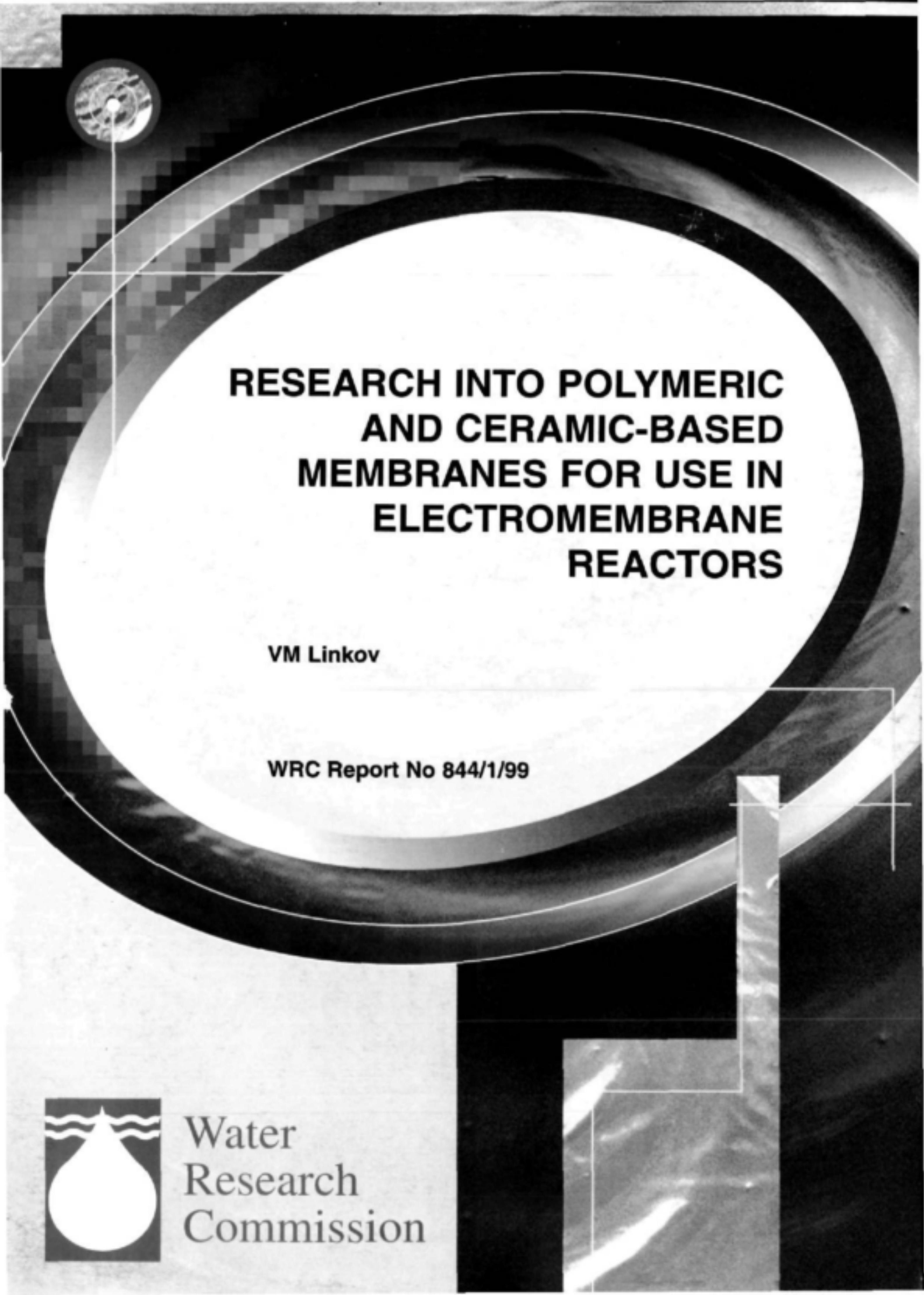

RESEARCH INTO POLYMERIC AND CERAMIC-BASED MEMBRANES FOR USE IN ELECTROMEMBRANE REACTORS

VM Linkov

WRC Report No 844/1/99

Water
Research
Commission

RESEARCH INTO POLYMERIC AND CERAMIC-BASED MEMBRANES FOR USE IN ELECTROMEMBRANE REACTORS

Final Report

to the

Water Research Commission

by

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EXECUTIVE SUMMARY

Background

South Africa needs newer and more advanced techniques for water treatment to remove an increasing number of intractable substances and microorganisms. Membrane processes form a major portion of the water treatment market. Electrodialysis (ED) is an electrochemical membrane process which is widely used for desalination of brackish water.

Although electrodialysis and electrodialysis reversal (EDR) processes have been commercial methods of demineralisation for more than two decades, a world-wide problem is the fouling of anion-exchange membranes by organic colloids present in water. This has detrimental effects on the membrane characteristics, and therefore the process economics. Membrane cleaning and replacement can amount to almost half of the cost of producing the demineralised product. Research is therefore required into methods to protect membranes against fouling, thereby extending their in-service lifespan.

This research project focuses on improved and novel ion-exchange membranes, both polymeric and ceramic-based types.

Motivation

Chemical and electrochemical pre-treatment techniques could be developed to reduce membrane-fouling problems. Methodology is especially required for the treatment of anion-exchange membranes (cation-exchange membranes are not as badly affected by fouling). Results of research carried out in Russia have shown that the fouling potential of modified anion-exchange membranes could be decreased by up to 20-fold. The availability and use of modified membranes could result in great savings in membrane replacement costs, the maintenance of steady current efficiencies and reasonable operating costs.

The transfer number of cation-exchange membranes for monovalent ions and selectivity of monovalent over bivalent ions may be increased by modification techniques similar to those used for the modification of anion-exchange membranes. This would make ED suitable for the production of water for irrigation.

The successful preparation and use of anion- and cation-transfer membranes made from alumina, silica and zirconia would permit the application of the ion-exchange membranes at high temperatures and in harsh chemical environments, over a wide pH range. They should be particularly suitable for the removal of heavy metal ions from hazardous effluents. Such membranes have potential to become lower cost alternatives to organic based membranes.

The use of newly-developed ceramic membranes would be as supports for electroconductive catalytic layers that are not soluble under anodic conditions. Such inorganic membranes would combine separation and electrode functions and would therefore be ideal for use in electromembrane reactors. These reactors are highly efficient in water disinfection processes and in the low-cost manufacturing of acids, alkalis, oxygen, hydrogen and halogens. The reactors maintain high specific productivity and low energy consumption, they are compact and easy to operate.

The overall objective of this project was the preparation of novel ion-exchange membranes for ED, EDR and electromembrane reactor processes, determination of their characteristics and evaluation of their suitability for ED water treatment, particularly mine water in South Africa.

The results of this research could find world-wide application in water-treatment industries. Anion-transfer membranes protected against fouling will not develop higher resistance and lower selectivities during electrodialysis of complex organic/inorganic feed mixtures. Specific target groups are the electroplating industry, electric power plants, and metallurgical industries.

Objectives

The objectives of this research programme, as set out in the contract, were as follows:

1 a) The development of new chemical (modification) and electrochemical pre-treatment methods to improve the fouling characteristics of existing polymeric ion-exchange membranes and b) the preparation of novel ceramic non-fouling membranes.

2 The development of cation-exchange membranes with increased transfer numbers for monovalent ions.

3 The fabrication of ceramic ion-exchange membranes with increased chemical stability.

4 Incorporation of these novel membranes into electrodialysis (ED) and electromembrane reactor units.

Participants

This research was a combined effort between Professor V Linkov from the University of the Western Cape and Professor V Belyakov from the Institute of General and Organic Chemistry in the Ukraine. ESKOM-TRI co-funded the part of research concerned with polymeric membranes.

Research methodology

Polymeric membranes (Ionics) were modified with a variety of surface active agents, and their fouling resistances determined in simulated solutions of mining water effluents. Changes in membrane permselectivity due to modification were also determined. The use of a pulsing mode to supply current to the membrane cell was investigated. Finally, the application of anodic oxidation for the destruction of organics was investigated. Inorganic ceramic-based membranes were prepared and evaluated for their anti-fouling properties.

Results

Of the polyelectrolytes investigated for use in membrane modification, the NB-8 agent allows us to obtain the highest resistance coefficient against fouling by organic substances. Although the membranes modified with LT-27 have lower resistance coefficients this modifier is also effective and can be used in considerably lower concentrations than NB-8. There is practically no difference in the measured properties of anion-transfer membranes modified under static or dynamic conditions. The layer of polyelectrolyte electroprecipitated under dynamic conditions is quite stable and effectively protects the membrane against fouling for a minimum of 20 days.

Inorganic ceramic membranes prepared on the basis of zirconium dioxide and aluminum oxide had similar osmotic properties to the polymeric Ionics membranes, although the diffusion permeability of the ceramic membranes for low-molecular electrolytes was 100-1000 times less. Modification of ceramic membranes by the incorporation of zirconium phosphate, pyrolytic precipitated carbon and manganese dioxide results in decreases in membrane permeability for water and electrolyte solutions. The modification of ceramic membranes by manganese dioxide results in a decrease in their electrical resistance in electrolyte solutions. This fact can be useful to make these membranes applicable as electrodes, for use in a wide range of electrochemical processes.

The modification of a ceramic membrane by zirconium phosphate increases its selectivity for cation transfer, making them suitable for use in electrolyte desalination and complex solution electrolysis.

Results of investigations with model solutions showed that the inorganic ceramic membranes are highly stable to fouling by humic acids (HA) and surface active compounds.

This was confirmed during the electrodialysis of simulated mine water solutions: the potential drop across the membranes remained unchanged after more than 10 days operation. The effective operation of inorganic membranes in electrodialysis installations requires the use of current pulsing and the reversal of power supply.

Polymeric membranes (Ionics), unmodified and modified, and the ceramic phosphate-containing membranes developed during the course of the study were compared for their main anti-fouling characteristics and selectivity. Inorganic membranes have specific properties that make them superior to polymeric membranes. First, they are not fouled by organic compounds, and they have a lack of limiting current even at significant voltage drops across the membrane. The transport characteristics of monovalent ions through inorganic membranes are similar to those through polymeric based ones (Na current efficiency not less than 95%). The transport of divalent ions (Ca and Mg), however, takes place to a lesser extent through the inorganic membranes than through the polymeric ones. This results in another important characteristic of inorganic electrodialysis membranes, namely their selectivity for monovalent ions.

In case of polymeric membranes, the coating by NB-8 has very little effect on the permselectivity of the anion exchange membrane. Coating by LT-27 results in an increase in permeability toward monovalent anions. Treatment of cation transfer membranes by 8-NB results in an increase in permeability towards divalent ions, whereas treatment with LT-27 increases permeability towards monovalent ions. These modified polymeric membranes as well as ceramic cation selective membranes can be used for production of potable water from a feed source with a high total hardness value.

The use of a pulsing mode increases membrane resistance toward fouling. By passing the feed solution through the anode compartment of the electrodialysis stack prior to desalination, the destruction of organic components will reduce their concentration, and therefore the effect of fouling on the membranes.

A further simple, and effective, method for the regeneration of membranes fouled by organic substances was chemical processing in a NaCl solution. Brine washing is utilised for cleaning of anion exchange membranes that are fouled with naturally occurring organics.

The characteristics of Ionics and MA-100 anion-transfer membranes (Russia) were compared. The Ionics membrane had better surface uniformity which provided better resistance to fouling by dodecyl benzyl sulfonate (DBS) and HA.

The characteristics of the Ionics and Neosepta (Japan) cation-transfer membranes were compared. Their electrical resistances to alternating current were very similar, but the resistance of Ionics membranes to direct current is about double that of the Neosepta membrane. The latter are practically impermeable to divalent ions and are well-suited for the selective concentration of Na salts from multicomponent systems.

Conclusions

The two high molecular weight surface active agents LT-27 and NB-8 can be used successfully to protect the Ionics membrane against fouling. Modification can be carried out under static or dynamic conditions. Coating by NB-8 has very little effect on the permselectivity of the Ionics anion exchange membrane. Treatment of cation transfer membranes by NB-8 results in an increase in permeability towards divalent ions, whereas treatment with LT-27 increases permeability towards monovalent ions. These membranes can be used for production of potable water from a feed source with a high total hardness value.

The following general conclusion is made regarding the development of stable, novel ceramic non-fouling membranes. As a result of the high stability of inorganic membranes in aggressive media, including oxidizing environments, and their insensitivity to the presence of high-molecular mass electrolytes, they can potentially be used in the following water-related fields: beneficiation of effluents of galvanic manufacturers or extraction of non-ferrous metals from different industrial solutions by electrodialysis, the electrodialysis of mine waters, the electrochemical synthesis of acids and alkalis, the preparation of disinfecting solutions, and others.

The use of a pulsing mode of power supply increases membrane resistance toward fouling.

By passing the feed solution through the anode compartment of the electrodialysis stack prior to desalination, the destruction of organic components will reduce their concentration, and therefore the effect of fouling on the membranes.

Washing with a NaCl or caustic brine solution is a useful way of cleaning anion-exchange resins that are fouled with naturally occurring organics.

Industrial perspective

Results of the studies conducted on polymeric have revealed significant opportunities to increase the efficiency of the process of electrodialysis, and also to reduce the effects of membrane fouling. To date, research has only been conducted on a laboratory scale. Opportunities of on-site work at the Tutuka Power Station or SASOL Secunda have arisen and are being further investigated.

Costs

The basic objective of the present project was merely to ascertain the potential and suitability of developing and using modified polymeric and novel ceramic membranes for the ED of organic-foulant containing feedwater. Operation costs can only be evaluated when membranes are operated under conditions which are very similar to those in an industrial application. At this stage any cost analysis can only be attempted with reference to the cost of electricity consumed during the ED process utilizing modified and unmodified membranes.

The main energy input in ED plants is the DC power supplied to operate the membrane stack; this parameter determines the competitiveness of the ED process with other desalination processes. The rule-of-thumb indication of the energy used per kg of salt removed suggests a figure of around 0.4 to 1 kWh/kg. In our experiments it has been shown that, as a result of membrane modification, voltage drop across ion-exchange membranes initially increases by not more than 29%. During the ED operation the voltage drop over unmodified membrane increases by approximately 60% in comparison with modified membrane. Thus, the overall decrease in voltage drop over the membranes and resulting DC power savings can potentially reach at least 30%, or from 0.12 to 0.3 kWh/kg.

Recommendations for future research

Results of investigations which were extensive in respect of humic acids and DBS have revealed that significant opportunities exist to increase the efficiency of the ED process for water desalination, by reducing the organic-fouling of Ionics membranes, by modification, and using ceramic membranes. Future research should be focused on the appropriate testing and cost benefits of our research findings in industrial-scale ED apparatus.

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The steering committee responsible for the project consisted of the following persons:

Dr. G Offringa	Water Research Commission (Chairman)
Mr. G.N. Steenveld	Water Research Commission
Dr E.P. Jacobs	University of Stellenbosch
Dr. J.J. Schoeman	Environmentek, CSIR
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Prof. R.D. Sanderson	University of Stellenbosch
Prof. V.M. Linkov	University of the Western Cape

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Mr. S. Peters	ESKOM TRI
Prof. V.N. Belyakov	IGICh, Ukraine
Prof. V.D. Grebenyuk	Ionics, USA

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1 INTRODUCTION

1.1 MOTIVATION

This research project focuses on novel and improved ion-exchange membranes. Such membranes could be useful for demineralisation, disinfection and ionisation.

The separation processes of both electrodialysis (ED) and electrodialysis reversal (EDR) are widely used for water demineralisation. There is, however, a world-wide problem with ED/EDR membranes, namely the fouling of anion-selective membranes by organic colloids present in the waters [1,2]. This has an adverse effect on the lifespan of the membranes and on the economics of the process.

Chemical and electrochemical pre-treatment techniques could be developed to reduce these problems [3]. Methodology is required for the treatment of especially anion-exchange membranes (cation-exchange membranes are not as badly affected by fouling). Grebenyuk [1] has shown that the fouling potential of modified anion-exchange membranes could be decreased by up to 20-fold. The use of modified membranes could result in great savings in membrane replacement costs, the maintenance of steady current efficiencies and reasonable operating costs.

The transfer number of cation-exchange membranes for monovalent ions may be increased by modification techniques similar to those used for the modification of anion-exchange membranes [4,5]. This would make ED suitable for the production of water of a quality desirable for irrigation [1].

The use of anion- and cation-transfer ceramic cation-exchange membranes from alumina, silica and zirconia would permit the application of the ion-exchange membranes at high temperatures and in harsh chemical environments, over a wide pH range. Such membranes could be a low-cost alternative to the well-known Nafion-type membranes [6]. They should be particularly suitable for the removal of heavy metal ions from hazardous effluents.

Newly developed ceramic membranes may be used as supports for electroconductive catalytic layers that are not soluble under anodic conditions. Inorganic membranes produced by this method can combine separation and electrode functions and will therefore be ideal for use in electromembrane reactors. These reactors are very efficient in water disinfection processes and in low-cost manufacturing of acids, alkalis, oxygen, hydrogen and halogens [7]. The reactors maintain high specific productivity and low energy consumption, they are compact and easy to operate.

The overall objective of this project will be the preparation of novel ion-exchange membranes for ED, EDR and electromembrane reactor processes, determination of their characteristics and evaluation of their suitability for water treatment, particularly mine water, in South Africa.

1.2 OBJECTIVES

The objectives of this research programme, as set out in the contract, are as follows:

1 A) The development of new chemical and electrochemical pre-treatment methods to improve the fouling characteristics of existing polymeric ion-exchange membranes and B) the preparation of novel ceramic non-fouling membranes.

2 The development of cation-exchange membranes with increased transfer numbers for monovalent ions.

3 The fabrication of ion-exchange membranes with increased chemical stability. Incorporation of these novel membranes into electrodialysis (ED) and electromembrane reactor units.

1.3 POTENTIAL RESEARCH PRODUCTS AND THEIR APPPICATIONS

Potential research products could eventually be:

- Anion-exchange membranes protected against fouling by organics.
- Cation-exchange membranes with increased transfer numbers for monovalent ions.
- Ion-exchange membranes with high chemical and thermal stabilities.
- Electromembrane reactors for water purification and disinfection.

Each of these research products would have specific target groups (as have been mentioned in the contract).

Potential applications of the envisaged research products could be as follows:

Anion exchange membranes protected against fouling by organic substances will not develop higher resistance and lower selectivity during the electrodialysis of complex organo-inorganic mixtures. The use of these membranes can therefore result in high energy-savings in the demineralisation of organo-mineral solutions in water-treatment and industrial waste processing.

The use of ion-exchange membranes with increased selectivity for monovalent ions will effect the selective removal of NaCl from irrigation and mining waters. After treatment the wastewater can be re-used in closed-circuit irrigation.

The availability of ion-exchange membranes of high chemical stability will mean that separations can be carried out at higher temperatures and in harsher environments than would otherwise have been possible. Such membranes (e.g. acid blocking membranes) could be used for the removal of 80% of pure mineral acids from acidic saline solutions, the drying of gasses and the removal of ammonia from water.

