

Chapter 1 Introduction

1.1 The Analytical process.

The analytical process can be defined as the set of operations separating the untreated, unmeasured sample from the results expressed as required in accordance with the “analytical black box”. Figure 1.1 indicates the three basic stages of this process. [1]

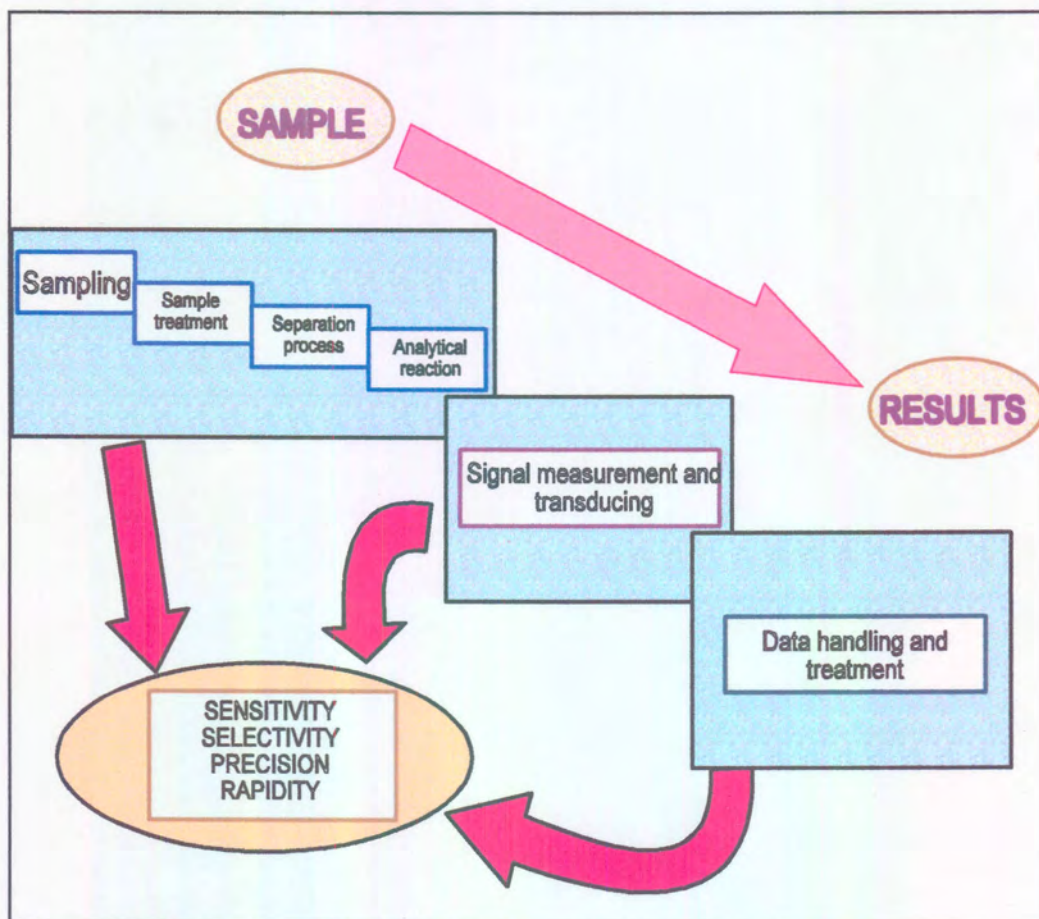


Figure 1.1 General stages of the analytical process.

- Notwithstanding the fact that each stage of the analytical process might determine its overall efficiency in every specific situation, the basic features of virtually every analytical methodology are affected by all three stages. [1]

1.2 Analytical chemistry and the need for automation.

Looking back to the not so distant past, it is impossible to mention all the researchers names in the field of instrumental analytical chemistry. Besides the analytical chemistry that developed, there was a need to make analytical chemistry in practice easier and more streamlined. For this reason instrumentation was developed to help the analyst with the number of samples that had to be analysed. Each year the quest for more samples in less time increased and man had to get help from a source which decreased the analysis time and increase the certainty of measurement, and saved on manpower.

Like many other branches of science and technology, analytical chemistry has experienced an enormous expansion in the last few decades of the twentieth century, promoted by scientific advances in general and by the occasionally pressing demands of a permanently, almost frantically changing society. All trends in analytical chemistry have an essential common aim, namely improving on the existing levels of such basic analytical features as sensitivity, selectivity, precision, rapidity, reliability, scope of application, analytical costs, versatility and sample throughput. [1]

The services of the analytical chemist are constantly increasing as more and better analytical tests are developed, particularly in the environmental and clinical laboratories. The analyst often must handle large number of samples and/or process vast amounts of data. Instruments are available that will automatically perform many or all of the steps of an analysis, greatly increasing the load capacity of the laboratory. The data generated can often be processes by the computer techniques; computers may even be interfaced to the analytical instruments. [2]

1.2.1 Flow-based techniques used for analysis

The history of flow-based techniques is well known to most people interested in the field. The concept of injecting a sample directly into a continuous-flow system, and then monitoring it on a continuous base, has been known since 1952. [3, 4] Skeggs's development of the segmented flow system in 1957, which led to the Auto Analyser, was one of the first automated pieces of equipment for general use in clinical and other laboratories. [5] In the late 1960's and early 1970's a new method in flow-based systems, the so called Flow Injection Analysis (FIA) technique, was developed. FIA led to dramatic improvements in the speed and quality of analysis.

Flow injection analysis has established itself nowadays as one of the methods of choice in various fields as an analytical technique which is suitable for automation and increasing sample output in most analytical laboratories. FIA is well documented in more than 5900 papers up to 1997. Since the early 1970's there was a rapid increase in the number of publications up to 1986 whereafter the publications per year stabilised around 500 per year. [6] FIA has been used to automate wet chemical techniques to improve analysis time, and quality and the reproducibility of the analysis.

1.2.2 Separation techniques

Separation and trace enrichment are two of the most fundamental steps in analytical chemistry. With increasing demand for fast and accurate analysis, it is not surprising that the automation of separation processes should play a major role. Separation is performed frequently on soluble species in solution.

Through the ages man has been aware of the importance of separating the valuable from the less valuable in nature's mixtures. This trait has persisted; it is difficult to single out an area of science or a science-based industry where separations do not play an important role. [6]

Separations can be very tedious and can be very labour intensive. For this reason separation, if possible, must be a part of the automation process.

The word separation classically conjures up a model of removing one component or species from a second component. [7] An analytical separation can be described as a process which is responsible for the separation of a mixture into at least two parts of different composition. The purpose of such a separation is to enrich the one fraction with at least one of the components of the mixture in comparison to the other components. To execute such a separation implies that two components must be separated from each other. For this reason transport (removal), which is differential in nature, must be part of the system. [8]

It is worth remembering that separation can only be achieved by exploiting differences between the components of mixtures. These differences may be of a physical nature such as variations in mass, density, size, shape, vapour pressure, or of a chemical nature such as differences in solubility or adsorption characteristics. A separation process may exploit either physical or chemical differences to effect separation, and in some cases a combination of these

factors are used to achieve the desired level of separation. [9]

Sample treatment (of which a separation process can be one of the processes involved) is one of the preliminary steps of the analytical process. It is therefore important to know that analytical separation techniques play a very important role in today's analytical chemistry. Separation techniques are one of three primary ways (the other two are chemical reactivity and signal discrimination) of achieving or enhancing selectivity. (Application of chemometric techniques further enhances selectivity in most instances). [1]

From a more practical view, separation techniques can be classified according to operativeness and efficiency into chromatographic and non-chromatographic techniques. The main thrust of this thesis will be concerned with the non-chromatographic separation techniques. Chromatographic techniques distinguishes itself from the non-chromatographic techniques due to the presence of not only a mobile phase but also a stationary phase for separation of the various analytes. This type of separation is characterised by the occurrence of at least the flow of one of the phases involved in the mass transfer. The implementation of non-chromatographic separation techniques relies on the principles behind, and developments in the field of automatic continuous analysers, both air-segmented and unsegmented. A continuous separation system can give rise to various types of interface across which mass transfer can take place (gas/liquid, liquid/liquid and liquid/solid).

The second phase, which collects the analytes or interferences, can be introduced into the system in a direct fashion (dialysis, liquid-liquid extraction or gas diffusion) or be a part of the separation system (e.g. the active material in a sorption micro column). Also, this second phase can be generated *in situ* by physical change (distillation), chemical change (precipitation) or a combination of the two.

Dynamic separation systems typically use continuous on-line detection systems through which the stream of the phase carrying the analyte are driven after separation.

1.2.2.1 Diayers in FIA systems acting as sample pretreatment tools

The technique of mass transfer in on-line analytical dialysers has been employed in continuous flow systems with gas-diffusion and dialysis membranes for many years, particularly in routine clinical laboratories. There are a number of thorough and authoritative reviews of the early history of membrane science and all the details are not repeated here. One of the milestones in this regard is a review by Lonsdale [11] in the growth of membrane technology up to 1982. Another article worth mentioning is the review article by Van Staden [12], which gives a detailed overview of the use of membranes in FIA systems.

Dialysis is a technique based on a diffusion process which involves the selective separation of sample species through a semi-permeable membrane. The technique can be divided into passive dialysis and active (or Donnan) dialysis. The classification of dialysis processes as passive or active (Donnan) depends on the nature of the membrane [1, 17]. In the passive process a neutral membrane differentiates between separations on a molecular scale with a preciseness of molecular order allowing species within a given range of molecular mass to diffuse across a neutral membrane. In active (Donnan) dialysis (see the definition and a detailed explanation in chapter 2), ions with a given type of charge are transferred across an ion-exchange membrane. Passive dialysis is a highly efficient molecular filter, but was found to be inefficient in terms of solute diffusion rates (0 - 7%) across a semi-permeable membrane. [12, 13].

Active Donnan dialysis is a promising technique for the preconcentration, recovery and speciation of ionic species, but with a limitation in the amount of

mass transfer of species through the membrane. Cox *et al.* [14, 15] have worked for many years on sample preparation on an analytical scale using Donnan dialysis, employing the technique for matrix normalization [14] and sample preconcentration [15].

According to Van Staden [12], the main use of the passive membrane in FIA systems relation is in-line sample dilution. Other methods of in-line sample dilution were also studied but are beyond the scope of this study. [16 - 21] Dilution can be advantageous in the sense of in-line sample preparation but, what about samples with already low analyte concentrations? Work has been done by Van Staden and Hattingh to circumvent the dilution effect and still retain the other advantages of the dialysis system (for example in-line sample cleanup). [22] In this work, a passive dialysis unit was incorporated into a dialysis system and the dialysate was concentrated on an ion-exchange resin. The detection limits decreased dramatically but at the expense of experimental time. This led to the search for a way in which one can lower the detection limit, have a rather short experiment time and at the same time retain all the advantages of the dialyser in the FIA system. Much work has been done on the use of electro dialysers, but most of this work is concerned with the use of ion-exchange membranes and also not as an analytical tool.

As the name implies, electro dialysis (ED) is a dialytic process in which an applied electric field is used to force ions through a membrane [23]. The main driving force which impels ions through the membrane is the potential gradient across the membrane. So far ion separation is affected through the use of selective ion-exchange membranes. In practical ED, many selective membranes are placed perpendicularly in the path of the electrical field. In all the research work reported to date [11, 23 - 26], conventional ED utilized ion-exchange membranes. ED with ion-exchange membranes was also utilized as suppressors in ion chromatography [29, 30] and for electro dialytic neutralization of samples prior to analysis in ion chromatography [29, 30]. The electro dialyser

units described by Cooper et al. [25] were designed with three compartments; a feed solution containing the sample was placed in a channel between a cation exchange membrane on the one side and an anion exchange membrane on the other side. Ions from the sample channel permeate under the influence of an electric field to the respective corresponding acceptor channels.

ED is a membrane-based separation technique that is also appealing because of its capability to deionize one stream while concentrating the electrolytes in another stream. ED therefore produces a purified stream that can either be discharged or reused and a concentrated electrolyte stream that can be disposed of or processed for reclamation of the dissolved salt. In most of these electrodialyser units, cation- and anion-permeable ion-exchange membranes were arranged in an alternating pattern. The series of cells became alternately diluting and concentrating compartments when a direct current was passed through the system. These stacks were mostly employed in desalination systems and industrial applications. Some applications of ED include desalination of brackish waters, desalting of whey and stabilisation of wine, purification of proteins solutions, recovery of metals from plating of rinse waters, recovery of acids, recovery of heavy metals from mining mill processes and the treatment of cooling-tower blowdown for water recovery and effluent volume reduction. [23, 24, 25, 26]

A literature survey showed that, to date, ED has only been exploited to a very limited extent in flow injection systems. ED has been reported for the separation of alanine and aspartic acid [31] and for extraction of ephedrine from spiked plasma [32]. [33] reported an application for the separation of leucine from ketoleucine during flow injection analysis with leucine dehydrogenase. The selectivity for L-amino acids in flow injection analysis was enhanced using ED with amino acid oxidation [30]. Conventional ED configurations [25] using cation- and anion-exchange membranes were employed in all the applications to date.

Although there is a perception in certain circles [29], that passive dialysis through a neutral membrane is a slow process requiring a large volume of sample, it has been reported [1, 12, 34], that membrane separation with passive dialysis is one of the most successful separation techniques in flow analysis. It was thought to combine the advantages of the passive dialysis system with that of the electro dialysis system. To obtain this result, an electro dialyser was designed which consisted of two compartments where a passive neutral membrane is incorporated between two channels (a donor and an acceptor) of the conduits of an FIA system, using the same dialyser configuration as in conventional dialysis. By using this concept it can be possible to enhance the transfer of certain sample components through a passive neutral membrane.

1.3 Objective of the project

From the foregoing paragraph it is obvious that there is an urgent need for the further development of tools to streamline the analytical procedure. Automation is one of the key concepts for the development of such tools. Flow injection analysis (FIA) in general lends itself to a great extent to be automated. One of the means by which FIA was made more streamline, as was mentioned in the previous paragraphs, is the introduction of a tools for in-line sample preparation. The tools of interest include the following;

- i. The dialyser unit equipped with a passive membrane for sample dilution and sample cleanup (separation).
- ii. Donnan dialysis for sample speciation and preconcentration.
- iii. Electro dialysis for the enhanced migration of charged species and the separation thereof.

By building a hybrid of the above mentioned tools, a new tool was envisaged to circumvent the disadvantages of the individual tools and enhance the advantageous points. By introducing a passive membrane into an electro dialyser unit, one should be

able to increase the mass transport of charged species across the membrane, thus a massive increase in the percentage dialysis can be expected. Furthermore a speciation of species due to different charges can be expected. Sample cleanup can be enhanced. It will be possible to remove interfering species to a great extent if there is a charge difference between the analyte and the interfering species. Since the proposed electro dialyser will operate in-line in the FIA system, automation will easily be introduced.

In the experimental chapters to follow, the planning, building, introduction into the FIA system, problems experienced and the solutions thereof will be discussed of the newly developed hybrid dialyser.

1.4 References

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Chapter 2

Introduction into Membranes and Membrane processes

2.1 Introduction

Over the past four decades or so the growth of several new industries, based on membrane technology, has observed. It is a highly fragmented technology, covering such wide-ranging applications as reverse osmosis (RO), gas separations, controlled-release pharmaceutical formulations and the artificial kidney. The scientific and engineering disciplines involved are also varied, and include physical and polymer chemistry, electrochemistry and chemical engineering. [1]

2.2 Definition of a Membrane and a Membrane process

Before discussing all the membrane processes in detail, it is imperative that one should have a sound knowledge of what a membrane and a membrane process implies.

As can be seen from paragraph 2.1, there are a wide variety of uses and applications for membranes in general. The difficulty in defining a membrane resides in the variety of uses and applications. The general definition of a membrane was also a problem HK Lonsdale experienced in an issue of *Journal of membrane science*. [2] In this mentioned article, Lonsdale put this question to various groups and individuals who are well established in the membrane field of operation or research. Following are some of comments that he received:

“A membrane can be regarded as a phase or group of phases that controls the transport of matter and energy between two essentially uniform phases which separates it.” (Patric Meares)

“A membrane is a permeable barrier characterised by flux and selectivity properties that provide functional transport across the partition.” (Harvey)

Hoehn)

“A membrane is a barrier film that allows selective and specific permeation under conditions appropriate to its function.” (Ashok K Vijh)

“A membrane is an interphase. It has distinct physicochemical properties and it is bounded by two surfaces, each of which joins it to a contiguous bulk phase. Generally it is “thin” in the sense that it has a large ratio of surface area to volume; as its thickness approaches molecular dimensions the interphase becomes an interface. The special separative/barrier/contacting properties of membranes derive from the fact that an interphase can communicate simultaneously with its two adjacent phases; this permits the establishment and maintenance of gradients across the membrane and allows exchange to occur at both surfaces. Thus, when viewed as a contacting device a membrane has an additional degree of freedom over conventional bulk phase operations which have but one bounding surface and it is this feature which is unique to membranes.” (John A Quinn)

As can be seen, all the answers given, can be reduced to a basic definition that includes all its applications and uses and it can be given as follows:

“A membrane is a thin barrier between two phases which restricts the movement of one or more components of one or both phases across the membrane barrier.” [3]

Membrane processes are an integral part of our every day life, for example: Every day over 20 million litres of brackish water are pumped out of the ground near Jeddah in Saudi Arabia and passed through thin sheets of cellulose acetate in a process known as reverse osmosis before being used as part of the city's water supply. Orange juice can be concentrated by membranes to make a concentrate which retains more of the

flavour than does evaporation. Milk can be concentrated slightly by means of a membrane before making cheese in a process which produces no whey. Gases rising from the ground in a waste tip can be piped away and the carbon dioxide separated from the methane by a membrane process allowing the methane then to be used as a fuel, simultaneously saving energy and reducing the greenhouse effect since methane is more effective as a greenhouse gas than carbon dioxide. In all of these processes materials are separated by a semi-permeable membrane which allows the passage of one or more of the materials much more readily than the others. [3]

A membrane process requires two bulk phases physically separated by a third phase, the membrane. The *membrane* as the definition implies, is an interphase between two bulk phases which can either be a homogeneous phase or a heterogeneous collection of phases. The membrane phase may either be one or a combination of the following:

- Nonporous solid.
- Microporous or macroporous solid with a fluid (liquid or gas) in the pores.
- A liquid phase with or without the second phase.
- A gel. [4]

Membranes are primarily used for separation and membrane processes are generally separation processes. Large scale commercial uses of membrane separations have displaced conventional separation processes. More of these displacements are expected in the future, for one since membrane separation processes are more energy and capital efficient than the conventional separation processes. [3, 4]

The membrane phase (or membrane), interposed between two bulk phases, controls the exchange of mass between the two bulk phases by means of a membrane process. In membrane separation processes the bulk phases are mixtures. One of the species in the mixture is allowed to be exchanged in preference to the others, in other words, the membrane is selective towards one of the species in the mixture. The one bulk

phase is then enriched with this species whilst the other is depleted thereof. A *membrane process thus is the selective and controlled transfer of a species from one bulk phase to the other.* [4]

A membrane may discriminate between two species because of difference in size, shape or chemical structure, and the separation will be achieved only to a *limited* extent. The membrane will *never* be able to separate the mixture completely. The separation of substances which mix spontaneously can be accomplished by some device which consumes energy supplied in the form of heat or mechanical work. The basic principle of any membrane or separation process is that a certain amount of energy is required to accomplish the separation. Two substances will mix spontaneously when the free enthalpy of the mixture is smaller than the sum of the free enthalpies of the pure substances. The minimum amount of energy (W_{\min}), necessary to accomplish complete separation is at least equal to or larger than the free enthalpy of mixing. [4]

$$W_{\min} \geq \Delta G_m = \Delta H - T\Delta S$$

Before discussing some membrane separation processes in more detail, a short key in the form of a table can serve to distinguish between the different processes (Table 2.1).



Table 2.1 A short key into some membrane processes

Membrane Process	Separation potential for	Driving force	Preferably permeating component
Reverse osmosis	Aqueous low molecular mass solutions	Pressure difference	Solvent
Ultrafiltration	Macromolecular solutions, emulsions	Pressure difference	Solvent
Microfiltration	Suspensions, emulsions	Pressure difference	Continuous phase
Gas permeation	Gas mixtures, water vapour/gas mixtures	Pressure difference	Preferably permeating component
Pervaporation	Aqueous/organic mixtures	Ratio of partial pressure to saturation pressure	Preferably permeating component
Liquid membrane	Aqueous low molecular mass solutions	Concentration difference	Solute
Osmosis	Aqueous solutions	Concentration difference	Solvent
Dialysis	Aqueous solutions	Concentration difference	Solute
Electrodialysis	Aqueous solutions	Electric field	Solute (ions)

2.3 Introduction to some of the membrane processes

There are quite a number of different membrane processes. Since there is no real cut-off point between the different membrane processes, (and the fact that some of them are very closely interrelated [4 -6]) the following very important and related processes will be discussed.

2.3.1 Osmosis

Osmosis, for this project, is most probably the second most important membrane process due to the fact that osmosis it is always accompanied by dialysis in real membranes. (Dialysis cannot take place if osmosis doesn't take place at the same time) [4 - 7]

Osmosis is a natural phenomenon in which water passes through a

semipermeable membrane from the one side with lower solute concentration to the higher solute concentration until equilibrium of solvent chemical potential is restored. At equilibrium the pressure difference between the two sides of the membrane is equal to the osmotic pressure difference. The solvent is transported through the membrane as a result of a difference in trans-membrane concentration. [4 -7]

2.3.2 Pressure driven Membrane Processes

The characteristic of these processes is that the solvent is the continuous phase and that the concentration of the solute is relatively low. Various processes, related to the particle size of the solute and consequently to membrane structure, can be distinguished. These processes are:

- Microfiltration
- Ultrafiltration
- Nanofiltration/Reverse osmosis

The principle of these three processes is illustrated in Figure 2.1.

Due to the driving force, namely applied pressure, the solvent and various solute molecules permeate through the membrane, whereas other molecules or particles are rejected to various extents dependent on the structure of the membrane. Upon comparing the three mentioned processes, in order from microfiltration, ultrafiltration to reverse osmosis,¹ the size (or the molecular mass) of the particles separated, diminishes and consequently the pore sizes (for the separation of these particles) in the membrane must also become smaller. This implies that the resistance of the membranes to mass transfer increases and hence also the applied pressure to obtain the same flux. [5]

1. *It should be note that no clear-cut distinction can be drawn between the various pressure driven membrane processes.*

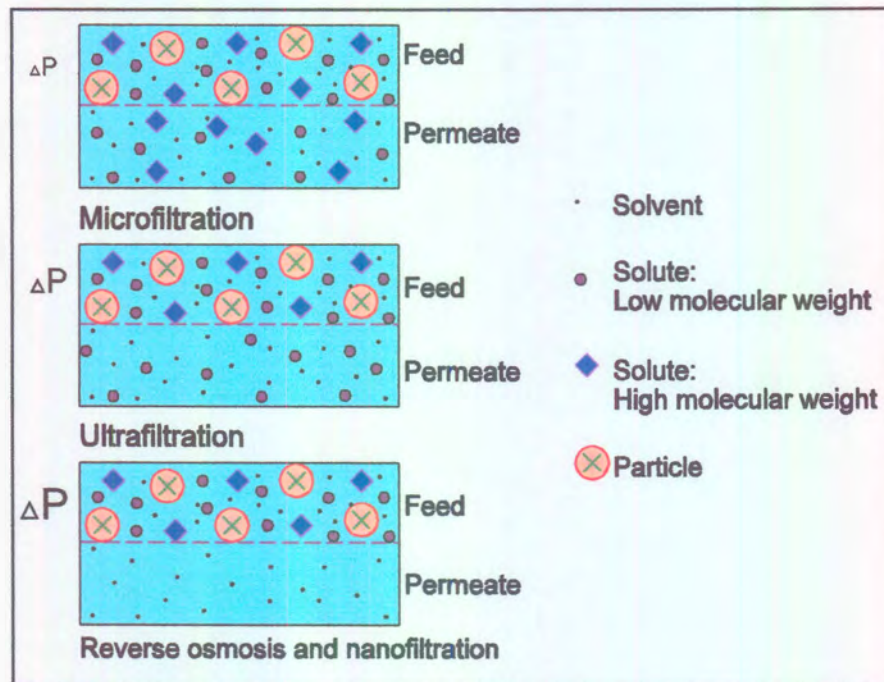


Figure 2.1 Schematic representation of some pressure driven membrane processes

2.3.2.1 Microfiltration

Microfiltration is the membrane process which most closely resembles conventional coarse filtration. The pore sizes of microfiltration membranes range from 10 - 0.05 μm , making this process suitable for retaining suspensions and emulsions. [5]

Applications of microfiltration include the following: [6]

- Concentration and /or washing of various colloidal suspensions.
- Separation of emulsions (oil-polluted industrial effluents).
- Pre-treatment for reverse osmosis plants.

