

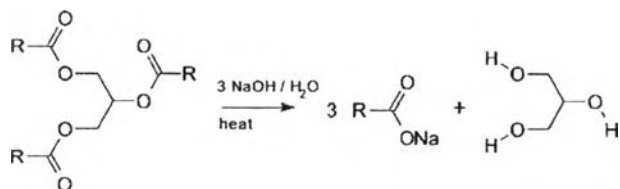
## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Glycerol

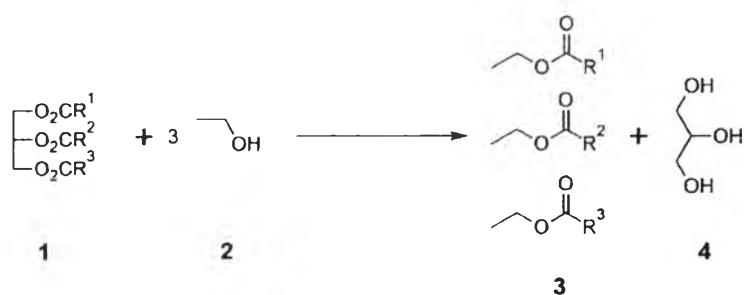
Glycerol (or glycerine, glycerin) is a simple polyol (sugar alcohol) compound (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>). It is a colorless, odorless, viscous liquid. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol backbone is central to all lipids known as triglycerides. Glycerol is sweet-tasting and of low toxicity. It is soluble in water in all proportions with evolution of heat. It has powerful solvent properties, combining in this respect those of water and alcohol.

Triglycerides found in fats and oils are by definition esters of glycerol with long-chain carboxylic acids; the hydrolysis (saponification) or transesterification of these triglycerides produces stoichiometric quantities of glycerol. In this scheme, glycerol is produced as a co-product in the production of long-chain carboxylate salts used as soaps.



**Figure 2.1** Glycerol produced from hydrolysis of triglycerides.

It is also a byproduct of the production of biodiesel via transesterification which is used in this research. This form of crude glycerol is often dark in appearance with a thick, syrup-like consistency. Triglycerides are treated with an alcohol such as ethanol with catalytic base to give ethyl esters of fatty acids and glycerol.



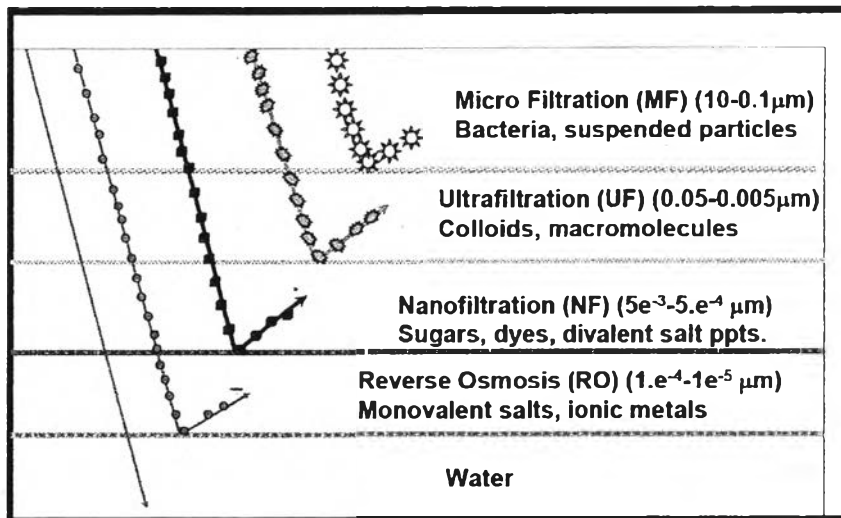
**Figure 2.2** Glycerol from biodiesel production via transesterification.

High-purity glycerol is one of the most important industrial feedstocks such as filler in commercially prepared low-fat foods, a thickening agent in liqueurs, a means of improving smoothness or providing lubrication in medical application. Glycerol is a component of glycerin soap. Essential oils are added for fragrance. This kind of soap is used by people with sensitive, easily-irritated skin. In addition, it is used to produce nitroglycerin, which is an essential ingredient of various explosives such as dynamite, gelignite, and propellants like cordite.

