feed solution is rejected. The difference between microfiltration, ultrafiltration, nanofiltration and reverse osmosis is the size of the separated molecule and membrane pore size. The pore size decreases from microfiltration to ultrafiltration to nanofiltration and finally to reverse osmosis, and as a result the applied pressure and the membrane resistance increases. The flux through these processes is inversely proportional to the membrane effective thickness.

Table 1.2: Membrane separation.

<table>
<thead>
<tr>
<th>Factors</th>
<th>MF</th>
<th>UF</th>
<th>NF</th>
<th>RO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driving Force</td>
<td>Pressure difference</td>
<td>Pressure difference</td>
<td>Pressure Difference</td>
<td>Pressure difference</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>0.2-3.5 bar</td>
<td>1-10 bar</td>
<td>15-40 bar</td>
<td>30-60 bar</td>
</tr>
<tr>
<td>Average flux</td>
<td>&gt;200 Lm$^{-1}$h$^{-1}$</td>
<td>5-200 Lm$^{-1}$h$^{-1}$</td>
<td>20-80 Lm$^{-1}$h$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Mechanism</td>
<td>Size exclusion</td>
<td>Size exclusion &amp; Solution diffusion</td>
<td>Pore flow</td>
<td>Solution diffusion</td>
</tr>
<tr>
<td>Performance affected by</td>
<td>Adsorption</td>
<td>Pressure Temperature Concentration Ionic environment</td>
<td>Pressure Temperature Concentration Ionic environment</td>
<td>Pressure Temperature Concentration</td>
</tr>
<tr>
<td>Filtration Type</td>
<td>Dead end</td>
<td>Cross flow</td>
<td>Electrostatic interaction</td>
<td>Dead end</td>
</tr>
</tbody>
</table>
1.1.3. An overview of nanofiltration

Nanofiltration (NF) is a recent development in membrane technology. It is a pressuredriven process falling in between Reverse Osmosis (RO) and Ultrafiltration (UF). RO has lower flux at higher operating pressure and is used for demineralization or total dissolved solid removal, while UF can provide higher flux at lower operating pressure and can remove macromolecules (humic acid, fulvic acid etc.). However, it can not remove salts, acids, sugars etc. On the other hand, the NF process combines the attributes of RO and UF with the ability to reject macromolecules and multivalent ions effectively at moderate operating pressure. Effective removal of salts, trihalomethane formation potential (THMFP), heavy metals, colour, virus, bacteria and parasites from water and wastewater is possible by NF. Thus, NF can play a significant role as an advanced treatment of water and wastewater.

In the 1970's, Israel Desalination Engineering coined the word "Hybrid Filtration" for a process which operates between RO and UF pressure ranges. This process showed sodium chloride rejection in the range of 50-70% and organics in the range of 90%. The main disadvantage of hybrid filtration is that it does not clearly describe the type of filtration. It might as well be something between media filtration and cartridge filtration. In the early 1980s, FilmTech developed a new type of membrane. At permeate flux of about 34 Lm⁻²h⁻¹, this membrane showed a solute rejection of about 10% for high strength sodium chloride solution and about 99% for sucrose solution. It did not seem right to call it a RO membrane because of its low rejection of sodium chloride, or to call it an UF membrane because of its almost complete rejection of sucrose. Again, there is no universally accepted
definition of RO and UF membrane, which would force this new membrane into one of these categories. It is widely accepted that solvent and solute transport through a RO membrane is by diffusion and through an UF membrane is by convection flow through pores. The new membrane should probably be a RO membrane. But to distinguish it from RO membrane with high rejection of sodium chloride, FilmTech coined the term \textit{nanofiltration} (NF) membrane. In fact the name NF is derived in way analogous to \textit{microfiltration} (MF). When more than 95\% of solute of minimum size in the order of $1 \, \mu m$ can be removed by a membrane, it is MF; that in the order of $1 \, nm$ can be removed by a membrane it is NF. NF membrane process is commercially available since 1986.