2.3.2.2 Ultrafiltration

The nature of ultrafiltration lies between microfiltration and reverse osmosis. The pore size varies between 0.05 μm and 1 μm . Ultrafiltration is typically used to retain macromolecules and colloids from a solution, the lower limit being solutes with molecular weights of a few thousand. For both microfiltration and ultrafiltration, the retention is determined by the size and the shape of the solutes relative to the pore size in the membrane. The transport of the solvent through the membrane is directly proportional to the applied pressure. [5]

The relatively large pores used for ultrafiltration (in comparison to reverse osmosis) allow both ionic and high molecular weight organic materials to pass through the membrane into the permeate stream. In metal finishing operations, ultrafiltration is typically employed to concentrate emulsified oils from rinses or to recover valuable detergents from cleaning rinse waters. In general osmotic pressure is not a problem when using ultrafiltration and the only energy requirements stems from running a low-pressure pump. Some general applications for ultrafiltration includes the following:

- Cleaners for one-piece steel and aluminum cans.
- Rinses for strip coil coating.
- Cleaning rinses for automobile and aircraft chassis.
- Coolant recovery. [9]

2.3.2.3 Nanofiltration/Reverse Osmosis

The first work in reverse osmosis towards water desalting was undertaken by Reid and his students at the university of Florida in the mid 1950s. This group made use of synthetic polymeric membranes which led to very low fluxes due to the fact that the thinnest these membranes could be cast without any imperfections was about 6 μm . Only in the late 1950s cellulose acetate fibres

were used which had much higher fluxes than the synthetic polymeric membranes. At about the same time Loeb and Sourirajan discovered a way to prepare very thin cellulose acetate membranes. This method is still in use today for the preparation of water desalination reverse osmosis membranes.

The process of reverse osmosis can be explained by Figure 2.2. Applied pressure is used to reverse the "normal" direction of water flow across a semipermeable membrane. If a pressure (ΔP) is applied to the concentrated solution just equal to the osmotic pressure difference between the two solutions ($\Delta \pi$), water flow ceases (or there is no net flow of water) and osmotic equilibrium is reached. At a higher pressure ($\Delta P > \Delta \pi$), water will flow from the concentrated to the dilute solution.

A high-pressure pump forces pure water (permeate/solvent) through the membrane that has the capability to reject salts and organics. As more permeate is removed from the feed stream, the remaining dissolved materials become more concentrated. [9]

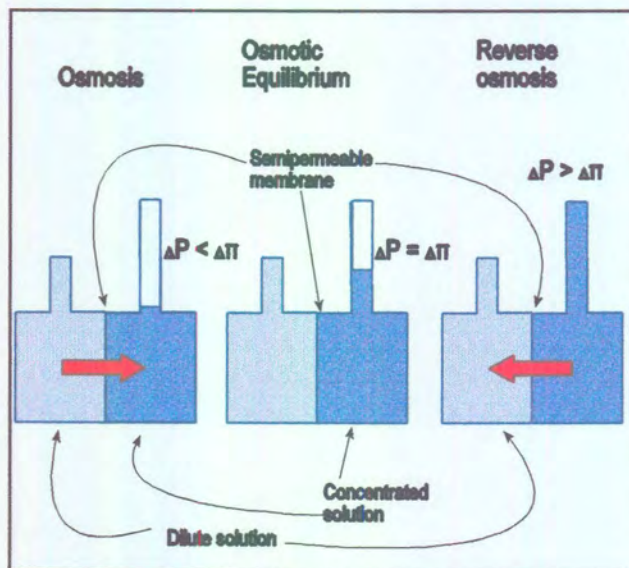


Figure 2.2 Osmotic phenomena.

If a trans-membrane pressure difference greater than that corresponding to osmotic equilibrium is applied to the test cell, then the solvent flux can be reversed so that the solution with the greater concentration is further concentrated. The reversal of the flux then is a direct reason for the name *reverse osmosis*. [6]

Nanofiltration and reverse osmosis are used when low molecular weight solutes such as inorganic salts or small organic molecules such as glucose and sucrose have to be separated from a solvent. Both these processes are considered as one process since the basic principles are the same. The difference between nanofiltration/reverse osmosis and the other pressure driven processes is based upon the difference in size of the solute. Consequently, the membranes required for nanofiltration/reverse osmosis systems are more dense with much higher hydrodynamic resistance. These membranes can be considered as being intermediate between open porous types of membranes (microfiltration and ultrafiltration) and dense non-porous membranes (pervaporation/gas separation). Because of these denser membranes, higher membrane resistance will be experienced and accordingly higher pressures must be applied for the same amount of solvent flux through the membrane. [5]

Reverse osmosis (RO) can be sub-divided into three types: [4]

- High pressure RO, 5.6-10.5 Mpa, (seawater desalination).
- Low pressure RO, 1.4 - 4.2 Mpa, (brackish water desalination).
- Nanofiltration or "loose" RO, 0.3 - 1.4 Mpa

Organic rejection depends on membrane polymer types and structures as well as membrane / solute interactions.

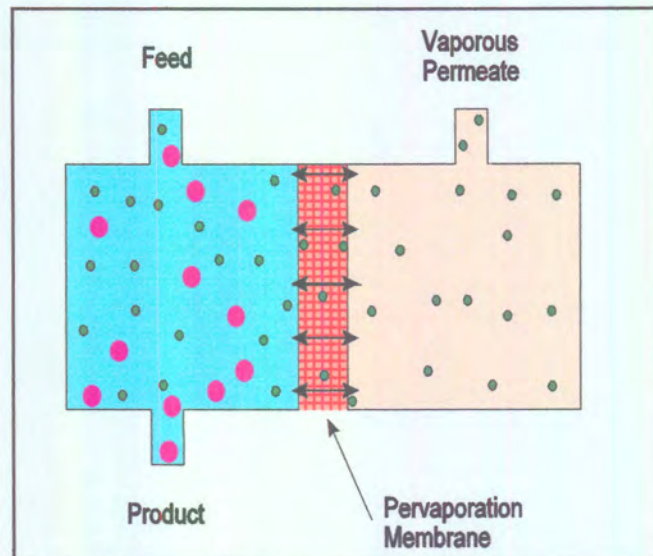


Figure 2.3 The Pervaporation process

2.3.3 Pervaporation

Pervaporation is characterized by the imposition of a barrier (membrane) layer between a liquid and a gaseous phase. [4 - 6] See Figure 2.3.

Pervaporation is distinguished from all other membrane processes by the phase change occurring during mass transfer. The driving force, unlike the applied pressure as discussed previously, is the reduction in activity (reduction of the partial pressure) on the permeate side. Mass transfer across the membrane occurs selectively towards the gas side. Because of the phase change required of the liquid solutes diffusing across the membrane (permselective "evaporation" of the liquid molecules), the process is termed pervaporation. Since different species permeate through the membrane at different rates, a substance at low concentration in the feed stream can be highly enriched in the permeate. Thus separation occurs with the efficacy of the separation effect being determined by the physicochemical structure of the membrane. [4, 6]

The liquid or liquid mixture in the feed side (Figure 2.3) is at atmospheric pressure. The permeate is removed as a vapour because of a low vapour pressure existing on the permeate side. This low (partial) vapour pressure can be achieved by employing a carrier gas or using a vacuum pump. The pervaporation process involves basically three steps namely:

- Selective sorption into the membrane on the feed side.
- Selective diffusion through the membrane.
- Desorption into a vapour phase on the permeate side. [5]

2.3.4 Liquid membranes

Liquid films on porous supports also form solution-diffusion membranes that can be used for gas separations. The liquids, which are held in place by capillary forces, naturally form defect-free layers. This reliance on capillary forces severely limits the allowable trans-membrane pressure difference that can be used. [4]

Two types of liquid membranes can be distinguished namely:

- The liquid film is immobilised within the pores of a porous membrane. This type is the so called Immobilized Liquid Membrane (ILM) or Supported Liquid Membrane (SLM).
- The second type is the so called Emulsion Liquid Membrane (ELM).

Selectivities of liquid membranes are based on the differences in the distribution coefficients of the components of the feed phase with the liquid in the membrane. If the components are similar, these differences are generally not very high. The diffusivities of components of comparable size are similar so that the selectivity, which is determined by differences in solubility and diffusivity, will not be high in general. To increase the selectivity, a carrier molecule can be added to the liquid in the membrane. This carrier molecule can have a high affinity for a specific

component in the feed phase and thus will it enhance the transport of this component over the membrane. [5, 10]

2.3.5 Dialysis

Concerning this project, dialysis (passive dialysis) is definitely the most important membrane process. For this reason it will be discussed in more detail than the other processes discussed so far.

2.3.5.1 The history and development of dialysis

Even though dialysis was the first membrane separation process to be discovered and studied, it has never really become industrially important. [1] By far and away the most important application of dialysis is in the medical field: hemodialysis for the treatment of chronic and acute uremia and for the removal of poisons from the bloodstream. Dialysis is not widely used on the industrial separations for the same two reasons membrane separation processes have failed in the past:

- It is a slow process, in part because it is driven by concentration differences, which are usually set by the system. (Time is a crucial factor in industrial processes)
- It is not highly selective, and species that are at all similar in chemistry or molecular size cannot be cleanly separated by dialysis. (Other methods of separation, for example electrodialysis and ion exchange, was much more effective) [1]

In fact, relative to other membrane processes that have come along since (such as reverse osmosis, ultrafiltration and electrodialysis), progress in dialysis has been quite slow.

The first significant application of dialysis occurred in the mid-1930s when

cellophane (regenerated cellulose) was first used to remove salts and other low molecular weight solutes from serum proteins and vaccines. At about the same time it was used for the recovery of caustic soda from hemicellulose solutions in the manufacture of rayon.

The dominant use of dialysis today is in the treatment of patients with kidney failure, to remove urea, uric acid, creatinine and other products of protein metabolism from their blood. In hemodialysis, arterial blood from the patient is passed over one side of the dialysis membrane while a dialysate solution containing a suitable mixture of ions is circulated on the other side. Hemodialysis was first reported by Abel, Rountree and Turner in 1914. However, the first practical unit was not assembled until 1944 by Kolff and Beck in Holland. [1, 11]

In 1950, dialysis membranes became commercially available. The concept of mass-transfer in on-line analytical dialysers was applied for a number of years in continuous flow systems. The use of on-line dialysis in segmented continuous flow systems was reported by Skeggs in 1957. In the mid 1960s, the first, non-segmented continuous flow system with a dialysis application, was introduced by Kadish and Hall. [11, 12] In 1975, Růžička introduced the first on-line flow injection dialysis application system.

2.3.5.2 Definition and the process of dialysis

The following definitions of dialysis was obtained:

Dialysis is the flux of dissolved lower molecular mass components through the membrane as a result of a difference in trans-membrane concentration. [5,6]

or in other words

Dialysis is a rate-governed membrane process in which a microsolute is driven across a semi-permeable membrane by means of a concentration gradient. [4]

The microsolutes **diffuses** through the membrane at a greater rate than the macrosolutes also present in the feed solution. (Depending on the pore size of the specific membrane, the smaller solutes that will diffuse through the pores with ease, will be classified as micro solutes whereas solutes that have difficulties in diffusing through the pores, will be classified as macrosolutes) If the receiving solution is not continuously renewed, the solute concentrations on both sides of the membrane will tend to equalize, negating the driving force for the separation. A good level of cleanup can be obtained from the process, provided that a concentration gradient can be maintained by continuous removal of the permeating components. Further more it is important to realize that dialysis is always accompanied by osmosis in normal operation. There is thus a reduction of the solute concentration in the feed because of osmosis which can seriously diminish the existing concentration gradient. [4 - 6]

If the feed and the dialysate are composed of the same solvent and differ only slightly in concentration, the assumption is made that the solute concentrations are proportional to their activities. When the feed and dialysate are composed of differing phases, these approximations are no longer valid since the standard states to which the activities are referenced may be different. For exact descriptions of driving forces, estimates of fugacities must be employed. [4]

Even though membrane composition and synthesis will be discussed, it was thought appropriate to give a short introduction into dialysis membranes.

The upper limits of pore dimensions in dialysis membranes are purposely chosen to minimize convective transport. (Convective transport is the transport of solutes due to the mechanical movement of the solution due to stirring, pumping or agitation) Consequently, the solute size that can permeate dialytic membranes has an upper bound determined by the above mentioned factor and by comprises made during membrane fabrication. Dialysis membranes usually have pore radii smaller than 60×10^{-8} cm. Macro molecules for example proteins like albumin, will

to a large extent, be retained. The effective pore size (of synthetic hydrophobic polymer membranes) can be reduced by the adsorption of proteins so that membranes with large pores will, during use in a dialysis system, develop improved protein retention. The hydrogel (celluloses) membranes with rather smaller pore radii (17×10^{-8} cm) do not adsorb the proteins and thus their transport properties will not be effected. To achieve selective mass transport in a dialytic process, one must rely upon a combination of solute and membrane properties. As an initial approximation, two solutes can be separated by dialysis if their diffusion coefficients in the feed differ by at least an order of magnitude. The solute diffusivity in the continuum within the membrane is an indicator of whether or not, and how fast a solute may permeate the membrane. This diffusivity is also modified by the matrix structure of the membrane, usually to a smaller value. In the simplest case of a hydrogel membrane, such as regenerated cellulose, the aqueous diffusion coefficient is reduced by a factor of ten for small solutes, with higher reductions for larger solutes. [4]

Many new terms were introduced in paragraph 2.2.5 which can leave the reader somewhat in the dark. This is an introductory description of dialysis and these terms will be explained in the paragraph concerned with membrane syntheses. The theory concerning dialysis and ion movement are discussed in detail in Chapter 3.

A matter which can be a cause of ambiguity, is the difference between normal dialysis and Donnan dialysis. Some disagreement and vagueness was encountered between the different references used. According to Ho and Sirkar [4] and Rautenbach and Albrecht [6], Donnan dialysis differs from other forms of dialysis in that it relies upon an ion-selective membrane to retard the transfer of either a cation or anion across the barrier. According to Mulder [5] normal dialysis is restricted to the diffusion of neutral solutes and that Donnan dialysis is the separation of electrolytes by either a neutral membrane or an ion-selective membrane. For the sake clarity in this thesis, the former of the two definitions will

be used.

2.3.6 Electrodialysis

2.3.6.1 History and development of electrodialysis

Electrodialysis is useful in a number of areas for example:

- Removal of electrolytes from aqueous solutions, e.g. water desalting.
- Concentration of electrolytes.
- Separation of electrolytes from non-electrolytes.
- Oxidation/reduction or acid/base formation.
- Double decomposition reactions.
- Separation of ions of like charge.

The first four of these applications have become substantial industrial applications. The principle application of electrodialysis today is the desalination of brackish water.

The history of electrodialysis dates back to the early 1930s, when aqueous solutions were first desalted in three-compartment cells consisting of an anode compartment, an anion-permeable and cation-permeable membrane forming a middle compartment, and a cathode compartment. Meyer and Strauss were the first to assemble a multicompartment electrodialysis apparatus.

With the advent of commercial reverse osmosis in the early 1970s, there has been considerable competition between electrodialysis and reverse osmosis for the brackish-water desalination market. Electrodialysis has found an important application in desalting foods, as in the removal of salts from cheese whey to produce a milk substitute, and in salt removal from sugar solutions. Another

important application of electrodialysis has been found in Japan, where there is essentially no indigenous supply of table salt. Seawater is treated by electrodialysis to produce a salt solution of about 20 wt % concentration that is then thermally evaporated to dryness.

2.3.6.2 The process of electrodialysis

In this process, electrically charged membranes are used to remove ions from an aqueous solution. A number of cation- and anion-exchange membranes are placed in an alternating pattern between a cathode and an anode. When an ionic feed is pumped through the cell, nothing will happen unless a direct current (dc) is applied. When a dc current is applied, cations and anions will migrate to the cathode and the anode respectively. The cations are obstructed in their migration by the anion-exchange membrane and so also the anions by the cation-exchange membrane. The overall effect is that the ionic concentration increases in alternating compartments accompanied by a simultaneous decrease in ionic concentrations in the other compartments. This principle is well explained in Figure 2.4. [4, 5, 9]

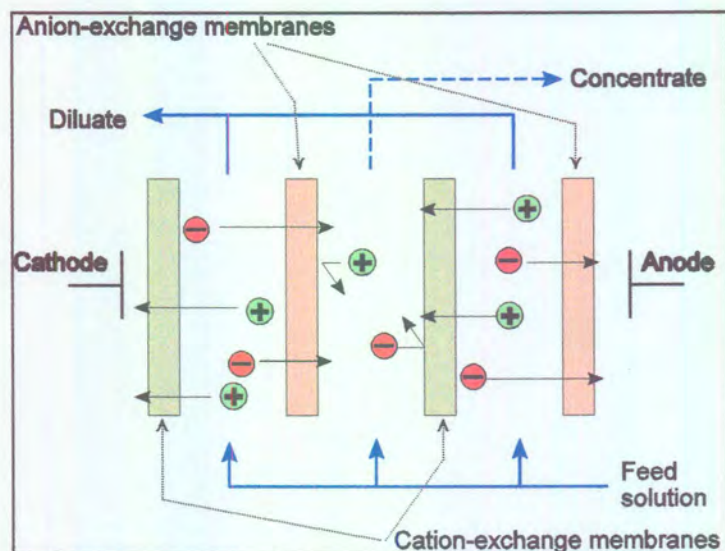


Figure 2.4 The Principle of Electro dialysis

2.4 Characterisation and Structure of Membranes

Membranes can be made of a large number of different materials. A classification of membranes can be divided into two main groups namely biological and synthetic membranes. Biological membranes are essential for life on earth. Every living cell is surrounded by a membrane, but these membranes differ fundamentally in structure, functionality etc. from synthetic organic and inorganic membranes. [5, 8] Synthetic membranes can be divided into organic (polymeric) and inorganic membranes, the most important class of membrane materials being the polymeric membranes. The choice of a given polymer as a membrane material is not arbitrary but based on very specific properties, origination from structural factors. Structural factors determine the chemical, thermal and mechanical properties of the polymer used. Such factors will also influence the permeability of the membrane. [5]

Polymers are high molecular weight components built up from a number of basic units, the monomers. The number of these monomers which link together to form a long chain molecule, will indicate the degree of polymerisation. The molecular weight of a long

chain is dependant on the degree of polymerisation. Basically all polymers can be used as barrier or membrane material but the chemical and physical properties differ so much that only a limited number can be used in practice. [4, 5]

Membranes need to be characterised to ascertain which can be used for specific separations or class of separations. A small change in one of the membrane parameters can change the structure and consequently have a drastic effect on membrane performance. Characterization is necessary to relate structural membrane properties such as pore size, pore size distribution, free volume and crystallinity to membrane separation properties. Membrane characterisation leads to the determination of structural and morphological properties of a given membrane.

Three basic types of membranes² can be distinguished based on their structure and separation principles:

- Porous membranes
- Non-porous membranes
- Carrier membranes

A schematic presentation of these various types of membranes is given in Figure 2.5.

² Not all membranes and membrane structures are covered by this classification. This approach is used for simplicity so that the basic principles can be understood. Further, there is no distinct transition from one type to the other.

2.4.1 Porous membranes

Membranes of this type induce separation by discrimination between particle size. High selectivities can be obtained when the solute or particle size is large relative to the pore size. [5]

Porous membranes contain fixed pores. The selectivity is mainly determined by the dimensions of the pores but the choice of material affects phenomena such as adsorption and chemical stability under condition of actual application and membrane cleaning. This implies that the requirements for the polymeric material are not primarily determined by the flux and selectivity but also by the chemical and thermal properties of the material. [4, 5]

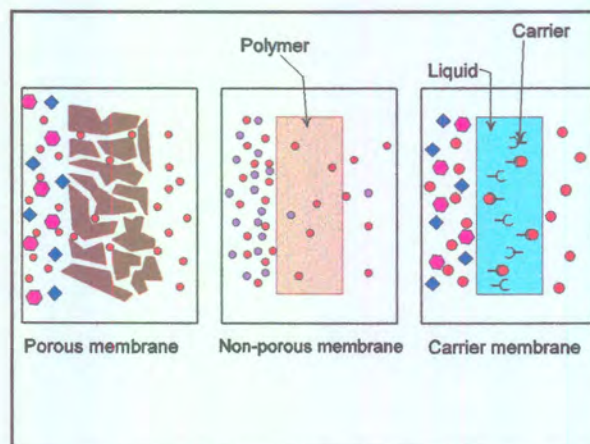


Figure 2.5 Schematic presentation of the three basic types of membranes

Even with the pore size and pore distribution determined exactly, the membrane performance is sometimes governed by other parameters such as concentration polarization and fouling. An important and often overlooked parameter is the pore geometry. Some characterisation techniques determine the dimensions of the pore entrance rather than the pore size to obtain information about permeation characteristics. Another important factor is the pore size distribution. The pores

in these membranes do not have the same size but exist as a distribution (Gaussian distribution) of sizes. In this case, the membrane can be characterised as nominal or absolute pore size. With an absolute rating, every particle of this specific size and larger will be retained whereas the nominal rating indicates that a certain percentage of the particles of a specific size or larger will be retained. It should be noted that this definition does not characterise the membrane nor the pores of the membrane, but rather the size of the particles retained by it. Another important factor is the surface porosity. This a very important variable in determining the flux through the membrane, in combination with the thickness of the top layer or the length of the pore.

Two different types of characterisation methods for porous membranes can be distinguished from the above mentioned considerations: [5]

- *Structure related parameters.* The determination of pore size, pore size distribution, top layer thickness and surface porosity.
- *Permeation-related parameters.* Determination of the actual separation parameters using solutes that are more or less retained by the membrane. (The so called cut-off measurements)

It is often very difficult to relate the structure-related parameters directly to the permeation-related parameters because the pore size and shape is not very well defined. The configuration of the pores (cylindrical, packed-spheres) used in simple model descriptions deviate sometimes dramatically from the actual morphology as depicted in Figure 2-6. [4, 5]

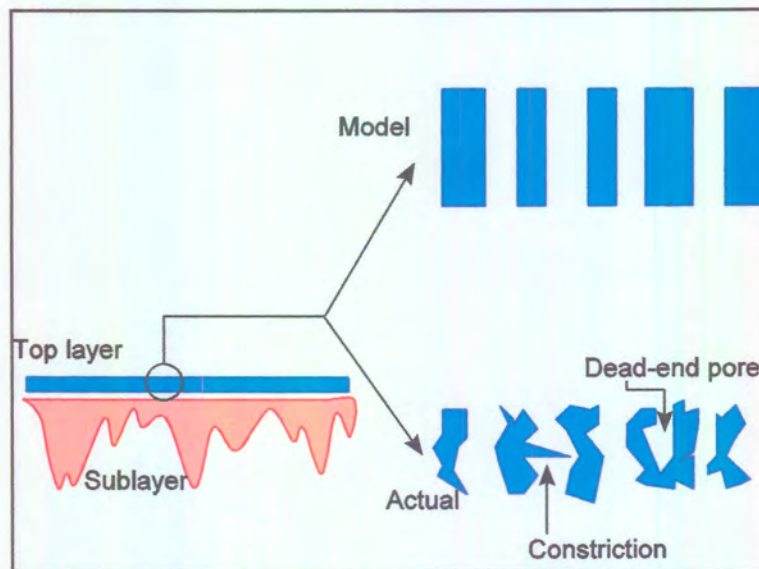


Figure 2.6 Comparison of an ideal and the actual structure of an Ultrafiltration membrane.