A great deal of research is being conducted to try to make value-added products from crude glycerol (typically containing 20% water and residual esterification catalyst) obtained from biodiesel production. The use of crude glycerin as an additive to biomass for a renewable energy source when burned or gasified is also being explored.

## 2.2 Ultrafiltration

Ultrafiltration (UF) is a variety of membrane filtration in which forces like pressure or concentration gradients leads to a separation through a semipermeable membrane. Suspended solids and solutes of high molecular weight are retained in the membrane, while water and low molecular weight solutes pass through the membrane in the permeate. This separation process is used in industry and research for purifying and concentrating macromolecular (103 - 106 Da) solutions, especially protein solutions. Ultrafiltration is not fundamentally different from microfiltration, nanofiltration or reverse osmosis except in terms of the size of the molecules which it retains as showed in Figure 2.3.



**Figure 2.3** Comparison of each-membrane separation capability.

For using as pretreatment of glycerol, Shee-Keat Mah et al., (2012) have investigated A feasibility on ultrafiltration of palm oil and oleic acid removal from glycerol solutions: Flux decline, fouling pattern, rejection and membrane characterizations. Ultrafiltration membrane is proven to be capable in removing palm oil and fatty acid from the glycerol solution with sustainable flux for approximately an hour if pH and the ratio of oil and acid is suitable.

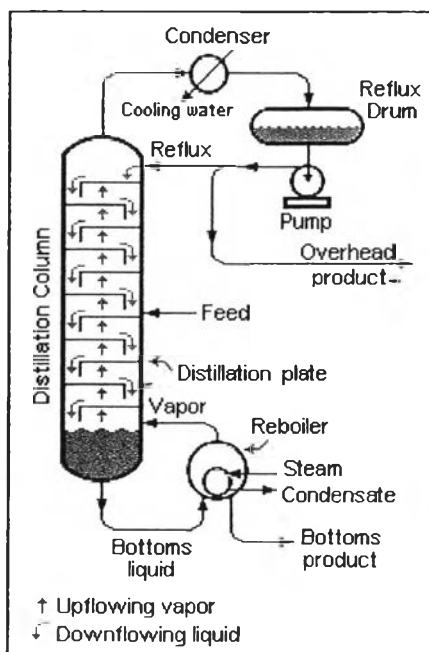
## 2.3 Desalination technologies

Desalination, demineralization or desalting refers to any of several processes that remove some amount of salt and other minerals from saline solution. Main technologies to desalinate the salt are the following.

### 2.3.1 Distillation

The well-known technology used for desalinate glycerol are thermal systems or distillation that heat brine solution in vacuum conditions, causing the solvent to evaporate and subsequently condense as pure solvent. Namely, it is an established technology that produces high-purity glycerin in high yield. However, The drawback of this technic is its intense energy consumption since it has a high heat capacity, which demands a high-energy input for vaporization . So the operating cost

will be very high and can only be founded in oil and gas industries. Distillation is the most commonly practiced method for purifying glycerin.



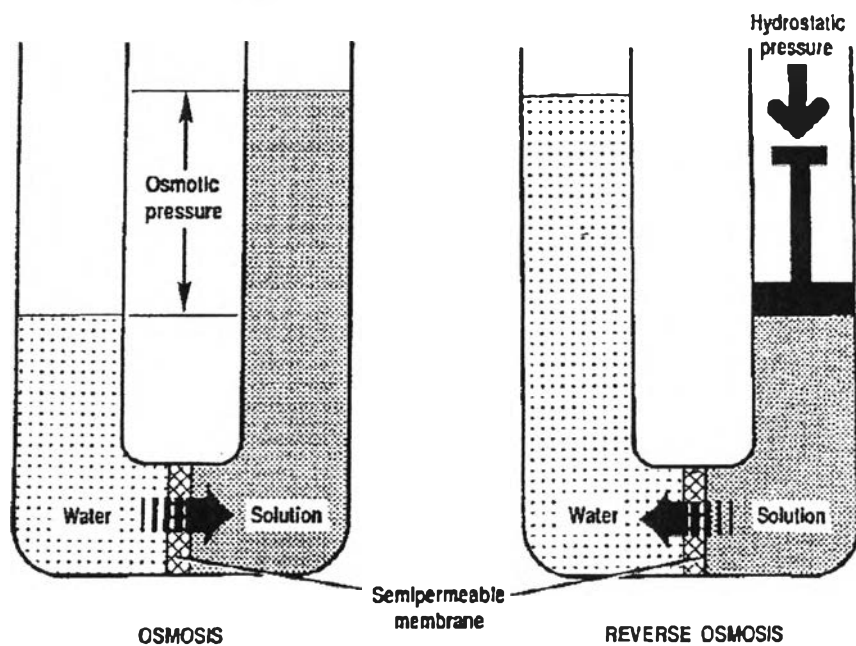
**Figure 2.4** Diagram of a typical industrial distillation tower.