Electromembrane reactors with highly stable ion-exchange membranes will allow for on-line complex water treatment. A variety of mineral salts and organic materials could thus be produced in an energy-saving and ecologically friendly manner, using electromembrane reactors.

1.4 ELECTRODIALYSIS

During the past two decades membrane methods have been developed for use in the separation of mixtures. These methods are low energy-intensive ones, suitable for a wide variety of applications. The modern membrane technological processes use the selective transfer of some component through the membranes under the influence of a potential gradient (electrodialysis) or pressure (ultrafiltration, reverse osmosis). These methods have found wide application, especially in the field of water purification.

Electrodialysis has a special place in the processes of membrane mixture separation. This is connected first of all with the fact that the electrical field gradient is used as a moving force in this process. The process of electrodialysis is based on the electrical migration (directional movement of ions towards electrodes of the opposite sign) of ionic mixtures when an electrical field is applied to the solution. Separation of the electrodes from the feed solution by ion-selective membranes (cation- and anion-exchange) allows cations and anions to selectively pass into the electrode spaces, from where they are removed from the solution.

The effectiveness of electrodialysis is therefore largely dependent on the characteristics of the membranes used in the process. It is only by the synthesis and use of highly selective membranes with satisfactory properties that meaningful advances will be made in the development and application of electrodialysis as an industrial method of water demineralisation and electrolyte concentration. The success of the significant industrial development of the implementation of electrodialysis for the selective concentration of sodium chloride from sea water is largely related to the development of novel charge-selective membranes.

During electrodialysis, discrimination of ions of the same sign and ion specificity, may be caused by the preferential uptake of one of the ions from solution [4,8]. In our studies the selective modification of ion-exchange membranes will be carried out with selected modifying agents, namely special surfactants [1]. The alteration of trans-membrane flow ratios of ions with different charges will be caused by the orientated surface layer of surfactants whose non-ionic groups impede the transport of polyvalent ions to a greater extent than monovalent ones.

Electrodialysis in the presence of polyelectrolytes is another treatment method that results in the alteration of the ion-specificity of ion-exchange membranes [9,10]. The deposition of polyelectrolyte molecules takes place on a membrane that is situated in the migration direction of macroions. Change in electro-diffusion fluxes is caused by a newly formed ion-exchange coating which 'encourages' the formation of an ionic near-membrane layer consisting mainly of mono-valent ions [3]. The formation of a polyamino compound layer on the surface of a cation-exchange membrane (for example a conventional sulfonic acid-type membrane) by acid-amide bonding is one examples of polyelectrolyte treatment [11].

The treatment of membranes with polyelectrolytes should also make it possible to prepare ion-exchange membranes that are highly resistant to fouling by large organic ions. Here the membrane is impregnated with an insoluble polyelectrolyte with a charge opposite to that of the membrane's functional group [12]. This results in the formation of a so-called 'mixed' ion-exchange membrane, characterised by lower ion-exchange capacity and a minimum decrease in resistance. An increase in electrical resistance that is due to the presence of large organic ions is easy to reduce by this method when the membrane is cross-linked and the molecular weight of the organic ions is high [13].

1.5 METHODOLOGY

In our studies a wide range of heterogeneous and homogeneous ion-exchange membranes were modified, using a specially developed electrodialysis cell. Modifications with various surfactants, poly-electrolytes and organic electrolytes were studied, as were chemical reactions and the structure of the ion-exchange coatings.

Methods for the incorporation of ion-exchange groups into ceramic membrane matrices and the coating of non-soluble layers of ion-exchange compounds onto inorganic membrane surfaces were developed. The effectiveness of the deposition techniques was studied by using specially designed methods for the determinations of diffusion, osmotic and electro-osmotic permeabilities of ceramic membranes and their volt-ampere characteristics [14]. The study of the novel ceramic ion-exchange membranes under conditions similar to those used for modified polymeric membranes and comparison of performances of both membrane types were carried out.

1.6 STRUCTURE OF THE REPORT

The report begins with an overall introduction to the present research project, including a motivation, methodology and the objectives (Section 1).

Hereafter, due to the length of the report and for the sake of simplicity, it is divided into two main sections: Part A – Polymeric membranes (Sections 2 – 11) and Part B – Ceramic membranes (Section 12 - 17). These were the two classes of membranes investigated. Each of these two parts (A and B) is a complete report in itself. Each includes the following sections: an introduction, objectives/tasks, experimental, results and discussion, conclusions, and references. At the end of the report, overall conclusions to all the results of the research are given i.e. for the project as a whole (Section 18). These 'dovetail' with the objectives as set out in the initial introduction (Section1.2).

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PART A - POLYMERIC MEMBRANES

2. INTRODUCTION

Research was carried out into the preparation of electrodialysis membranes with enhanced fouling characteristics, specific ion selectivity and increased pH resistance.

It is known that humic acid (HA) and sodium dodecylbenzensulfonate (DBS) have fouling effects on anion-transfer membranes during the process of electrodialysis. Their presence in the feed water undergoing electrodialysis results in:

- an increase in the voltage drop across the membranes;
- an increase in the transfer of sulfate ions.

These have detrimental effects of the overall process of electrodialysis, causing an increase in power consumption during operation, and the precipitation or formation of calcium sulfate in the concentrate compartments. This problem could probably be solved by modifying the anion-transfer membranes with selected organic polyelectrolyte solutions, e.g. NB-8. Considering that there may be undesirable compounds other than HA and DBS present in the water to be treated, studies of the influence of further organic compounds on the electrochemical characteristics of anion-transfer membranes were performed. In particular, the influences of a number of saturated hydrocarbons were investigated.

Earlier, ion-exchange membranes had been successfully modified by us. This was done by fabrication under static conditions, i.e. before the membranes were installed in the electrodialysis cell. Results of further studies showed, however, that during operation there was a gradual removal of the modifying substance from the membrane surface. This necessitated the periodic treatment of membranes with a modifier and involved disassembly of the electrodialysis cell. Further studies were therefore undertaken to provide an improved technique. The possibility of treating the membrane within the volume of the electrodialysis cell was investigated. This was done by the periodic coating of a layer of the modifier onto the membrane surface, under dynamic conditions. A solution of modifying substance was circulated through the electrodialysis cells.

The dynamic method of membrane modification also means that the modifying substance can be used for cation-transfer membranes, and change their electrochemical characteristics. In particular, application of the modifier solution can result in changes in the electrical resistance and permselectivity (selective permeability) of cation-transfer membranes toward cations of various charges. Hence, the present research work also involved studying the influence of modifying substances on the characteristics of cation-transfer membranes.

Further, it also included studying the increase in permselectivity of a membrane toward divalent cations. This would be applicable to the production of softened water during electrodialysis, i.e. water with a low hardness. A change in membrane permselectivity toward monovalent cations permits the concentration of the salts of monovalent metals in the concentrate compartments. This is the method used for the production of sodium chloride by electrodialysis. Both cationic (positively charged) and anionic (negatively charged) polyelectrolytes were included in the procedures to investigate the modification of cation-transfer membranes.

Increasing the efficiency of the electrodialysis process is not limited to an improvement in the characteristics of the membranes used for this process. In efforts to further reduce the effects of hardness and organic substances on the membrane's surface, modes of current reversal or a pulsing current supply were used. Studies of the influence of pulsing current and its reversal on the electrochemical characteristics of Ionics membranes, during the electrodialysis of solutions containing foulants (organic substances), were conducted.

The main areas of research reported on therefore include the following:

- Studies of the fouling action of organic substances on modified and unmodified anion transfer membranes;
- Development of a dynamic method for the modification of a membrane surface, directly in electrodialysis cells;
- Studies of membrane modification with various polyelectrolytes under dynamic conditions, and the influence on the electrochemical properties of both anion- and cation-transfer membranes;
- Studies of the modification of membranes by various polyelectrolytes and the resulting influence on the permselectivity of cation-transfer membranes;
- Determination of the influence of a pulsing current supply and its reversal on changes in the electrochemical characteristics of Ionics anion-transfer membranes during the electrodialysis of solutions containing foulants.

3. LITERATURE SURVEY

3.1 INTRODUCTION

Several methods of water desalination are known; these include: reverse osmosis, electrodialysis, distillation and ion exchange. The ranking of water desalination methods for treating water with a dissolved solid concentration below 10 $g.l^{-1}$ (including capital costs), is the following:

electrodialysis > reversal osmosis > ion exchange > distillation

Hence, electrodialysis is the most viable method for desalination of water with a dissolved solids concentration of below 10 $g.l^{-1}$. The environmental and economical aspects of electrodialysis may be greatly enhanced (above those for any of the other desalination method) if present effluents (for example, mine shaft water) could be used as feed water for the production of fresh water. In certain European countries, legislation is in place where fines are imposed on enterprises which discharge saline waters into the environment. In these cases the cost savings achieved by installing desalination plants to treat this water warrant the capital expenditure required.

There are, however, problems associated with the desalination of saline effluents. The most significant is the fouling of anion-transfer membranes during desalination [1]. Studies [2] have shown that a substantial reduction in the cost of water desalination cannot be achieved by the use of only so-called conventional methods to improve membrane selectivity, or for reducing membrane electrical resistance. The reason is that the selectivity of modern membranes is rather high (95-98 %) and their resistance is low. Membrane resistance constitutes no more than 10 % of the total resistance of the electrodialyser. Therefore, an increase in selectivity hardly affects the total electrical power consumption during water desalination. As a result, further advances in the field of electrodialysis should be researched, using novel means. An analysis has shown that approximately half the cost of water desalination by membrane methods is associated with pre-treatment, prior to the actual separation process. This usually involves the removal of organic and colloid substances, iron etc. [3]. It is firmly believed that future progress in the field of membrane methods for water desalination will only result from the synthesis and application of new membranes, the use of which could lead to substantial decreases in the requirements for water pre-treatment.

The problem associated with improving the stability of anion-transfer membranes towards fouling by organic substances is the most topical in the field of electrodialysis. The same conclusion was reached by Eskom, after they determined requirements for water desalination at the Tutuka Power Station, South Africa, where it was found that during a one year period it may be necessary to replace 11 % of the anion-transfer membranes and 22 % of heavy anion-transfer membranes. The cost of chemicals, as a percentage of the cost of product water, was the following:

- 40 % - pre-treatment of feed water
- 7.4 % - membrane cleaning
- 40 % - replacement of membranes, separators and electrodes.

Thus, the cost of pre-treatment, cleaning of membranes and replacement parts constitutes 87% of the cost of producing desalinated water. Improvement of membrane stability with regard to fouling is therefore considered a good way to reduce the total cost of this water desalination method.

3.2 BASIC PRINCIPLES OF ELECTRODIALYSIS

Demineralisation of water by electrodialysis is based on the ability of swollen ion-exchange membranes to allow the transfer of monovalent ions. This ability may be explained by the high concentrations of immobilised (fixed) ions, which are chemically bonded to the membrane network or matrix. The charge of fixed ions is neutralised by an equivalent number of ions of opposite charge (gegen-ions). An ionic bond exists between fixed ions and gegen-ions. In a swollen membrane, therefore the fixed ion/gegen-ion pair is dissociated. Since the concentration of fixed ions is high when the membrane is at equilibrium with dilute aqueous solutions, ions (co-ions) which have a similar charge to the fixed ions, permeate the membrane to a very small degree. Consequently, gegen-ions appear to be practically the only current carriers in ion-exchange membranes. Electrodialysers, prepared for demineralisation, are usually produced in the form of filter-press installations.

A schematic representation of a multi-chamber electrodialysis unit, with cation-transfer and anion-transfer membranes, is shown in Figure 3.1

Electrode chambers are located between two frames or end plates, at opposite ends of the stack. The stack consists of alternating cation- and anion-transfer membranes, with flow spacers inserted between each membrane.

Electrodes, located at opposite ends of the stack, allow for the maintenance of a DC potential across the stack. The selective properties of cation- and anion-transfer membranes allow for the process of desalination and concentration of the solution in alternating compartments. Multi-cell installations are advantageous because the electric power requirements and consumption (during water decomposition reactions), and the need to overcome the ohmic resistance of the solution in the electrode chambers, are minimal.

The most basic functional components of electrodialysers are the membranes. If these did not possess selectivity with respect to an ionic charge, the process would not function as a desalination process. In order to meet the requirements for minimal electrical power consumption, ion-transfer membranes have to possess maximum selectivity, i.e. large numbers of gegen-ions to facilitate transfer and conduct electrical current. The membrane thickness should be low, in order to minimise electrical resistance, but yet sufficient to provide mechanical strength against the hydraulic pressure in the desalinating (depleted) and concentrating chambers.

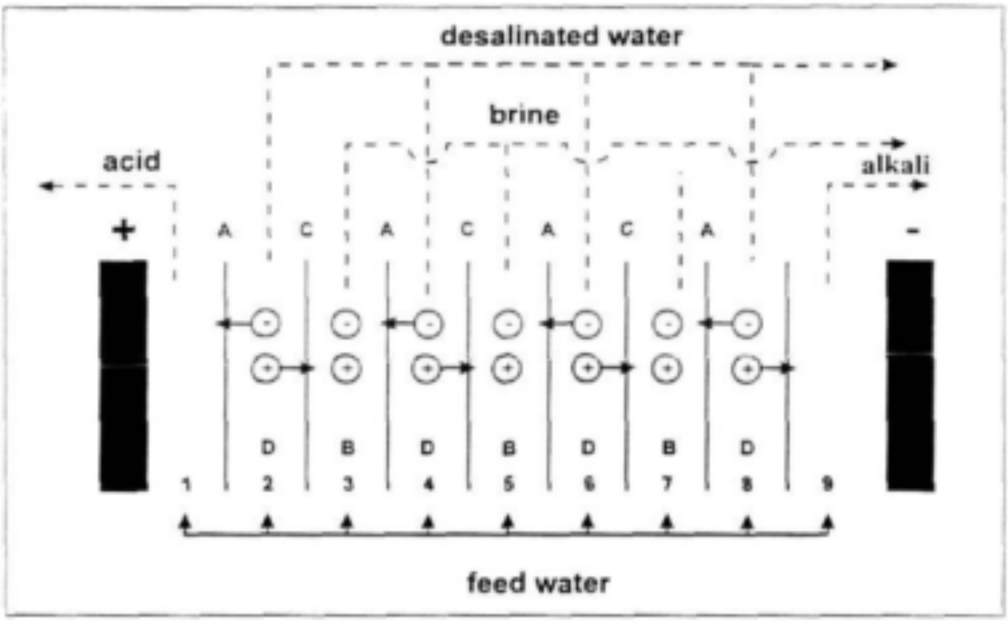

Figure 3.1: Schematic representation of a multi-chamber electrodialysis unit with cation-transfer (C) and anion-transfer (A) membranes. D - demineralisation chambers, B – concentrating, or brine, chambers.

The membrane selectivity determines the current efficiency. Current efficiency of a specific chamber (η) and membrane selectivity are related as follows:

$\eta = 1 - t^c_k - t^c_a$

where:

> t^c_k and t^c_a are the co-ion transfer numbers through cation- and anion-transfer membranes, respectively.

Current efficiency is reduced by current leakage and by salt diffusion from the depleted and concentrating chambers.

The degree of solution concentration during electrodialysis is always limited, since osmotic and electro-osmotic water transfer is, as a rule, directed to the same site as salt transfer. Experience has shown that the critical concentration of a brine solution is approximately 4.5 M sodium chloride. This corresponds to the transfer of 12 moles of water per mole of salt.

During the desalination of natural waters, containing Ca^{2+} and SO_4^{2-} ions, the degree of brine concentration is limited by the probability of the precipitation of these salts in the concentrating chamber. In order to prevent this it is necessary that the concentrations of the above-mentioned ions do not exceed the solubility-product of calcium sulphate. During the desalination of 'hard' waters it is necessary to prevent the undesirable deposition of $CaSO_4$ on the membrane surfaces, as well as in the connecting channels. This implies that a high consumption of feed water is necessary for rinsing. In this case, the ratio of solution volume to the volume of rinse water is 1:1.

The current density in electrodialysers fluctuates within the limits of 0.2 - 1.0 $A.dm^{-2}$. The higher the current density is the higher is the productivity of the system. This, however, leads to an increase in the consumption of electrical power per cubic meter of product. For each specific case there is an optimal current density which ensures a sufficiently high process productivity at the lowest possible electrical power consumption. Depending on the number of chambers and the mineral content of the feed and desalinated water, the voltage across the electrodialyser should be 300-500V. In certain cases the values could be as high as 900-1000 V. Such increased voltages are undesirable for reasons of safety. The number of chambers connected electrically, in series, in a stack of the desalination installation varies between 100 and 1000.

Depending on the quality of the feed water electrodialysis installations can be divided into two types. The first is where the degree of desalination is achieved by a single-pass through the system. In the second water is passed through the installation several times. Installations of a mixed type also exist. For example, for the desalination of sea-water: certain low capacity installations recirculate the water (to be desalinated) through the system several times and the rinse water, in the concentrating chamber, is discharged after a single pass.

For hydraulic staging, membranes are inserted between an electrode pair. Such an apparatus may have an in-series or in-parallel connection of chambers. For an in-series connection the long flow-path allows for good desalination. However, the mechanical loading on the membranes increases due to the oscillation of pressures in the neighbouring chambers. For a parallel connection, better conditions are created for air pockets to be removed from the chambers and the hydraulic pressure of the liquid stream is more evenly distributed.

Demineralisation by electrodialysis is based on the separation of relatively low concentrations of dissolved solids from a large volume of water and this has to be taken into account for any further developmental work in this field.

Electrodialysis is not only used for the desalination of water. It can also be used for the following:

- the desalination of organic liquids (for example, diethyleneglycol which is used for gas-drying [4]),
- the production of alkalis and acids from salts for ion-exchange resin regeneration [5] (including mixed bed ion-exchangers without bed separation) [6,7],
- the production of sulfur and carbon dioxide from vent gases,
- the absorption of heavy metals from wash-waters.

Electrodialysis methods for the separation of predominantly monovalent salts (for instance, sodium chloride) have been developed. These methods allow for the possibility of not only preventing hardening of membranes during water desalination, but to substantially decrease the electrical power consumption required to desalinate water for irrigation purposes.

In order for the process to be economically viable, it is believed that the saline content in feedwater for the electrodialysis process should be limited to between 1 and 10 $g.l^{-1}$. At concentrations higher than 10 $g.l^{-1}$ it is more economical to make use of evaporation, because the cost of producing 1 m^3 of desalinated water by this process is only slightly dependant on the initial salt content. In the case of the electrodialysis of water containing less than 1 $g.l^{-1}$ of dissolved salts, the cost of electrical power for overcoming the ohmic resistance of the solution in the depleted chambers is significant, and the process becomes less cost-efficient than the method of ion- exchange.

The growth of membrane technology is largely related to the 'simplicity' of the apparatus, the possibility of carrying out the separations at room temperature, and the high selectivity of substance separation. The development of high-productivity, temperature-stable and chemically-stable membranes has led to opportunities by which different substances can be removed from a solution, as well as the separation of mixtures into single components. The spheres of application of membrane processes embrace numerous industries, ranging from food processing to electronics production.