There are a number of characterisation techniques available for porous media and although both microfiltration and ultrafiltration membranes are porous, different techniques are used for the characterization. [5]

For microfiltration:

- Scanning electron microscopy
- Bubble-point method
- Mercury intrusion porometry
- Permeation measurements

*For ultrafiltration:*³

- Gas adsorption-desorption
- Thermoporometry
- Permporometry
- Liquid displacement
- Rejection measurements

3

The structure is more asymmetrical compared to microfiltration membranes. Such membranes consist of a thin top layer supported by a porous sublayer, with the resistance to mass transfer being almost determined completely by the top layer.

- Transmission electron microscopy

2.4.2 Non-porous membranes

These membranes are commonly used in gas and vapour separation, pervaporation and dialysis. For the abovementioned processes, either composite or asymmetric membranes are used. In this type of membrane the performance permeability and selectivity is determined by the intrinsic properties of the material. The choice of material is determined by the type of application, and the polymer type can range from an elastomer to a glassy material. Membranes in this class are capable of separating species of approximately the same size from each other. Separation takes place through differences in solubility and/or differences in diffusivity. This means that the intrinsic properties of the polymeric material determine the extent of selectivity and permeability. [4]

Nonporous membranes are used to perform separations on a molecular level. However, rather than molecular weight or molecular size, the chemical nature and morphology of the polymeric membrane and the extent of interaction between the polymer and the permeants are the important factors to consider. Transport through nonporous membranes occurs by a solution-diffusion mechanism and separation is achieved either by differences in solubility and/or diffusivity. The determination of the physical properties of these membranes and hence the characterisation of the membrane can be accomplished by one of the following methods:

- Determine the permeability towards gasses and liquids.
- Determine the physical properties of the membrane by means of DSC/DTA methods, density measurements, and XRD.
- Measurement of the thickness of the membrane with plasma etching.
- Surface analysis. [5]

2.4.3 Carrier membranes

In this case, transport is not determined by the membrane or membrane material but by a very specific carrier-molecule which facilitates specific transport. Through the use of specially tailored carriers, extremely high selectivities can be obtained. [4, 5]

2.5 Membrane materials

Hydrophobic materials (see Figure 2.7) such as polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF) and isotactic polypropylene (PP) are often used for membranes. PTFE is highly crystalline and exhibits excellent thermal stability. It is not soluble in any common solvent and hence also shows good thermal and chemical resistance. PVDF also shows good thermal and chemical resistance although not as good as PTFE. (It is soluble in aprotic solvents.) PP is also excellent solvent resistant when in the isotactic configuration. (Isotactic: where all the side groups lie on the same side along the main chain). The three polymers PTFE, PVDF and PP cannot be wetted by water spontaneously, i.e. when used in aqueous mixtures have to be pre-wetted. These three materials are commonly used for microfiltration. [5]

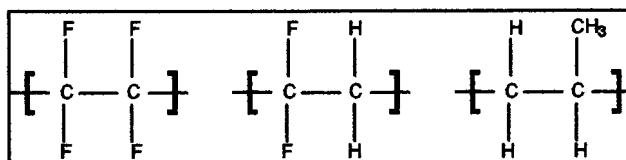


Figure 2.7 Structure of PTFE, PVDF and PP respectively

Cellulose (or regenerated cellulose) is mainly used as a material for dialysis membranes. Cellulose is a polysaccharide that can be obtained from plants. Its molecular weight varies from 500 000 to 1 500 000 implying that the number of segments (single carbon chains) is roughly between 3000 and 9000. The glucose segment contains three hydroxyl groups which are very susceptible to chemical reaction by forming esters and ethers. The glucose repeating units in cellulose are connected by β -1,4 glycosidic



linkages (see Figure 2.8). Because of its structure, cellulose is quite crystalline, and although the polymer is very hydrophilic, it is not water soluble. This is due to the crystallinity and intermolecular hydrogen bonding between the hydroxyl groups. Cellulose derivatives such as cellulose nitrate and cellulose acetate are used for microfiltration/ultrafiltration applications, whereas cellulose triacetate exhibit good properties as a reverse osmosis membrane in desalination applications. Cellulose esters have got excellent membrane properties but are very sensitive to thermal, chemical and biological degradation. [5]

Another class of membrane polymers are the polyamides. These polymers are characterised by the amide group. Although the aliphatic polyamides comprise a very large class of polymers, the aromatic polyamides are to be preferred as membrane materials because of their outstanding mechanical, thermal, chemical and hydrolytic stability, as well as their permselective properties, particularly in reverse osmosis.

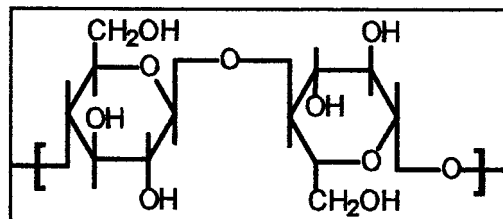


Figure 2.8 The chemical structure of cellulose

2.6 References

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Chapter 3

Theoretical Background to the Movement of Particles in a Solution and across a Membrane

3.1 Introduction.

One of the main objectives of this study was to enhance the mass transfer of particles (analyte) across a passive membrane. It therefore was of utmost importance that one should be equipped with a sound knowledge on the movement of these particles in a solution and across a membrane. This project was based, specifically, on the movement of charged particles (ions) under the influence of an applied potential across a passive membrane. Figure 3.1 is a schematic presentation of a longitudinal cross section of the proposed electrolysers. In Figure 3.1 the movement of the fluid in the electrolysers, due to the pumping action of the peristaltic pump, is from left to right. If one considers Figure 3.1, it is clear that there were two categories of movement for the analyte ions namely : (All definitions to follow are based upon analytical and physical chemistry and are not only for Flow Injection Analysis)

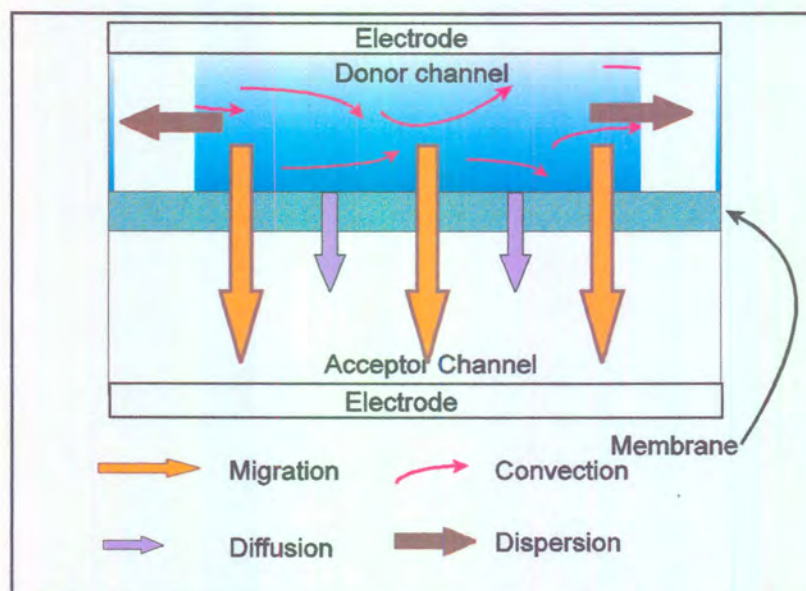


Figure 3.1 Means of movement of a charged particle in the proposed dialyser unit.

1. The transport of the ions from the bulk of the solution to the membrane surface.

There are three ways by which an ion can be transported namely: (See Figure 3.1)

1. Dispersion (sample ion distribution in the Flow injection electrolysers unit): Can be subdivided into convective- (due to the flow of the solvent in the tubing and in the donor channel in the case of Figure 3.1) and diffusional transport (axial and radial concentration gradients that exist due to the form of the injected sample bolus).
2. Diffusion: Ions are transported due to the concentration gradient that exist. (This diffusion must not be confused with the diffusion that do exist due to the form of the sample bolus, but it is rather due to the inhomogeneous composition of the sample bolus.)
3. Migration: Ions are transported due to the influence of the applied potential. [1, 2, 3]

In the bulk of the solution (that is in the donor channel of the dialyser), it is clear that two of these types of transport will predominate namely, the convective transport due to the pumping action through the donor channel and migration due to the applied potential. Diffusion will only be possible as the dispersion process [1], since the analyte solution will be a homogeneous mixture of the analyte ions.

2. The transport of the ions across the membrane.

Various membrane processes (of which electro dialysis and dialysis are the predominant) must be considered. Neutral membranes are used in an electro dialysis system, thus it is not only conventional electro dialysis

across an ion-exchange membrane that was under study but also other membrane processes.

It is clear that this theoretical chapter can be subdivided into the sections as described above. As an introduction into the general theory of ion transport under the influence of an applied potential, it was thought appropriate to make use of the theoretical work as explained by Atkins. [4] Some guidelines are also given by Wesselingh and Krishna. [5] It is furthermore important to note that the Fick's description of mass transfer was used in this theoretical chapter. Mass transfer can also be described by the Maxwell-Stefan relation. [4]

3.2 Ion Transport (the movement of a charged particle under the influence of an applied potential)

In solution, cations move towards a negatively charged electrode (cathode) and anions move towards a positively charged electrode (anode). This migration is a transport process, in principle the same as kinetic theory of gases, with the main differences being the support of the solvent and the drift of ions under the influence of an electrical field. The presence of the field is a simplification, because the average motion of the ions is easy to describe. The presence of the solvent (and the ion-ion interactions) is a complication which is still the subject of current research.

3.2.1 Ion motion : the empirical facts

The conductivity of a solution is determined by measuring its electrical resistance, and the standard method is to incorporate a conductivity cell, of the type shown in Figure 3.2, into one arm of a Wheatstone bridge and to search for the balance point. The main complication is that alternating current must be used because a direct current would lead to electrolysis and to polarisation. The use of alternating current (with a frequency of about 1 kHz) avoids polarisation because

the charging that occurs on one half of the cycle is undone during the second half. By studying the transport of charge through electrolyte solutions it is possible to build up a picture of the events that occur.

The resistance (symbol: R) of a sample increases with its length ℓ and decreases with its cross-sectional area A : $R \propto \ell/A$. The proportionality coefficient is called the resistivity (symbol: ρ), and it can be written as $R = \rho\ell/A$. The conductivity (symbol: κ) is the inverse of the resistivity therefore

$$R = \frac{1}{\kappa} \frac{\ell}{A} \quad \text{or} \quad \kappa = \frac{\ell}{RA} \quad 3.1$$

Resistance is expressed in ohm (Ω). The reciprocal ohm, Ω^{-1} , is called the siemens (symbol: S , $1 S = 1\Omega^{-1}$). It follows that the units of conductivity are $S\text{m}^{-1}$ (or $S\text{cm}^{-1}$). The conductivity of a solution, which is due to contributions from both cations and anions, depends on the number of ions present, and it is normal to introduce the molar conductivity (symbol: Λ_m) defined as

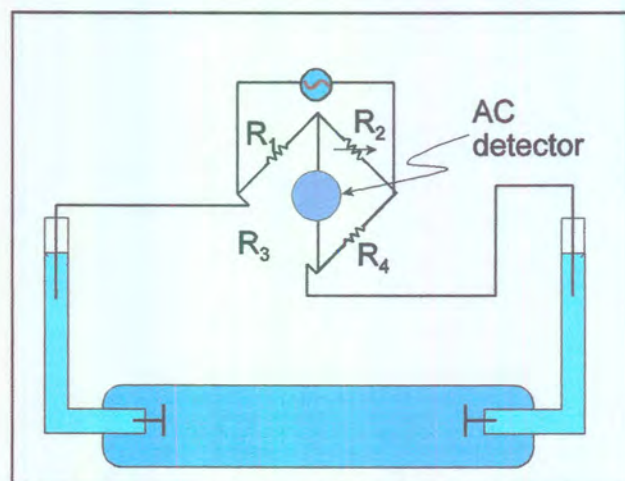


Figure 3.2 The conductivity of an electrolyte solution is measured by making the cell one arm of a Wheatstone bridge and measuring its resistance.

$$\Lambda_m = \frac{\kappa}{c}$$

3.2

with c being the (molar) concentration of the added electrolyte. The equivalent conductivity is also sometimes used. This takes into account the fact that some ions are multiply charged, and so might transport more charge even though they may be moving more slowly. The equivalent conductivity treats all ions as being singly charged. For example, in $\text{NaCl} (aq)$, each ion carries unit charge in each direction, and the equivalent conductivity is the same as the molar conductivity. In $\text{CuSO}_4 (aq)$, however, each ion transports two units of charge, and the equivalent conductivity is half the molar conductivity.

Molar conductivities depend on the concentration of the electrolyte. (They would be independent of concentration only if the conductivity was exactly proportional to the concentration, and for such strongly interacting particles as ions this is unlikely to be the case.) Measurement of the concentration dependence of molar conductivities shows that there are two classes of electrolyte. In one, the strong electrolytes, the molar conductivity decreases slightly as the concentration is increased (illustrated in Figure 3.3) but the effect is not large. In the other, the weak electrolytes, the molar conductivity is normal at concentrations close to zero, but drops sharply to low values when the concentration departs from zero. (illustrated in Figure 3.3) The classification depends on the solvent employed as well as the solute: lithium chloride, for example, is a strong electrolyte in water,

$$\Lambda_m = \Lambda_m^0 - K\sqrt{c} \quad 3.3$$

This is called Kohlrausch's Law. Λ_m^0 is called the limiting molar conductivity and K is a coefficient that is found to depend more on the nature of the electrolyte (i.e. whether it is of the form MA , or M_2A , etc.) than on its specific identity.

Kohlrausch was also able to confirm that the value of Λ_m^0 for any electrolyte can be expressed as the sum of contributions from its individual ions. If the molar conductivity of the cations is denoted λ_+ , and that of the anions λ_- , then Kohlrausch's Law of the independent migration of ions is

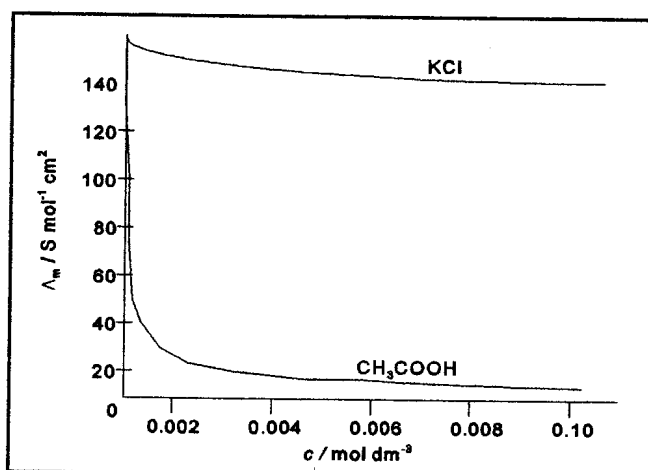


Figure 3.3 The concentration dependence of the molar conductivities of a strong and weak electrolyte respectively.

$$\Lambda_m^0 = \nu_+ \lambda_+ + \nu_- \lambda_- \quad 3.4$$

where ν_+ and ν_- are the numbers of cations and anions per formula unit of electrolyte (e.g. $\nu_+ = \nu_- = 1$ for HCl , NaCl , and CuSO_4 , but $\nu_+ = 1$, $\nu_- = 2$ for

MgCl₂). This simple result, which can be understood on the grounds that the ions behave independently when the solution is infinitely dilute.

Weak electrolytes are substances that are not fully ionised in solution, and include weak acids and bases. The marked concentration dependence of their conductivities arises from the displacement of the MA(aq) ⇌ M⁺(aq) + A⁻(aq) equilibrium towards the right at high dilutions. The conductivity depends on the number of ions in the solution, and therefore on the degree of ionisation, α, of the electrolyte. If the ionisation equilibrium constant of some weak 1:1 electrolyte, MA, is denoted K, then then it is present at a concentration c,

$$K = \frac{[M^+(aq)][A^-(aq)]}{[MA(aq)]} = \frac{(a\alpha)(\alpha c)}{(1-\alpha)c} = \left\{ \frac{\alpha^2}{1-\alpha} \right\} c \quad 3.5$$

where a is the activity and c is the concentration. The degree of ionisation when the concentration is c is therefore

$$\alpha = \frac{1}{2} (K/c) \left\{ \left(1 + 4c/K \right)^{\frac{1}{2}} - 1 \right\} \quad 3.6$$

If the molar conductivity of the hypothetical fully ionised electrolyte is Λ'_m, then since only a fraction α is ionised in the actual solution, the measured molar conductivity (Λ_m) is given by

$$\Lambda_m = \alpha \Lambda'_m \quad 3.7$$

with a α given by equation 3.6. The value of Λ'_m may be approximated by Λ⁰_m, and so, if K is known, equation 3.6 can be used to predict the concentration dependence of the molar conductivity. The dependence agrees quite well with the experimental curve shown in Figure 3.3.

Alternatively, the concentration dependence of Λ_m can be used in measurements

of the limiting molar conductivity. It is quite easy to manipulate the equilibrium constant expression into the form

$$1/\alpha = 1 + \alpha c/K,$$

and so, with

$$\alpha = \Lambda_m / \Lambda_m^0$$

then

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K(\Lambda_m^0)^2} \quad 3.8$$

This is called Ostwald's Dilution Law, and it shows that if $1/\Lambda_m$ is plotted against $c \Lambda_m$, the intercept is $1/\Lambda_m^0$.

3.2.2 The mobilities of ions

At this point it is important to become acquainted with some definitions:

The rate of migration of a property (ions in this case, but it can also refer to heat or any other physical property) is measured by its flux (J), which is the quantity passing through unit area per unit time. The flux of a property is usually proportional to the gradient of a related property of a system. (The flux of a species is proportional to its concentration gradient in other words the flux is proportional to a concentration difference times a mass transfer coefficient. [4])

Two kinds of flux can be distinguished namely:

J_z with respect to the (moving) mixture and

N_z with respect to an interface. See Figure 3.4.

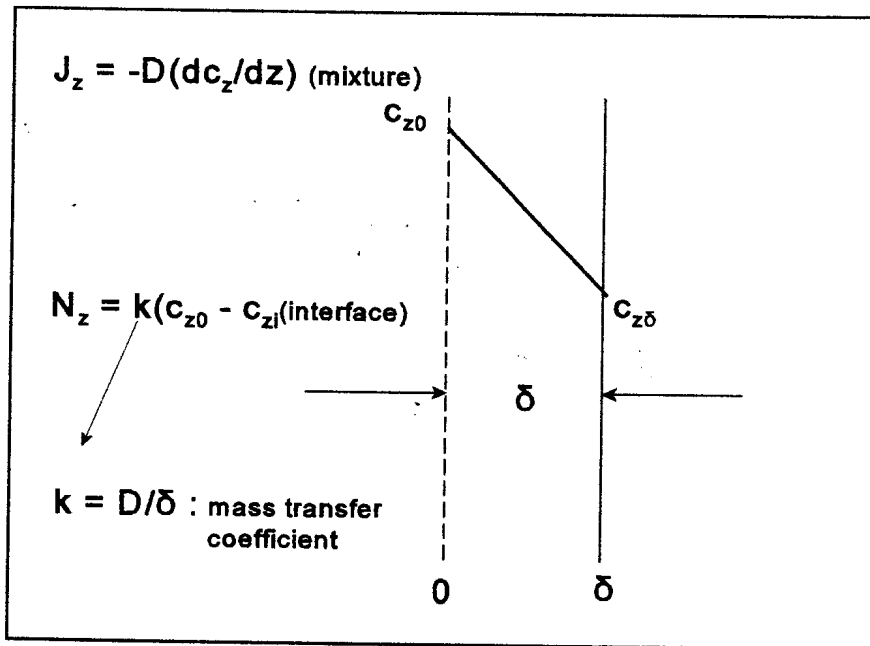


Figure 3.4 Fluxes with respect to J and N .

J is the more fundamental of the two. [4]

The rate of diffusion (the flux of matter) parallel to some axis z (J_z) is found to be proportional to the concentration gradient along that axis, thus

$$J_z \propto \frac{dN}{dz}$$

where N the number density.

J_z is a component of a vector, and the positive sign indicates flow towards increasing z . Matter flow occurs down a concentration gradient and so if dN/dz is negative, J_z is positive. (See Figure 3.5). Therefore, the coefficient of proportionality in the matter flux expression must be negative and it is denoted $-D$ (diffusion coefficient). This leads to Fick's first law of diffusion.

$$J_z = -D \left(\frac{dN}{dz} \right) \tag{3.9}$$

This law will be discussed later in this chapter. Please note that concentration is denoted as c in Figure 3.4 whereas for the same equation (equation 3.9) the number density, N , was used.

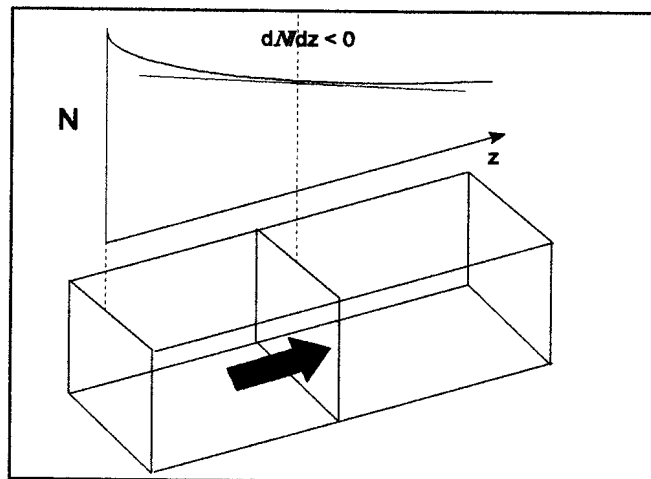


Figure 3.5 The flux of particles down a concentration gradient.

Ions in solution are subject to a variety of forces. They experience the random bombardment of the solvent particles, but since these occur in random directions they do not result in net motion if the solution is uniform. In an electric field they also experience an electric force. When two electrodes a distance ℓ apart are at a potential difference $\Delta\phi$, there is a uniform electric field of magnitude $E = \Delta\phi/\ell$ between them. An ion of charge ze experiences a force (Γ) of magnitude.

$$\Gamma = zeE = \frac{ze\Delta\phi}{\ell} \quad 3.10$$

With e the elementary charge and z the sign of the charge.

A cation responds by accelerating in the direction of the negative electrode (cathode) and an anion accelerates towards the positive electrode (anode).

As the ion rubs through the solvent a frictional force, Γ' , retards it with a strength

that increases with its speed. If we assume that the Stokes formula ($F = fs$, $f = 6\pi\eta a$) for a sphere of radius a , speed s and solvent viscosity η applies even on a microscopic scale, then a terminal speed, called the drift speed, is reached when the accelerating force ($F = zeE$) is balanced by the viscous drag ($F = fs$). This occurs when

$$s = \frac{zeE}{f} \quad 3.11$$

Where E is the electric field applied and f is the frictional constant.