### 2.3.2 Reverse Osmosis

Reverse osmosis (RO) is a purification technology that uses a semipermeable membrane. This membrane technology is not properly a filtration method. In reverse osmosis, an applied pressure is used to overcome osmotic pressure, a colligative property, that is driven by chemical potential, a thermodynamic parameter. Reverse osmosis can remove many types of molecules and ions from solutions, and is used in both industrial processes and the production of potable water. The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. To be "selective", this membrane should not allow large molecules or ions through the pores (holes), but should allow smaller components of the solution (such as the solvent) to pass freely.

In the normal osmosis process, the solvent naturally moves from an area of low solute concentration (high water potential), through a membrane, to an area of high solute concentration (low water potential). The movement of a pure solvent is driven to reduce the free energy of the system by equalizing solute

concentrations on each side of a membrane, generating osmotic pressure. Applying an external pressure to reverse the natural flow of pure solvent, thus, is reverse osmosis. The process is similar to other membrane technology applications. However, key differences are found between reverse osmosis and filtration. The predominant removal mechanism in membrane filtration is straining, or size exclusion, so the process can theoretically achieve perfect exclusion of particles regardless of operational parameters such as influent pressure and concentration. Moreover, reverse osmosis involves a diffusive mechanism, so that separation efficiency is dependent on solute concentration, pressure, and water flux rate. Reverse osmosis is most commonly known for its use in drinking water purification from seawater, removing the salt and other effluent materials from the water molecules.



**Figure 2.5** Reverse osmosis process.

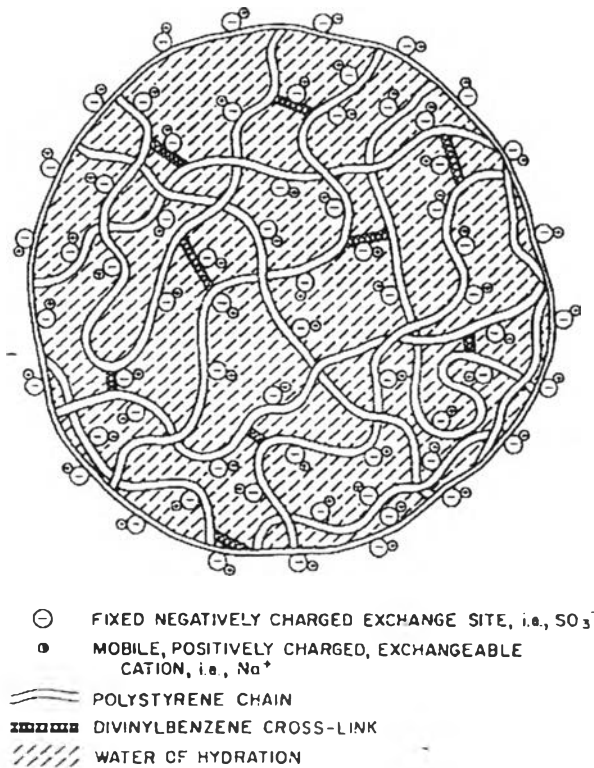
However, this process can not be operate with viscous liquid since it require too much pressure and it is impossible for membrane to handle this. So it can not be used to treat glycerol solution which is very viscous compared to the water.