One can estimate the rate of expansion of membrane processes by noting the volumes of membrane sales in the West-European market. An illustration of the growth in sales from 1983 to 1990 is shown in Figure 3.2 [8]. According to an estimate in 1990 [10] 2 billion dollars worth of membrane units (including operating expenses) were applied in the field of biotechnology alone. World-wide the annual sales of membranes grew from USD 2250 million in 1989 to USD 4000 million in 1994 [9].

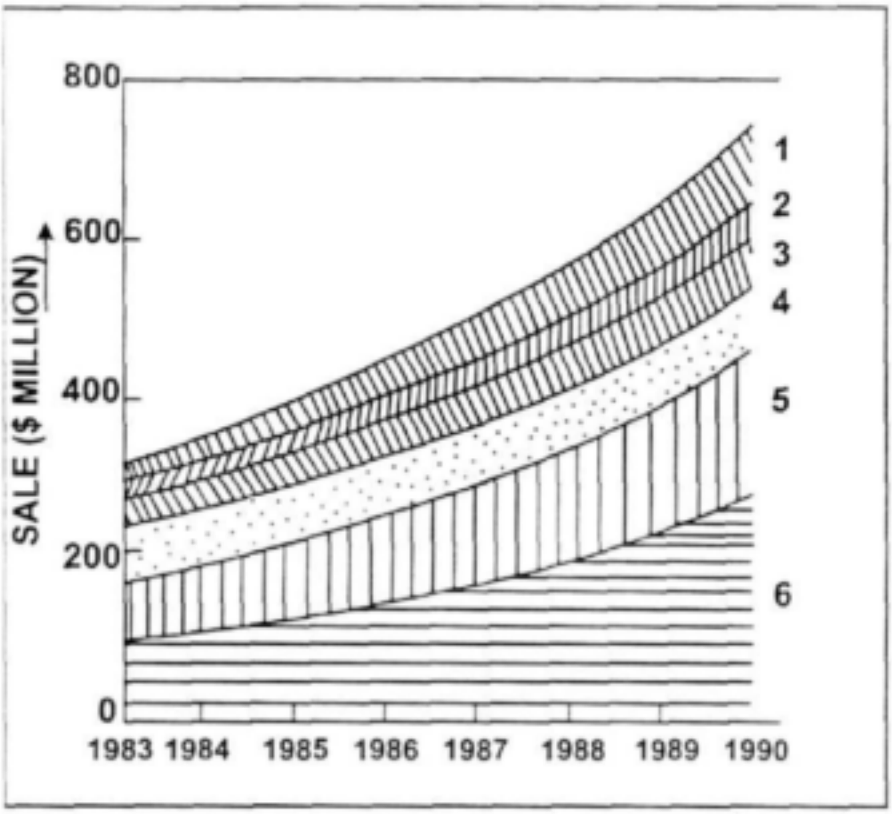

Figure 3.2: Increase in volumes of membrane sales in Western Europe.

Membrane types: 1 - gas separation, 2 - electrodialysis, 3 - reverse osmosis, 4 - ultrafiltration, 5 - haemodialysis, 6 – microfiltration.

The largest desalination units were created for the desalination of mineralised waters for industrial or potable water supply. Earlier, desalination units were only used in arid regions [11]. At present, the scope of their application has expanded significantly, due to increases in the volume of discharged mining effluent, as well as drainage waters [12-14].

The scale of use of desalinated water depends largely on the cost-effectiveness of the desalination process. When using membrane methods for desalination, the basic cost includes the cost of water pre-treatment, the cost of membranes and production equipment, the electrical power consumption for desalination and auxiliary operations [13,14].

Owing to the continuing improvement in existing methods of water desalination and the development of new methods, a substantial increase in the productivity of desalination methods has been observed [15]. Table 3.1 shows a summary of the increase in productivity of desalination units with a capacity greater than 95 $m^3.24h^{-1}$.

Table 3.1: Summary of the increase in productivity of desalination units with capacities greater than 95 $m^3.24h^{-1}$.

Year	1955	1960	1970	1975	1980	1985	1987	1994
Number of desalination units	15		675	1036	2207	4600	6300	
Productivity, ($m^3.24h^{-1}$)	18.9	240	601	1680	7275	9920	12869	27000
Product yield ($km^3.annum^{-1}$)	0.007	0.09	0.219	0.610	2655	3621	4607	9855

Until recently, the application of electrodialysis (ED) as a desalination method was placed second - after distillation. At present, this method has made way for another membrane method, namely reverse osmosis (RO).

In 1994 the annual sales of membranes for ED units reached approximately USD 500 million and these totalled 12 % of all membrane sales world-wide [9]. In At present ED plants for sea water desalination operate at an electric power consumption of 16-20 $kWh.m^{-3}$. For future projected units this value is estimated at 6.7 $kWh.m^{-3}$ [16]. The search for methods by which to reduce the costs of desalination is carried out not only in the field of electric power consumption, but also by considering ways by which to reduce the cost of membrane purchases. The cost of membranes constitutes approximately 50 % of the cost of the apparatus. Therefore, it is of vital importance to increase the lifetime and effectiveness of membrane use.

3.3. THE PRESENT STATUS OF IMPROVEMENTS IN THE STABILITY OF ANION-TRANSFER MEMBRANES AGAINST FOULING BY ORGANIC SUBSTANCES

The accumulation of great practical experience in the operation of industrial units has revealed that membrane lifetime depends largely on the amount and chemical nature of substances that are present in the feed water. Further, the degree of influence of fouling components on membranes depends on the apparatus construction and the applied process of water desalination.

Any improvement in a membrane's in-service lifetime, and consequently the duration of operation of the desalinators, depends firstly on the volume of water which is fed into the plant, and also on membrane's stability against fouling.

The first steps in the direction of achieving the above are:

- the selection of criteria for an estimation of the water quality entering the plant,
- the selection of methods of feed-water pre-treatment, and

- the search for methods of protecting membranes against fouling by organic substances and colloids.

The effects of many substances on membrane fouling have not been adequately studied to permit a formulation of general requirements as to their concentration limits in feed water. Therefore, when selecting a desalination method it is necessary to first determine membrane fouling (contaminating) components in the feed water, as well as their maximum permissible contents.

Basic classes of substances present in most naturally occurring and discharged waters, which are detrimental to membranes, are:

- colloidal and suspended solids,
- micro-organisms,
- organic compounds,
- mineral components of solutions which are able to produce poorly soluble compounds in membrane pores or on their surface.

Concentration polarisation, i.e. the increase in concentration of separate components at the membrane surface, increases the fouling effect of these substances.

The removal of, for example, surfactants from water is complicated, labour-intensive, and costly [17]. Simultaneously, the presence of surfactants lowers the performance of purification plants, thus contributing to the retention of a residual complex of contaminants in the water. Surfactants, on account of their high sorption capacity on various surfaces, are some of the most detrimental components to ion-exchange membranes. Their presence in most waste waters and effluents make the study of the influence of surfactants on membrane properties one of crucial importance.

3.3.1. Applications of surfactants and methods to remove surfactants from water

Synthetic surfactants are obtained mainly from petroleum distillation products. At present, surfactants are used in more than 100 sectors of national economies. Industry accounts for some 80 % of the Russian surfactant production for the manufacture of fabrics and articles based on natural, artificial, and synthetic fibres [18]. Surfactants are widely used in agriculture: as insecticides and herbicides, for improving the wettability of mineral fertilisers, for improving the soil-water balance (which is conducive to the greater activity of micro-organisms in soil) and for growth intensification and raising crop yields. Surfactants are also used in the construction of roads (to stabilise and strengthen the ground support). The wide use of surfactants in the oil-producing industry expands the possibility of polluting underground waters, although the principal path by which surfactants penetrate environmental water is via surface waters. Even this relatively short list of surfactant applications shows that there will be an increase in environmental pollution by detergents. Of the total mass of surfactants used as chemicals for domestic purposes, 42 % enters municipal sewage, 22 % fouls atmospheric air, and 12 % is discharged to city disposal sites [19]. Simultaneously, those portions of surfactants that do not enter water directly after use are gradually introduced into these systems by rain and floods. Therefore, in the long run, both surface- and underground water tables become contaminated.

At present the main types of surfactants produced by industry are anionic surfactants (>60 %) and non-ionic surfactants (≈30 %). Cationic and amphoteric surfactants account for 5-7 % of volumes [20,21]. Among the anionic surfactants, the most widely used are the alkylbenzenesulfonates [22]. These substances belong to a grade of so-called 'hard' substances, i.e. they are decomposed with difficulty [23]. The presence of surfactants in effluents aggravates the biological purification of heavy metals present in these effluents [24,25]. The permissible concentration of petroleum products in water subjected to biological treatment is decreased from 25 to 12 mg.L^{-1} in the presence of surfactants [26]. It has been established that the degree of biological degradation depends on the chemical nature and structure of the surfactant molecules.

Biological destruction is more easily accomplished for compounds with an alkyl chain, and more easily with non-ionic surfactants than ionic surfactants [27-30]. Certain industrially developed countries have passed laws banning the production and use of surfactants that cannot be degraded by biological methods. The main requirement to obtain permission for the manufacture and use of surfactants is the "compatibility of detergents and cleaning remedies with the environment". This implies a high compatibility with biodegradation, or surfactant removal from wastewater, using other treatment methods [31 - 33]. In addition to the most widely used, most economical, and the most environmentally-safe method of biodegradation for the removal of surfactants from water, and physico-chemical destruction methods (ozonation, chlorination, gamma-irradiation, treatment with an electric charge, etc.), the methods of separation, extraction, and adsorption also appear very promising [11,17]. Sorption methods are widely used for purifying wastewater from surfactants. There are numerous reports describing the purification of water from surfactants. Since this area of research is not encompassed by this project, only a few selected methods will be mentioned here [34 - 38]. It must be noted that each of the methods has its optimum area of application, with concentration limitations for the surfactant and its associated impurities in water.

During biological treatment, the surfactant concentration in water should not exceed 10-20 mg.l^{-1} [39-41]. At higher concentrations other removal methods have to be employed prior to biodegradation. The removal of surfactants from solutions using physico-chemical methods (adsorption, separation, extraction, etc.) permits their concentration and recycling. The degree of economically substantiated water purification by biological methods is not more than 90 % [42]. More complete removal of surfactants is feasible using adsorption and ion exchange methods. This means that, as a rule, no more than 10 % of impurities enters the environment together with the effluent. The surfactants contained in the effluent are the most resistant to destruction, and highly resistant to oxidation [43]. Given the modern tendency to increase the production and use of surfactants, and the employment of existing methods for purification of the environment from these compounds, the contamination of the environment and water bodies is ever increasing [44]. Therefore, an investigation into the mechanisms governing the interaction of surfactants with the basic elements of electrodialysis desalination plants, namely the ion-exchange membranes, and the search for methods of protecting them from fouling by surfactants, is an important practical task.

3.3.2. The influence of surfactants on the properties of ion-exchange membranes

The type of interaction that takes place between a surfactant and an ion-exchange membrane is determined by the chemical nature and the structure of both the membrane and the surfactant. The molecular chains of surfactants have a bifilar nature, i.e. a water-repellent hydrocarbon radical and a polar or ionic group. The most widely used anionic surfactants are alkyl sulfates, alkyl-aryl sulfonates and carbonic acids. The most widely used cationic surfactants are alkyl pyridine compounds, nitriles, amines and quaternary ammonium bases [45].

In recent years the selection and production volumes of non-ionic surfactants (NIS) have increased. They have the lowest cost and are chemically resistant over a wide pH range. The wettability and solubility of NIS in water are determined by the availability of polar groups in the molecule. These polar groups are capable of forming hydrogen bonds with water molecules. The presence of mineral ions, which form complexes with the NIS molecules, is conducive to the solubility of NIS in water [46]. Very recently a new class of surfactants has been introduced; these are oligomeric anion- and cation-active bi-anchor surfactants, with regulated lengths of the hydrocarbon radical, and a number of charged end/tail groups [47]. This has generated a number of papers dealing with issues relating to the use of these surfactants, also for membrane modification.

During the interaction of silicon organic based surfactants (dissolved in organic solvents) with wettable membranes the water content on the membrane surface is affected [48]. This is therefore a potentially effective method for the modification of membranes that will repel water. The sorption of surfactants and polyelectrolytes from water solutions onto the surface of low-charged polymer membranes, for instance, nuclear filters, also increases their hydrophilicity. In this case, the adsorption is reversible [49]. During the washing of nuclear filters with water or an electrolyte solution, nearly complete surfactant removal from the surface is achieved.

Dispersive interactive forces are the determining forces in surfactant adsorption by low charged, wettable, cellulose-based membranes. In true solutions, below the critical micelle concentration (CMC), the orientation of adsorbed surfactants in relation to the membrane surface varies from vertical (for lowly homogeneous compounds) to horizontal (for highly homogeneous compounds) [50].

The water-repellent part of the surfactant faces the membrane, while its wettable part faces the solution. These surfactants are adsorbed onto the surface of the uncharged membranes for surfactant concentrations between the values of CMC_1 and CMC_2. Since ion-exchange membranes have a wettable surface, due to the presence of charged functional groups, the surfactant adsorption is accomplished by either an electrostatic or ion-exchange mechanism. Thus, adsorption of bi-anchor surfactants onto the surface of ion-exchange membranes results in a reduction in the membrane fouling effect by other organic gegen-ions (counter-ions) present in water (for instance, by humic acid or fulvic acids) [75,76]. During surfactant adsorption onto ion-exchange membranes in the presence of an electric field, concentration generally occurs in the 'accepting' layer. The portion of surfactants that have been absorbed but not bound by ion-exchange groups, gradually increases. An energy barrier hampering the transfer of gegen-ions from the solution to the membrane appears on the surface of the membranes. On account of this, the respective transfer of ions having different charges may vary. In particular, the permeability of divalent ions is limited, while the transfer of monovalent ions increases [53-57].

The structure and nature of the functional groups on the membrane exert a substantial influence on the specific selectivity index P^2_1 [53], determined in terms of the formula:

$$P^2_1 = \eta_2 . C_1 / (\eta_1 . C_2)$$

where:

> C_1, η_1, and C_2, η_2 are current efficiency (η) and concentration (C) outputs of the mono- (1) and divalent ions (2).

Table 3.2 shows the changes in cation exchange membrane transport properties in the presence of hexadecyl pyridine chloride (HPC). The maximum decrease in P^2_1 occurred in the Amfion C-313 membrane, manufactured by American Machine Federation [53].

The fact that competing ions have different charges also has a substantial influence on the P^2_1 value. This is shown in Table 3.3.

Table 3.2: Change of cation-exchange membrane transport properties in the presence of hexadecyl pyridium chloride (HPC).

Membrane Type	P^2_1		Current efficiency, η		Amount of absorbed HPC (10^{-6}, M.cm^{-2})
	Without HPC	With HPC	Without HPC	With HPC	
NeoseptaCl-25T	2.52	1.26	98.6	99.5	4.8
Amfion C-310	2.14	1.00	91.1	93.5	7.6
Amfion C-313	2.15	0.87	92.8	95.6	7.5
Ionac MC-3470	2.01	1.03	91.1	94.3	2.8
Nepton CR61CZ4-183	1.39	0.73	76.7	83.3	4.4
Permaplex C-20	2.11	1.08	92.0	94.8	3.3

Table 3.3: Transport properties of Neosepta Cl-25T membranes in the presence of HPC.

Ions	Solution concentration (g-eq.dm^{-3})	Current density (A.cm^{-2})	Electrodialysis duration (min)	Without surfactants		With surfactants	
				P^2_1	η	P^2_1	η
Mg/Na	0.0832	1	60	4.12	-	0.69	-
Mg/Na	0.4160	10	60	1.68	99.5	0.78	99.4
Ca/Na	0.0832	1	60	6.06	-	1.25	-
Ca/Na	0.4160	10	60	2.52	98.6	1.26	99.5
Sr/Na	0.0832	1	60	6.70	-	0.93	-
Sr/Na	0.4160	10	60	2.68	95.9	0.84	95.2
Ba/Na	0.0832	1	60	8.14	-	0.69	-
Ba/Na	0.4160	10	60	3.55	95.3	0.52	95.7
Co/Na	0.4160	5	120	1.69	100.0	1.04	100.0
Al/Na	0.4160	5	120	2.72	94.6	0.07	94.0

Membranes in solutions containing trivalent aluminium ions and monovalent sodium ions [$P_{Al/Na}$ = 0.07] have the highest selectivity with respect to monovalent ions. For mixtures of single- and double-charged ions the P^2_1 index for the Neosepta CL-25T membrane is not lower than 0.52.

Thus, surfactants can be used for modifying the transport properties of ion-exchange membranes. However, it should be noted that in this case the membrane electric resistance increases due to the low mobility of the organic ion (surfactant).

3.3.3. Mechanisms of surfactant interaction with ion-exchange membranes

Investigations into surfactant adsorption interaction processes with ion-exchange membranes were carried out by Kotov [58 - 64]. Results showed that the process of establishing the sorption equilibrium of aliphatic surfactants on ion-exchange membranes takes place in two stages. First, inorganic anions are replaced with organic anions. The so-called 'non-exchange absorption' proceeds once 80-90 % of the ion-exchange groups have been bound with surfactant [59]. The velocity of ion exchange during the second stage is much lower than the velocity during the non-exchange sorption. This is shown in an analysis of the kinetic curves of alkyl sulfate ion sorption (AS^-) and Cl^- ion desorption on MA-40 and MA-41 membranes in Figure 3.3.

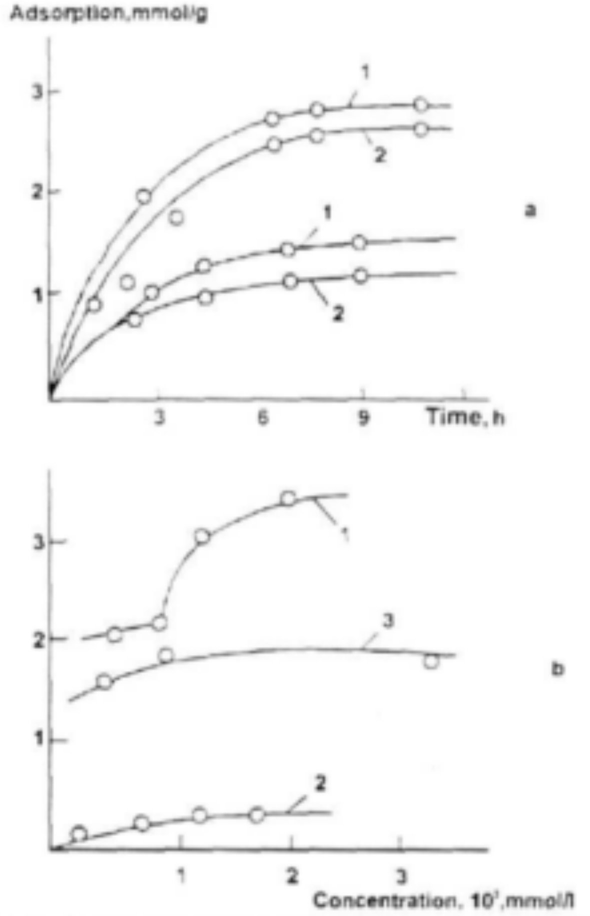

Figure 3.3: Kinetics of sorption (1,2) and desorption (1, 2 [lower]) of (a) sodium alkyl sulfonate on MA-40L membrane (1,1 [lower]), MA-41L membrane (2,2 [lower]); (b) sorption isotherm on MA-40L membrane (1), MK-40L membrane (2), and ion-exchange isotherm on MA-40L membrane (3).