Since the drift velocity governs the rate at which charge is transported, the conductivity is expected to decrease with increasing solution viscosity and increasing ion size.

Experimental results confirm these predictions for bulky ions (such as R_4N^+ and $RCOO^-$), but not for small ions. For example, the molar conductivities of the alkali metal ions increase from Li^+ to Cs^+ , even though the ionic radii increase. The discrepancy is resolved when we realize that the radius in Stokes' formula is the hydrodynamic radius of the ion, its effective radius in the solution taking into account all the solvent molecules it carries. Small ions give rise to stronger electric fields than large ones (it is a result from electrostatics that the electric field at the surface of a sphere of radius R is proportional to ze/R^2 , and so the smaller the radius the stronger the field). For this reason small ions are more extensively solvated than big ions. This means that an ion of small ionic radius has a large hydrodynamic radius because it drags many solvent molecules through the solution as it migrates. Therefore, it also has a lower molar conductivity than a bigger ion of the same charge. Friction will be discussed again in paragraph 3.3.

The proton, however, although it is very small, has a very high molar conductivity. This is because it conducts by a mechanism (the Grotthuss mechanism) that does not involve its actual motion through the solution. Instead of a single, highly solvated proton moving through the solution, it is believed that there is an effective motion of a proton which involves the rearrangement of bonds through a long chain of water molecules, and the conductivity is governed by the rates at which the water molecules can rotate into orientations in which they can accept or donate protons. (See Figure 3.6)

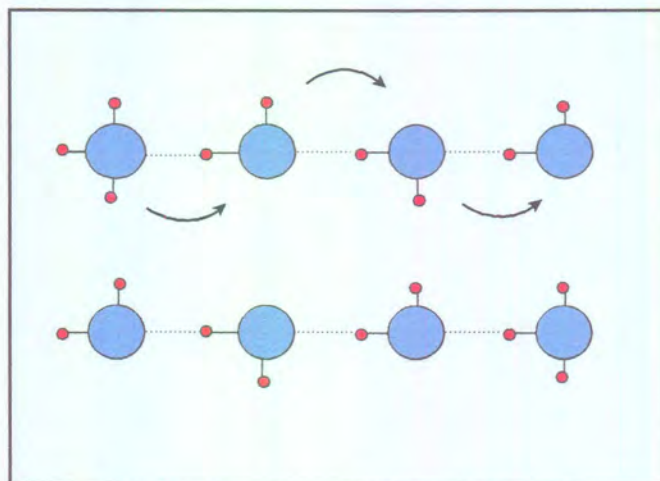


Figure 3.6 The mechanism of conduction in water.

The drift speed is proportional to the strength of the applied field. The coefficient of proportionality is called the mobility of the ion (symbol : u) and we write

$$S = uE \quad 3.12$$

This means that at a stage in an alternating current (AC) cycle when there is a potential difference of 1 V across a solution of length 1 cm (so that $E = 1 \text{ V cm}^{-1}$), the drift speed is typically about $6 \times 10^{-4} \text{ cm s}^{-1}$. This might seem slow, but not when expressed on a molecular scale, for it corresponds to an ion passing about 10 000 solvent molecules per second.

The usefulness of ionic mobilities is that they provide a link between measurable and theoretical quantities. As a first step the relation between mobility and conductivity is established. In order to keep the calculation simple, signs are ignored with the concentration being on the magnitude: The direction of flux can always be decided by common sense.

Consider a solution of a strong electrolyte at a concentration c . Let each formula unit give rise to v_+ cations of charge z_+e and v_- anions of charge z_-e . The concentration of each type of ion is therefore vc (with $v = v_+$ or v_-) and the number density of each type is vcN_A (N_A is Avogadro's number) The number of cations that pass through an imaginary window of area A (See Figure 3.7), during an interval Δt is equal to the number within the distance $s_+\Delta t$, and therefore to the number in the volume $s_+\Delta tA$. The number in this volume is equal to $(s_+\Delta tA)(v_+cN_A)$. The number passing through the window per unit area per unit time, the cation flux, is therefore

$$J_{\text{cations}} = (s_+\Delta tA)(v_+cN_A) / \Delta tA = s_+v_+cN_A$$

Each cation carries a charge z_+e , and so the flux of charge is

$$J(\text{charge}) = z_+s_+v_+ceN_A = z_+s_+v_+cF$$

where $F = eN_A$ is Faraday's constant. Since $s = uE$ this becomes

$$J(\text{charge}) = z_+s_+v_+cFE.$$

The current through the window due to the cations (I_+) is the charge flux times the area, $I_+ = JA$. The electric field is the potential gradient $\Delta\phi/\ell$. Therefore,

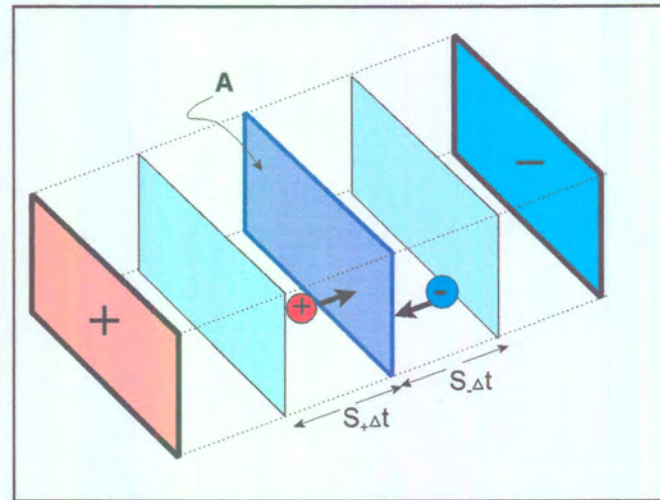


Figure 3.7 In the calculation of the current, all the cations within a distance $s_+\Delta t$ will pass through the area A and likewise for the anions

$$I_+ = \frac{z_+ u_+ v_+ c F A \Delta \phi}{l} \quad 3.13$$

Current and potential difference are related by Ohm's Law, $I = \Delta\phi/R$, and the resistance R is related to the conductivity by equation 3.1. Therefore, for the cations, $I_+ = \kappa_+(\Delta\phi A/l)$. Comparison of this with the last expression gives

$$\kappa_+ = z_+ u_+ v_+ c F,$$

and so the molar ionic conductivity is

$$\lambda_+ = z_+ u_+ F \quad 3.14$$

Exactly the same argument leads to the corresponding expression for the anion molar conductivity.

$$\lambda_{\pm} = z_{\pm} u_{\pm} F \quad 3.15$$

It follows that the limiting molar conductivity of a solution is related to the individual ion mobilities by

$$\Lambda_m^0 = \{z_+ u_+ v_+ + z_- u_- v_-\} F \quad 3.16$$

In case of a symmetrical z:z electrolyte (e.g. CuSO_4), this simplifies to

$$\Lambda_m^0 = z(u_+ + u_-)F \quad 3.17$$

Ions that are very mobile carry a large fraction of the total current. The transference number or transport number (symbol: t) is defined as the fraction of total current carried by the ions of a specified type. In the case of a solution of two kinds of ion, the cation transport number is defined as

$$t_+ = \frac{I_+}{I} \quad 3.18$$

with a similar expression for the anion transport number t_- . Since the total current I is the sum of the cation and anion currents, $t_+ + t_- = 1$. The cation current is related to the cation mobility by equation 3.12, with a similar expression for the anions, and so the relation between the limiting value t^0 and u is

$$t_+^0 = z_+ v_+ u_+ / (z_+ v_+ u_+ + z_- v_- u_-) \quad 3.19$$

In the case of a symmetrical electrolyte this simplifies to

$$t_+^0 = \frac{u_+}{(u_+ + u_-)}, \quad t_-^0 = \frac{u_-}{(u_+ + u_-)} \quad 3.20$$

Moreover, since the ionic conductivities are related to the mobilities, from equations 3.13 and 3.14 it follows that

$$t_+^0 = \frac{v_+ \lambda_+}{(v_+ \lambda_+ + v_- \lambda_-)}, \quad t_-^0 = \frac{v_- \lambda_-}{(v_+ \lambda_+ + v_- \lambda_-)} \quad 3.21$$

and therefore that

$$v_+ \lambda_+ = t_+^0 \Lambda_m^0, \quad v_- \lambda_- = t_-^0 \Lambda_m^0 \quad 3.22$$

Consequently, since there are independent ways of measuring transport numbers of ions, we can determine the individual ionic conductivities and through equations 3.14 and 3.15 the ionic mobilities.

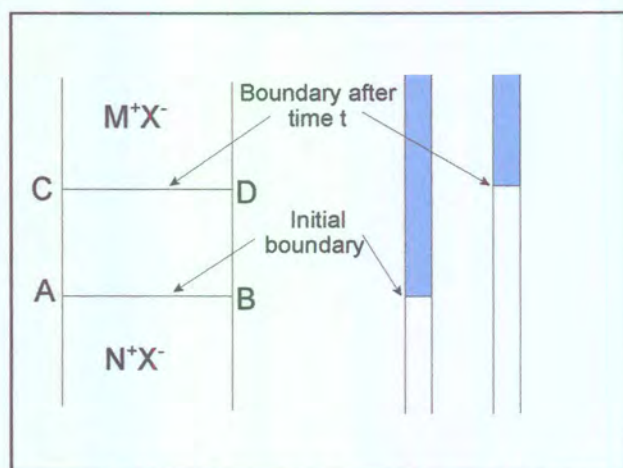


Figure 3.8 the moving boundary method for the measurement of transference numbers

3.2.3 The measurement of transport numbers

One of the most accurate methods for measuring transport numbers is the moving boundary method in which the motion of a boundary between two ionic solutions having a common ion is observed as a current flow.

Let MX be the salt of interest and NX (the indicator) a salt giving a denser solution. The indicator solution occupies the lower part of a vertical tube, Figure 3.8, and the MX solution, the leading solution, occupies the upper part with a sharp boundary between them. The indicator solution must be denser than the leading solution, and the mobility of the N ions must be greater than the mobility of the M ions. When a current I is passed for a time t the boundary moves from AB to CD , and so all the M ions in the volume between AB and CD must have passed through CD . That number is cVN_A (where V indicates volume), and so the charge they transfer through the plane is $z_+cVeN_A = z_+cVF$. However, the total quantity of charge transferred when a current I flows for a time t is It . Therefore, the fraction due to the motion of the M ions, which is their transport number, is

$$t_+ = \frac{z_+ c V F}{I t} \quad 3.23$$

Hence, knowing the diameter of the tube and the distance moved by the boundary in the time t , the transport number, and hence the ion conductivity and mobility, may be determined.

In the Hittorf method an electrolytic cell is divided into three compartments and an amount $I t$ of electricity is passed. An amount $I t / z_+ F$ of cations are discharged at the cathode but an amount $t_+(I t / z_+ F)$ of cations migrate into the cathode compartment. The net change in the amount of cations in that compartment is therefore $(t_+ - 1)(I t / z_+ F)$, or $-t_-(I t / z_+ F)$. Therefore, by measuring the change of composition in the cathode compartment, t_- , the anion transport number, can be deduced. Likewise, the change in composition of the anions in the anode compartment is $-t_+(I t / z_+ F)$.

3.2.4 Conductivities and ion-ion interactions

Having accounted for the form of the law of independent migration of ions, the remaining problem is to account for the $c^{1/2}$ dependence of the Kohlrausch Law, equation 3.1. Note that we have to account for a reduction of the conductivity below its value at zero ionic strength. The activity coefficients of ions also depend on $c^{1/2}$, and depend on their charge type rather than their specific identities. That was explained in terms of the properties of the ionic atmosphere around each ion, and it is suspected that the same explanation applies here.

When an electric field is applied to a solution of ions and all the ions drift in a definite direction, we have to modify the picture of the ionic atmosphere as being a spherically symmetrical haze of charge around each ion. In the first place, the ions do not adjust to the moving ion infinitely quickly, and the atmosphere is

incompletely formed in front of the moving ion and incompletely decayed in its wake, Figure 3.9. The overall effect is the displacement of the centre of charge of the atmosphere a short distance behind the moving ion. Since the two charges are opposite, the result is a retardation of the moving ion. This reduction of the ions' mobility is called the relaxation effect, because the rearrangement of the ionic atmosphere is a relaxation of the ions into an equilibrium distribution. The electrophoretic effect is a second consequence of the ionic atmosphere. As we have seen, the central ion experiences a viscous drag as it moves through the solution. When the ionic atmosphere is present, this effect is enhanced because the ionic atmosphere moves in an opposite direction to the central ion. The enhanced viscous drag reduces the mobility of the ions, and hence also reduce their conductivities.

The quantitative formulation of these effects is far from simple, but the Debye-Hückel-Onsager theory is an attempt to obtain quantitative expressions at about the same level of sophistication as the Debye-Hückel theory itself. The theory leads to a Kohlrausch-like expression, equation 3.3, with

$$K = A + B_m^0 \quad 3.24$$

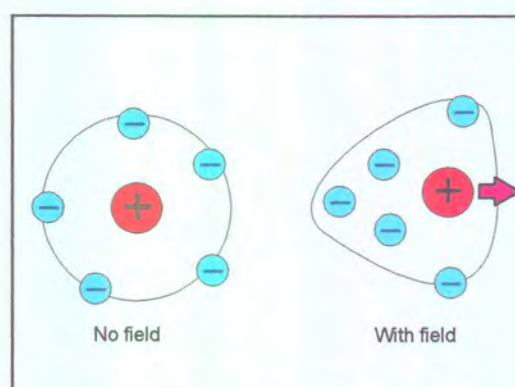


Figure 3.9 Ionic atmospheres without and with an applied field respectively.

$$A = \left(\frac{z^2 e F^2}{3 \pi \eta} \right) \left(\frac{2}{\epsilon R T} \right)^{\frac{1}{2}}, \quad B = q \left(\frac{z^3 e F^2}{24 \pi \epsilon R T} \right) \left(\frac{2}{\pi \epsilon R T} \right)^{\frac{1}{2}} \quad 3.25$$

where ϵ is the electric permittivity of the solvent and $q = 0.50$ for a 1:1 electrolyte. R is the gas constant and T is the temperature. The slopes of the conductivity curves are predicted to depend on the charge type of the electrolyte, as the Kohlrausch measurements require.

The success of the Debye-Hückel-Onsager theory suggests that the model is substantially correct. A further test is to examine what happens when the effects of the ionic atmosphere are eliminated in some way. One way of doing this is to measure the conductivity at very high frequency, for when the central ion moves backwards and forwards very rapidly the retarding effect of the asymmetric atmosphere ought to average to zero. The Debye-Falkenhagen effect is the observation of this increase in conductivity. Another way of eliminating the atmosphere is to cause the ions to move so quickly that they outrun it. The first Wien effect is the observation of higher conductivities at high electric fields, as this predicts. (The second Wien effect is the observation of an increased conductivity as a result of the enhancement of the degree of ionisation of a weak electrolyte when a strong field is applied.)

The simple picture of ions surrounded by a diffuse ionic atmosphere fails at higher concentrations because ions stick together as pairs, triples, and so on. This can be seen from X-ray diffraction by ionic solutions, where peaks in the diffraction pattern can be interpreted in terms of definite ion-ion distances.

3.3 Diffusion and transport

For the discussion of this section, Atkins [4] was used extensively as well as Mulder [6] and Ho and Sirkar [7]

3.3.1 Diffusion: The thermodynamic view

In section 3.2 it was shown that the thermodynamic quantity that governs the direction of spontaneous change under conditions of constant temperature and pressure is the chemical potential. When a unit amount of solute particles moves from a region where their chemical potential is $\mu(1)$ to one where it is $\mu(2)$, the work (w) required is $w = \mu(2) - \mu(1)$. Suppose the chemical potential depends on the position x in the system, then the work required to move material from x to $x + dx$ is

$$dw = \mu(x+dx) - \mu(x) = \{\mu(x) + (d\mu/dx)dx\} - \mu(x) = (d\mu/dx)dx \quad 3.26$$

The derivatives ought to be partial, under the constraints of constant pressure and temperature. In classical mechanics the work required to move an object through a distance dx against a force Γ is $dw = -\Gamma dx$. Therefore, by comparing these expressions, it was found that the slope of the chemical potential is an effective force. It can be written as the thermodynamic force:

$$\Gamma = - \left(\frac{\partial \mu}{\partial x} \right)_{p,T} \quad 3.27$$

There is no real force pushing the particles down the slope of the chemical potential, for that is their natural drift as a consequence of the Second Law of thermodynamics and the hunt for maximum entropy. Another point is that the quantity is a molar force, the effective force per unit amount of substance. This will be discussed again in section 3.5

In a solution where the activity of the particles is a , the chemical potential is :
 $\mu = \mu^\ominus + RT \ln a$. If the solution is not uniform the activity depends on the position and it can be written as:

$$\Gamma = -\left(\frac{d}{dx}\right)\{\mu^0 + RT \ln a\} = RT\left(\frac{\partial \ln a}{\partial x}\right)_{p,T}$$

If the solution is ideal a may be replaced by the concentration c , and so

$$\Gamma = -(RT/c)\left(\frac{\partial c}{\partial x}\right)_{p,T} \quad 3.28$$

because $(d/dx) \ln c = (1/c) dc/dx$. This shows that the thermodynamic force pushes in the direction of decreasing concentration (Γ is positive when dc/dx is negative). (Compare with equation 3.53)

From equation 3.28 it is possible to once again derive Fick's first law of diffusion from a thermodynamic viewpoint. (See also the derivation of equation 3.9) It is supposed that the flux of particles is a response to a thermodynamic force due to the concentration gradient. As a result of the balancing of the force Γ , and the viscous drag on the particles, they settle down to a drift speed s . This drift speed is proportional to the thermodynamic force, and so $s \propto \Gamma$. If the number density of particles is N , the flux of particles through an imaginary window in the fluid is equal to sN . All the particles within a distance $s\Delta t$, and therefore in a volume $s\Delta tA$, pass through the window of area A in the time Δt . (See section 3.2.2 and figures 3.5 and 3.7). Thus, $J = sN = scN_A$. But since s is proportional to Γ , which in turn is proportional to $(1/c)(dc/dx)$, it follows that J is proportional to dc/dx .

Since $J=scN_A$, equation 3.9 can be written as

$$scN_A = -D(dN/dx) = -DN_A(dc/dx).$$

Expressing dc/dx in terms of Γ using equation 3.27 gives



$$s = -\left(\frac{D}{c}\right) \frac{dc}{dx} = \left(\frac{D}{RT}\right) \Gamma \quad 3.29$$

Therefore, once the effective force and D is known, the drift speed of the particles (and vice versa) can be calculated, and this will be true whatever the origin of the force.

There is one case where we already know the drift speed and the effective force acting on a particle is known: An ion in solution has a drift speed $s = uE$ (equation 3.12) when it experiences a force ezE , so that the force per mole is zFE . Therefore, substituting these known values into equation 3.29 gives

$$uE = \left(\frac{D}{RT}\right)(zeF), \text{ or } u = \frac{ezD}{kT} \quad 3.30$$

This rearranges into the very important result known as the Einstein relation between the diffusion coefficient and the ionic mobility:

$$D = \frac{ukT}{ez} \quad 3.31$$

The Einstein relation thus points out the relation between Fick's first law of diffusion and the drift speed of a particle.

The Einstein relation can be developed in two ways. In the first place, it can be used to find the Nernst-Einstein relation between the molar conductivity of an electrolyte and the diffusion coefficients of its ions. First from equation 3.14 it follows that for a cation



$$\lambda_+ = u_+ z_+ F = \frac{e z_+^2 D_+ F}{kT} = \frac{z_+^2 D_+ F^2}{RT} \quad 3.34$$

and a similar expression for the anion. Then the sum of the two weighted by the numbers of ions from each formula unit, equation 3.30, is the limiting molar conductivity:

$$\Lambda_m^0 = (F^2 / RT) \{v_+ z_+^2 D_+ + v_- z_-^2 D_-\} \quad 3.33$$

This is the so called Nernst-Einstein relation. One application of this expression is the determination of ionic diffusion coefficients from conductivity measurements; another is the prediction of conductivities using models of ionic diffusion.

The other development of the Einstein relation leads to the Stokes-Einstein relation between the diffusion coefficient and the viscosity of the solution. By combining the expressions $s = iE$ and $s = ezE/f$ (which comes from equation 3.11), one obtains

$$u = \frac{ez}{f} \quad 3.34$$

as a relation between an ion's mobility and its hydrodynamic radius. However since $u = ezD/kT$, it can be written that

$$D = \frac{kT}{f} \quad 3.35$$

This is the so called Stokes-Einstein relation. Therefore, since $f = 6\pi\eta a$ (see section 3.2.2), and if the hydrodynamic radius (Stokes radius) of the ion is known, the diffusion coefficient of the solution can be calculated from the viscosity of the solution. An important feature of this result, however, is that it is independent of the charge of the diffusing particle. Therefore, it also applies in the limit of a vanishingly small charge; that is, it also applies to neutral particles. This means that viscosity measurements can be used to estimate the diffusion coefficients for molecules in solution.

3.4 Diffusion

The following discussion will concern the time-dependent diffusion processes, where the interest will be in the spreading of inhomogeneities. An example is the concentration distribution in a solvent to which a solute is added.

3.4.1 The diffusion equation

This explanation concentrates on the diffusion of particles, but similar arguments also apply to the diffusion of properties. The aim is to obtain an equation for the rate of change of the concentration of particles in some inhomogeneous region.

Consider a thin slab of cross-sectional area A and extending from x to $x+\Delta x$, Figure 3.10. (Compare with Figures 3.5 and 3.7) Let the number density at x be N at the time t . J_A is the number of particles that enter the slab per unit time, and so the increase in concentration inside the slab (which has volume $A\Delta x$) on account of the flux from the left is

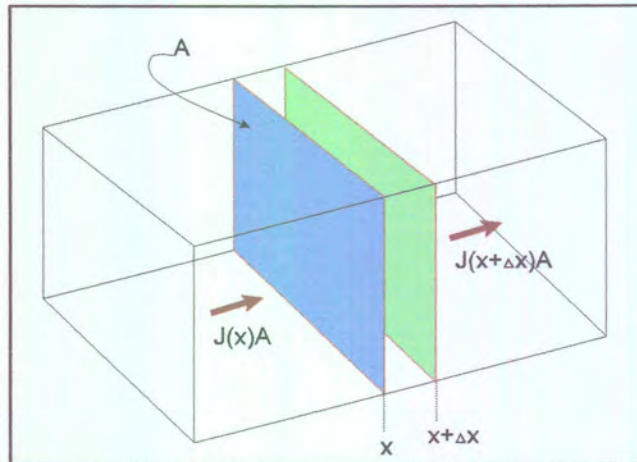


Figure 3.10 The net flux in a region is the difference between the flux entering the region from a high concentration and the flux leaving to the region of low concentration.

$$\frac{\partial N}{\partial t} = J(x) A / \Delta x = J(x) / \Delta x.$$

There is also an outflow through the right-hand window. The flux there is $J(x+\Delta x)$, and the change of concentration due to this efflux is

$$\frac{\partial N}{\partial t} = -J(x+\Delta x) A / \Delta x = -J(x+\Delta x) / \Delta x.$$

The net rate of change of concentration is therefore

$$\frac{\partial N}{\partial t} = \{J(x) - J(x+\Delta x) / \Delta x\} / \Delta x.$$

The fluxes are proportional to the concentration gradients at the two windows. Using Fick's first law it can be written as:

$$\begin{aligned} J(x) - J(x + \Delta x) &= -D \left(\frac{\partial N(x)}{\partial x} \right) + D \left(\frac{\partial N(x + \Delta x)}{\partial x} \right) \\ &= -D \left(\frac{\partial N}{\partial x} \right) + D \frac{\partial}{\partial x} \left\{ N + \left(\frac{\partial N}{\partial x} \right) \Delta x \right\} = D(\partial^2 N / \partial x^2) \Delta x \end{aligned}$$

(Unless otherwise specified, N means $N(x,t)$.) Substitution of this relation into the

expression for the rate of change of concentration in the slab leads to the diffusion equation :

$$\partial N / \partial t = D(\partial^2 N / \partial^2 x) \quad 3.36$$

This is also called Fick's Second Law of Diffusion.