### 2.3.3 Ion Exchange Resin

Ion exchange resins are polymers that are capable of exchanging particular ions within the polymer with ions in a solution that is passed through them. This ability is also seen in various natural systems such as soils and living cells. The synthetic resins are used primarily for purifying water, but also for various other applications including separating out the salt.

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers).

The resins are prepared as spherical beads 0.5 to 1.0 mm in diameter. These appear solid even under the microscope, but on a molecular scale the structure is quite open. Figure 2.6 show that a solution passed down a resin bed can flow through the crosslinked polymer, bringing it into intimate contact with the exchange sites.



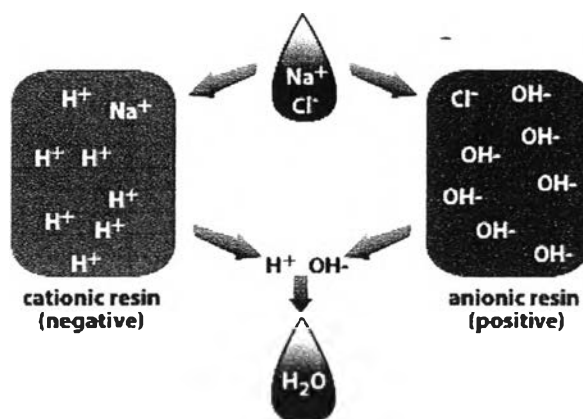
**Figure 2.6** Expanded view of polystyrene bead.

A bed of resin can be used either to remove unwanted ions from a solution passed through it or to accumulate a valuable mineral from the solution which can later be recovered from the resin. Examples of the removal of unwanted ions are the removal of heavy metals from metal trade wastes, the demineralisation of the whey used to manufacture specialized dairy products and the removal of salts from fruit juices.

In desalination process, Complete deionization can be achieved by using two resins. The solution is first passed through a bed of cation exchange resin contained in a vessel. This is in the hydrogen ion form brought about by the use of a strong

acid regenerant (either hydrochloric or sulphuric). During service, cations in the solution are taken up by the resin while hydrogen ions are released. Thus the effluent consists of a very weak mixture of acids. The solution now passes through a second vessel containing anion exchange resin in the hydroxide form for which sodium hydroxide is used as the regenerant. Here the anions are exchanged for

hydroxide ions, which react with the hydrogen ions to form water. Such twin bed units will reduce the total solids content to approximately  $1\text{-}2\text{ mg L}^{-1}$ . With larger units it is usual to pass solution leaving the cation unit through a degassing tower. This removes most of the carbonic acid produced from carbon dioxide and bicarbonate in the feed solution and reduces the load on the anion unit.



**Figure 2.7** Ion exchange resin principle.

Advantages of this method are the very low running costs. Very little energy is required, the regenerant chemicals are cheap and if well maintained resin beds can last for many years before replacement is needed. There are, however, a number of limitations which must be taken into account very carefully during the design stages when ion exchange resin is used such as Calcium sulphate fouling, Iron fouling, Adsorption of organic matter, Organic contamination from the resin, Bacterial contamination, Chlorine contamination and especially Environmental implications.