From an analysis of the adsorption dependencies of membranes presented in Figure 3.3, a and b, it is concluded that two adsorption surfactant layers are formed. One of the layers is formed by the exchange of absorbed ions, while the other appears due to a water-repellent action. However, surfactant adsorption by the water-repellent mechanism on uni-polar membranes (adsorption on the MK-40 membrane) is approximately one order of magnitude lower than on the MA-40 anti-polar membrane. The term uni-polar denotes like charges on both membrane and surfactant, while anti-polar denotes opposite charges.

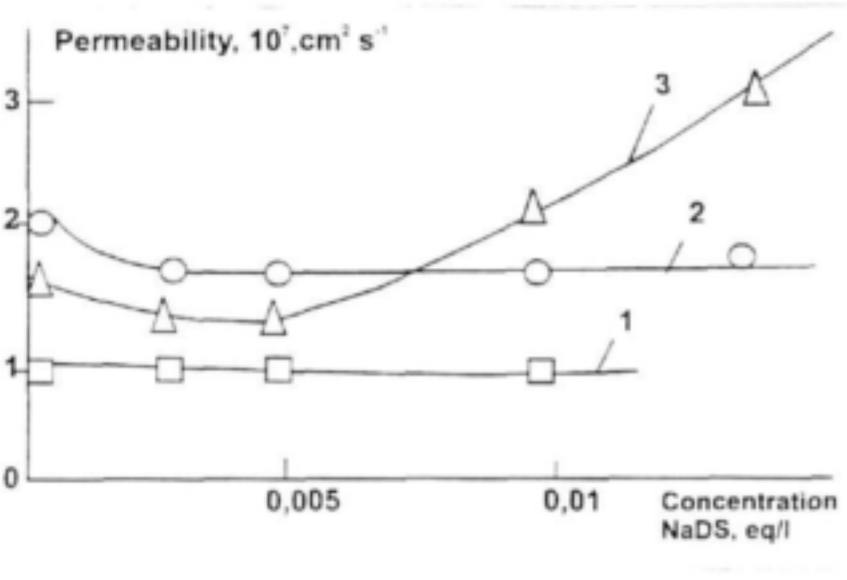

Figure 3.4: Permeabilities of the anion-exchange membranes MA-41 (1), MA-41L (2), and MA-41P (3) versus concentration of a solution of sodium dodecylsulfate (Na DS).

It was therefore concluded that the surfactant adsorption layer on the surface of the anti-polar membrane is formed by anionic surfactant dimers, of which the charged groups are oriented in different directions. Others [17] also arrived at the same conclusion when using the polymer skeleton of an EDE-10P ion-exchange resin, which forms the base material from which the MA-40 membrane is manufactured. Here it was also shown that the dimensions of the free spaces in the ion-exchange resin permits only individual ions or their binary associates (formed by virtue of Van der Waals forces) to penetrate these spaces. In addition to free spaces emerging close to the functional groups in swollen ion-exchange materials, these materials have larger pores that contain a small number of charged groups, with respect to the volume of the threshold space. However, the dimensions of these pores do not meet the condition of micelle formation within them, as these micelles possess a high association factor. In this case, the surfactant concentration in the resin-phase threshold space is much higher than the CMC. This occurs even though saturation of the resin by a surfactant takes place via the transfer of individual ions and their gradual accumulation. Given the increase of the surfactant concentration in the free solution, in excess or above the CMC, the micelle shape changes. The degree of ion association increases, thereby leading to an increase in the molecule (ion) packing density, as well as the micelle dimensions [65]. During the likely penetration of the micelles into the membranes, an isotherm would reflect the increase in association. This is related to the increase in concentration in the region above the CMC, and the line of the graph is parallel to the abscissa (x) axis. This is illustrated in Figure 3.3 b.

The concentration of the free surfactant ions above the CMC does not increase, but actually decreases. This has been shown in experimental work [66-68], and predicted theoretically as early as 1935 [69]. The thermodynamic equilibrium in the membrane-surfactant-solution system is established between the surfactant ion concentration in the free solution, and the concentration in the membrane threshold space.

During surfactant adsorption the first stage comprises the build-up of the first layer of surfactant with the simultaneous rejection of inorganic gegen-ions from the membranes. Depending on the size of the water-repellent tail of the organic ion it is either located perpendicular to the surface or lies in the membrane water-repellent section. It chooses the most advantageous position in terms of energy. It is likely that at a low concentration the surfactant ion chooses to orientate itself along the surface [66].

A number of papers [59, 70 - 79] report that the electrochemical properties, the structural changes and the regeneration capacity of a membrane (Q) depend on the degree of membrane saturation with surfactant ions. The value of Q is defined by the ratio of the amount of absorbed organic counter-ions to the membrane ion-exchange capacity [98]. The volume fractions of individual phases present in a heterogeneous membrane were calculated using an approach suggested by Gnusin [78]. These fractions are those of a dry resin, inert filler, water incorporated by the resin, and the structural defects formed between the resin particles and the inert filler. The experimental data and calculations showed that at a low degree of filling ($Q \approx 0.1$) adsorption takes place in active centres of the membrane-solution interface. This stage is referred to as a dynamic fixation [80]. The adsorption does not bring about any performance or structural changes to the membranes.

At a filling degree of $0.1 < Q < 0.4$ the structure starts to become hydrophobic. This phenomenon is related to an increase of the inert filler fraction. It is accompanied by a decrease in electrical conductivity, diffusion permeability, and maximum current allowed through the membrane. At a filling degree of $0.4<Q< 0.8$ the membrane is characterised by numerous irreversible structural changes. This leads to changes in the orientation of sorbed ions in inter-gel sections, and to the enhancement of water-repellent and inter-ion interactions. In this case, the formation of a bipolar section in the membrane takes place. The membrane may become amphoteric, or the charge may become opposite to that of the original membrane [81,82]. This method is sometimes used for the modification of the properties of existing membranes. An increase in the water volume-fraction contained in the structural defects, the channels between the resin particles and the inert filler, or the volume fraction of the swollen resin in the membrane structure, was found for maximum membrane saturation by surfactants ($0.8 < Q <1$) [83]. Given their maximum saturation with the surfactant ions, the structural changes in the membrane are determined by the solvation of water-repellent polymer chains of the matrix, and a destruction of polymer chains occurring due to disjoining pressures. A sharp decrease in the limiting current, electric conductivity, and diffusion permeability occurs with the membrane in this state. Irrespective of the method of membrane saturation by surfactants (adsorption from the solution or by applying an electric field), the nature of structural changes is normal. It is dependent, in the former case, on the duration of the chemical treatment and, in the second case, on the amount of electricity applied.

Thus, given the saturation of the surface layer, it is only possible to speak of the modified state of the membrane that is determined by reversible changes. If the surfactant penetration is too deep, the membrane loses its separation abilities, and such a saturation degree is termed "fouling".

The introduction of organic non-electrolytes (such as fructose or carbamide) which do not possess surface activity, into the membrane, has practically no effect on the magnitude of the limiting current (i_{lim}) [84]. The addition of camphor and similar compounds is accompanied by an increase in i_{lim}, irrespective of the degree of saturation and the nature of the membrane functional groups. This has been ascribed this unusual phenomenon to a decrease in the thickness of the diffusion layer. This decrease is determined by the 'insular' nature of the adsorption of the camphor diffusion layer, and an increase in the spontaneous convection near the external interface related to this layer [70]. In contrast to this, a change in the state of the internal interfaces between gel and intergel sections in the membrane occurs during the electro-sorption of surfactant ions, leading to the formation of a double-layer structure.

During the electro-sorption of surfactant the structural changes take place firstly in the 'accepting' surface-layer of the membrane. This is reflected by the electro-diffusion properties of the membrane. An asymmetrical effect appears in the transport properties. The most sensitive variable by which to estimate the degree of asymmetry is the integral coefficient of permeability (D), calculated from the formula

$D = \sigma.V / (S.\Delta C)$

where:

σ and S are the membrane thickness and area, respectively;

V is the volume of the concentration chamber;

ΔC is the concentration difference (between solutions).

The difference in the permeability coefficients is used to characterise the asymmetry of the membrane permeability. These permeability coefficients are measured in an arrangement of the modified layer in relation to the electrolyte solution (D_e) and water (D_w). The integral coefficient of surfactant permeability through the membrane is only slightly dependent on the concentration of the surfactant in the solution. The membranes MA-40 and MA-41L have gelled and isoporous structures and the surfactants contain aliphatic hydrocarbon radicals. The absence of the permeation of surfactant through the membranes in concentrations higher than the CMC is possibly due to a sieving effect. Inasmuch as permeability through a coarsely porous membrane (MA-41P) increases with an increase in surfactant concentration, above the CMC, this membrane is permeable not only to individual ions, but also to micelles.

In the sub-critical area of concentrations (5.10^{-4} mol.l^{-1}) the adsorption of anionic surfactant does not exert any noticeable influence on the electric conductivity and polarisation curve of the MK-40 cation-transfer membrane. However, there is a great decrease in the limiting current in anion-transfer membranes. The higher the molecular weight of the organic anion, the larger this decrease is. When the surfactant concentration exceeds the CMC then degradation of the polarisation curves of all membranes is found. The graphs of the polarisation curves are linear [77,78].

The hydrocarbon radical of the surfactant is essentially a gegen-ion for the membrane. This radical is adsorbed by an electrostatic interaction with the membrane ionic groups. This considerably reduces membrane swelling. In such a case, given an increase in the length of the hydrocarbon radical, i.e. its volume, the degree of hydrophobicity of the membrane increases [60,85]. This is evident in the moisture content and electrical conductivity of the membrane, although an increase in the ion-exchange capacity of the membrane is found. This phenomenon is shown in Table 3.4 [60].

Table 3.4: Physicochemical properties of the MA-41 membrane.

Gegen-ions	E', ($M.m^{-3}$)	$V \cdot 10^{30}$, (m^3)	E, ($kM.m^{-3}$)	h,%	K, ($M.M^{-1}$)	$\lambda \cdot 10^6$, $Ohm^{-1}.m^3.M^{-1}$	E_a, ($kJ.M^{-1}$)
Chlorine	-	24.8	1.43	32.0	13.6	77.00	19.3
Hexylsulfonate	425	170	1.60	39.5	14.9	8.88	23.9
Octylsulfonate	192	214	1.63	32.3	11.8	5.55	25.1
Decylsulfonate	65.6	258	1.99	29.0	8.6	2.94	25.1
Tetradecylsulfonate	15	346	2.45	27.2	6.4	1.94	29.6
Hexadecylsulfonate	1.8	390	3.25	26.9	4.8	1.80	32.0

Note: E' is the critical micelle concentration (CMC) of sodium salts; V is the gegen-ion volume; E is the volume capacity; h is moisture content; K is the moisture content coefficient; λ is the molar electric conductivity; E_a is the energy of electric conductivity activation.

The increase in membrane ion-exchange capacity during sorption of the surfactant is most likely determined by the disordering action of large organic anions in the membrane matrix. This causes solvation of the polymer microstructures in the membrane, and leads to the formation of micro-defects, allowing for greater access to the functional groups. To some extent this explanation seems plausible, but it is thought that the most likely reason for the increase in the membrane ion-exchange is the non-exchange sorption of the surfactant ions. It then becomes clear why the non-exchange sorption, the increase of the organic ion dimensions, and the decrease of the surfactant CMC value in the solution results in an increase in non-exchange sorption of surfactant ions. This explanation is supported by data in the literature [61].

Those surfactants of which the charge coincides with the membrane charge are sorbed in negligibly small quantities and therefore any change in the properties of uni-polar membranes is negligible [60,61]. Perhaps the main factor limiting the surfactant sorption in these cases is the electrostatic repulsion of like-charged ions. This weakens the water-repellent interaction of hydrocarbon radicals with the matrix. At the same time, it is necessary to take into consideration that the adsorption of non-ionic surfactants by ion-exchange membranes causes substantial changes in their performance. This is especially true after extended contact. The interaction of non-ionic surfactants OP-7 and DS-10, and anionic-surfactants of alkyl sodium sulfonate, on MA-41L, MA-40L and MK-40L membranes have been compared. It was shown [76] that the MA-41L membranes are the least affected, while the MA-40L membranes are affected the most, as shown in Figure 3.5.

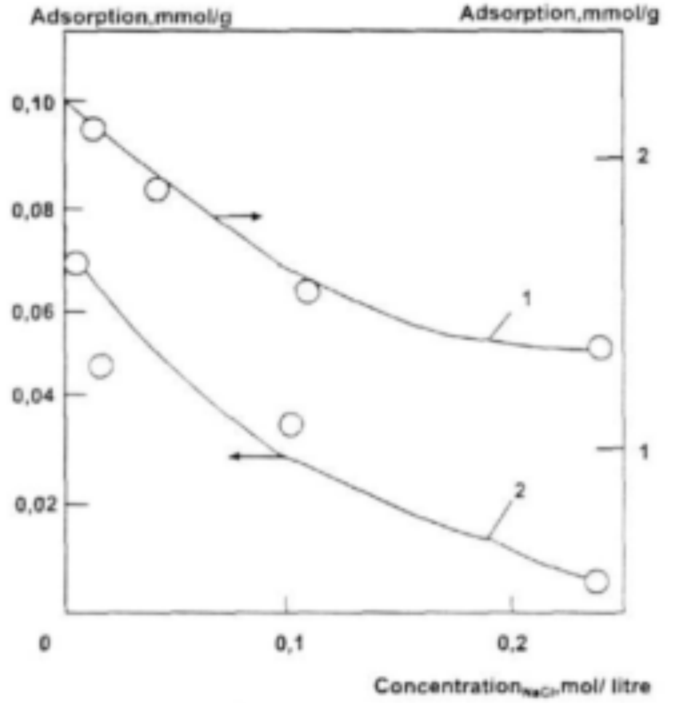

Figure 3.5: The effect of NaCl content in solution on the sorption of sodium alkyl sulfonate on membranes MA-40L (1) and MK-40L (2). Concentration of the sodium alkylsulfonate: $1.5.10^{-3}$ mol.L^{-1}.

During the sorption of non-ionic surfactants changes in the membrane physico-chemical properties (electrical conductivity, ion exchange and swelling capacity) occur to a lesser extent than during the sorption of anionic surfactants. After a 12-month contact with a solution containing 100 mg.l^{-1} OP-7, which is higher than the CMCell, the MK-40L membrane deteriorated to such an extent that it was impossible to determine its strength.

3.3.4. The influence of inorganic electrolytes on surfactant interaction with ion-exchange membranes

The presence of inorganic salts leads to a decrease in the sorption capacity of exchange materials (including membranes) towards surfactant ions. This is determined, to a considerable extent, by the competing sorption between inorganic ions and surfactants [17,86]. As the inorganic salt concentration increases, the surfactant sorption by ion-exchange membranes decreases [17]. For an increase in inorganic salt concentration in the solution to 10-15 millimol.l^{-1}, the surfactant adsorption by EDE-10P anion-exchanger decreases. With a further increase in the mineral content of the solution, the adsorption of surfactant virtually does not change. A sharp increase in adsorption occurs at a surfactant concentration equal to that of the mineral salt.

The surfactant distribution coefficient (K_d) between a solid and liquid phase depends on the membrane structure. For macro-lattice ion-exchange membranes (AV-17MS) K_d is much higher than for the AV-17P microporous anion-exchange membrane. This is determined by the possibility of the surfactant penetrating the three-dimensional polymer lattice of macro-lattice ion-exchange membranes. These macro-lattice structures are obtained by using long-chain cross-linking agents during membrane manufacture.

The low mobility of surfactant gegen-ions (organic gegen-ions) in membranes determines the low values of membrane electric conductivity. With an increase in the concentration of inorganic salts in the solution, however, at the expense of the sorbed ions, redistribution occurs to the benefit of the inorganic ions (Donnan sorption of electrolyte). The electric conductivity for the mixed form increases, as shown in Table 3.5 [64].

Table 3.5: Electric conductivity of the MA-41L membrane in the and in the presence of sodium alkyl sulfonate (2.10^{-4} M.L^{-1}) in absence a Na Cl solution.

Membrane salt form	Electric conductivity (x10^{-3}, Ohm^{-1} cm^{-1}) of the NaCl concentration in the equilibrium solution, M.L^{-1}					
Hydroxide	0.01	0.05	0.10	0.20	0.50	1.00
Chloride	3.5	4.8	7.0	0.20	12.35	18.5
Chloralkylsulfonate	0.2	1.2	2.7	4.0	9.0	12.5

The exchange capacity of the MA-40 membrane, in basic medium, depends on the pH of the medium. The sorption of inorganic ions increases with a decrease in the pH of the equilibrium solution [76]. These factors are illustrated in Figure 3.6 a and b. These phenomena are determined by a decrease in the degree of dissociation of the amino groups, which are the functional groups of the MA-40 membrane, and not the influence of the surfactant. The influence of the pH of the solution on the surfactant sorption by strongly basic ion exchange membranes is negligible [87,88]. The capacity of the MK-40 membrane (highly basic) in the presence of surfactants does not depend on the pH. See Figure 3.6 a.

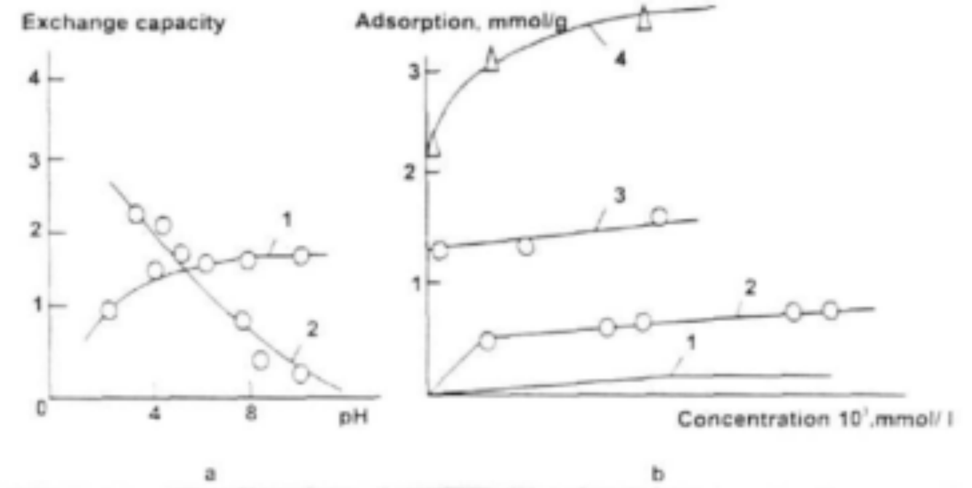

Figure 3.6: Exchange capacity (a) and sorption isotherm (b) of sodium dodecylsulfate.
MK-40 (1) and MA-40 (2) membranes versus pH in 1N NaCl solution; MK-40 (1) and MA-40 membranes (2,3,4) in OH^- form (2), mixed form (3), Cl^- form (4).