Concerning the diffusion equation (the above mentioned equation) it shows that the rate of change of concentration is proportional to the curvature (more precisely, the second derivative) of the concentration with respect to distance. If the concentration changes sharply from point to point (if the distribution is highly wrinkled) then the concentration changes rapidly with time. If the curvature is zero, then the concentration is constant in time. For example, if the concentration decreases linearly with distance, then the concentration at any point is constant because the inflow of particles is exactly balanced by the outflow. The diffusion equation can be regarded as exactly balanced by the outflow. The diffusion equation can be regarded as a mathematical formulation of the intuitive notion that there is a natural tendency for the wrinkles in a distribution to disappear.

The diffusion equation is a second-order differential equation with respect to space and a first-order differential equation with respect to time. Therefore, in order to arrive at a solution two boundary conditions must be specified for the spatial dependence and a single initial condition for the time-dependence. This can be illustrated by the specific example of a solvent in which the solute is initially coated on one surface (e.g. a layer of sugar on the bottom of a deep beaker of water). The initial condition is that at $t = 0$ all N_0 particles are concentrated on the yz -plane (of area A) at $x = 0$. The boundary conditions are a), that the concentration must everywhere be finite and b), that the total number of particles present is N_0 at all times. The solution of the diffusion equation under these conditions is

$$N = \left\{ N_0 / A(\pi Dt)^{\frac{1}{2}} \right\} e^{-x^2/4Dt} \quad 3.37$$

as may be verified by direct substitution. Another solution is for the case of a localised concentration of solution in a three-dimensional solvent (a sugar lump suspended in a large flask of water): The concentration distribution is spherically symmetrical, and at a radius r is

$$N = \left\{ N_0 / 8(\pi Dt)^{\frac{3}{2}} \right\} e^{-r^2/4Dt} \quad 3.38$$

The solutions are useful for experimental determinations of diffusion coefficients. In the capillary technique a capillary tube, open at one end and containing a solution, is immersed in a well stirred larger quantity of solvent, and the change of concentration in the tube is measured at a series of times. The solute diffuses from the open end of the capillary at a rate that can be calculated by solving the diffusion equation with the appropriate boundary conditions, and so D may be determined. In the diaphragm technique the diffusion occurs through the capillary pores of a sintered glass diaphragm separating the well-stirred solution and solvent. The concentrations are monitored and then related to the solutions of the diffusion equation corresponding to this arrangement.

3.4.2 Properties of the solutions

The solutions of the diffusion equation, such as those above, can be used to predict the concentration of particles (or the value of some other physical quantity, such as the temperature in a non-uniform system) at any location. The solutions may also be used to calculate the mean distances through which the particle diffuse in a given time.

The number of particles in a slab of thickness dx at x is $NAdx$, and so the

probability that any of the N_0 particles is there is $NAdx/N_0$. If the particle is there, then it has travelled a distance x from the origin. Therefore, the mean distance travelled by all the particles is the sum of each x weighted by the probability of its occurrence:

$$\langle x \rangle = \int_0^{\infty} \frac{xNA dx}{N_0} = \sqrt{\frac{1}{\pi Dt}} \int_0^{\infty} x e^{-\frac{x^2}{4Dt}} dx = 2\sqrt{\frac{Dt}{\pi}} \quad 3.39$$

The average distance of diffusion varies as the square root of the lapsed time. If the Stokes-Einstein relation is used for the diffusion coefficient, the mean distance traveled by particles of radius a in a solvent of viscosity η is

$$\langle x \rangle = (2kT / 3\pi^2\eta a)^{\frac{1}{2}} \sqrt{t} \quad 3.40$$

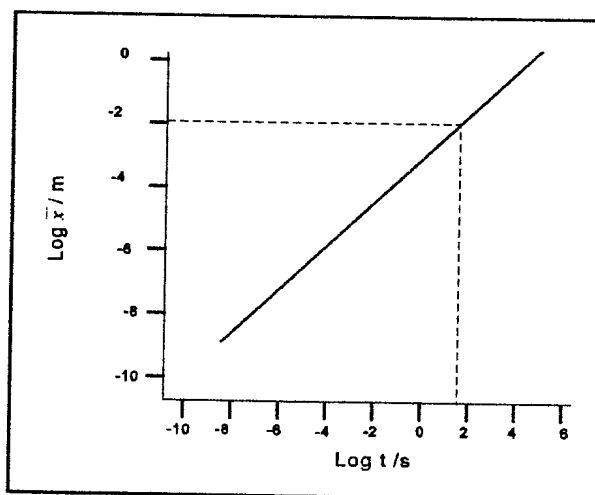


Figure 3.11 The root mean square distance covered by particles with $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

The root mean square distance traveled by diffusing particles is

$$\bar{x} = \left\{ \int_0^{\infty} x^2 N A dx / N_0 \right\}^{\frac{1}{2}} = (2DT)^{\frac{1}{2}} \quad 3.41$$

This quantity is a valuable measure of the spread of particles when they can diffuse in both directions from the origin (for then $\langle x \rangle = 0$ at all times). The value of x for particles with a typical diffusion coefficient ($D = 5 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$) is shown in Figure 3.11: This shows how long it takes for diffusion to increase x to about 1 cm in an unstirred solution: **diffusion is a very slow process.**

The proportion of particles that remain within a distance \bar{x} of the origin is a useful number because it indicates how many particles remain close to their original position. Since the number in the slab at x is $N A dx$, the total number in all the slabs up to the one at \bar{x} is the sum (integral).

$$N(x \leq \bar{x}) = \int_0^{\bar{x}} N A dx = 0.68 N_0 \quad 3.42$$

It follows that the proportion of particles inside the range $0 \leq x \leq \bar{x}$ is 0.68. Therefore, over two-thirds of the particles are still close to the origin and only 32 % have escaped beyond \bar{x} (but do not forget that \bar{x} increases with time). (The 0.68 and 32 % values are determined statistically)

3.4.3 Diffusion with convection

Because diffusion is so slow, reaction vessels are generally stirred and the slow diffusion of particles is dominated by brute-force mixing. The transport of particles arising from the motion of a streaming fluid is called convection. If diffusion is ignored, the flux of particles through an area A in a time Δt when the fluid is streaming at a velocity v can be calculated in the way we have used

several times before (counting the particles within a distance $v\Delta t$), and is

$$J = (Nv\Delta t)/A\Delta t = Nv \quad 3.43$$

J is called the convective flux. This flux contributes to the concentration of particles in a region, and a calculation similar to the one already done gives the rate of change of concentration in a slab of thickness Δx and area A as

$$\begin{aligned} \partial N / \partial t &= \{AJ(x) - AJ(x + \Delta x)\} / A\Delta x \\ &= v\{N - [N + (\partial N / \partial x)\Delta x]\} / \Delta x = -v(\partial N / \partial x) \end{aligned} \quad 3.43$$

Velocity was assumed constant.

When both diffusion and convection are of similar importance the total change of concentration in a region is the sum of the two effects, and so the generalised diffusion equation is

$$\partial N / \partial t = D(\partial^2 N / \partial x^2) - v(\partial N / \partial x) \quad 3.45$$

A further important refinement, which is important in chemistry, is the possibility that the concentrations of particles may change as a result of reaction. When this is incorporated into the last equation, a powerful differential equation for discussing the properties of reacting, diffusing, convecting systems: it is the basis of reactor design in chemical industry and of the utilisation of resources in living cells.

3.4.4 The statistical view of diffusion

An intuitive picture of diffusion is that the particles move in a series of small steps and gradually migrate from their original positions. To explore this idea by building a model which assumes that the particles can leap through a distance d in a time τ , so that the distance traveled by a particle in a time t is $(t/\tau)d$. This does not mean that the particle will be found at that distance from the origin. The direction of each step may be different, and the net distance traveled must take this into account. To simplify the discussion allow the particles to travel only along a straight line (the x -axis), and for each step (to the left or the right) to be through the same distance d each time, to obtain the one-dimensional random walk.

When the calculation is carried through, it turns out that the probability of being at a distance x from the origin after an interval t is

$$P = (2\tau / \pi t)^{\frac{1}{2}} e^{-x^2 / 2t\tau d^2} \quad 3.46$$

This has precisely the same form as equation 3.37, the difference of detail arising from the fact that in this calculation the particles can migrate in either direction from the origin and may reside only at discrete points separated by d instead of being anywhere on a continuous line. This suggests that diffusion can indeed be interpreted as the outcome of a large number of steps in random directions. Furthermore, the details of the calculation also show that the diffusion equation is not valid when the particles have had time to take only very few steps.

Comparison of the two exponents in equations 3.37 and 3.46 leads to the Einstein-Smoluchowski relation between the diffusion coefficient and the step length and rate. From the identification $2d^2/\tau=4D$ it follows that:

$$\text{Einstein-Smoluchowski relation : } D = d^2/2\tau \quad 3.47$$

The Einstein-Smoluchowski relation is the central connection between the microscopic details of particle motion and the macroscopic parameters relating to diffusion (e.g. the diffusion coefficient and, through the Stokes-Einstein relation, the viscosity). It also brings us back full circle to the properties of gases. For if d/τ is interpreted as a mean speed of particles \bar{c} , and d is interpreted as a mean free path (λ), then the Einstein-Smoluchowski relation turns into $D = \frac{1}{2}\lambda \bar{c}$, which is the same expression that we obtained from the kinetic theory of gases. This shows that the diffusion of a perfect gas can be interpreted as a random walk with an average step size equal to the mean free path.

3.5 Transport in membranes.

Transport in membranes can be subdivided into two main groups namely transport through porous membranes and transport through non-porous membranes. Some features of the different transport mechanisms, for example the driving force, stay the same. For this reason, both porous and non-porous transport were considered and at the end a unified mechanism was investigated.

3.5.1 Introduction

A membrane may be defined as a permselective barrier between two homogeneous phases. A molecule or a particle is transported across the membrane from one phase to the other because a force acts on that molecule or particle. The extent of this force is determined by the gradient in potential, or approximately by the difference in potential, across the membrane (ΔX) divided by the membrane thickness (ℓ), i.e. (also compare the derivation of equation 3.28)

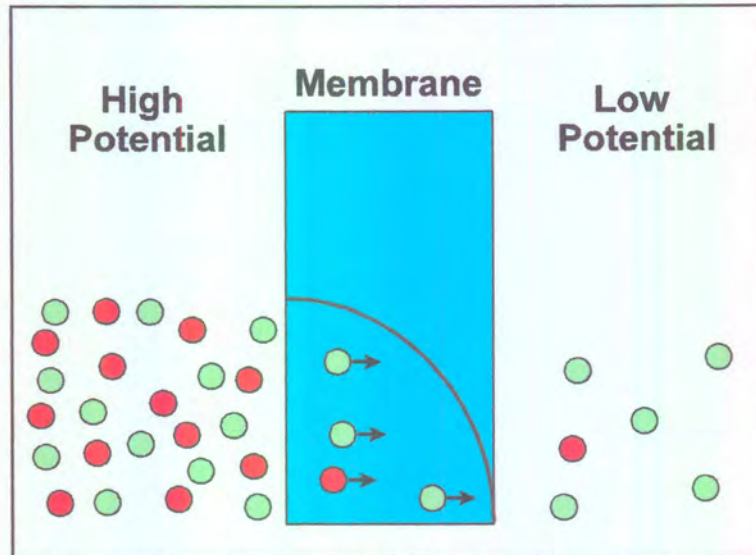


Figure 3.12 Passive membrane transport from a phase with a high potential to one with a low potential.

$$\text{driving force} = \frac{\Delta X}{l} \quad 3.48$$

Two main potential differences are important in membrane processes, the chemical potential difference ($\Delta\mu$) and the electrical potential difference (ΔF). (The electro-chemical potential is the sum of the chemical potential and the electrical potential). Other possible forces such as magnetic fields, centrifugal fields and gravity will not be considered.

In passive transport, components or particles are transferred from a high potential to a low potential (See Figure 3.12, section 3.2.2 and section 3.3)

The driving force, in passive transport, is the gradient in potential ($\partial X/\partial x$). Instead of differentials it is often more useful to use differences ($\partial X/\partial x \approx \Delta X/\Delta x$). The average driving force (F_{ave}) is equal to the difference in potential across the membrane divided by the membrane thickness: (Compare with Figure 3.4)

$$F_{ave} = - \frac{\Delta X}{l} \quad 3.49$$

If no external forces are applied to this system, it will reach equilibrium when the potential difference has become zero. When the driving force is kept constant, a constant flow will occur through the membrane after establishment of a steady state. There is a proportionality relationship (A) between the flux (J) and the driving force (X), i.e.

$$J = AX \quad 3.50$$

The proportionality factor A, determines how fast the component is transported through the membrane or A is a measure of the resistance exerted by the membrane as a diffusion medium. [6, 7]

Another form of passive transport is facilitated or carrier-mediated transport (active transport). Here, transport of a component across a membrane is enhanced by the presence of a carrier. The carrier specifically interacts with one or more specific components in the feed and an additional mechanism (besides free diffusion) results in an increase in transport. It is possible that components can be transported against their chemical potential gradient in carrier-mediated membrane transport. Active transport is mainly found in living cell membranes where the energy is provided by ATP. [6, 8] Facilitated transport however, is beyond the scope of this thesis.

3.5.2 Driving Forces

Transport across a membrane takes place when chemical or electrical potential difference acts on the individual components in the system. The potential differences arises as a result of differences in either pressure, concentration,

temperature or electrical potential. Most transport processes take place because of a difference in chemical potential $\Delta\mu$. Under isothermal conditions (constant temperature), pressure and concentration contribute to the chemical potential of component i according to; (Compare with equation 3.28)

$$\mu_i = \mu_i^\circ + RT \ln a_i + V_i P \quad 3.51$$

with a_i (which is part of the concentration term) and V_i the activity and molar volumes of component i . P indicates pressure (part of the pressure term). The term μ_i° is a constant.

$$a_i = \gamma_i x_i \quad 3.52$$

where γ_i is the activity coefficient and x_i the mole fraction. For ideal solutions the activity coefficient $\rightarrow 1$, and the activity becomes equal to the mole fraction. The chemical potential difference $\Delta\mu_i$ can be subdivided into a difference in composition and a difference in pressure according to

$$\Delta\mu_i = RT \Delta \ln a_i + V_i \Delta P \quad 3.53$$

The composition contribution is equal to the product RT and the logarithm of the composition (activity or mole fraction).

A simple method of comparing driving forces is to make them dimensionless. As shown in Figure 3.12, the driving force is the potential gradient, and the average driving force is the potential difference across the membrane divided by the membrane thickness. (equation 3.48) If the chemical potential and the electrical potential are considered to be the driving forces and assuming ideal conditions,

i.e. $a_i = x_i$ and $\Delta \ln x_i \approx x_i^{-1}$. Equation 3.49 becomes

$$F_{ave} = \frac{RT}{\ell} \frac{\Delta x_i}{x_i} + \frac{z_i \Gamma}{\ell} \Delta E + \frac{V_i}{\ell} \Delta P \quad 3.54$$

On multiplying equation 3.54 by the factor ℓ/RT (= mol/N), the driving forces become dimensionless:

$$F_{dim} = \frac{\Delta x_i}{x_i} + \frac{z_i \Gamma}{RT} \Delta E + \frac{V_i}{RT} \Delta P \quad 3.55$$

or

$$F_{dim} = \frac{\Delta x_i}{x_i} + \frac{\Delta E}{E^*} + \frac{\Delta P}{P^*} \quad 3.56$$

where $P^* = RT/V_i$ and $E^* = RT/(z_i \Gamma)$

The magnitude of the various driving forces being the pressure, electrical potential or the concentration, can easily be compared with each other using equation 3.56. The concentration term $\Delta x_i/x_i$ is often equal to unity, while the pressure term is strongly dependent on the kind of component involvement. The electrical potential depends on the value of z_i . Electrical potential is a very strong driving force in comparison to pressure, which is very weak.

3.5.3 Transport through porous membranes

In porous membranes a large variety of pore geometries are possible. Some possible geometries of porous membranes can be seen in Figure 3.13. In some membranes, such geometries (or structures) exist over the whole membrane

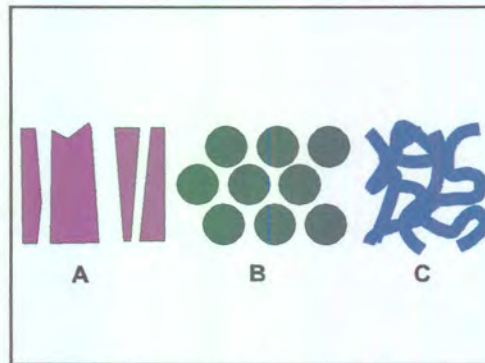


Figure 3. 13 Some characteristic geometries found in porous membranes.

thickness and here the resistance is determined by the total membrane thickness. On the other hand, some membranes are asymmetric in their structure. This implies that the resistance is determined only by the porous top layer of the membrane. The existence of these different pore geometries also implies that different models have been developed to describe the transport adequately. [6, 7] The simplest representation is one in which the membrane is considered as a number of parallel cylindrical pores, perpendicular to the membrane surface. (See Figure 3.13 A).

The length of each of the cylindrical pores is equal to the membrane thickness. The volume flux through these pores may be described by the Hagen-Poiseuille equation. Assuming that all the pores have the same radius, it can be written as follows:

$$J = \frac{\varepsilon r^2 \Delta P}{8\eta \tau \Delta x} \quad 3.57$$

This indicates that the solvent flux is proportional to the driving force (the pressure difference, ΔP), across a membrane of thickness Δx and inversely proportional to the viscosity η . The quantity ε is the surface porosity, which is the fractional pore area. (ε is equal to the ratio of the pore area to the membrane

area A_m multiplied by the number of pores n_p , $\varepsilon = \pi r^2/A_m$), while τ is the pore tortuosity (which for cylindrical perpendicular pores, the value will be equal to unity).

Membranes consisting of the structure depicted in Figure 3.13 B, i.e. a system of closed packed spheres, can be found in organic and inorganic sintered membranes of in phase inversion membranes with a nodular top layer structure. Such membranes can best be described by the Kozeny-Carman relationship:

$$J = \frac{\varepsilon^3}{K\eta S^2(1-\varepsilon)^2} \frac{\Delta P}{\Delta x} \quad 3.58$$

ε is the volume fraction of the pores, S the internal surface area and K the Kozeny-Carman constant, which depends on the shape of the pores and the tortuosity.

Phase inversion membranes frequently show a sponge-like structure, as schematically depicted in Figure 3.13 C. The volume flux through these membranes are described either by the Hagen-Poiseuille or the Kozeny-Carman relation, although the morphology is completely different.

3.5.4 Transport through nonporous membranes

Even though the following discussion is concerned with the transport of gases, it is imperative to understand the basic mechanism of transport across the membrane (which is the same for solute particles), before the process of dialysis will be discussed in more detail.

When the sizes of molecules or particles are in the same order of magnitude, porous membranes cannot affect the separation. In this case nonporous membranes must be used. However, the term nonporous is rather ambiguous

because pores are present on a molecular level in order to allow transport even in such membranes. The existence of these dynamic “molecular pores” can be adequately described in terms of free volume.

Initially transport through these dense membranes will be considered via a somewhat simple approach. Although there are some similarities between gaseous and liquid transport, there are also a number of differences. In general, the affinity of liquids and polymers is much greater than that between gases and polymers (The solubility of a liquid in a polymer is much higher than that of a gas.). A high solubility has a tremendous influence on the diffusivity, making the polymer chains more flexible and resulting in an increased permeability.

The transport of a gas, liquid or a vapour through a dense, nonporous membrane can be described in terms of a solution-diffusion mechanism:

$$\text{Permeability (P)} = \text{solubility (S)} \cdot \text{Diffusivity (D)} \quad 3.59$$

Solubility is a thermodynamic parameter and gives a measure of the amount of penetrant sorbed by the membrane under equilibrium conditions. The solubility

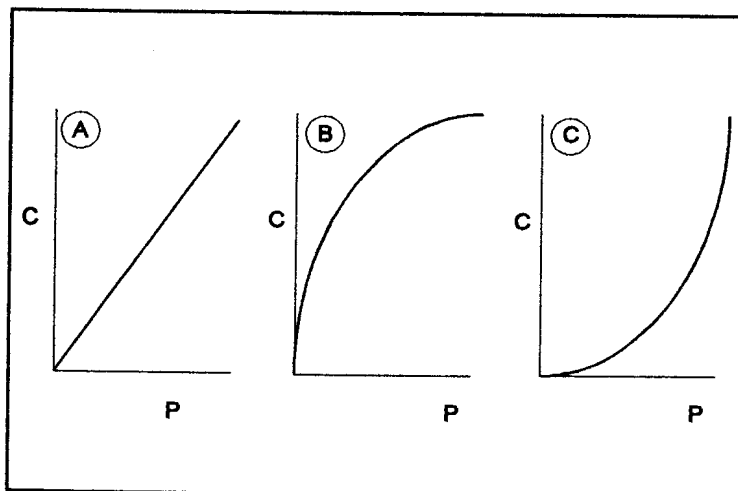


Figure 3.14 Schematic drawing of sorption isotherms for ideal and non-ideal systems.

of gases in a polymer is very low and can be described by Henry's law. With vapours and liquids however, the situation is not ideal, and Henry's law does not apply. The diffusivity on the other hand is a kinetic parameter which indicates how fast a penetrant is transported through the membrane. Diffusivity is dependant on the geometry of the penetrant for as the molecular size increases, the diffusion coefficient decreases. However, the diffusion coefficient is concentration dependent with interacting systems and even large molecules, having the ability to swell the polymer, can have large diffusion coefficients.

The solubility of gases in polymers is generally quite low and it is assumed that the gas diffusion coefficient is constant. Such cases can be considered as ideal systems where Fick's first law of diffusion (see equation 3.9) is obeyed. On the other hand, the solubility of liquids and vapours can be relatively high and the diffusion coefficient is now assumed to be concentration dependent, thus the diffusivities increase with increasing concentration.

Two separate cases must therefore be considered, ideal systems where both the diffusivity and the solubility are constant, and concentration-dependent systems where the solubility and the diffusivity are functions of the concentration. (Other cases can be distinguished where the solubility and the diffusivity are functions of other parameters, such as time and place. These phenomena, often termed "anomalous", can be observed in glassy polymers where relaxation phenomena occur or in heterogeneous (porous) types of membranes.

For ideal systems, where the solubility is independent of the concentration, the sorption isotherm is linear (Henry's law), i.e. the concentration inside the polymer is proportional to the applied pressure (Figure 3.14 A). This behaviour is normally observed with gases in elastomers. With glassy polymers the sorption isotherms is generally curved rather than linear (see Figure 3.14 B), whereas such strong interactions occur between organic vapours or liquids and polymer, the sorption isotherm is generally non-linear, especially at high vapour pressures (Figure 3.14

C). Such non-ideal sorption behaviour can be described by free volume models and Flory-Huggins thermodynamics.