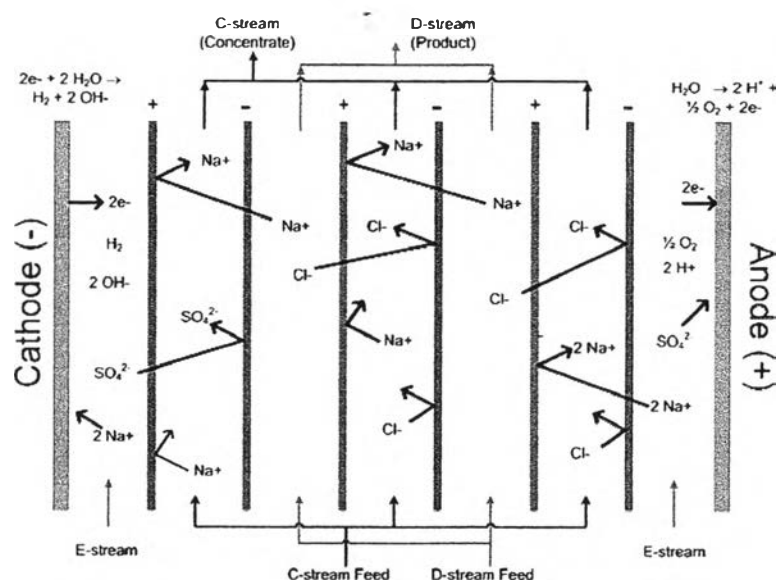
Studies of salt removal from the glycerol-water mixture were carried out by different authors and mainly using the ion exchange process. Carmona et al., (2009a, 2009b) have reported the equilibrium studies of ion exchange for the removal of NaCl or KCl from synthetic mixture of different glycerine/water portion at different temperatures. The sodium removal was studied using strongly acidic cation-exchange resins one of gel-form Amberlite IR-120 and other macroporous Amberlite 252. The best results were obtained using the resin Amberlite 252 which has the biggest pore size at low temperature and 10% water content. According to these



results, Hydrate ionic radius for potassium and sodium are 1.65 and 2.2 Å, respectively, and this lower value for the  $K^+$  ion can be the cause that Amberlite IR-120 exhibits a higher selectivity for this ion.

### 2.3.4 Electrodialysis

Electrodialysis (ED) is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. This is done in a configuration called an electro dialysis cell. The cell consists of a feed (diluate) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. In almost all practical electro dialysis processes, multiple electro dialysis cells are arranged into a configuration called an electro dialysis stack, with alternating anion and cation exchange membranes forming the multiple electro dialysis cells. Electro dialysis processes are different compared to distillation techniques and other membrane based processes (such as reverse osmosis) in that dissolved species are moved away from the feed stream rather than the reverse.



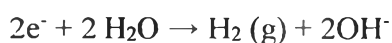
Courtesy EET Corporation  
www.eetcorp.com

**Figure 2.8** Electro dialysis diagram.

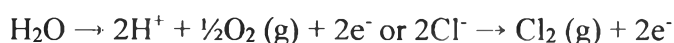
According to figure 2.8, in an electrodialysis stack, the diluate (D) feed stream, brine or concentrate (C) stream, and electrode (E) stream are allowed to flow through the appropriate cell compartments formed by the ion exchange membranes. Under the influence of an electrical potential difference, the negatively charged ions (e.g., Cl<sup>-</sup>) in the diluate stream migrate toward the positively charged anode. These ions pass through the positively charged anion exchange membrane, but are prevented from further migration toward the anode by the negatively charged cation exchange membrane and therefore stay in the C stream, which becomes concentrated with the anions. The positively charged species (e.g., Na<sup>+</sup>) in the D stream migrate toward the negatively charged cathode and pass through the negatively charged cation exchange membrane. These cations also stay in the C stream, prevented from further migration toward the cathode by the positively charged anion exchange membrane. As a result of the anion and cation migration, electric current flows between the cathode and anode. Only an equal number of anion and cation charge equivalents are transferred from the D stream into the C stream and so the charge balance is maintained in each stream. The overall result of the electrodialysis process is an ion concentration increase in the concentrate stream with a depletion of ions in the diluate solution feed stream.

The E stream is the electrode stream that flows past each electrode in the stack. This stream may consist of the same composition as the feed stream (e.g., sodium chloride) or may be a separate solution containing a different species (e.g., sodium sulfate). Depending on the stack configuration, anions and cations from the electrode stream may be transported into the C stream, or anions and cations from the D stream may be transported into the E stream. In each case, this transport is necessary to carry current across the stack and maintain electrically neutral stack solutions.

Reactions take place at each electrode. At the cathode,



while at the anode,



Small amounts of hydrogen gas are generated at the cathode and small amounts of either oxygen or chlorine gas (depending on composition of the E stream

and end ion exchange membrane arrangement) at the anode. These gases are typically subsequently dissipated as the E stream effluent from each electrode compartment is combined to maintain a neutral pH and discharged or re-circulated to a separate E tank.