The problems of fouling are topical both for pressure-driven membrane processes as well as for electrodialysis, where highly charged ionic membranes are used. Basically, the mechanism of membrane fouling by various components involves the interaction of these components with the surface of membrane functional groups, penetration of membrane pores by large molecules or particles, and decreases in their transport characteristics.

One of the most reliable but expensive methods of protecting the membranes against fouling has been the pre-treatment of water to remove fouling substances. Thus, during the processing of untreated mining effluents the specific productivity of cellulose acetate membranes decreases from 12 $l.m^{-2}$ h^{-1} to practically a zero after only 15 hours of operation [8]. This is illustrated in Figure 3.7.

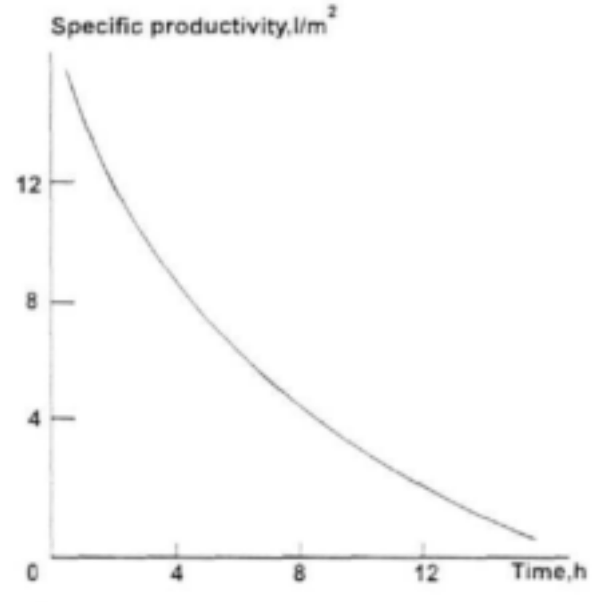

Figure 3.7: Specific productivity of cellulose acetate membranes versus operation time, during the treatment of mining effluents without any pre-treatment.

On the other hand, if water is pre-treated to remove fouling substances then membranes may operate for several years without significant decreases in their characteristics, and therefore decreases in plant productivity. Therefore, the use of 'customary membranes' for the purification of water containing organic and colloid mixtures requires multi-step pre-treatment. A detailed discussion of the pre-treatment of mining effluents prior to RO and ED has been given by Pilipenko *et.al.* [12]. Pre-treatment includes the preliminary removal of colloids by means of thin-layer polyelectrolytes, and the removal of micro-organisms and organic substances using coagulation of sulfo-acidic aluminium in flaking chambers. This is followed by secondary cleaning, the filtration of water through large-grain filters, final treatment in clarifiers, and disinfection with liquid chlorine. The pre-treatment flow-chart also includes the removal of sludge by pumps, de-watering of the deposit on sludge platforms, and utilisation of the sludge. In order to prevent precipitation of low-soluble calcium and magnesium salts, water softening is employed, sometimes in combination with coagulation. For each of these processes reagents are necessary, and also systems for the treatment and utilisation of the sludge.

No less complicated pre-treatment is necessary for the desalination of sea- or drainage waters. Thus, for the reverse osmosis of drainage waters collected from 30 hectares in the state of Arizona (USA) (total productivity of units by filtrate - 250.10^3 $m^3.24$ hrs^{-1}), pre-treatment of the water is necessary. This involves: chlorination, sand filtration, softening with lime at a pH of 9.7, acidification of the water to a pH of 7.5, filtration through double-layer filters, secondary chlorination to maintain a residual free chlorine, the introduction of sulphur (IV) oxide to maintain the residual chlorine concentration in water, acidification to pH 5.5 to reduce hydrolysis of the cellulose-acetate membranes, and the addition of sodium hexametaphosphate as a sequestering agent, to prevent deposition [89]. However, even such a complex pre-treatment does not prevent the membranes from fouling (membrane productivity dropped by 2-4 % per each 1000 h of operation, contrary to the estimates of 1%). The problem of reducing membrane surface contamination was successfully achieved by additional water treatment by ultrafiltration. After ultrafiltration, the losses in productivity of the RO units were reduced by 80-100 %. The introduction of additional water pre-treatment units, using further membranes, increases the expenditures of desalination by 20 to 40 % [90].

In Los Banos, California, the agricultural drainage water intended for RO desalination undergoes complex pre-treatment [91]. Initially the water passes through marsh ponds where the suspended solids are reduced and algae growth is inhibited. After the drainage water leaves the marsh ponds it passes through a charcoal, sand and gravel filter to remove more suspended solids. The water is then conditioned by adjusting its acidity and reducing its bacterial concentrations. Next, a technique similar to domestic water softening removes scale-forming constituents that hamper the desalting process. After these pretreatment phases, the drainage water is fed through the reverse osmosis membranes.

As a result of the complexity of preventing the fouling of membranes by preliminary water treatment, an intensive search for methods of membrane protection from fouling was initiated. In some cases the water to be treated contains substances with quite high molecular weights. These substances do not penetrate the membrane, but form a layer on the surface. This layer provides for the electrostatic repulsion of like-charged particles in the solution. In this way, so-called dynamic membranes are generated [92,93]. This is the easiest and the cheapest method of membrane protection, but it is only suitable for specific types of waters. An example is the purification of lignin-containing effluents [92]. In order to achieve this function, the feed solution has to contain substances that form a protective support layer on the membranes. In the absence of such substances, the once saturated support layer is gradually washed off by the flow of solution. For instance, the application of a hydrogel (charged or non-charged water-soluble polymer) to the membrane surface, chemically unbonded with the membrane, preserves the modifying action for no longer than one month [94]. For improved adhesion of the modifying layer with the membrane, the treatment with the hydrogel is carried out at an elevated temperature [95]. Often, to reduce the solubility of the hydrogel support, the layer is affixed using heat and radiation [96].

Along with the use of non-charged hydrogels, the methods of modifying membranes with electrolytes have been gaining application [97-99]. The layer of charged polyelectrolyte is more stable on a negatively charged membrane. Furthermore, this type of modification alters the transport properties of membranes. The layer of positively charged polyelectrolyte on the negatively charged surface of a cation-transfer membrane reduces its permeability to divalent cations. These membranes may be usefully applied in the production of potable water from saline water [97]. This same layer reduces the possibility of depositing low-soluble salts onto the membrane, by reducing the relative concentration of depositing ions compared to monovalent ions. The layer of polyelectrolyte can be applied to a membrane by submerging the membrane into a solution containing the polyelectrolyte [99]. It can also be achieved by means of direct electro-deposition of the polyelectrolyte onto membranes, during the process of electrodialysis [100, 101]. The last method is the chemical bonding of polyelectrolyte chains to a membrane surface [93,103-104].

Membranes prepared by the latter method are more stable. However, in order to produce these membranes their surface has to contain functional groups with which the polyelectrolyte can react. After this reaction the membrane has to exhibit a charge opposite to that of the unmodified membrane [104-106]. The use of monomeric modifiers allows one to obtain membranes with the most stable properties. However, the danger exists that these compounds may penetrate the membrane matrix, and therefore alter its transport properties [107]. Chemical modification of anion-transfer membranes, which results in the formation of negatively charged groups in the surface layer, firmly protects the membranes from fouling by negatively charged particles and large anions present in feed- and discharged waters [108, 109]. Hence, the chemically bound layer of sulfo groups has a stabilising effect for protection from both surfactants and fulvic acids (present in practically any type of naturally occurring water). The voltage across modified membranes hardly increases during operation, and the relative transfer of Cl^- ions in comparison to SO_4^{2-} increases. This is illustrated in Figures 3.8 and 3.9.

A stabilising effect from fouling by fulvic acids and humic compounds is obtained when membranes are treated with high-molecular weight anionic surfactants (HS) which contain a flexible polar chain [103, 112]. In contrast to low-molecular weight surfactants, which have a single charged radical on a hydrophobic chain, the non-polar radical of HS consists of alternating hydrophobic and hydrophilic groups. The HS locates itself in an horizontal position on the membrane surface, in contrast to non-polar radicals of low-molecular weight surfactants (LS) which are located vertically. Thus, HS have a higher surface activity at the interface than LS do [113]. The treatment of membranes by these compounds is easily accomplished by submersion of the membrane into an aqueous solution of HS with concentrations ranging from 50 to 500 $mg.l^{-1}$ [114]. The modified membranes are sufficiently stable during electrodialysis over a period of time, as illustrated in Figure 3.10.

An interesting method of membrane surface modification is the fixation of the modifying layer by means of plasma spraying. By using plasma discharge it is possible to carry out the polymerisation of film-forming charged monomers, for instance 4-vinylpyridine. This leads to the formation of a thin layer on the membrane surface [115]. This method was suitable for the production of ultra-thin ionic membranes with a thickness < 1 mm.

The development of new methods for the production and modification of membranes to enhance their anti-fouling essentially broadens their fields of application.

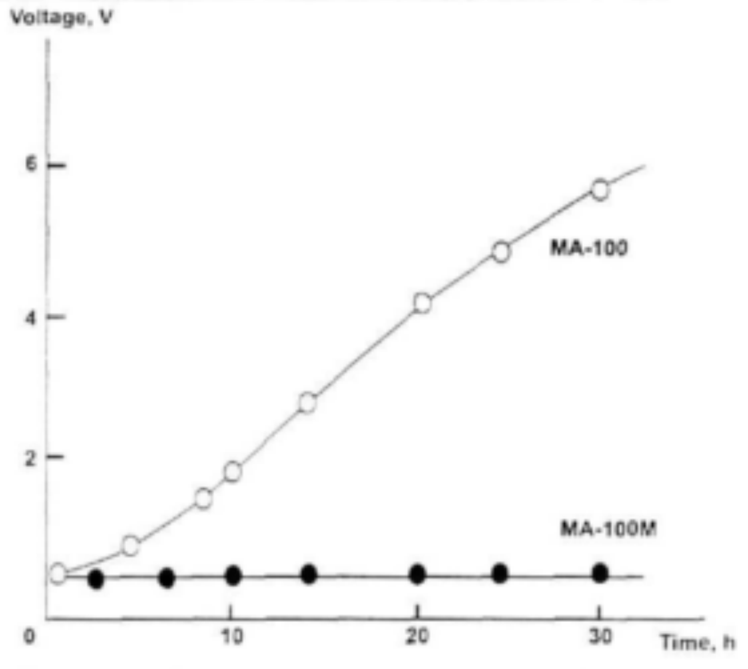

Figure 3.8: Potential drop (V) across MA-100 and MA-100M membranes.

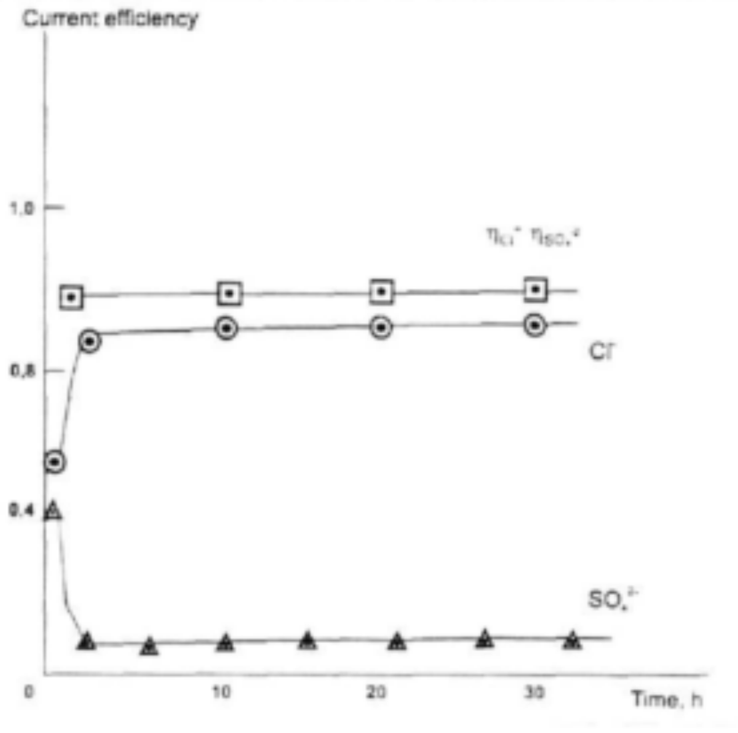

Figure 3.9: Current efficiency of MA-100 and MA-100M membranes.

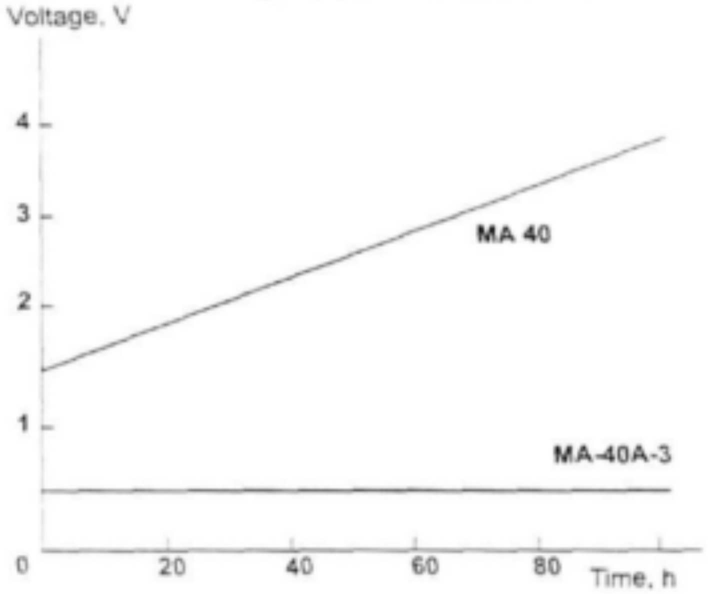

Figure 3.10: The successful modification of anion-transfer membranes towards fouling. Electrodialysis in a solution containing 30 $mg.l^{-1}$ HA, with non-modified MA-40 membrane and modified MA-40-A-3 membrane.

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4. MATERIALS AND EXPERIMENTAL METHODS

4.1. COMPOSITIONS OF SOLUTIONS USED FOR THE DETERMINATION OF ELECTRODIALYSIS MEMBRANE CHARACTERISTICS

The model solutions used to study the electrochemical properties of membranes were based on mine water solutions supplied by Eskom for desalination. The compositions of the solutions are given in Tables 4.1 and 4.2.

Table 4.1: Concentrations of the main salt components in Eskom mine water

No	Compounds	Concentration, mg·l^{-1}
1	NaCl	1170
2	Na_2SO_4	852
3	$NaHCO_3$	336
4	$CaCl_2$	220
5	$MgSO_4$	60
	Total:	2638

In all cases the basic solution (an imitation mine-water solution) was prepared according to the data in Table 4.1 and was termed SIMW. All the salts used for the preparation were of a 'chemically pure' analytical grade.

The majority of the organic components present in the water are saturated hydrocarbons of varying molecular weight and with no dissociating functional groups, and are therefore not capable of forming charged ions in solution. The number of organic compounds capable of forming ions is less diverse. These are benzene dicarboxylic acid, humic acid (HA) and dodecyl benzene sulfonate (DBS), present in concentrations of up to 1 mg·l^{-1}. Using the data contained in Table 4.2 a number of model solutions containing the main organic components were prepared. The compositions of the model solutions are shown in Table 4.3.

Table 4.3 shows that the concentrations of organic substances selected for many of the model solutions exceed the true concentration of these substances in mine water. This is due to the fact that when polarising currents are lower than the limiting current density, and the concentrations of organic substances in solution are less than 20 mg·l^{-1}, the process of membrane fouling takes from 1 month to a year, depending on the nature of fouling substances. Therefore, in order to accelerate the membrane fouling process (in our experiments) the organic substances were added to the model solutions in considerably higher quantities than otherwise. Despite the shortcoming/s of such solution modelling, it is assumed that the use of this approach will allow us to conduct a comparative evaluation of initial and modified membranes in relatively short periods of time.

Table 4.2: Concentrations of the main organic components in mine water.

No	Organic compounds in mine water	Molecular formula	Content, mg·l^{-1}
1	decane	$C_{10}H_{22}$	Not detectable
2	undecane	$C_{11}H_{24}$	Not detectable
3	1-dodecane	$C_{12}H_{24}$	Not detectable
4	1-tetradecene	$C_{14}H_{28}$	Not detectable
5	tetradecane	$C_{14}H_{30}$	2.4
6	5-tetradecene	$C_{14}H_{28}$	Not detectable
7	3-tetradecene	$C_{14}H_{28}$	Not detectable
8	1-hexadecene	$C_{16}H_{32}$	Not detectable
9	hexadecane	$C_{16}H_{34}$	0.16
10	7-hexadecene	$C_{16}H_{32}$	Not detectable
11	1-octadecene	$C_{18}H_{36}$	1.0
12	1,2-bebzendicarboxylic acid, dibutyl ester	$C_{16}H_{22}O_4$	1.0
13	5-eicosene	$C_{20}H_{40}$	Not detectable
14	6-choro-3-[3,5-dimethyl-pyrasol-1-yl-pyridazine-3,5	$C_9H_{11}ClN_5$	Not detectable
15	humic acid		1.0
16	dodecyl benzene sulfonate		1.0

Table 4.3: Model solutions used to study the fouling of anion-transfer membranes.

No.	Model solutions*	Main org. compounds	Content, mg·l^{-1}
1	SIMW Ia	hexadecane	0.2
2	SIMW Ib	tetradecane	2.0
3	SIMW Ic	decane	5.0
		tetradecane	5.0
		hexadecane	5.0
		octadecane	5.0
4	SIMW II	dodecyl benzene sulfonate	30 - 100
5	SIMW III	humic acid	30-90

*All the model solutions were prepared using the basic SIMW solution.

4.2. STUDIES OF THE ELECTROCHEMICAL CHARACTERISTICS OF MEMBRANES

4.2.1 Background

It is well known [1-12] that during electrodialysis the presence of organic substances in feed solutions can result in changes in the transport characteristics of ion-exchange membranes. This is due to the fact that some organic ions, especially those with low mobility, can penetrate into the bulk of the membrane, become affixed there and block the transport of other ions. A marked decrease in the characteristics of electrodialysis membranes is observed when surface-active substances and substances of humus origin are present in the feed solution. These substances are able to penetrate into the pores of the membranes and remain there, due to an electrostatic interaction with the functional ion-exchange groups of the membranes. Hydrophobic interaction with non-charged sections of the membranes is also possible.