The solubility can be obtained from equilibrium measurements in which the volume of gas taken up is determined when the polymer sample is brought into

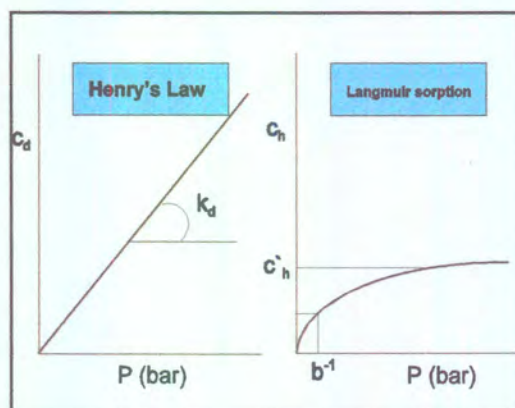


Figure 3.15 The two contributions in the dual sorption theory.

contact with a gas at a known applied pressure. For glassy polymers where the solubility of a gas often deviates in the manner shown in Figure 3.14 B, such deviation can be described by the dual sorption theory, in which it is assumed that two sorption mechanisms occur simultaneously, i.e. sorption according to Henry's law and via a Langmuir type sorption. This is shown in Figure 3.15.

In this case, the concentration of gas in the polymer can be given as the sum produced by the two sorption modes

$$C = C_d + C_h \quad 3.60$$

or

$$c = k_d P + \frac{c'_h b P}{1 + b P} \quad 3.61$$

where k_d is the Henry's law constant [k_d]: $\text{cm}^3(\text{STP}) \cdot \text{cm}^3 \cdot \text{bar}^{-1}$ which is equal to the solubility coefficient S , b is the hole affinity constant ($[b]$: bar^{-1}) and c'_h is the saturation of constant [c'_h]: $\text{cm}^3(\text{STP}) \cdot \text{cm}^{-3}$). The dual sorption model often gives a good description of observed phenomena and it is very frequently used to describe sorption in glassy polymers. From a physical point of view, however, it is difficult to understand the existence of two different sorption modes for a given membrane which implies the existence of two different types of sorbed gas molecules (the dual sorption theory can also be considered as a three parameter fit).

Permeability is both a function of solubility and diffusivity (see equation 3.58). The simplest way to describe the transport of gases through membranes is via Fick's first law (equation 3.9).

At this point in time it is imperative to once again discuss the diffusion equations which are applicable for transport across membranes. It will be noted that some of these equations were mentioned earlier in section 3.4. It was however thought appropriate to mention them again (sometimes in a different form) to show their applicability to membrane processes.

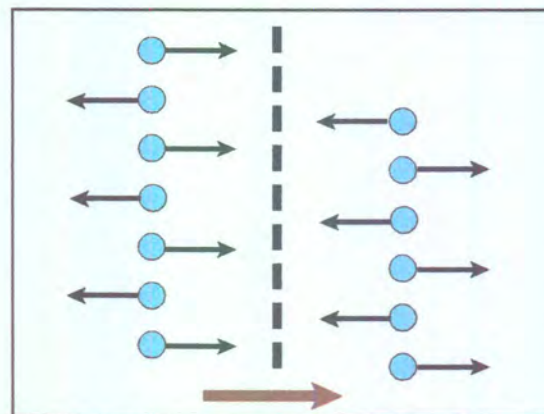


Figure 3.16 Schematic drawing of diffusion as a result of random molecular motions.

Diffusion may be considered as statistical molecular transport as a result of the random motion of the molecules. A (macroscopic) mass flux occurs because of a concentration difference. Imagine a plane with more molecules on one side than on the other, then a net mass flux will occur because more molecules move to the right than to the left. (As shown schematically in Figure 3.16 and see also Figure 3.10). Now, consider two planes (e.g. a thin part of a membrane) at the points x and $x + \delta x$ (Figure 3.17). The quantity of penetrant which enters the plane at x at time δt is equal to $J \cdot \delta t$. The quantity of penetrant leaving the plane at $x + \delta x$ is $[J + (\partial J/\partial x)\delta x]\delta t$.

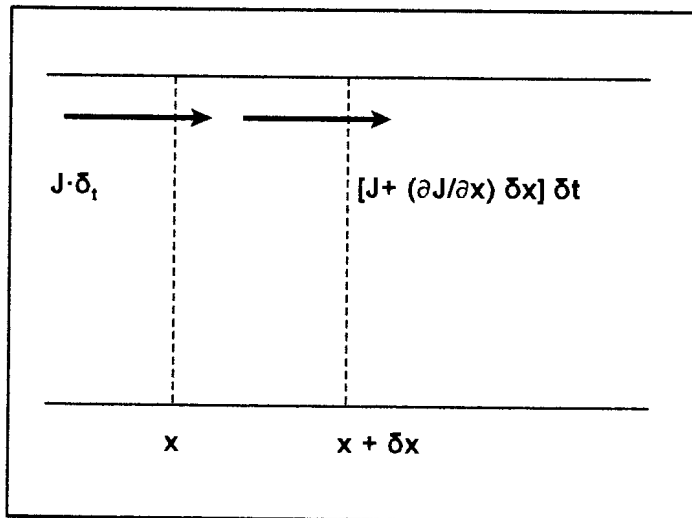


Figure 3.17 diffusion across two planes situated at the points x and $x + \delta x$ in the cross section of a membrane.

The change in concentration (dc) in the volume between x and $x + \delta x$ is

$$dc = \frac{[J \delta t - (J + \left(\frac{\partial J}{\partial x}\right) \delta x) \delta t]}{\delta x} \quad 3.62$$

which yields

$$dc = - \left(\frac{\partial J}{\partial x} \right) \delta t \quad 3.63$$

For an infinite small section and an infinite small period of time $\delta x \Rightarrow 0$, $\delta t \Rightarrow 0$), equation 3.63 becomes

$$\frac{\partial c}{\partial t} = - \frac{\partial J}{\partial x} \quad 3.64$$

Substitution of equation 3.9 into equation 3.64 yields

$$\frac{\partial c}{\partial t} = - \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad 3.65$$

If it is assumed that the diffusion coefficient is constant, then

$$\frac{\partial c}{\partial t} = - D \frac{\partial^2 c}{\partial x^2} \quad 3.66$$

This expression, also known as Fick's second law (compare with equation 3.36), gives the change in concentration as a function of distance and time.

The order of magnitude of the diffusion coefficients of molecules permeating through non-porous membranes depends on the size of the diffusing particles and on the nature of the material through which diffusion occurs. In general, diffusion coefficients decrease as the particle size increases (compare the Stokes-Einstein equation 3.35).

Another example of diffusion being very dependent on the medium through which



it proceeds is shown in Figure 3.18 (left-hand figure), a schematic representation of the values of the diffusion coefficients in water (or in another low molecular liquid) and in a rubbery polymer as a function of the molecular weight of the diffusing component. In water, the diffusion coefficient decreases only slightly with increasing molecular weight compared to the situation with rubber. This is the normal behaviour when diffusion occurs in non-interacting systems. When concentration-dependent systems are involved, however, the membrane may swell considerably and the diffusing medium may also change significantly. Such strong interactions can have a large impact on diffusion phenomena.

Because of swelling the penetrant concentration inside the polymer will increase. The size will become less important. In general, it can be said that the effect of concentration will increase as the diffusion coefficients decrease at lower swelling values. This is shown schematically in Figure 3.18 (right-hand figure), where the diffusion coefficients of a given low molecular component are plotted versus the degree of swelling. This Figure 3.18 shows clearly that the diffusion coefficients vary by some orders of magnitude with different degrees of swelling, resulting in the occurrence of different types of separation.

Another way of describing diffusion processes is in terms of friction. The penetrant molecules move through the membrane with a velocity v because of a force $\partial\mu/\partial x$ acting on them. This force (the chemical potential gradient) is necessary to maintain the velocity v against the resistance of the membrane. If the frictional resistance is denoted as f , the velocity is then given by

$$v = -\frac{1}{f} \left(\frac{\partial\mu}{\partial x} \right) \quad 3.67$$

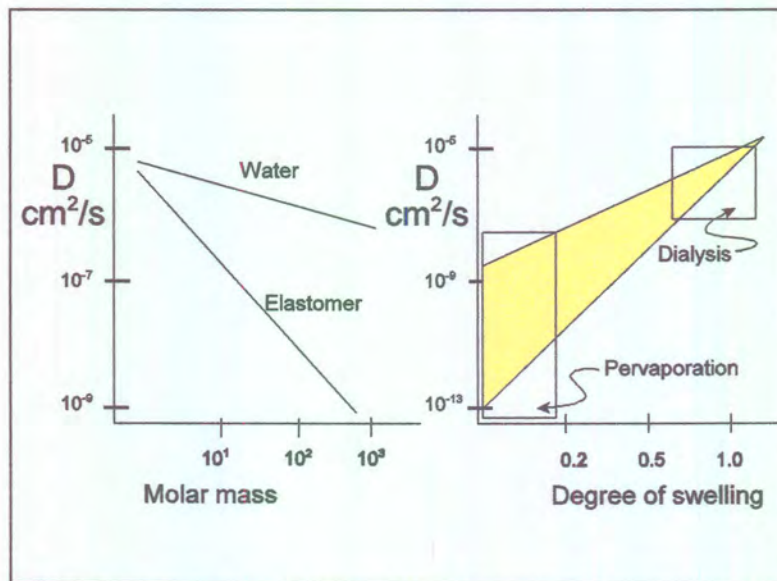


Figure 3.18 Diffusion coefficients of components in water and in an elastomer membrane as a function of the molar mass and in a polymer as a function of the degree of swelling for a given low molar mass penetrant.

It can be shown from a frictional model that equation 3.67 can be written as:

$$v = -m \left(\frac{\partial \mu}{\partial x} \right) \quad 3.68$$

and the quantity of molecules passing through the cross-sectional area per unit time is given by

$$J = v c = mc \left(\frac{\partial \mu}{\partial x} \right) \quad 3.69$$

(Note that the reciprocal of the friction coefficient is the mobility coefficient m .)

The thermodynamic diffusion coefficient D_T is related to the mobility by the relation

$$D_T = m \cdot RT \quad 3.70$$

and since the chemical potential μ is given by (see equation 3.28 and 3.51)

$$\mu = \mu^\circ + RT \ln a \quad 3.71$$

equation 3.69 can be rewritten as

$$\begin{aligned} J &= -\frac{D_T}{RT} c \left(\frac{\partial \ln a}{\partial x} \right) \\ &= -D_T \left(\frac{\partial \ln a}{\partial \ln c} \right) \left(\frac{\partial c}{\partial x} \right) \end{aligned} \quad 3.72$$

and by comparison with Fick's law the following is obtained

$$D = D_T \left(\frac{d \ln a}{d \ln c} \right) \quad 3.73$$

Since for ideal systems the activity a is equal to the concentration c and $D = D_T$, equation 3.72 will reduce to Fick's law. However, for non-ideal systems, (organic vapours and liquids) activities must be used rather than concentrations. The fact that D_T changes with the concentration (or activity) indicates that the presence of the penetrant modifies the properties of the membrane.

3.5.5 Transport through membranes. A unified approach.

A number of 'macroscopic' models have been given in the preceding paragraphs in an attempt describe the large differences in the separation principles involved in various membrane processes and membranes, with the extremes being

observed for porous membranes (microfiltration/ultrafiltration) and nonporous membranes (gas separation/pervaporation/dialysis). The model descriptions can be classified as those based on a phenomenological approach and on non-equilibrium thermodynamics, and those mechanistic models such as the pore model and the solution-diffusion model. The phenomenological models are so-called 'black-box' models and provide no information as to how the separation actually occurs. Mechanistic models try to relate separation with structural-related membrane parameters in an attempt to describe mixtures. These latter models also provide information on how separation actually occurs and which factors are important.

The objective is now to unify all the membrane processes under one mode, in order to relate the various membrane processes with each other in terms of driving forces, fluxes and basic separation principles. To do so, the starting point must be a simple model, such as a generalised Fick equation or a generalised Stefan-Maxwell equation (for the use in defining friction coefficients). In order to describe transport through a porous membrane or through a nonporous membrane, two contributions must be taken into account, the diffusional flow (v) and the convective flow (u). The flux of component i through a membrane can be described as the product of velocity and concentration, i.e.

$$J_i = c_i(v_i + u) \text{ (see Figure 3.19)} \quad 3.74$$

The contribution of convective flow is the main term in any description of transport through porous membranes. In nonporous membranes, however, the convective flow term can be neglected and only diffusional flow contributes to transport. It can be shown by simple calculations that only convective flow contributes to transport in the case of porous membranes (microfiltration). Thus, for a membrane with a thickness of $100 \mu\text{m}$, an average pore diameter of $0.1 \mu\text{m}$, a tortuosity τ of 1 (capillary membrane) and a porosity ε of 0.6, water flow at 1 bar pressure difference can be calculated from the Poiseuille equation

(convective flow), i.e.

$$J_w = \frac{\varepsilon r^2 \Delta P}{8\eta \tau \Delta x} \approx \frac{0.6 \cdot 0.25 \cdot (10^{-7}) \cdot 10^5}{8 \cdot 10^{-3} \cdot 10^{-4}} \approx 2 \cdot 10^{-3} \text{ m/s}$$

The driving force for diffusion is the difference in chemical potential, and both the concentration (activity) and the pressure contribute to this driving force. However, it can be assumed that the “concentration” (or activity) on either side of the membrane is equal in microfiltration and hence the pressure difference must be the only driving force. Indeed, diffusive water flow as a result of this driving force is very small, as can be demonstrated as follows. The chemical potential difference can be written as:

$$\Delta \mu_w = v_w \cdot \Delta p = 1.8 \cdot 10^{-5} \cdot 10^5 = 1.8 \text{ J/mol}$$

$$J_w = L_p \frac{d\mu}{dx} \approx \frac{D_w}{RT} \frac{\Delta \mu_w}{\Delta x} = \frac{10^{-9} \cdot 2}{2500 \cdot 10^{-4}} \approx 10^{-8} \text{ m/s}$$

and a comparison of the value for the convective and diffusive contributions indicates quite clearly that diffusion can be neglected in this case.

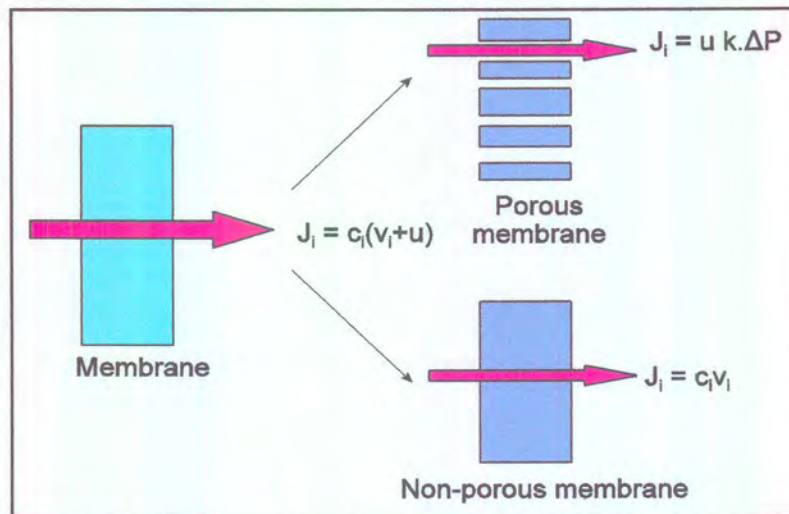


Figure 3.19 Convective and diffusive flow in a porous and a non-porous membrane.

Considering only the extreme cases, it can be stated that transport in porous membranes occurs by convection and in nonporous membranes by diffusion. However, in going from porous to nonporous membranes, an intermediate region exists where both contributions have to be taken into account.

The last part of this chapter will be devoted to a comparison of membrane processes where transport occurs through nonporous membranes. A solution-diffusion model will be used where each component dissolves into the membrane and diffuses through the membrane independently. As a result, simple equations will be obtained for the component fluxes involved in the various processes which allows to compare the processes in terms of transport parameters.

The flux of a component through a membrane may be described in terms of the product of the concentration and the velocity, i.e. convective flow makes no contribution (see equation 3.74). Hence,

$$J_i = c_i v_i \quad 3.75$$

The mean velocity of a component in the membrane is determined by the driving force acting on the component and the frictional resistance exerted by the membrane, i.e.

$$v_i = \frac{X_i}{f_i} \quad 3.76$$

The driving force is given by the gradient $d\mu/dx$. The frictional coefficient can be related to the thermodynamic diffusion coefficient D_T . If ideal conditions are assumed, i.e. if the thermodynamic diffusion coefficient is equal to the observed diffusion coefficient, equation 3.75 then becomes

$$J_i = \frac{D_i c_i}{RT} \frac{d\mu_i}{dx} \quad 3.77$$

The chemical potential can be written as

$$\mu_i = \mu_i^\circ + RT \ln a_i + V_i (p - p^\circ)$$

And substitution of equation 3.53 into equation 3.77 gives

$$J_i = \frac{D_i c_i}{RT} \left[RT \frac{d \ln a_i}{dx} + V_i \frac{dP}{dx} \right] \quad 3.78$$

Figure 3.20 gives a representation of the process conditions necessary for describing transport through nonporous membranes, where the superscripts m and s refer to membrane and feed/permeate side, respectively. If it is assumed

that thermodynamic equilibrium exists at the membrane interfaces, i.e. that the chemical potential of a given component (liquid or gas) at the feed/membrane interface is equal in both the feed and the membrane, and furthermore, that the pressure inside the membrane is equal to the pressure on the feed side, the following equations may be obtained:

at the feed interface (phase 1/membrane):

$$\mu_{i,2}^m = \mu_{i,1}^s \Rightarrow a_{i,1}^m = a_{i,1}^s \quad 3.79$$

and at the permeate interface (membrane/phase 2):

$$\mu_{i,1}^m = \mu_{i,2}^s \Rightarrow a_{i,2}^m = a_{i,2}^s e^{\left[\frac{-V_i(P_1 - P_2)}{RT} \right]} \quad 3.80$$

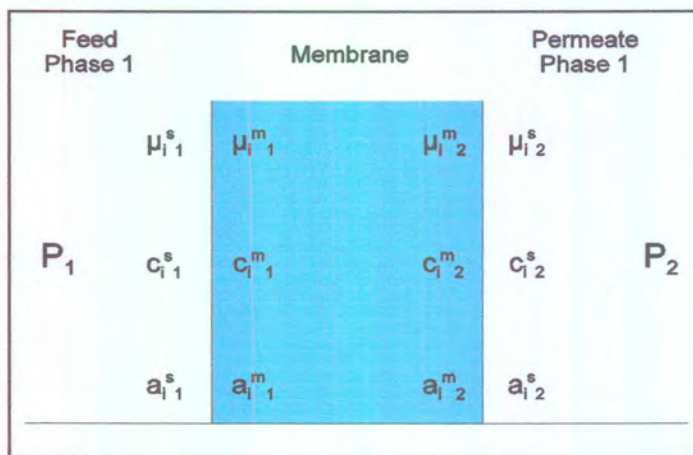


Figure 3.20 Process conditions for transport through non-porous membranes.

The activities at the feed interface can be written as

$$c_{i,1}^m \cdot \gamma_{i,1}^m = c_{i,1}^s \cdot \gamma_{i,1}^s \quad 3.81$$

while the activities at the permeate interface are

$$c_{i,1}^m \gamma_{i,2}^m = c_{i,2}^s \gamma_{i,2}^s e^{\left[\frac{-V_i(P_1 - P_2)}{RT} \right]} \quad 3.82$$

If the solubility constant K_i is defined as the ratio of the activity coefficients, we can write:

$$K_{i,1} = \frac{\gamma_{i,1}^s}{\gamma_{i,1}^m} \text{ and } K_{i,2} = \frac{\gamma_{i,2}^s}{\gamma_{i,2}^m} \quad 3.83$$

or

$$c_{i,1}^m = K_{i,1} c_{i,1}^s \text{ and } c_{i,2}^m = K_{i,2} c_{i,2}^s \quad 3.84$$

Furthermore, if it is assumed that the diffusion coefficient is concentration-independent, Fick's law (equation 3.9) can be integrated across the membrane to give

$$J_i = -\frac{D_i}{\ell} (c_{i,2}^m - c_{i,1}^m) \quad 3.85$$

After substitution of equations 3.81, 3.82 and 3.83 into equation 3.85 one arrives at



$$J_i = \frac{D_i}{\ell} \left(K_{i,1} c_{i,1}^s - K_{i,2} c_{i,2}^s e^{\left[\frac{-V_i(P_1 - P_2)}{RT} \right]} \right) \quad 3.86$$

and if $\alpha_i = K_{i,2} / K_{i,1}$ (i.e. the solubility coefficient are similar at both interphases) and $P_i = K_i D_i$, then equation 3.86 converts into

$$J_i = \frac{P_i}{\ell} \left(c_{i,1}^s - \alpha_i c_{i,2}^s e^{\left[\frac{-V_i(P_1 - P_2)}{RT} \right]} \right) \quad 3.87$$

Equation 3.87 is the basic equation used to compare various membrane processes when transport occurs by diffusion. The phases involved in such processes are summarised in table 4.1.

Table 4.1 Phases involved in diffusion controlled membrane processes
(L = Liquid, G = Gas)

Process	Phase 1	Phase 2
reverse osmosis	L	L
dialysis	L	L
gas separation	G	G
pervaporation	L	G

3.5.5.1 Reverse osmosis

Reverse osmosis is normally used with aqueous solutions containing a low molecular weight solute, which is often a salt. It can also be used for aqueous solutions containing very small amounts of organic solutes. This process involves the application of pressure to the liquid feed mixture as driving force, the total flux being given by the sum of the water flux J_w and the solute flux J_s . However, since this project is more concerned with the flux of ions across a

dialysis membrane, this section will not be discussed in detail.

3.5.5.2 Dialysis [7]

In general, the driving force for mass transfer is the potential gradient across the membrane thickness. Phenomenological models used to describe mass transfer processes are concerned with the relationship between the driving force and the resulting flux. In dialysis, the primary flux is that due to diffusion, which is driven by the concentration gradient component of a gradient in chemical potential. While other driving forces may exist, (migration or pressure gradient component of chemical potential causing bulk flow) dialysis is fundamentally a diffusive process and is modelled as such by solution-diffusion theory. The cornerstone of this theory of course is Fick's first law of diffusion. This law is a simple phenomenological model that describes the potential/flux relationship for diffusive mass transfer. It states that the diffusive flux is proportional to the gradient in concentration, mole fraction or chemical potential at constant pressure. In the strictest sense, a system consisting of solute, solvent, and membrane is ternary rather than binary. However, a pseudobinary approach can be taken in which solute A diffuses through component B, where B can be defined as both the membrane and the solvent. The molar flux can be described by the following general form of Fick's first law of diffusion:

$$J_{Ay} = x_A (J_{Ay} + J_{By}) - c_t D_{AB} \frac{dx_A}{dy} \quad 3.88$$

where J_{ay} and J_{by} are the molar fluxes of A and B in the y-direction, x_A is the mole fraction of solute A, c_t is the total concentration of A and B, and D_{AB} is the binary diffusion coefficient. The first term on the right represents bulk flow resulting from unequal counter diffusion of A and B, whereas the second term gives the diffusive flux. In reasonably dilute solutions, the bulk flow term may be neglected

and the total molar concentration, c_t may be considered constant. Now equation 3.88 can be simplified to

$$J_{Ay} = -D_{AB} \frac{dc_A}{dy} \quad 3.89$$

which is similar to equation 3.9. In dialysis, liquid phases containing the same solvent are present on both sides of the membrane in the absence of a pressure difference. The pressure terms can therefore be neglected and the following equation may be obtained from equation 3.87 if $\alpha_i = 1$. Assuming a linear concentration gradient and integrating equation 3.89 across the membrane,

$$J_{Ay} = \frac{D_{AB}(c_{1m} - c_{2m})}{\ell} \quad 3.90$$

where c_{1m} and c_{2m} are concentrations within the membrane at each of its interfaces and ℓ is the membrane thickness.