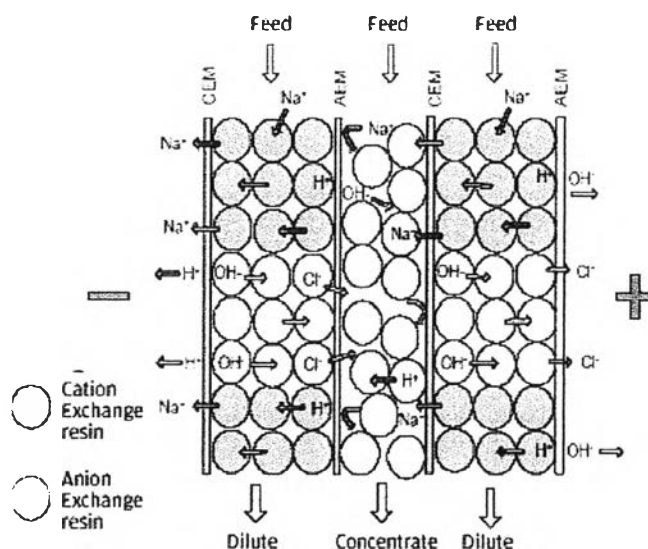
Electrodialysis has inherent limitations, working best at removing low molecular weight ionic components from a feed stream. Non-charged, higher molecular weight, and less mobile ionic species will not typically be significantly removed. Furthermore, the concentration that can be achieved in the electrodialysis C stream is limited by the membrane selectivity loss due to the Donnan exclusion mechanism and water transport from the diluate to the brine caused by osmosis; in particular, at very high concentration differences across the membrane between the concentrate and diluate streams, diffusion of ions from the concentrate stream back into the diluate stream and transport of water across the membranes can offset separation resulting from the applied electric potential, resulting in a poor (i.e., higher ion concentration than desired) product. Despite this disadvantage, in general, significantly higher brine concentration can be achieved by a properly configured electrodialysis than by reverse osmosis and the problem of scaling is also less severe in electrodialysis than in reverse osmosis.

In contrast to reverse osmosis, electrodialysis becomes less economical when extremely low salt concentrations in the product are required and with sparingly conductive feeds: current density becomes limited and current utilization efficiency typically decreases as the feed salt concentration becomes lower, and with fewer ions in solution to carry current, both ion transport and energy efficiency greatly declines. Consequently, comparatively large membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions. Innovative systems overcoming the inherent limitations of electrodialysis are available in the name of Electrodeionization (EDI). These integrated systems work synergistically, providing the least overall operating and capital costs for a particular application.

### 2.3.5 Electrodeionization

Electrodeionization (EDI) is a process that removes ionizable species from liquids using ionically active media and an electrical potential to influence ion transport. The EDI process employs anion and cation permeable ion exchange membranes, with ion exchange resins packed between them. Applying a DC electric potential causes ions to move from one compartment to another, effecting a separation. This mechanism is the same as of Electrodialysis. In addition, the capital equipment and worker skill required for EDI is significantly less than distillation.

An EDI cell combines the benefits of ion exchange and electrodialysis while minimizing the problems associated with each of these separate technologies. Traditional ion exchange requires regeneration of the exchange media with acids and bases, which generates waste and takes significant time. Electrodialysis become less efficient as salt concentrations decrease because the fluid is becomes increasing less conductive as ions are removed. An EDI cell uses the ion exchange resin to provide high ionic conductivity to decrease the high resistance normally found in the diluate compartments of an electrodialysis cell. The resin's high ionic capacity increases the residence time of the ionic contaminants inside the cell allowing more time for the current to transport these ions into the appropriate compartments. The electrodes generate a potential gradient for ionic movement within the cell. At cation/anion (resin/resin and resin/membrane) interfaces water is dissociated into its constituent ions,  $H^+$  and  $OH^-$ , which regenerate the resins on-line, so there is no down time or need for regenerative chemicals as in ion exchange.