The characteristics relating to membrane transport properties that are most likely to change during fouling are selectivity and electrical resistance [13-27]. The method of membrane polarography is a method by which the voltammetric characteristics of individual membrane samples can be recorded [4-6]. Chronopotentiometry [13,15,16] is a method widely used to study the effects of a membrane's interaction with organic components in a feed solution. In particular, chronopotentiometry allows us to study the process of membrane interaction with fouling substances under dynamic conditions of electrodialysis. During the present research programme chronopotentiometry was used to determine the resistance of membranes towards fouling by organic substances.

Membrane polarography was used to determine the voltammetric characteristics of membranes, from which useful information on their behaviour could be obtained. During polarisation by an electric current, ion-exchange membranes are frequently operated in overlimiting conditions. It is possible to determine the value of the limiting current density from the voltammetric curve, and to calculate the resistance of the membrane to the direct current. Electrical resistance is one of the main characteristics of the membrane. The same electrical configuration was used for both methods, i.e. membrane polarography (volt-ampere curves) and chronopotentiometry (chronopotentiometric curves). See Figures 4.1 and 4.2.

4.2.2 Apparatus used for studying the voltammetric and chronopotentiometric characteristics of membranes

The hydraulic and electrical circuits of the apparatus used for studying the voltammetric and chronopotentiometric characteristics of membranes are shown in Figures 4.1 and 4.2. A stabilised NIIRIT B5-49 power supply was used to provide current. A high-resistance NIIRIT SC-4313 voltammeter was used to measure the voltage drop.

The electrodialyser used during the experiments (Figure 4.1) consisted of six cells, two of which contained electrodes. The remaining four cells contained the probes, mounted for measuring voltage drop across the membranes - AM_1, AM_2 and AM_3. The working area (cross-section) of the cells was 2 x 5 cm^2 and the width was 0,5 cm. A 2 mm-thick platinum wire was used as electrode.

The measuring probes were glass capillaries and were positioned in the centre of the inter-membrane spaces, through an outer wall of the cell (Figure 4.2). The capillaries were supported by flexible tubing, closed by dense filters, and incorporated into a saturated potassium chloride (KCl) solution, into which silver/silver chloride (Ag/AgCl) reference electrodes were placed. Prior to commencing with the experiment the capillaries were filled with a freshly prepared, saturated KCl solution, providing low electrical resistance for the measuring system. The electrical resistance is an important parameter for estimating the voltage drop across membranes during the electrodialysis of dilute solutions.

4.2.3. Techniques used for the determination of volt-ampere curves and voltage-drop measurements across the membranes

Membranes were installed and the electrodialysis cells tested for leakages. All trapped air had to be removed from the capillaries. After this, the feed solution was passed through the cells of the electrodialyser, and electrical current applied. The vessel containing the feed solutions (the model solution of mine water) and electrode solutions (0.05 M Na_2SO_4) were placed 50 cm above the cell. Each solution volume was 5 litres. The set-up permitted gravitational feed of the solutions to the cell. The solution-velocity was controlled by means of a valve.

Prior to taking measurements, the cells of the electrodyaliser were conditioned in a pre-determined mode of solution velocity and current density, for 15 to 30 minutes. The conditioning time was determined by the current density of the membranes. Measurement of the voltage drop between the probes could then proceed.

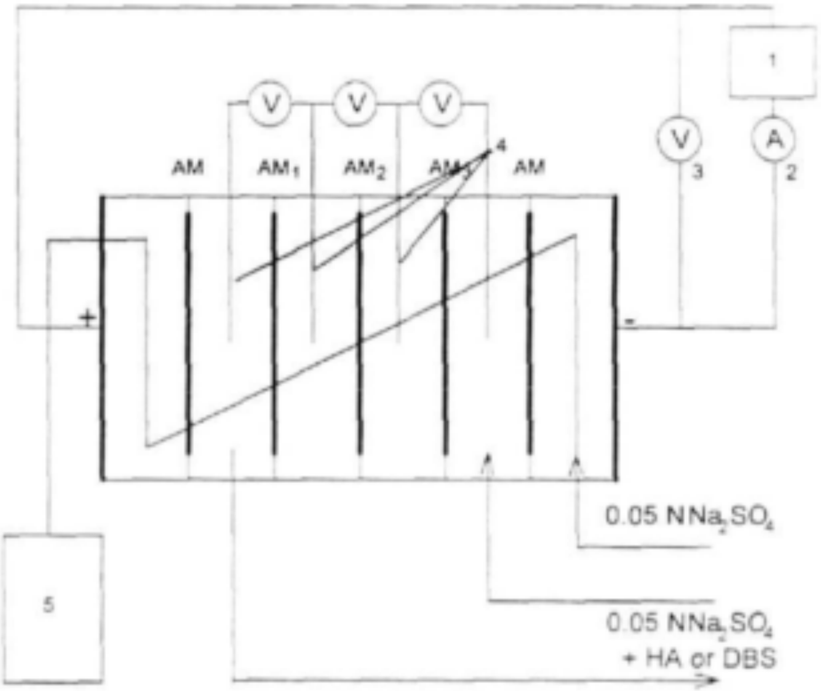


Figure 4.1: Electrical and hydraulic circuits of the apparatus used to study the volt-ampere and chronopotentiometric characteristics of membranes.

1 - power supply, 2 - ammeter, 3 - high ohmic voltmeter, 4 - measuring probe, 5 - vessel containing electrode solution, AM – anion-transfer membranes AM_1, AM_2 and AM_3 (test membranes).

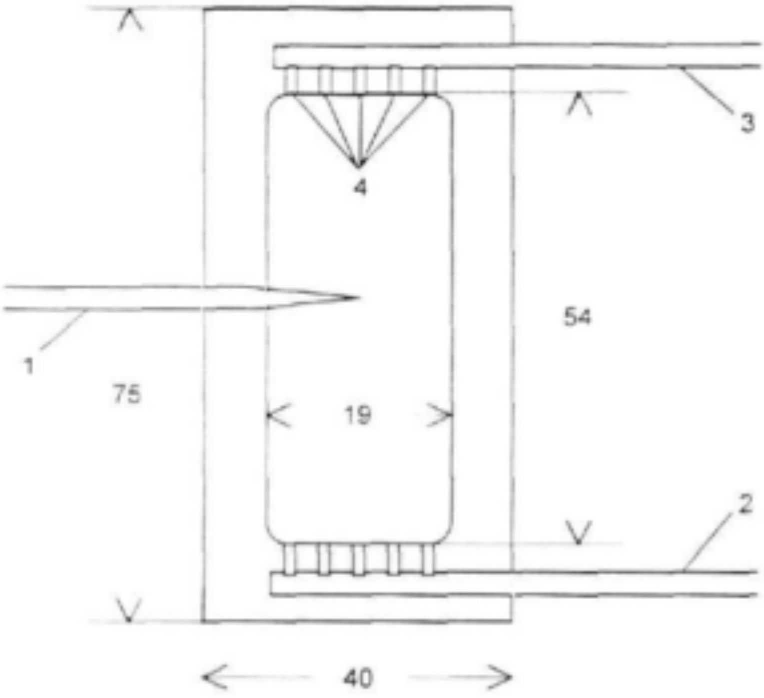


Figure 4.2: Measuring cell.

1 - the probe, 2 and 3 – tubing, for the supply and removal of the electrolyte, 3 - a distribution slot. Numerical figures are dimensions (mm).

The electrodialysis apparatus for volt-ampere and chronopotentiometric measurements was equipped with only anion-transfer membranes. The absence of cation-transfer membranes in the cell excluded the influence of concentration differences on the results of measurements. Such a concentration difference can arise between the concentrate and demineralising cells during electrodialysis when the unit is equipped with alternate membranes. By including only anion-transfer membranes in the electrodialysis cell, the concentration changes were observed mainly in the near-membrane diffusion layer, at significant distances from the measuring probes. The ends of the capillary probes were placed in the centre of the electrolysis chambers at a distance of 2.5 ± 0.5 mm from the membranes. It is known [28, 29] that the thickness of the diffusion layer in which the concentration changes occur does, as a rule, not exceed 100 μm.

The volt-ampere curves of three anion-transfer Ionics membranes in an electrodialysis cell are shown in Figure 4.3. The values were measured under identical conditions. The feed solution was supplied to the working cells at a velocity of 0.1 $cm \cdot s^{-1}$. The shapes of the curves are similar but their gradients differ.

4.2.4. Technique used for the determination of membrane electrical resistance to alternating current

4.2.4.1. Chemicals and equipment

- 0.6 M sodium chloride (NaCl) solution
- R577 Alternating current bridge;
- LPU-01 pH-meter;

- Measuring cell, consisting of two adjacent electrode chambers.

4.2.4.2 *Preparation of membrane samples prior to measurements*

The membrane samples (sizes 3 x 7 cm) were conditioned in a 0.6 M sodium chloride (NaCl) solution, whilst stirring. The conditioning was complete once the resistance of the solution was at a constant value, equal to that of the original solution. The NaCl solution in contact with the membrane was periodically replaced.

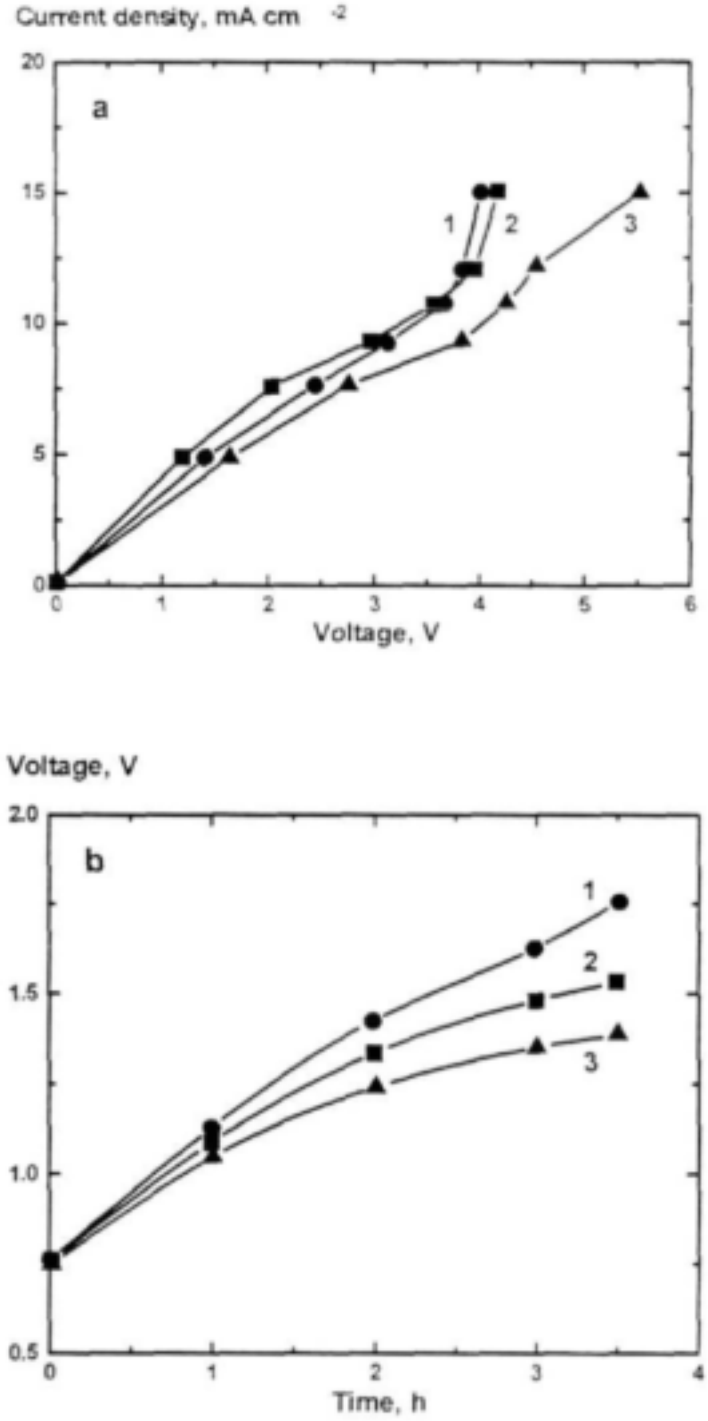


Figure 4.3: Volt-ampere (a) and chronopotentiometric (b) curves of Ionics anion transfer membranes 1, 2 and 3. SIMW contained 50 mg·l^{-1} DBS, current density 6.0 mA·cm^{-2}.

4.2.4.3 *Creation of a circuit for the determination of membrane electrical resistance*

The membrane under investigation was clamped between cell halves containing the measuring electrodes. Leakages were prevented by rubber o-rings, used for sealing. The measuring cell was filled with the electrolyte solution; it entered the cell from the bottom and exited from the top, so eliminating trapped air.

4.2.4.4. *Experimental*

The measuring cell with no membranes was filled with a 0.6 M NaCl solution. The solution velocity was 0.1±0.05 $cm \cdot s^{-1}$. After 2 minutes, the solution flow was interrupted and an alternating current bridge used to determine the resistance of the cell. The resistance was then determined in the presence of the conditioned membranes. Three measurements were conducted for each method, and the mean of the values taken as the result. The accuracy of the measurements was 14%.

4.2.4.5. *Determination of electrical resistance*

The electrical resistance of a membrane with a known surface area can be calculated by the following formula:

$$\rho = (R_{cm} - R_c) \cdot S, \qquad (4.1)$$

where:

R_{cm} and R_c - the Ohmic resistance of the cell with and without a membrane, respectively;

S - working surface area of the membrane, equal to the area of the electrode (cm^2).

4.3. MODIFICATION OF ION-EXCHANGE MEMBRANES BY POLYELECTROLYTES

4.3.1 Introduction

The most reliable method for the preparation of ion-exchange membranes with specific end goals (properties) in mind (for example, permselectivity toward a certain class of ions, increased stability toward fouling by various substances, or increased chemical stability) is to impart the properties during synthesis of the membrane [30-32]. In practice, however, many properties are imparted by post-manufacture modification. One of the most simple and widespread methods is by coating a modifying substance onto the surface of the membrane. Important requirements are that the modifying substance does not penetrate into the bulk of the membrane and no decrease of the physico-chemical characteristics occurs. The stability of the coated layer, determined by the forces of interaction between the modifier-substance and the surface of the membrane, is of considerable significance. If the structure of the membrane contains reactive functional groups then the process of coating with polyelectrolytes can include chemical interaction with the surface of the membrane. This method has been quite widely used for the modification of membranes containing sulfochloride functional groups by polyelectrolytes [32,33].

The interaction between a polyelectrolyte and a membrane containing no reactive groups is based on electrostatic forces. Thus, a dynamic membrane is formed on the surface of a base membrane in contact with the polyelectrolyte. As the dynamic membrane contains charge, it can reject antipolar ions and thus change the permeability of the base membrane.

Results of our earlier research, funded by Eskom, have shown that a bianchor (double-charged), high molecular weight, surface active substance NB-8 could be used to increase the stability of Ionics anion transfer membranes toward fouling by DBS and HA. It was also shown that modification of the membrane did not influence its permeability toward Cl^- and SO_4^{2-} ions, because of the low charge density in the coated layer of NB-8. A NB-8 molecule with a molecular weight of 2760 contains only two sulfo groups. A sufficient potential-barrier, which is essentially able to limit the transfer of SO_4^{2-} ions through the modified membrane, can therefore not be generated on the surface layer of the membrane.

Attempts have recently been made to find other polyelectrolytes that are capable of modifying anion-transfer membranes, to protect them against fouling by organic substances, and to increase their permselectivity to monovalent ions.

The main criteria relevant to the choice of new substances are:

- availability and low/non-toxicity;
- solubility in water or other solvents suitable for coating the polyelectrolyte layer onto the surface of the Ionics membranes;
- availability of charged groups, able to provide for an electrostatic interaction with the surface of the membrane;
- sufficient charge density, to electrostatically repel large organic anions.

4.3.2. Polyelectrolytes used for the modification of anion-transfer membranes

Based on the above criteria, alternatives to NB-8 were carboxymethylcellulose (CMCell), LT-26 and LT-27. The latter two are flocculants of the "Magnafloc" range, and are described in more detail below.

1. NB-8 is a disodium salt of α,ω-olygooxypropylene-bis (o-urethan-2,4,2,6-toluene ureilene benzenesulfonic acid), with the following chemical formula:

   $NaO_3S\text{-}R''\text{-}RNCONH\text{-}R'\text{-}NHCOO(RO)_x\text{-}CONH\text{-}R'NHCONH\text{-}R''\text{-}SO_3Na$,

   Where R = $CH_2CH(CH_3)$

   R' = $2,4\text{-}2,6\text{-}C_6H_3(CH_3)$

   R'' = $1,4\text{-}C_6H_4$; $x=36$.

2. "Magnafloc" is a registered trade name of Applied Colloid Ltd (Applied Colloids Limited, P O Box 38, Low Moor, Bradford, Yorkshire). "Magnafloc" products are synthetic, high molecular weight, water-soluble polymers, based on acrylamide and its copolymers. Magnafloc LT-26 and LT-27 Anionic Flocculants have very high molecular weights and are non toxic. The anionic polyacrylamide flocculant is supplied as a free flowing granular powder. Typical properties of LT-26 and LT-27 are listed in Table 4.4.

3. Carboxymethylcellulose (CMCell) is the sodium salt of a simple ether of cellulose and glycolic acid, with the general formula:

   $$[C_6H_7O_2\,(OH)_{3-x}\,(OCH_2COONa)_x]_n$$

   R-COOH and R'-OH are the main functional groups. The degree of replacement of hydroxyl groups is 1,2 (on account on the one elementary linkage). The degree of polymerisation is 1500. Prior to using CMCell it is separated by fractionation with acetone from an aqueous solution.

Table 4.4:Typical characteristics of Magnafloc LT-26 and LT-27 anionic flocculants

Physical form	white granular powder
Particle size	98% < 750µ
Bulk density	0.5 – 0.6
pH of 1% solution at 25 °C	5.5 – 6.5
Free acrylamide	less than 0.05

4.3.3 Polyelectrolytes used for the modification of cation-transfer membranes

Cationic flocculants with a positive charge and macromolecules of a type R^+Cl^- were first chosen for the modification of cation-transfer membranes. Such macromolecules are only able to interact with the surface groups of membranes by an electrostatic mechanism, although a hydrophobic interaction may also contribute. Further possible flocculants, capable of forming strong bonds with the membrane surface, were also investigated.

The following polyelectrolytes were selected with which to treat the cation-transfer membranes:

1. Cationic flocculant LT-22, of the "Magnafloc" type.
2. Flocculants of the "Magnifloc" type, produced by Cytec (USA), based on dimethylamine-epichlorohydrin-ethylenediamine polymers:
    - Magnifloc 573C;
    - Magnifloc 581C.