A partition coefficient K can be defined as the ratio between membrane and external solution concentrations at equilibrium:

$$K = \frac{c_{1m}}{c_{1s}} = \frac{c_{2m}}{c_{2s}} \quad 3.91$$

which is similar to the partition coefficient in general chromatography. Combining equations 3.90 and 3.91 and simplifying by eliminating the subscripts:

$$J = \frac{KD\Delta c}{\ell} \quad 3.92$$

Since separation on a membrane is determined by the permeability, it is essential to once again illuminate this principle. The permeability can be defined as

$$P = \frac{KD}{\ell} \text{ and } R = \frac{\ell}{KD} \quad 3.93$$

with R the membrane mass transfer resistance. Equation 3.92 can now be written as

$$J = P\Delta c = \frac{\Delta c}{R} \quad 3.94$$

This simple equation describe the solute flux in dialysis indicating that it is proportional to the concentration difference. Separation arises from differences in permeability coefficients: thus macromolecules have much lower diffusion coefficients and distribution coefficients than low molecular weight components.

3.5.5.3 Gas permeation

In gas permeation or vapour permeation, both the upstream and downstream sides of a membrane consist of a gas or a vapour. However, once again this is not relevant to the membrane processes of interest.

3.5.5.4 Pervaporation

Pervaporation is a membrane process in which the feed side is a liquid while the permeate side is a vapour as a result of applying a very low pressure downstream.

3.5.5.5 Electrodialysis [6,7]

As discussed in paragraph 3.5.5.2, the concentration gradient of the solute species across the membrane is the driving force for solute transport across the membrane. Due to this reason, the extent of solute transfer in dialysis is limited by the condition of zero concentration gradient, at which time dialytic transfer stops. In electrodialysis, the continuous supply of electrical energy ensures a positive driving force. In classical electrodialysis electrolytes are usually transported from low concentrations to high concentrations. The practical requirements for ion (electrolyte) transfer can be described as follows:

The total electrical potential drop across an electrodialysis cell consist only partly of the concentration potential. The other part is to overcome the ohmic resistance of the cell. This ohmic resistance is caused by the friction of various ions with the membranes and water while being transferred from one solution to the other, resulting in an irreversible energy dissipation in the form of heat generation. The technical feasibility of electrodialysis as a mass separation process, that is its ability to separate certain ions from a given mixture, is mainly determined by the membranes used in the system. In a cation-exchange membrane, the fixed anions are in electrical equilibrium with the mobile cations in the interstices of the polymer. In contrast the mobile anions (co-ions) are more or less completely excluded from the polymer matrix because of their electrical charge which is identical to the fixed ions. This type of exclusion is called the Donnan exclusion.

3.6 References

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Chapter 4

The evaluation of passive membranes for use in electro dialysis systems:

Determination of chloride.

4.1 Introduction

As is evident from chapter 1, the use of an electro dialysis (ED) system as an analytical application is a rather rare and unexploited device. The use of ion-exchange membranes in the electro dialyser system as part of a water purification system was the norm for use in ED systems. A new dimension in analysis was opened with the introduction of the ED into the conduits of the FIA (Flow Injection Analysis) system. ED (equipped with an ion-exchange membrane) had been reported for the separation of alanine and aspartic acid by Strathmann and Chmiel. [1] Debets *et al.* [2] reported on the extraction of ephedrine from spiked plasma by also making use of an ED system equipped with an ion-exchange membrane. An application for the separation of leucine from ketoleucine in a flow injection system was reported by Kittsteiner-Eberle *et al.* [3] The latter group, however, was the first group to use an ED/FIA system equipped with a passive membrane instead of the usual ion-exchange membrane. This group, however, did not evaluate the ED/FIA system but was rather concerned with the separation of the amino acids.

The use of passive membranes in an ED/FIA system was thus going through its growing pains. To ascertain the right of existence of the use of an ED system equipped with a passive membrane, the system was evaluated bearing in mind the following points:

- The main thrust in the initial stages of this investigation was to ascertain whether or not there will be an increase in the mass transfer across the passive membrane with the introduction of the applied potential across the passive membrane.

- The next important part of the investigation was to establish if a change in the applied potential would lead to an improvement in the enhanced mass transfer (if any).
- Another important aspect that had to be considered was if there was, to be an increase in the mass transfer across the passive membrane, how would different membranes react to such an applied potential.

Since the evaluation of the ED/FIA system was a priority at this stage of the investigation, a suitable analyte had to be found. The main prerequisite for the analyte chosen was that the FIA system used for its analysis must be simple, pose few as possible interferences and the electro dialyser must be easily introduced into this FIA system.

The determination of chloride was studied extensively in various FIA systems by making use of quite a number of possible detection methods. Potentiometric detectors were used rather extensively for the determination of chloride in FIA systems. Linear relationships were found to vary considerably depending on the application. Potentiometric methods were applied for the analysis of bottled water [5], natural water [6, 7], electroplating baths [8] and wine [9], just to name a few. Another very popular method was the indirect determination of chloride by the spectrophotometric measurement of the coloured $\text{Fe}(\text{SCN})^{2+}$ complex (the mercuric thiocyanate method). [11, 12]. Other spectrophotometric methods include the liberated chlorinilate ions [13] and the phenolphthalein reaction [14]. Methods, other than spectrophotometry and potentiometry, included precipitation (indirect method) [15] and FIA titration methods [16].

Initially an ISE (Ion Selective Electrode) was preferred (as described by Van Staden [17]) since this FIA system was very simple to use. However, tremendous problems were encountered with this detection system. Massive baseline drift occurred the moment the potential was applied across the membrane and distorted peaks were observed no matter how well the electro dialyser and other equipment were grounded.

For this reason electroanalytical methods combined with the ED/FIA system were avoided. The next most suitable detection method was the spectrophotometric determination of chloride using the mercuric thiocyanide colour reaction. [11,12]

Dialysis was employed quite often in the determination of chloride in FIA systems. [18 - 23]. The percentage dialysis max of 7% obtained in all the abovementioned references confirms the values mentioned by Van Staden in a review article on membranes. [24] Slight deviations were observed from the micro dialysis system that was described by Sundqvist [25]. It was thus crucial to confirm that there would be an increase of mass transport across the membrane (a percentage dialysis of higher than 7%) with the applied potential to confirm the credibility of the proposed ED system.

4.2 Experimental

4.2.1 Reagents and solutions

All reagents were prepared from analytical grade chemicals unless otherwise specified. Deionized water from a Modulab system (Continental Water Systems, San Antonio, TX) was used for dilution. The water was tested for traces of chloride before use. All solutions were degassed before measurement with a water vacuum pump system. The main solutions were prepared as follows:

4.2.1.1 Standard chloride solution

A standard stock chloride solution containing $10\,000\text{ mg l}^{-1}$ was prepared by dissolving 32.97 g of dried sodium chloride in water and diluting to 2ℓ with de-ionized water. Working standard solutions were prepared by appropriate dilutions to cover the working ranges as discussed in the text.

4.2.1.2 Colour reagent

The colour reagent was prepared by dissolving 1.26 g of mercury(II)thiocyanate in 300 ml of methanol, 1 ℓ of de-ionized water was added and shaken to mix well. 10 ml concentrated nitric acid (specific gravity 1.42) and 31g ferric nitrate nona hydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were added, dissolved and diluted to 2 ℓ with de-ionized water. The colour reagent was filtered if necessary. The reagent was found to be stable for several months at room temperature if stored in a dark bottle.

4.2.2 Instrumentation

The FIA system (Figure 4.1) used in this work, was composed from the following components: a six-roller Cenco peristaltic pump rotating at 10 rpm, a Valco (Houston, Texas) 10-port electrically actuated injection valve with a sample loop of 70 $\mu\ell$, reaction manifold system and a laboratory-made electro dialyser. The electro dialyser used (see Figures 4.2 and 4.3) was a slightly modified version of the dialyser unit as described by Van Staden [26, 27]. The dialyser unit consisted of two, mirror image, PVC blocks. Embedded into each of these blocks were graphite electrodes which acted as the anode (acceptor side) and the cathode (donor side) respectively. Placed onto each of the PVC blocks was a 0.6 mm thick Perspex spacer. Into each of the Perspex blades, a groove of 0.6 mm diameter and 300 mm length was cut so as to form a channel when placed onto each of the PVC blocks respectively. The PVC blocks were then fitted onto each other in such a way that the Perspex blades facing each other and the grooves in the respective Perspex blades coincided with each other. The membrane was then sandwiched between the two Perspex blades as the only separation between the two tubes so formed. The walls of the tubes that were formed thus consisted of, at the far end, the graphite (which was embedded into the PVC blocks), the side walls of Perspex and the common wall, the membrane. A Leader LPS 156 potentiostat was used to apply the d.c. potential. Two different passive membranes were used namely, a Spectrapore membrane (MW cut-off

6000-8000, pore size 2.5-4 nm, thickness 0.031 mm) and a Technicon type C membrane (pore size 4-6 nm, thickness 0.015mm). Tygon tubing (0.76 mm id) was used to construct the manifold system. For current and potential measurements a Prema 5000 intergrating multimeter was used. The detector used was a Unicam 8625 UV/VIS spectrophotometer equipped with a 10 mm Hellma-type flow-through cell (volume 80 μl). The spectrophotometer and the injection valve were coupled to a personal computer equipped with the FlowTEK program [28].

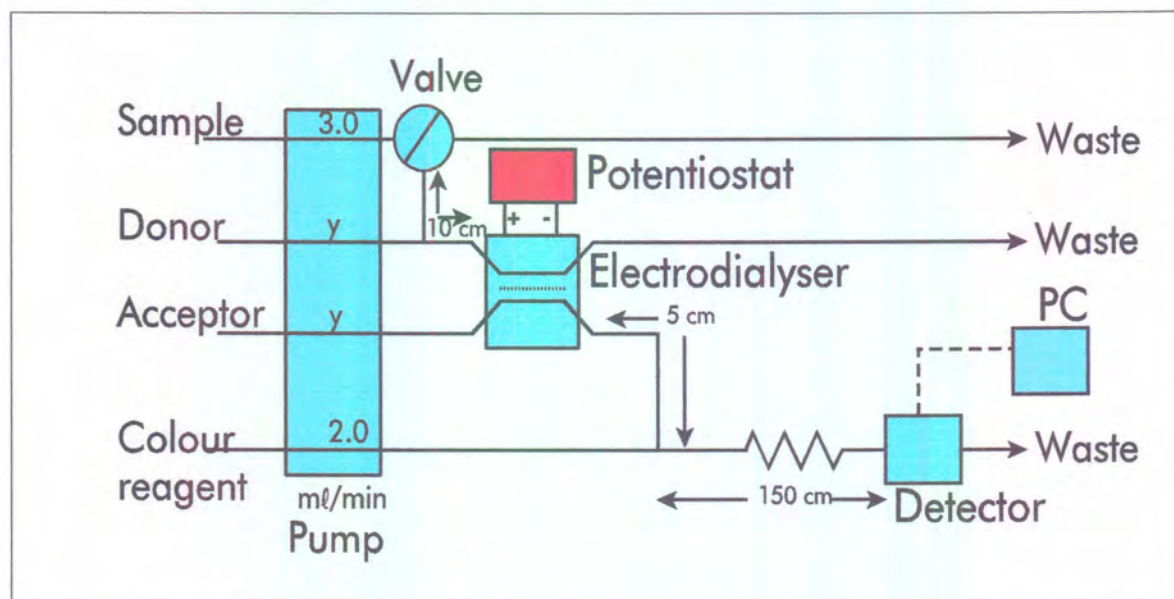


Figure 4.1 Schematic flow diagram of the electrolysers/flow injection system for the determination of chloride.

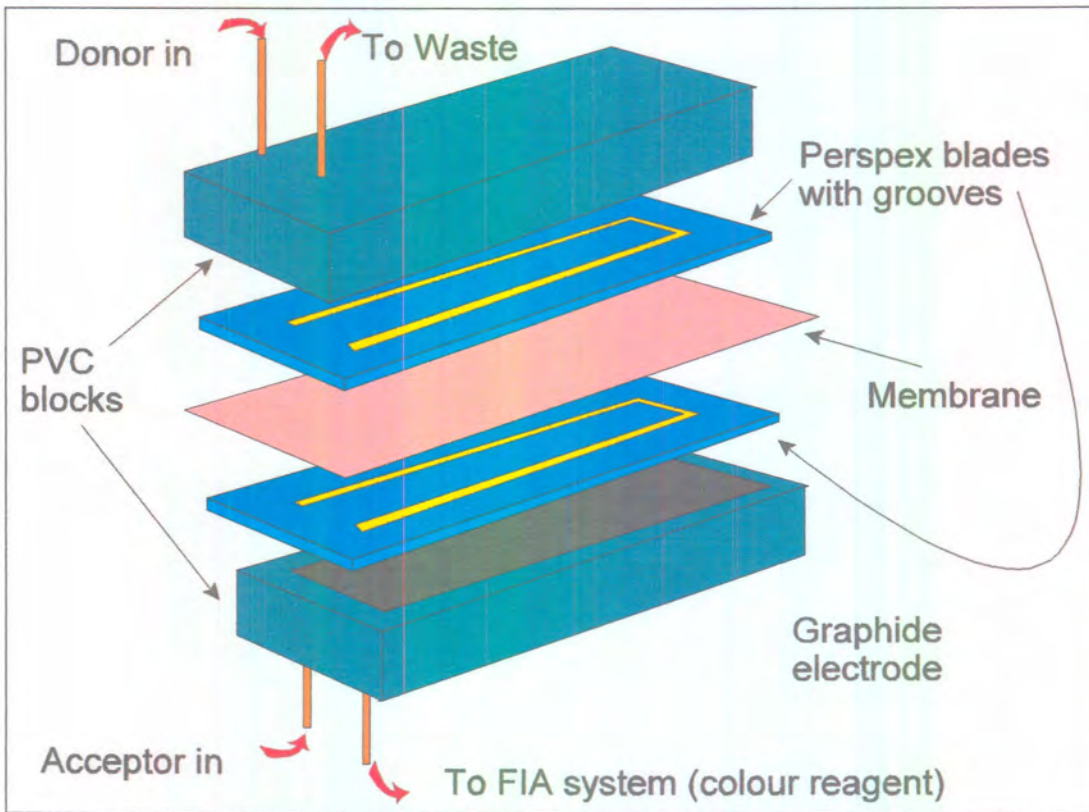


Figure 4.2 3-D Representation of the electrolysers indicating the placement of the different components.

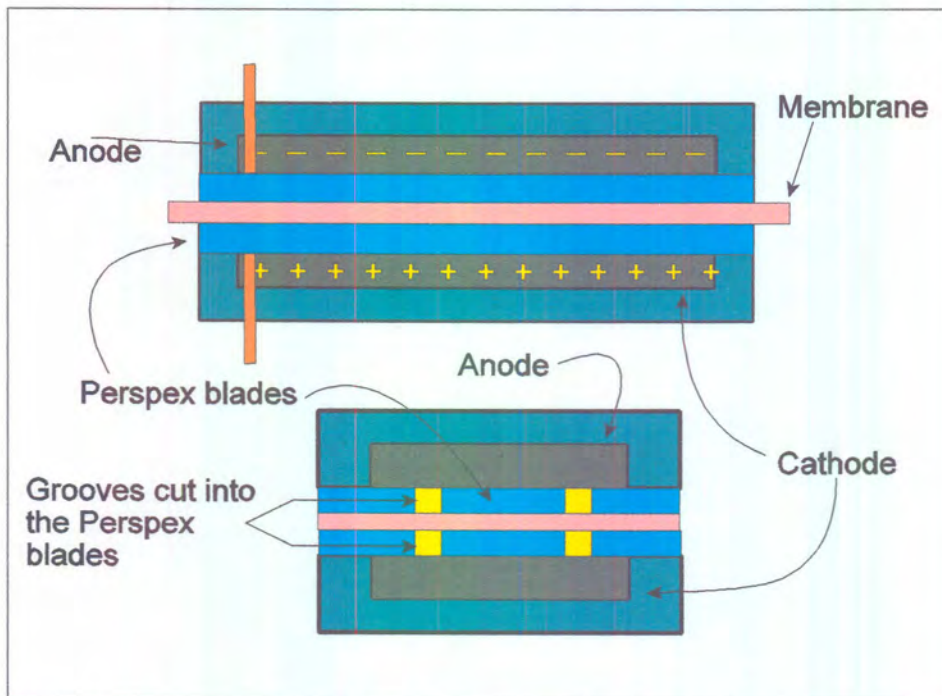
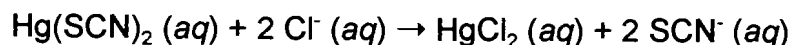


Figure 4.3 Longitudinal- and diagonal cross sections of the dialyser unit indicating the fitting of the different components.

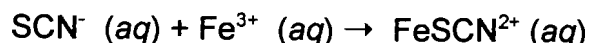
4.2.3 Flow system

The flow system used is depicted in Figure 4.1. Sample solutions were drawn up into a 70 $\mu\ell$ sample loop of the Valco valve from where it was injected into the carrier donor stream and transported into the electro dialyser. Analytes in the sample donor stream were electro dialysed under the influence of an applied d.c. potential through the passive neutral membrane to the acceptor channel. The electro dialysate ions were swept from the electro dialyser unit and mixed with iron(III)/mercury(II)thiocyanate chromogenic reagent in the reaction manifold system. The following reactions took place:

With the addition of the analyte (chloride) ions, which have a larger affinity for the mercury than the thiocyanide ions, the thiocyanide ions were displaced from the mercury/thiocyanide complex in amounts proportional to the added analyte chloride ions:



The displaced thiocyanide ions were then free to react with the Fe^{3+} ions to form the FeSCN^{2+} complex which has an absorption maximum at a wavelength of 480 nm.



Some higher order ferric/thiocyanide complexes may also form, but at low concentrations of thiocyanide, the major species will be FeSCN^{2+} . The displacement of the thiocyanide and therefore the initial concentration of the thiocyanide (that is the concentration before the commencement of the second reaction) was very low since the volume (70 $\mu\ell$) and concentration (200 - 3200 mg l^{-1}) of the analyte chloride ions injected was very low. For this reason,

according to Lewin and Wagner [29], the major ferric/thiocyanide complex that would form, would be FeSCN^{2+} .

This coloured reaction product was transported to the spectrophotometer for measurement at a wavelength of 480 nm.

Data acquisition and device control were achieved using a PC30-B interface board (Eagle Electric, Cape Town, South Africa) and an assembled distribution board (MINTEK, Randburg, South Africa). The FlowTEK [28] software package (obtainable from MINTEK) for computer aided flow-analysis was used throughout for device control and data acquisition. All the data given (mean height values) are the average of 10 replications.

4.3 Results and discussion

In order to enhance the mass transfer of chloride anions through the passive neutral membrane as an accurate and precise measurable product, optimum system conditions were of critical importance in the design and operation of the electrolysers/flow injection system. The first main target of the optimisation was to ensure that the maximum amount of chloride ions were drawn across the neutral membrane into the conduits of the acceptor channel by applying a d.c. potential gradient across the two sides of the membrane. The second goal was to prevent any gas evolving reactions that might occur at the anode. Since rather high potentials were used (5 - 27 V), most oxidizable species that migrated to the anode would have reacted. Any of the gas evolving anode reactions had to be avoided at all costs since the debubblers developed up to this stage of the investigation were not very effective for the removal of the gaseous products that ended up in the FIA system. This was done by optimising the acceptor stream flow rate so that the dialysate analyte ions would be rushed out of the acceptor channel into the reaction manifold before the ions could come in contact with the anode. Thus it was essential to optimise flow rates of the donor and acceptor

channels and the applied potential over the membrane. Initially therefore, this part of the project concentrated on the design of the ED system.

4.3.1 Applied potential

The sensitivity and reproducibility of the electrodialysed chloride analyte sample plugs in the electrolysers unit depended on the potential gradient applied on the system. The applied potential was therefore evaluated using the detector signal for response and %RSD as indicators. The d.c. potential was varied between 0 and 27 V for both membranes, while the flow rates in the donor and acceptor streams were kept constant at 1.6 ml min^{-1} . The results in Figure 4.4 revealed that the precision at low applied potentials was poor (%RSD > 8% for the Technicon membrane and > 13 % for the Spectrapore membrane), indicating that the contribution of detectable chloride ions drawn through the neutral membrane was unstable. As the applied voltage was increased to 6.8 V, the %RSD decreased significantly, reaching an optimum value of 2.8% for the Spectrapore membrane and 1.9% for the Technicon membrane. It can be assumed that the majority of electrolysate chloride ions were drawn into the core of the acceptor stream and that the anode electrode had a minor influence at the applied potential of 6.8 V. It is furthermore apparent that there is a slight increase of the %RSD from very low voltages (6.8 V) to higher voltages (27 V) in both the membranes. This is probably due to the stronger attraction forces exerted on the chloride anions from the anode resulting in a loss of anions from the main acceptor stream and also to possible electrode reactions. A rather sharp increase in the %RSD is observed from 20 V and higher. This was due to the formation of gas at the anode. From equation 3.10, it is evident that with an increase in the applied potential there should be an increase in the movement of the ions in solution, and thus the chloride ions should reach the anode in a shorter period of time. The precision of the Spectrapore membrane deteriorated faster than the precision of the Technicon membrane with the increase of applied voltage above 6.8 V. The influence of applied potential on the peak height is depicted in Figure

4.5. The results in Figure 4.5 show an increase in peak height when the applied potential was increased from 0 to 24 V. The results in Figure 4.5 reveal that the peak height of the Technicon membrane increased faster than the peak height of the Spectrapore membrane when the applied potential was increased from 0 to 24 V. This is probably due to the larger pore size and smaller thickness of the Technicon membrane. The increase in peak height of the Technicon membrane flattened off for applied potentials larger than 24 V.

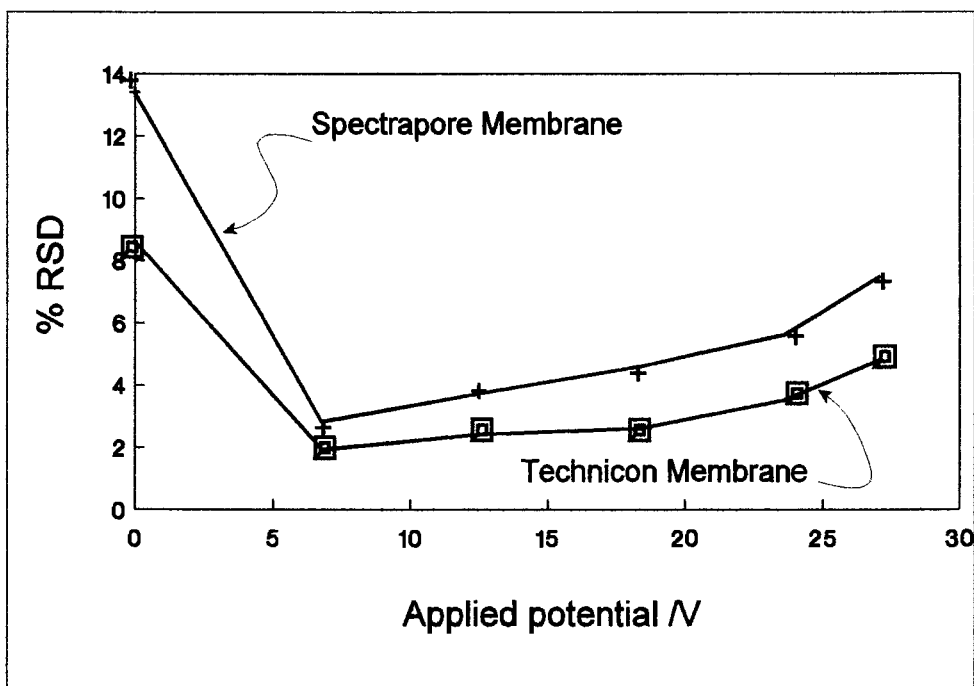


Figure 4.4 Evaluation of relative standard deviation as a function of applied potential.