The material used for NF membrane fabrication is organic in nature and most NF membranes are multiple layer thin-film composites of organic polymer. The active membrane layer usually consists of negatively charged chemical groups. The membranes comprise of pores, with an average pore diameter of $2 \, nm$. The modules used for NF are flat sheets (plate and frame type), hollow fibre and spiral wound. Hollow fibre and spiral wound type are suitable for pilot and industrial scale, while flat sheet type is used for laboratory scale operation. Flux in spiral wound is higher than that of hollow fibre, but the major advantage of hollow fibre module is that its removal efficiency is comparatively high so pretreatment of feed water is less required. Since pore size of NF membrane is very small, like RO, NF membranes are sometimes characterized by molecular weight cut-off (MWCO) (the lowest molecular size efficiently rejected by membrane). The MWCO for NF ranges from 100-200. The MWCO for UF is greater than 1000 and that for RO is less than 500. In fact, no membrane has a sharp cut-off range. There must be some grey area
between RO, NF and UF. The cut-off range for NF may be closer to RO or UF or in between the two, depending on the rejection requirements.

Separation by NF membrane follows two mechanisms, namely:

1. **Physical**: Due to very small pore size (in the order of few nm), neutral organic compound with molecular weight above 200 are rejected by the sieving mechanism.

2. **Electrostatic interaction**: In general NF membranes are negatively charged and salt rejection occurs by electrostatic repulsion of anions. The higher the charge on the anion, greater the salt rejection.

Most NF membranes contain negatively charged hydrophilic groups attached to a hydrophobic UF support membrane and they possess higher water flux. This is due to the favourable orientation of dipole of water molecules. Again due to the surface active groups, they also possess improved fouling resistance against hydrophobic colloids, oils, proteins and other organics.

Industrial applications of nanofiltration are quite common in food and dairy sector, chemical processing, pulp and paper industry, and textiles, although the chief application is in the treatment of fresh, process and waste waters. In treatment of water, NF is specifically used in polishing at the end of conventional processes. It cannot be used for water desalination, but it is an effective means of water softening, as the main hardness chemicals are divalent. NF membranes are also used for the removal of natural organic matter from water, especially tastes, odours and colours, and in the removal of trace herbicides from large water flows. They can also be used for the removal of residual quantities of disinfectants in drinking water. In processing of sugar, dextrose syrup and thin sugar juice
are concentrated by NF, while ion exchange brines are demineralised. NF is used for
degumming of solutions in the edible oil processing sector, for continuous cheese
production, and in the production of alternative sweeteners. There are probably as many
different applications in the whole chemical sector (including petrochemicals and
pharmaceuticals) as in the rest of industry put together. Many more are still at the
conceptual stage than are in plant use, but NF is a valuable contributor to the totality of the
chemicals industry. The production of salt from natural brines uses NF as a purification
process, while most chemical processes produce quite vicious wastes, from which valuable
chemicals can usually be recovered by processes with NF. The high value of many of the
products of pharmaceutical and biotechnical sectors allows the use of NF in their
purification processes. The paper pulp industry uses a great quantity of water in its
production processes, a quantity that the industry is striving to reduce, mainly by “closing
the water cycle” – a system in which the purification properties of NF have a major role.
All of these specifically mentioned applications have been water based, but nanofiltration is
not restricted to the treatment of aqueous suspensions. Indeed one of the largest NF plants
was installed at a petroleum refinery for the dewaxing of oils. Boam and Nozari [72], in
their review of organic solvent nanofiltration, point out that many organic system
separation processes are quite highly energy intensive, and that, by contrast, OSN can be
quite an energy saving alternative (for example, by comparison with distillation). In
aqueous systems, nanofiltration uses hydrophilic polymeric materials, such as
polyethersulphone, polyamides and cellulose derivatives. These materials, in contact with
organic solvents, quickly lose their stability. Special membranes have therefore been
developed to provide the same kind of performance as in aqueous systems, and they are now used for solvent exchange, solvent recovery and separation for catalyst recovery and also for heavy metal removal. An overview of the applications of NF in various industrial areas is shown in Table 1.3.