4.4. VISCOSITY STUDIES OF THE POLYELECTROLYTE SOLUTIONS USED FOR MEMBRANE MODIFICATION

One of the main properties characterising polyelectrolyte solutions is their viscosity-concentration dependence. Usually this relationship is non-linear, although in certain ranges of polyelectrolyte concentrations it is close to linear. It is possible to use the linear graph of this dependency as a calibration curve for determining the concentration of polyelectrolyte in solution. Such a method was used in this study, for determining the amount of polyelectrolyte fixed onto the membrane during modification.

A study of the viscosity-concentration dependence has shown that for an increase in polyelectrolyte concentration up to 1 $g \cdot l^{-1}$ the viscosity of the solution increases nearly linearly (see Figures 4.4 and 4.5). The forms of the curves indicate that LT-26, LT-27, CMCell and MF 581C solutions typically behave as electrolytic solutions. An exception is LT-27, where a change in curvature on the graph is seen at a concentration of 0.1 $g \cdot l^{-1}$.

As seen in Figure 4.7 the viscosity of an aqueous NB-8 solution decreases as its concentration increases. This phenomenon is characteristic of a substance with high surface activity [13]. It is possible to conclude that, notwithstanding a high molecular weight and two sulpha- groups on each end of the polymer chain, this substance is a typical surfactant. Hence, it can bond with a membrane not only by an electrostatic interaction, but also by a hydrophobic mechanism. Simultaneously, NB-8 can be tangentially affixed to the membrane surface, instead of in a vertical position, as has been observed for low-molecular surfactants [34].

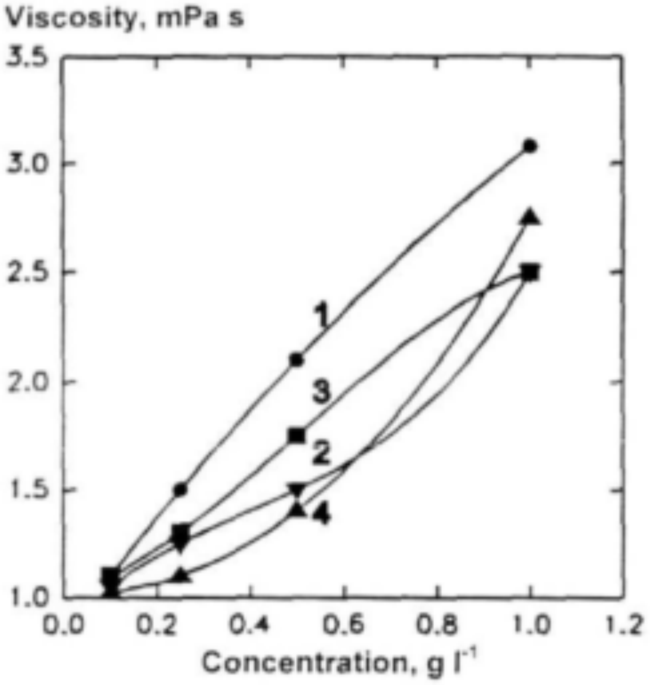


Figure 4.4: The viscosity-concentration dependence of aqueous solutions of LT-27 (1), LT-26 (2), CMC (3) and MF581C (4).

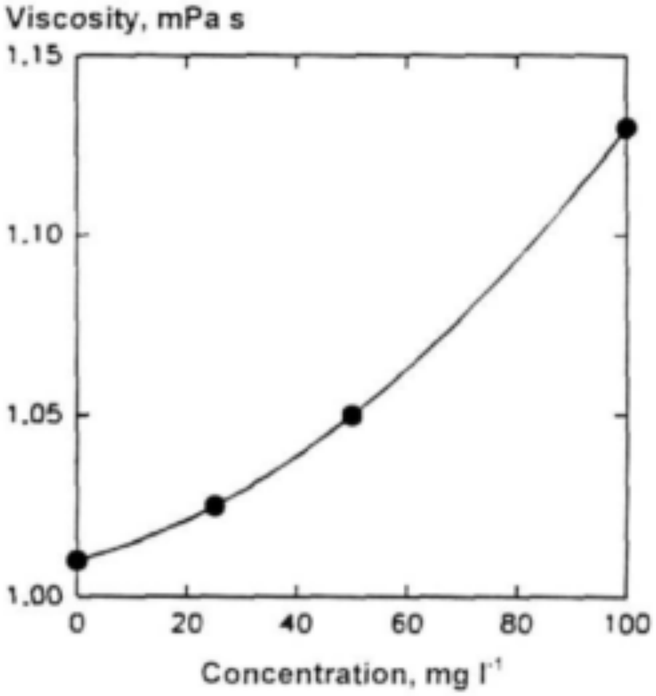


Figure 4.5: The viscosity-concentration dependence of an aqueous solution of LT-27.

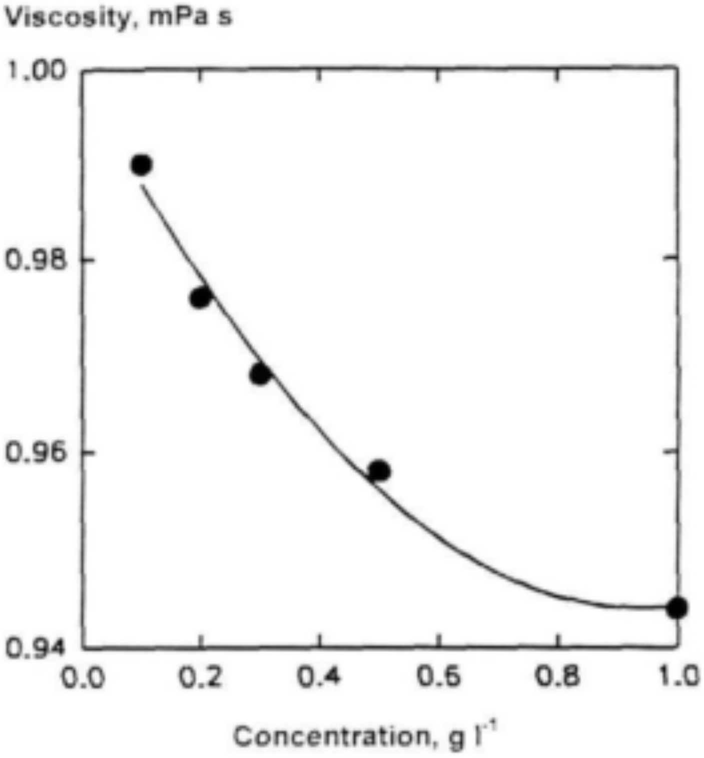


Figure 4.6: The viscosity-concentration dependence of an aqueous NB-8 solution.

Based on the dependencies seen in Figures 4.4 and 4.5, the ranges of polyelectrolyte concentrations to be used for modifying the membranes were chosen from the areas of the curves with the lowest gradients. This concentration was below 100 mg·l^{-1} for all the polyelectrolytes investigated.

4.4.1. Method of deposition of polyelectrolyte onto ion-exchange membranes

Two methods were used for the deposition of polyelectrolytes onto the surfaces of ion-exchange membranes.

4.4.1.1 *The deposition of aqueous solutions of polyelectrolytes onto membranes, under static and dynamic conditions.*

Taking the low stability of dilute aqueous solutions of polyelectrolytes into account the modifying solutions were prepared from a 1 g.l^{-1} stock solution directly before use. Such solutions retain their properties (viscosity, conductivity and pH) for over a week if refrigerated.

The modification of membranes under static conditions was carried out in 100 ml of solution, whilst stirring. Membranes were modified with LT-27 for a modification time of 30 minutes (see Figure 4.7) and with NB-8 for a time of 5-10 min.

Membrane modification was performed under dynamic conditions in the electrodialysis apparatus itself. The polyelectrolyte solution was circulated through the demineralisation compartments of the cell for 30 minutes.

4.4.1.2 *The deposition of organic-solvent based polyelectrolyte solutions onto membranes.*

An amount of polyelectrolyte was dissolved in an organic solvent capable of wetting the surface of the membrane, but not dissolving the base membrane. An adhesive was added and the solution was applied to the membrane surface by brush.

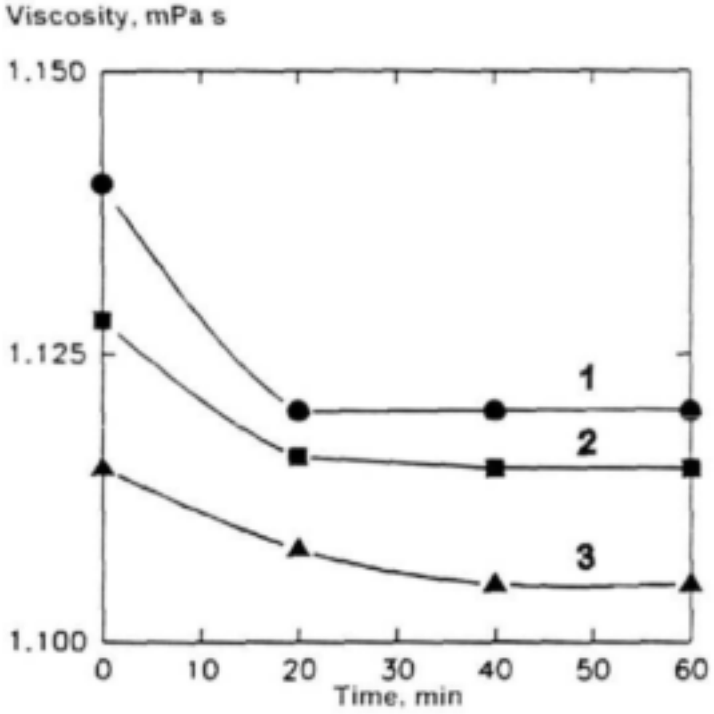


Figure 4.7: Changes in the viscosities of solutions LT-27-100 (1), LT-27-50 (2) and CMCell-100 (3) after contact with Ionics membranes.

4.4.2. Designations used for the modified membranes

I:	initial Ionics membrane;
$I_{NB\text{-}8\text{-}50\text{-}10}$:	membrane modified by a 50 mg.l^{-1} aqueous solution of NB-8 for 10 minutes;
$I_{LT\text{-}27\text{-}50}$:	membrane modified by a 50 mg.l^{-1} aqueous solution of LT-27 for 30 minutes (if the standard time of 30 minutes was used for static treatment then the time is omitted in the designation).

To distinguish the abovementioned membranes (prepared under static conditions) from those modified under dynamic conditions, and therefore under an applied current, the following designations were used:

$I_{LT\text{-}22\text{-}5/15}$:	Ionics membrane modified by a 5 mg·l^{-1} aqueous solution of LT-22, at a current density of 15 mA·cm^{-2};
$I_{MF\text{-}573C\text{-}5/15}$:	Ionics membrane modified by a 5 mg.l^{-1} aqueous solution of MF 573C flocculant, at a current density of 15 mA·cm^{-2}.

5. STUDIES OF THE RESISTANCE OF MODIFIED ANION-TRANSFER MEMBRANES TO FOULING BY ORGANIC SUBSTANCES

5.1. ELECTROCHEMICAL PROPERTIES OF ANION-TRANSFER MEMBRANES MODIFIED UNDER STATIC CONDITIONS

Research was undertaken to determine the influence of a certain hydrocarbons, present in mine drainage water, on the characteristics of Ionics membranes. For this purpose the chronopotentiometric measurements of a number of characteristics of membranes in SIMWs were conducted (SIMW I a, 1b and 1c – see Table 4.3). The results obtained are shown in Table 5.1, where the values of the voltage drop across the membranes are shown for the electrodialysis of SIMW at current densities of 3.0, 6.0 and 10.0 $mA \cdot cm^{-2}$.

Table 5.1: The influence of SIMW compositions on polarised Ionics anion-transfer membranes.

(Δu_0 and Δu_3 - initial voltage drop and final value after three hours of polarisation.)

Membrane type	Current density (i) $mA \cdot cm^{-2}$	Voltage drop (Δu) V					
		SIMW I a		SIMW I b		SIMW I c	
		Δu_0	Δu_3	Δu_0	Δu_3	Δu_0	Δu_3
I	3	0.46	0.48	0.48	0.50	0.50	0.51
I	6	0.82	0.84	0.82	0.86	0.88	0.90
I	10	1.10	1.12	1.15	1.14	1.18	1.18
$J_{NB\text{-}8\text{-}100}$	6	0.86	0.86	0.86	0.88	0.90	0.91

On analysing the data in Table 5.1 it is noticed that three hours of polarisation does not result in a significant increase of the voltage drop across the membranes for all three SIMW types. The slight increases of the voltage drops observed for SIMW Ic could be due to the hydrophobisation of the membrane surface by organic substances. From the data in Table 5.1, and also from the polarisation curve in Figure 5.1, it is concluded that concentrations of saturated hydrocarbons in the range 0.2 - 20.0 $mg \cdot l^{-1}$ in the dialysis solution have practically no effect on the fouling characteristics of the membranes. More specifically, both the unmodified Ionics membrane and the membrane modified with NB-8 are stable in the SIMW solutions

When hydrocarbon concentrations were greater than 2.0 $mg \cdot l^{-1}$ a phase separation of the weakly soluble hydrocarbons and water occurred. The hydrocarbon phase of the SIMW solution covered the glass vessels and piping, and then precipitated on the surface of the membrane.

As no influence of the selected hydrocarbons on the membrane characteristics could be noticed, use of the SIMW 1 solution was discontinued. Instead, solutions of SIMW II and SIMW III, containing various concentrations of humic acid (HA) and dodecylbenzenesulfonate (DBS) were used in further resistance studies of modified anion transfer membranes toward fouling by organic substances.

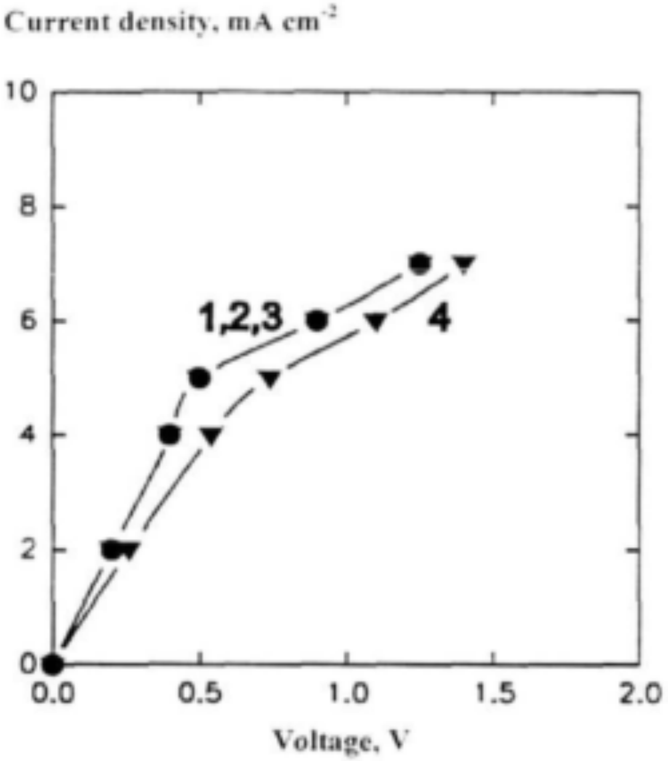


Figure 5.1: Volt-ampere characteristics of I_A (•) and $I_{A\text{-}NB\text{-}8\text{-}100}$ (▼) membranes in SIMW (1), SIMW Ia (2), SIMW Ib (3) and SIMW Ic (4) solutions. Solution velocity 0.2 cm·s^{-1}.

The volt-ampere curves obtained for the initial membrane and modified membranes in SIMW are shown in Figure 5.2. When analysing the curves it is seen that, in all cases, modification of membranes causes a decrease in the limiting current density. For instance, when NB-8 and LT-27 are used it decreases from 5.5 to 5.0 mA·cm^{-2}. When LT-26 and CMCell are used then this decrease is more significant; the limiting current decreases to 4.0 mA·cm^{-2}. This is associated with the fouling of membranes that have been modified by polyelectrolytes. The decrease in the limiting current density is associated with the formation of a bipolar layer, beyond the membrane-polyelectrolyte layer interface. When NB-8 is used, hydrophobisation of the membrane surface could occur.

From the results of the chronopotentiometric studies shown in Figure 5.3 one notices that modifications of the Ionics membranes by LT-27 and NB-8 influence the electrochemical characteristics of membranes to a considerably lesser degree than modifications with LT-26 and CMCell do. Furthermore, the graph and data presented in Table 5.2 show that much greater fouling protection is achieved when the membranes are modified with LT-27 and NB-8.

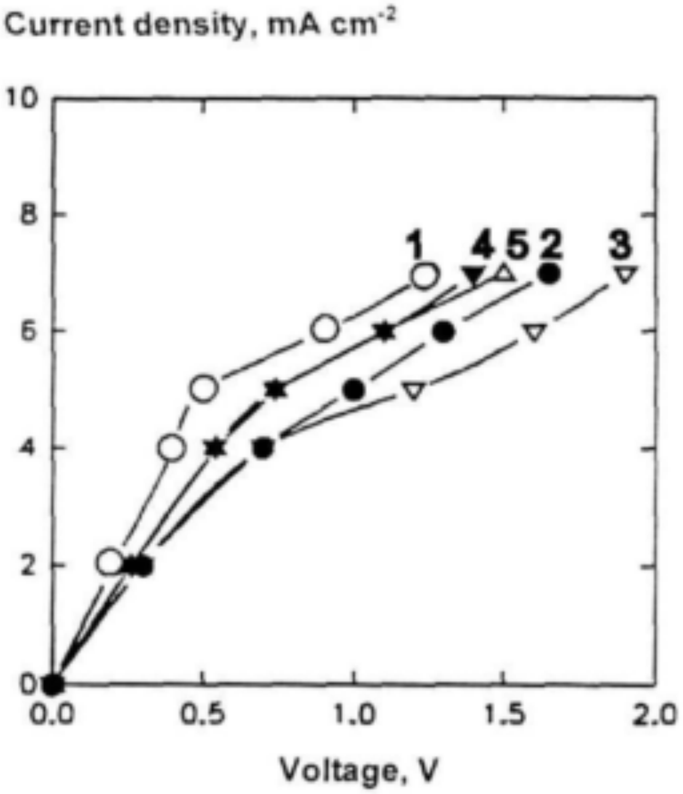


Figure 5.2: Volt-ampere characteristics of I_A (1), $I_{LT-26-100}$ (2), $I_{CMC-100}$ (3), $I_{NB-8-100}$ (4) and $I_{LT-27-100}$ (5) membranes in SIMW containing 100 mg·l^{-1} DBS. Solution velocity 0.2 cm·s^{-1}.