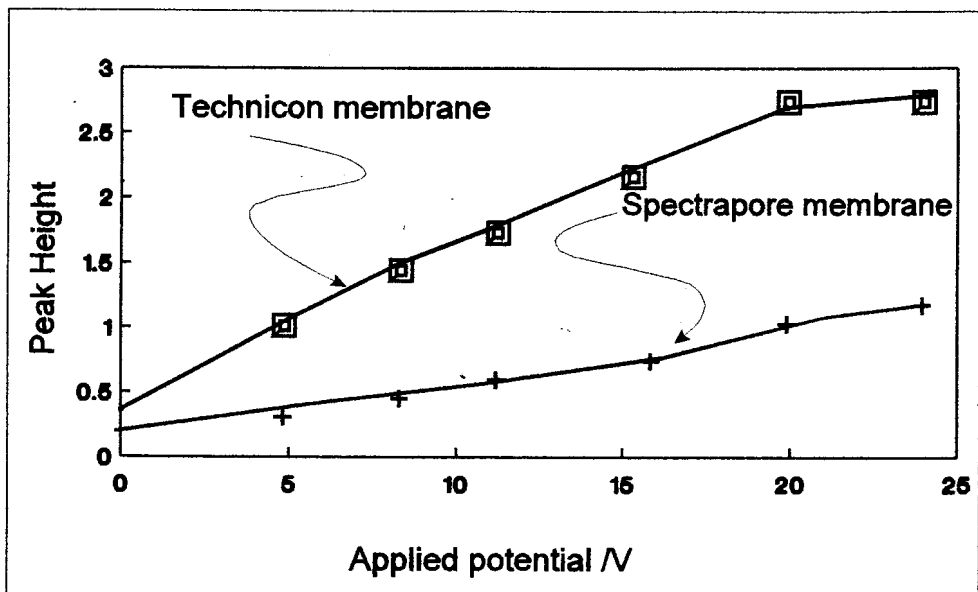


Figure 4.5 Evaluation of the response as a function of applied potential.

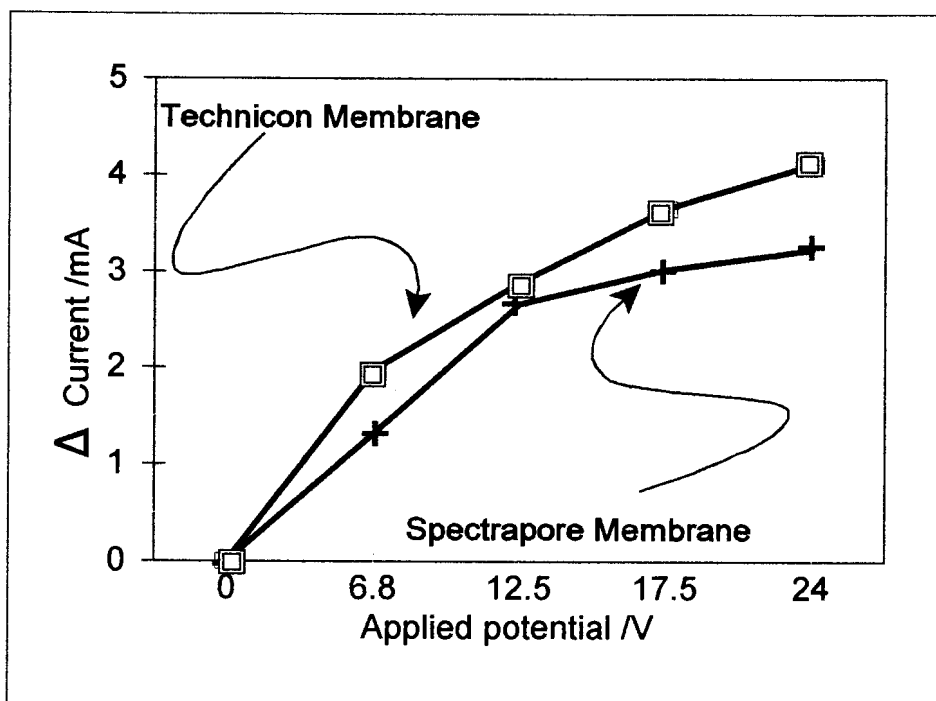


Figure 4.6 Effect of applied potential on the change in current on the acceptor channel indicating the flux of ions through the passive membrane .

From Figure 4.6 it is evident that there was a definite increase in the current across the membrane, for both membranes, with an application of a dc potential. The change in current was negligible at an applied potential of 0 V. The current however increased dramatically, for both membranes, with increasing applied potential. For the Technicon membrane this increase flattened off only slightly with increasing applied potential. For the Spectrapore membrane however there was a definite flattening in the curve after potential was increased above 12.5 V. This phenomenon, most probably, was due to the increased membrane thickness of the Spectrapore membrane in comparison to the thickness of the Technicon membrane.

4.3.2 Flow rates of the donor and acceptor streams

The main purpose of flow rate of the acceptor stream was to flush the dialysate chloride anions immediately, as they emerged from the membrane, to the reaction manifold to prevent any anions to reach the surface of the anode. Evaluation of the flow rates of both the donor and acceptor streams revealed that the best results were obtained with the flow rates of both streams in the same direction when applied in the continuous mode. Sensitivity and precision were used as indicators in the optimisation of the flow rates. In all the experimental work done, the same flow rate was applied for both the donor and acceptor streams. The reason for this is that previous studies indicated that the best precision and sensitivity was obtained when the same flow rate was used in both the donor and the acceptor channels. [21] During these experiments the applied potential was kept constant at 15 V while the flow rates of the donor and acceptor streams were varied. The influence of the flow rates, for both membranes, was first compared on the basis of %RSD, as illustrated in Figure 4.7. It is clear from the results that the precision deteriorated remarkably for flow rates below 1.4 mL min^{-1} for the Spectrapore membrane and for the flow rates below 1.6 mL min^{-1} for

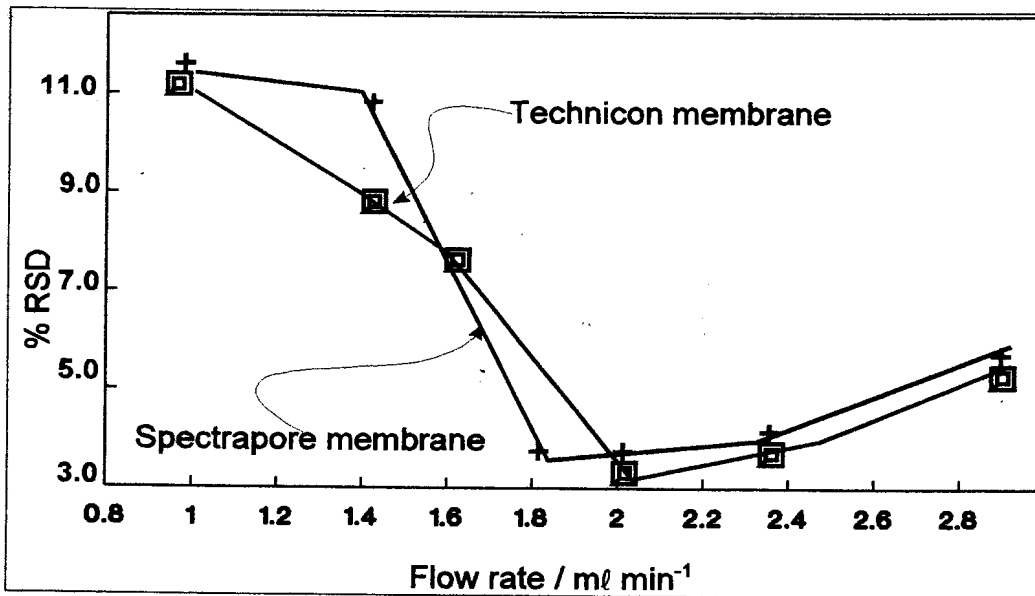


Figure 4.7 Evaluation of relative standard deviation as a function of the flow rate of both membranes.

the Technicon membrane. It is obvious that at low flow rates the dialysate chloride ions tended to move through the core of the acceptor stream and were able to reach the anode where possible electrode reactions could cause sufficient disturbance to increase the %RSD. Another contribution to this increase is the

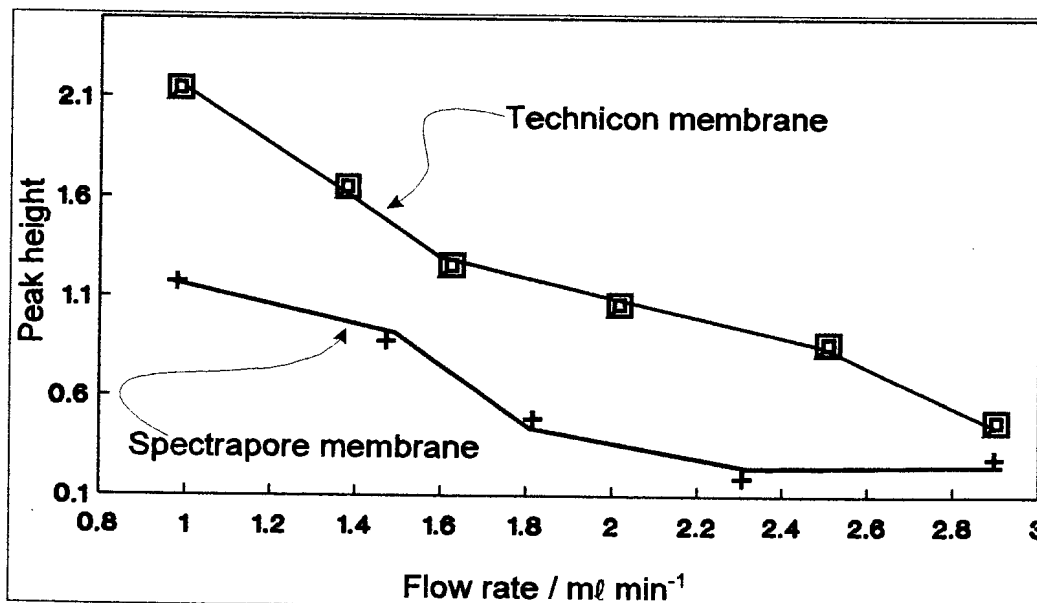


Figure 4.8 Evaluation of response as a function of the flow rate of both membranes.

irregular flow patterns at lower flow rates. The precision improved at higher flow rates with the best precision obtained at a flow rate of 2 mL min^{-1} for both membranes. If one considers the peak height versus the flow rate (Figure 4.8), the best response was obtained with flow rates of 1 mL min^{-1} for both membranes. A possible explanation for the decrease in sensitivity with higher flow rates was that although the flux of ions across the neutral membrane under the influence of the applied electric field remained the same, it could not match the influence of the higher flow rate with dilution effect on the dialysate anions in the acceptor channel of the FIA system. The best compromise between sensitivity and precision for employment of the proposed electrolysers/FIA system was obtained with a flow rate of 1.6 mL min^{-1} for the Technicon membrane and 2.0 mL min^{-1} for the Spectrapore membrane. The proposed electrolysers/FIA system is, however, very flexible and it is therefore possible to use the influence of donor and acceptor stream flow rates to apply the system in other analyte concentration ranges when required.

4.3.3 Interferences

The ions, Br^- , I^- and NH_4^+ were found to have an influence on the response of chloride ions in the ED/FIA system. It was found that bromide and iodide ions interfered positively with the determination of chloride, starting at levels as low as the detection limit for chloride. An evaluation revealed that the bromide and the iodide interfered whether they were injected into the donor or the acceptor streams. The conclusion of this was that the bromide and iodide being anions, experienced the same driving force exerted by the applied potential as the chloride ions. Additionally, however the main interference was that the bromide and iodide ions also reacted with iron(III)/mercury(II)thiocyanate chromogenic reagent to give coloured reaction products absorbing at the same wavelength as the colour product from the chloride ions. The influence of ammonia/ammonium

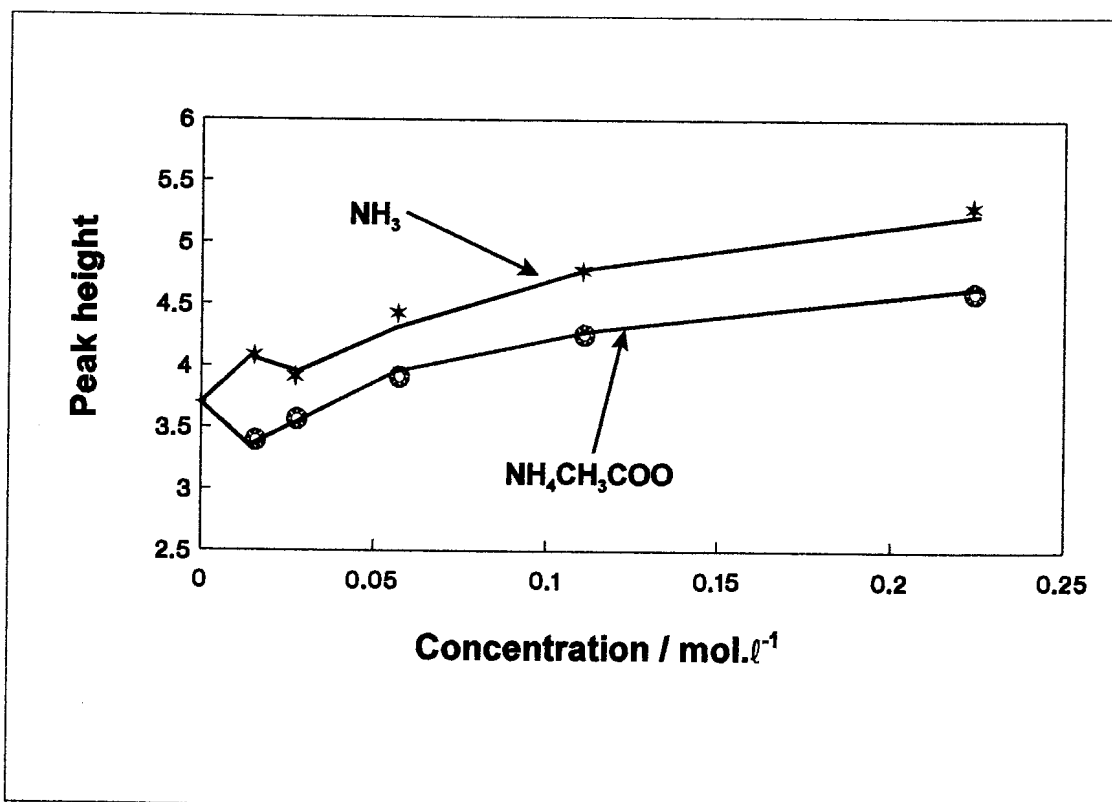


Figure 4.9 Influence of interferences: Technicon membrane.

ion is illustrated in Figure 4.9. The interference of ammonia depends on the type of compound used. When ammonium hydroxide was used as the primary source of ammonia, interference occurred when very low concentrations of the ammonia salt were injected into the donor stream of Technicon membrane as seen from Figure 4.9. Interference also started at a concentration of 0.011 mol l^{-1} when the Spectrapore membrane (Figure 4.10) was used. Gas and molecular diffusion was probably the main cause for this interference as the ammonium cations were not able to reach the anode. Two factors contributed to this: the total effective cross-sectional area of pores available for gas and molecular diffusion were big enough to allow for the ammonia/ammonium ions to diffuse through the passive neutral membranes. Secondly, the thinner Technicon membrane dimensions were probably responsible for the ability of the ammonium acetate to diffuse through the membrane, whereas the Spectrapore membrane was just thick enough to prevent diffusion through the membrane even at higher concentrations, as is evident in Figure 4.10. The ammonia/ammonium ion that diffused through both membranes had a buffer effect on the acidic colour reagent. The influence of the buffer effect was reduced by increasing the amount of HNO_3 used in the colour reagent about five to ten fold.

4.3.4 Calibration and comparison of the Spectrapore and Technicon membranes

A comparison between the performances of Spectrapore and Technicon membranes in the electrolysers/flow injection system is outlined in table 3. 1. The linearity of the ED/FIA system for the determination of chloride was evaluated under optimum running conditions for both membranes (2.0 ml min^{-1} and 1.6 ml min^{-1} for the Spectrapore and Technicon membranes respectively with an applied potential of 15 V for both membranes). As can be seen from table 3.1, the linear range for the Spectrapore membrane was between 400 and 3200 mg l^{-1} with the straight line equation $y = 0.002039x - 0.8556$ and $r^2 = 0.9974$. The linear range for Technicon membrane was found to be between 200 and 1200 mg l^{-1} with the equation for the straight line $y = 0.003975x - 0.2557$ and

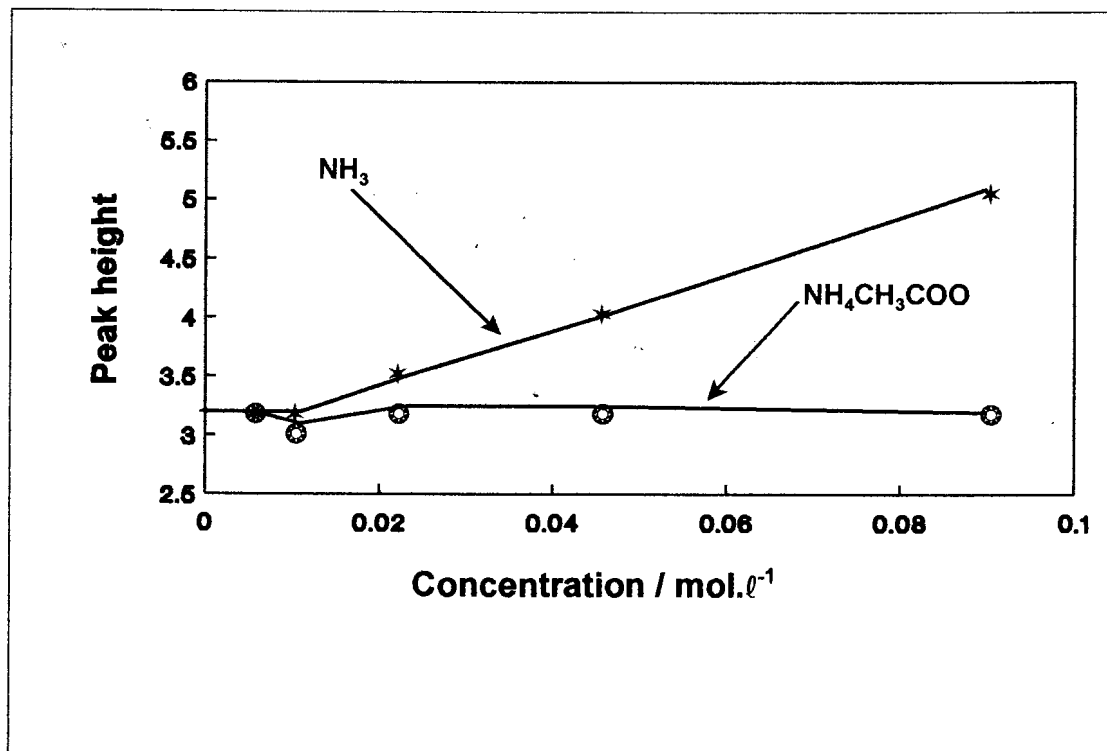


Figure 4.10 Influence of interferences: Spectrapore membrane.

$r^2 = 0.9941$. The mass transfer was increased to 10% and 37% for the Spectrapore and Technicon membrane respectively, which was a remarkable improvement on the values possible with conventional dialysis. Sample interaction was 0.23% for the Spectrapore membrane and 0.32% for the Technicon membrane at sample frequencies of 26 and 23 samples per hour respectively. These sample interactions are negligible.

Table 4.1 Comparison of the performance of the Spectrapore and Technicon membranes in the electrodialyser/flow injection system.

Parameter	Spectrapore Membrane	Technicon Membrane
% Electrodialysis	10	37
Runs h ⁻¹	26	23
Experimental time (s)	140	160
Sample interaction (%)	0.23	0.32
Linear range (mg ℓ ⁻¹)	400 - 3200	200 - 1200
Applied potential (V)	15	15
Flow rate (ml min ⁻¹)	2	1.6

Note should be taken that the percentage dialysis at an applied potential of 0 V could not be detected. Reason for this was the high flow rates. As was mentioned previously, the expected percentage dialysis is 0 -7 % [24] at optimal conditions. Higher than optimum flow rates were used in both membrane systems and consequently percentage dialysis will be extremely low. For this reason the concentration of the analyte in the acceptor stream, without the applied dc potential, will nearer zero concentration.

4.3.5 Samples

Real samples from industrial effluents were analysed with the proposed ED/FIA system. The results obtained for both membranes were compared with the results obtained from a standard titration method for the determination of chloride. The results, as shown in Table 2, revealed a good correlation between the ED/FIA system and the standard titration procedure.

Table 4.2

Comparison of the results of a number of samples as determined with the Spectrapore and Technicon membranes in the electrolysers/flow injection system and a standard titration procedure.

Sample	Spectrapore membrane	Technicon membrane	Standard titration procedure
1	1054	1060	1063
2	435	444	439
3	2004	2007 ^a	1997

^a Diluted to fall within the linear range.

4.4 Conclusion

The aim of the project was to investigate the viability of ED in the enhancement of mass transfer over passive neutral membranes in FIA systems. Chloride anions were selected to evaluate the electrolysers/FIA system. The system proved to be very successful and it was possible to retain all the advantages of passive dialysis in flow systems, but at the same time, increase mass transfer through the membrane. The flexibility of the ED/FIA system is also shown by variation in the working range to fit a specific application, a commodity that was possible with alternation in the applied voltage and flow rates of the donor and acceptor streams.

To return to the points of evaluation mentioned in paragraph 4.1: Will there be an increase in the mass transfer across the membrane? The answer is undoubtedly yes. There was a massive increase in the % dialysis, especially in the case of the Technicon membrane and to a lesser extent also in the case of the Spectrapore membrane. The reasons why the Technicon membrane performed better than the Spectrapore membrane can be one of, or a combination of the following:

The Spectrapore membrane is thicker than the Technicon membrane thus the value of ℓ in equation 3.92 is higher for the Spectrapore membrane than for the Technicon membrane. Since the flux, J , is inversely proportional to the membrane thickness, ℓ , ($J \propto \ell^{-1}$), the flux is expected to decrease with increasing membrane thickness.

The pore diameter of the Technicon membrane is slightly larger than those of the Spectrapore membrane. Considering equation 3.57, it is clear that the flux is directly proportional to the surface porosity. ($J \propto \epsilon$) Thus the flux will increase with increasing pore size.

The optimum flow rate for the Spectrapore membrane is slightly higher than for the Technicon membrane. This led to a higher dilution factor in the acceptor channel of the Spectrapore membrane.

Even though the $\text{NH}_3/\text{NH}_4^+$ had less influence on the signal in the case of the Spectrapore membrane, the influence in the Technicon membrane was easily circumvented by the addition of more nitric acid to the colour reagent mixture. For this specific FIA system, the Technicon membrane was found to suit the system better than the Spectrapore membrane.

This newly developed ED/FIA system is of great value for the determination of any charged species. The main problem encountered with this system was the formation of gaseous products at the anode (acceptor channel of the dialyser) as a result of anode reactions. The detection system used was very sensitive towards bubbles in the flow system. For this reason rather high flow rates through the dialyser unit was used to prevent the dialysate chloride ions (or any species that will oxidise at the anode) from reaching the anode. This procedure however, limited the time the sample bolus spent in the dialyser unit and thus reducing the time available for movement of the analyte across the membrane. It is therefore recommended that for ED/FIA systems which make use of the same type of detector, some kind of de-bubbler must be incorporated into the flowing stream before the dialysate ions reach the detector.

4.5 References

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