**Figure 2.9** Electrodeionization module.

In continuous electrodeionization for the preparation of deionized solution, the process operates in two regimes. In the first regime, at higher salinity or at the inlet portion of the resin bed, the resins in the diluting streams remain in the salt forms, and efficiencies are derived from the resin-enhanced electrical conductivity of the ion-depleting compartments. In the second regime, at low salinity or at the outlet portion of the resin bed, the DC electric potential causes water to dissociate into its constituent ions,  $H^+$  and  $OH^-$ , electrochemically converting the resins to the hydrogen and hydroxide forms. This phenomenon, known as electroregeneration, accounts for the ability of EDI systems to produce multi-megohm water, much like a continuously regenerated mixed bed ion-exchange column.

## 2.4 The Transport Number and Membrane Permselectivity

The feed of ED and EDI is electrolyte solution. In an electrolyte solution the current is carried by both ions. However, cations and anions usually carry different portions of the overall current. In ion-exchange membranes the current is carried preferentially by the counterions. The fraction of the current that is carried by a certain ion is expressed by the ion transport number which is given by:

$$T_i = \frac{|z_i|J_i}{\sum_j |z_j|J_j} \quad (1)$$

Here  $T_i$  is the transport number of the component  $i$ ,  $J_i$  is its flux, and  $z_i$  its valence, the subscript  $j$  refers to all ions involved in the charge transport.

The transport number  $T_i$  indicates the fraction of the total current that is carried by the ion  $i$ , the sum of the transport number of all ions in a solution is 1.

The membrane permselectivity is an important parameter for determining the performance of a membrane in a certain ion-exchange membrane separation process. It describes the degree to which a membrane passes an ion of one charge and retains an ion of the opposite charge. The permselectivity of cation- and anion-exchange membranes can be defined by the following relations.

$$\Psi^{cm} = \frac{T_c^{cm} - T_c}{T_a} \quad \text{and} \quad \Psi^{am} = \frac{T_a^{am} - T_a}{T_c} \quad (2)$$

Here  $\Psi$  is the permselectivity of a membrane,  $T$  is the transport number, the superscripts  $cm$  and  $am$  refer to cation- and anion-exchange membranes, and the subscripts  $c$  and  $a$  refer to cation and anion, respectively.

The permselectivity of an ion-exchange membrane relates the transport of electric charges by a specific counterion to the total transport of electric charges through the membrane and the transport number of the ion in the solution. An ideal permselective cation-exchange membrane would transmit positively charged ions only, i.e. for a transport number of a counterion in an cation-exchange membrane is  $T_c^{cm} = 1$  and the permselectivity  $\Psi^{cm} = 1$ . The permselectivity approaches zero when the transport number within the membrane is identical to that in the electrolyte

solution, i.e. for  $T_c^{cm} = T_c$  is  $\Psi^{cm} = 0$ . For the anion-exchange membrane holds the corresponding relation.

The transport number of a certain ion in the membrane is proportional to its concentration in the membrane which again is a function of its concentration in the solutions in equilibrium with the membrane phase, due to the Donnan exclusion. For a monovalent salt and a dilute salt solution and assuming the activity coefficients of the salt in the membrane and the solution to be 1 the co-ion concentration is given to a first approximation by:

$${}^m C_{co} = \frac{{}^s C_s^2}{C_{fix}} \quad (3)$$

Here  $C$  is the concentration, the subscripts  $co$ ,  $s$  and  $fix$  refer to co-ion, salt and fixed ion of the membrane, the superscripts  $s$  and  $m$  refer to membrane and solution.

Equation 3 indicates that the co-ion concentration in the membrane is decreasing with increasing salt concentration in the solution and will vanish when the salt concentration in the solution is identical to the fixed ion concentration of the membrane.

According to Indusekhar (1965) who research the diffusion effect during Electrodialysis, when the salt concentration of solution increase, the membrane permselectivity will decrease due to the transport of the ions resulting from Donnan diffusion. And if the concentration of salt reach about 27,000 ppm, it cannot be demineralize by electrodialysis anymore. Thus, the %desalination increase for later cycle that amount of salt decrease since the permselectivity of membrane approach the ideal.