Table 1.3: Possible applications of nanofiltration in various industries.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food</td>
<td>Demineralisation of whey [73-75]</td>
</tr>
<tr>
<td></td>
<td>Demineralisation of sugar solutions [76]</td>
</tr>
<tr>
<td></td>
<td>Recycle of nutrients in fermentation processes [77]</td>
</tr>
<tr>
<td></td>
<td>Separation of sunflower oil from solvent [78,79]</td>
</tr>
<tr>
<td></td>
<td>Recovery of Cleaning-In-Place solutions [80,81]</td>
</tr>
<tr>
<td></td>
<td>Recovery of regeneration liquid from decolouring resins in sugar industry [82-85]</td>
</tr>
<tr>
<td></td>
<td>Effluent treatment [86]</td>
</tr>
<tr>
<td></td>
<td>Purification of organic acids [87-89]</td>
</tr>
<tr>
<td>Textile</td>
<td>Separation of amino acids [90, 91]</td>
</tr>
<tr>
<td></td>
<td>Removal of dyes from waste water [92]</td>
</tr>
<tr>
<td>Clothing and leather</td>
<td>Recovery of water and salts from waste water [93-99]</td>
</tr>
<tr>
<td>Paper and graphical</td>
<td>Recovery and reuse of chromium(III) and chromium(II) [100-102]</td>
</tr>
<tr>
<td>Chemical</td>
<td>Recovery of water from waste water or waste water treatment effluent [103-106]</td>
</tr>
<tr>
<td></td>
<td>Recovery of bleaching solution [107-109]</td>
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<tr>
<td></td>
<td>Sulfate removal preceding chlorine and NaOH production [110, 111]</td>
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<tr>
<td></td>
<td>CO₂-removal from process gasses [108]</td>
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<tr>
<td></td>
<td>Preparation of bromide [107]</td>
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<tr>
<td></td>
<td>Recovery of caustic solutions in cellulose and viscose production [110]</td>
</tr>
<tr>
<td></td>
<td>CaSO₄ precipitation [112]</td>
</tr>
<tr>
<td>Metal plating and</td>
<td>Separation of heavy metals from acid solutions [87]</td>
</tr>
<tr>
<td>product/electronic and</td>
<td>Removal of metal sulfates from waste water [110]</td>
</tr>
<tr>
<td>optical</td>
<td>Cleaning of machine rinsing solutions [108]</td>
</tr>
<tr>
<td></td>
<td>Removal of Nickel [113]</td>
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<tr>
<td></td>
<td>Recovery of Cu-ions from ore extraction liquids [107]</td>
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</tbody>
</table>
Table 1.3 shows the diversity of opportunities for nanofiltration and it can be expected that many are to follow or already exist. However, most of the examples mentioned above are developed on a trial and error basis and not from basic process knowledge.

This means that these processes can run at sub-optimal conditions and even membranes with better properties for the application might be available. Improvement of these processes either by finding the optimal conditions or using better membranes will result in economic gain.

1.2. Theoretical Aspect

The host-guest interactions play an important role in recovery of organic solvents. Therefore, knowledge of the interactions between the two is significant for better understanding of membrane phenomena.
Quantum mechanical methods such as Hartree-Fock or density functional theory (DFT) are quite useful in understanding the interactions in molecular systems (hydrogen bonding and electrostatic). This method is widely used to quantify interactions and its success in this aspect is documented well [137]. Even though CD drew the attention of many researchers, because of computational cost, only few computational studies have been reported earlier [138-140]. Different methods are used to understand the host-guest interactions in larger systems like complexes of CDs or their derivatives [141-149]. An intermediate value of interaction energy indicates that the rate of adsorption of alcohols on CD membrane is governed by the host-guest interaction [150].

In recent years, density functional theory (DFT) has proved its applicability to interpret chemical reactivity in complex phenomenon [150]. Moreover, density functional reactivity theory (DFRT) is used to estimate reactivity parameters. The reactivity descriptors, defined within the framework of DFT, are global hardness, electrophilicity, chemical potential, local softness, Fukui functions etc [151]. These descriptors have been tested and studied by several research groups and are found to be very useful in explaining the reactivity patterns in the molecular systems [152-155].

1.3. **Aim of the Present Study**

The main objectives of the research work are:

1. Preparation of CD composite nanostructured membranes and characterization of the membranes in respect of thickness, pore size and distribution, critical surface tension etc. To study the solvent effect on membrane formation and establish the phase diagram for ternary system.
2. To study the adsorption of certain organic solvents such as acetic acid, methanol, ethanol, butanol on membrane and interpretation of adsorption isotherms.

3. To study the separation of organic solvents from aqueous solvent by nanostructured membrane. Also, to develop a suitable flux model for permeation of organic solvents through NF membrane and to calculate the interaction energies between membrane components and permeate.

4. To perform QM/MM studies on for understanding of cyclodextrin-alcohol interaction.

5. To observe the effect of external electric field on CD-alcohol adduct.
1.4. References


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