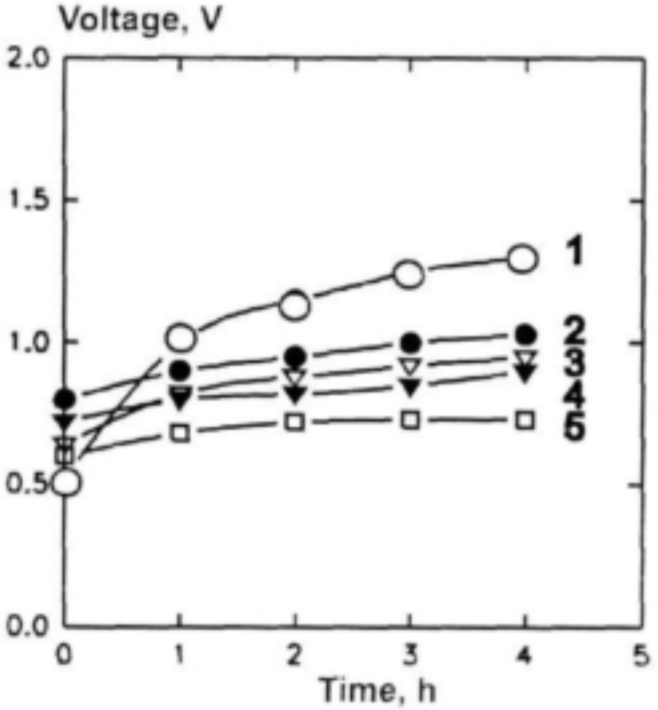


Figure 5.3: Chronopotentiometric characteristics of I_A (1), $I_{LT-26-100}$ (2), $I_{CMC-100}$ (3), $I_{NB-8-100}$ (4) and $I_{LT-27-100}$ (5) membranes in SIMW containing 100 mg·l^{-1} DBS. Current density 6.0 mA·cm^{-2}.

Table 5.2: Resistance coefficients (K_s) of Ionics anion-transfer membranes modified by four different polyelectrolytes (calculated from chronopotentiometric curves).

Membrane	Resistance coefficients (K_s)*
I	1
$I_{LT\text{-}26\text{-}100}$	1.22
$I_{CMC\text{-}100}$	1.30
$I_{LT\text{-}27\text{-}100}$	1.43
$I_{NB\text{-}8\text{-}100}$	1.64

* K is explained in Appendix A2

From the data in Table 5.2 it is seen that the highest value for K_s is obtained for membranes modified with NB-8. This value is slightly lower than the value obtained after modification with LT-27. When comparing the forms of the chronopotentiometric curves, one sees that the curves for LT-27 and NB-8 are similar, although the initial point of the curve for LT-27 corresponds to the higher value for Δu_0. It is believed that the lower K_s value for LT-27 is due to the greater thickness of this modifier layer that forms on the membrane during modification with 100 mg.l^{-1} solution. To verify this assumption, research was conducted into the influence of the concentration of an LT-27 solution on the electrochemical parameters of such modified membranes.

Therefore, after terminating electrodialysis, the volt-ampere curves were measured for a further four hours. They are shown in Figure 5.4a and, after current reversal for I hour, in Figure 5.4b. The curves obtained for membranes modified with NB-8 and LT-27 practically coincide. This data confirms the assumption of the unjustifiably thick layer of polyelectrolyte that is formed on the membrane during modification with an LT-27 solution of 100 mg·l^{-1} concentration The layer is washed of during electrodialysis, and the current is subsequently reversed.

Based on the data in Figure 5.5 it is possible to consider 10 mg·l^{-1} as the optimum concentration for a LT-27 modifying solution; the lower concentration has the best effect. The resistance coefficient of the membrane is 1.4. Solutions of lower concentrations of modifier with will also be effective, but a large excess of the modifier solution volume (in relation to the volume of the membrane) and an increase in the modification time will then be necessary.

5.2. ELECTROCHEMICAL PROPERTIES OF ANION-TRANSFER MEMBRANES MODIFIED UNDER DYNAMIC CONDITIONS

The main advantage of carrying out membrane treatment under dynamic conditions is that the membranes may be modified without dismantling the electrodialysis apparatus. There are two ways in which membranes can be treated within the volume of an electrodialysis cell. First, the modifying solution can be supplied only to the demineralisation cells or compartments, processing only one side of the membrane. Second, the modifier solution can be passed through all the cells, with the exception of the electrode compartments. In the first case the layer of polyelectrolyte will be affixed mainly onto the accepting surface of the antipolar membrane, both in the absence or application of electrical current, and one surface of the membrane will form a bipolar interface with the layer of polyelectrolyte. At currents close to the limiting current density, hydrogen (H^+) and hydroxyl (OH^-) ions will be generated.

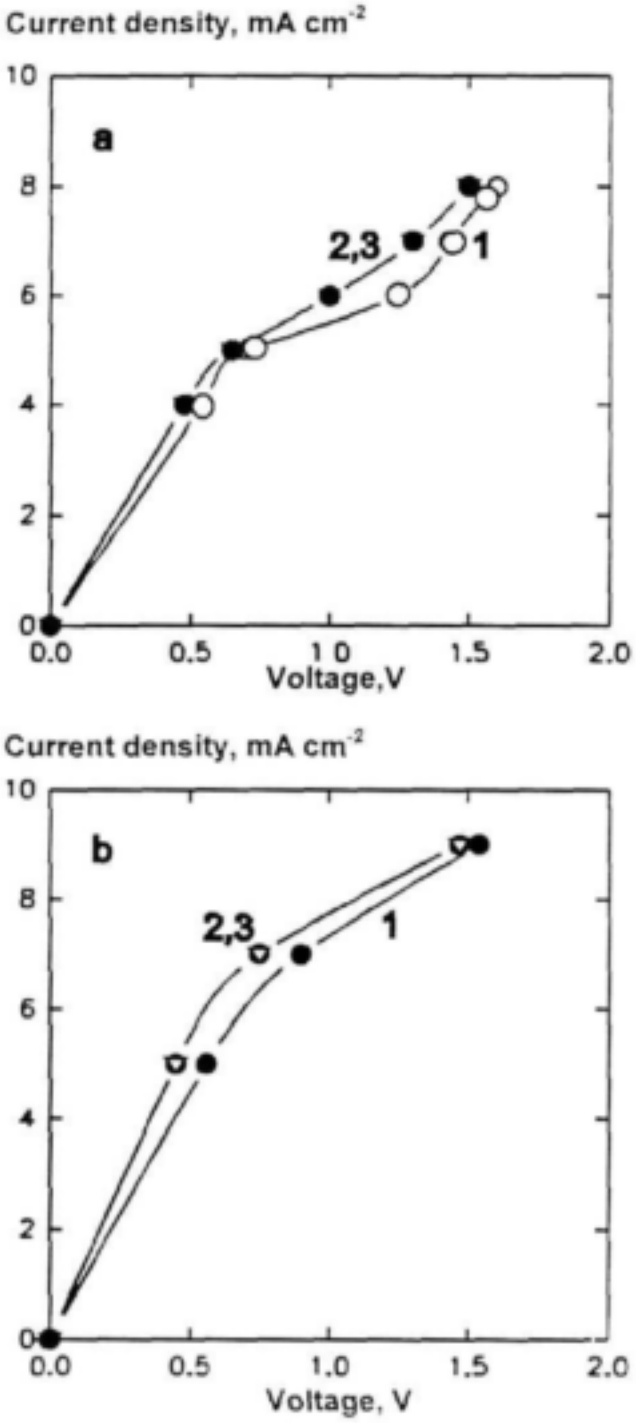


Figure 5.4: Volt-ampere characteristics of I_A (1), $I_{NB\text{-}8\text{-}100}$ (2) and $I_{LT\text{-}27\text{-}100}$ (3) membranes in SIMW containing 100 mg·l^{-1} of DBS, before (a) and after (b) current reversal over a period of 1 h. Solution velocity 0.2 cm·s^{-1}.

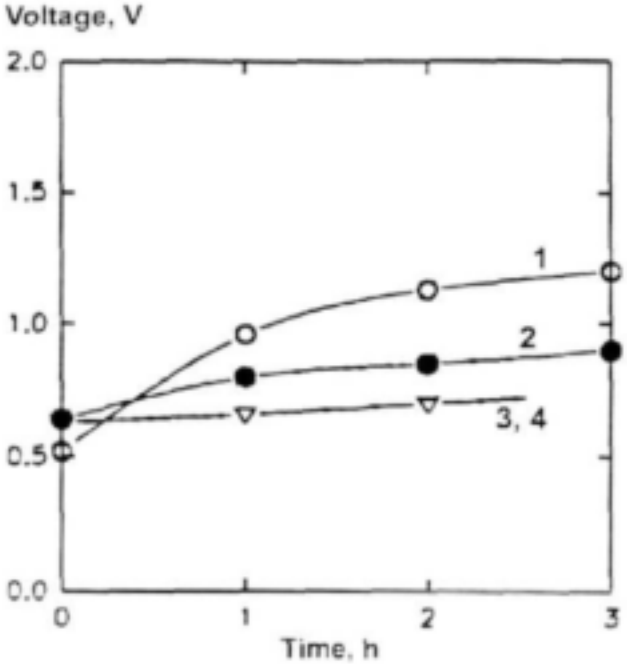


Figure 5.5: Chronopotentiometric characteristics of a standard Ionics membrane (1) and membranes modified with LT-27 solutions of concentrations 100.0 (2), 50.0 (3), 10.0 (4) and 5.0 (5) mg·l^{-1}.

The volt-ampere curve in Figure 5.6 for membranes modified under dynamic conditions illustrates this phenomenon. The polyelectrolyte solutions were introduced at the accepting side of the membrane whilst simultaneously applying an electrical current (density 3 mA·cm^{-2}). When analysing the graph one notices that except for the plateau, representative of the limiting current, there is a further curve, associated with the generation of H^+ and OH^- ions on the bipolar membrane-polyelectrolyte interface. This is observed for the three modifying substances NB-8, LT-27 and CMCell.

In the second case, where the membrane's surface is modified with modifier solution on both sides, i.e. processing through both demineralisation and concentrate compartments, the second curve in the graph is not noted. The graph has a normal, expected form. Based on this, it is concluded that the dynamic method of modification is preferable.

An analysis of the limiting current values for membranes modified under both static and dynamic conditions shows that these values are the same, and they are presented in Table 5.3.

5.3 CONCLUSIONS

Research into the resistance of modified Ionics anion-transfer membranes to fouling by organic substances present in electrodialysis feed-water has shown that:

- The presence of saturated hydrocarbons in mine drainage water, in concentration of up to 20 mg·l^{-1}, has no influence on the power consumption of the electrodialysis process when using Ionics membranes.
- Of the polyelectrolytes investigated for use in membrane modification, the NB-8 agent allows us to obtain the highest resistance coefficient against fouling by organic substances;

- Although the membranes modified with LT-27 have lower resistance coefficients, this modifier is also effective and can be used in considerably lower concentrations than NB-8;
- There is practically no difference in the measured properties of anion-transfer membranes modified under static or dynamic conditions;
- The layer of polyelectrolyte, electroprecipitated under dynamic conditions, is quite stable and effectively protects the membrane against fouling for a minimum of 20 days.

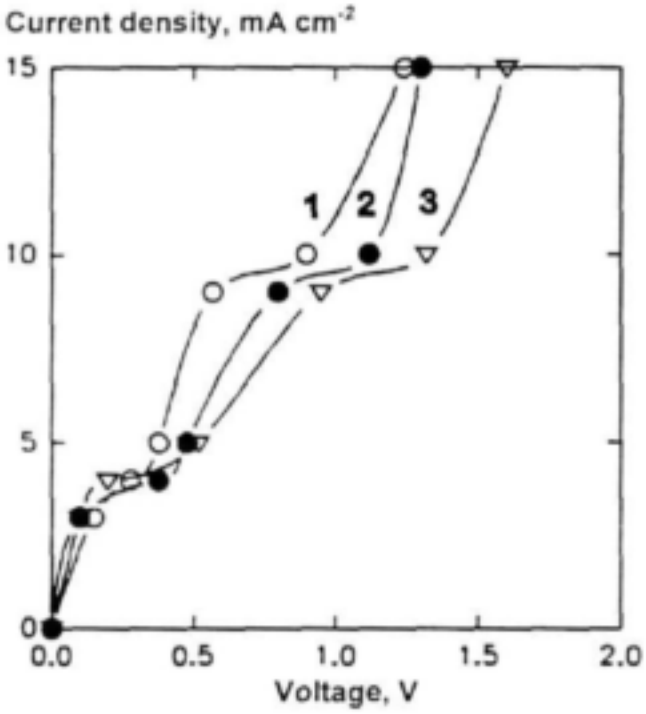


Figure 5.6: Volt-ampere characteristics of Ionics membranes modified with 100 mg·l^{-1} aqueous solutions of NB-8 (1), LT-27 (2) and CMCell (3) during 0.5 h electrodialysis with SIMW. Current density 3.0 mA·cm^{-2}. (Modifying solution passed through demineralisation cells only).

Table 5.3: The limiting current values for initial and modified Ionics anion-transfer membranes (modified under both static and dynamic conditions)

No.	Membrane designation	Limiting current value (i) mA·cm^{-2}	
		Under static conditions	Under dynamic conditions
1	I	5.5	
2	$I_{LT\text{-}26\text{-}100}$	4.0	4.0
3	$I_{CMC\text{-}100}$	4.0	4.0
4	$I_{NB\text{-}8\text{-}100}$	5.0	5.0
5	$I_{LT\text{-}27\text{-}100}$	5.0	5.0

6. STUDIES OF THE PERMSELECTIVITY OF THE IONICS MEMBRANE AND CHANGES DUE TO MEMBRANE MODIFICATION

6.1. INTRODUCTION

An electromigrative flow of polyelectrolyte to the antipolar membrane and the diffusion of polyelectrolyte to the unipolar membrane are observed when membranes are modified by passing solution through the demineralising cell of the electrodialysis apparatus. Therefore, the negatively charged NB-8 modifier, as well as similar polyelectrolytes, are delivered electroforetically to the positively charged anion-transfer membrane, precipitating on the membrane surface and forming a layer [35]. Adsorption of macro-ions by the unipolar membrane is unlikely [10,16] but, due to the high surface activity of NB-8, one may expect their deposition onto the surface of the unipolar membrane. This occurs by a hydrophobic mechanism. The deposition of a polyelectrolyte layer onto the surfaces of both anion- and cation-transfer membranes may result in changes in their specific selectivities towards differently charged ions. The influence of the modification of the Ionics membrane on selectivity was studied.

Various methods can be used to increase the permselectivity of membranes. In essence, an additional layer has to be created which is able to function as a potential barrier towards the penetration of divalent ions on the surface of the membrane. As a rule, this is accomplished by chemical bonding or physical adsorption of a substance (polyelectrolyte) onto the surface of a membrane containing positive charge [27,30-32,35-41]. It is possible to create membranes that are selective towards different ions [34,42-47], e.g. SO_4^{2-}, NO_3^-, and H^+ ions. Plasma evaporation or the plasma polymerisation of modifying compounds onto the surfaces of membranes [48,49] has recently gained wide acceptance.

Two factors were used in estimating the permselectivities of the initial and the modified membranes. The first, the separation factor, was proposed by Gelferich [50]:

$$T_{Na}^{Me} = \frac{\overline{C}_{Me}}{C_{Me}} \times \frac{C_{Na}}{\overline{C}_{Na}}, \tag{6.1}$$

where:

$\overline{C}_{Me}/\overline{C}_{Na}$:	the ratio of concentrations of multivalent ions towards monovalent ions, adsorbed by an ion-exchanger (in solid phase);
C_{Na}/C_{Me}:	the ratio of the concentrations of the ions in solution.

If $T_{Na}^{Me} > 1$ then the ion-exchanger selectively absorbs multivalent ions. However, the selective absorption of ions by the ion-exchanger does not imply selective permeability of an ion through the membrane. As an ion interacts with the ion-exchanger in the membrane, the specific permeability of the membrane towards this ion can be extremely low.

Based on the above, a further factor for determining the specific selectivity of membranes was proposed [3]:

$$P_{Na}^{Me} = \frac{\bar{t}_{Me}}{\bar{t}_{Na}} \times \frac{C_{Na}}{C_{Me}}, \tag{6.2}$$

where:

t_{Me}/t_{Na} is the ratio of the transfer numbers of the relevant ions through the membrane.

The latter factor, based on transfer numbers, more accurately describes the processes in ion-exchange membranes, and allows one to compare the transfer of differently charged ions through the membrane. In order to use this factor in laboratory practice, it is usually the ratio of current efficiencies for differently charged ions, instead of the transfer numbers, that is used. Use of this ratio is more appropriate to the conditions of the electrodialysis process. The current efficiencies are determined by an analytical method involving the concentrations of ions being transferred through the membrane, for a defined time interval and at a specific current density. As the ratio of the concentrations of the various ions is used when calculating the P_{Na}^{Me} coefficient, it is convenient to conduct a comparative estimation of the permselectivity of the membranes at the same ratio of concentrations for monovalent and divalent ions. To estimate the permselectivity of a membrane during the electrodialysis of a solution containing NaCl and $CaCl_2$, the concentration of each species is 0.1 M [3]. In such a case the expression used for determining the coefficient acquires the following form:

$$P_{Na}^{Me} = \frac{\eta_{Me}}{\eta_{Na}}. \qquad (6.3)$$

Solutions of 0.1 M NaCl and 0.1 M Na_2SO_4 are used when determining the permselectivity of Cl^- and SO_4^{2-} ions through an anion-transfer membrane.

6.2. EXPERIMENTAL

A five-compartment electrodialysis apparatus, with platinum electrodes (surface area 4 cm^2), was used for determining the current efficiency of ions being transferred through cation and anion transfer membranes (see Figure 6.1). Solutions of 0.1 M NaCl and 0.1 M $MgSO_4$ were supplied to the central cell of the apparatus at a velocity of 1.0 $cm \cdot s^{-1}$. A 0.2 M KNO_3 solution was circulated through the electrode compartments at a velocity of 2.0 $cm \cdot s^{-1}$. A 0.05 M KNO_3 solution was supplied to the concentrate compartments at a velocity of 0.1 $cm \cdot s^{-1}$.

The apparatus was assembled, the compartments filled with their respective solutions and electrical current applied. Preliminary polarisation of the membranes was carried out until steady-state conditions of electrodialysis were achieved. The time necessary to establish steady-state conditions is determined by the time required for formation of the concentration profile in the membrane, and is dependant on current density, membrane thickness, and membrane permeability towards ions. This was determined during preliminary experiments. When using Ionics membranes and a current density of 3 $mA \cdot cm^{-2}$, the time required to establish steady state conditions or a stationary mode was 40 minutes. For MA-100 and MK-100 membranes the time was 1.5 h. Based on this finding, the time for the preliminary treatment of the membranes was standardised to 1.5 hours, in order to ensure reproducibility of the results. The time chosen was more than twice the amount of time necessary to attain steady state conditions.

After the stationary condition was reached, the supply of power to the cell was interrupted. The concentrate cells were filled with 50 cm^3 0.05 M KNO_3 solution and the power was returned to the cells. After an hour the process was terminated, the power interrupted and the solutions drained from the cell. The concentrations of Na^+

and Mg^{2+} ions in the concentrate and the concentrations of Cl^- and SO_4^{2-} in these compartments were determined. Each experiment was repeated in triplicate. The mean value was determined and used as the final experimental result.

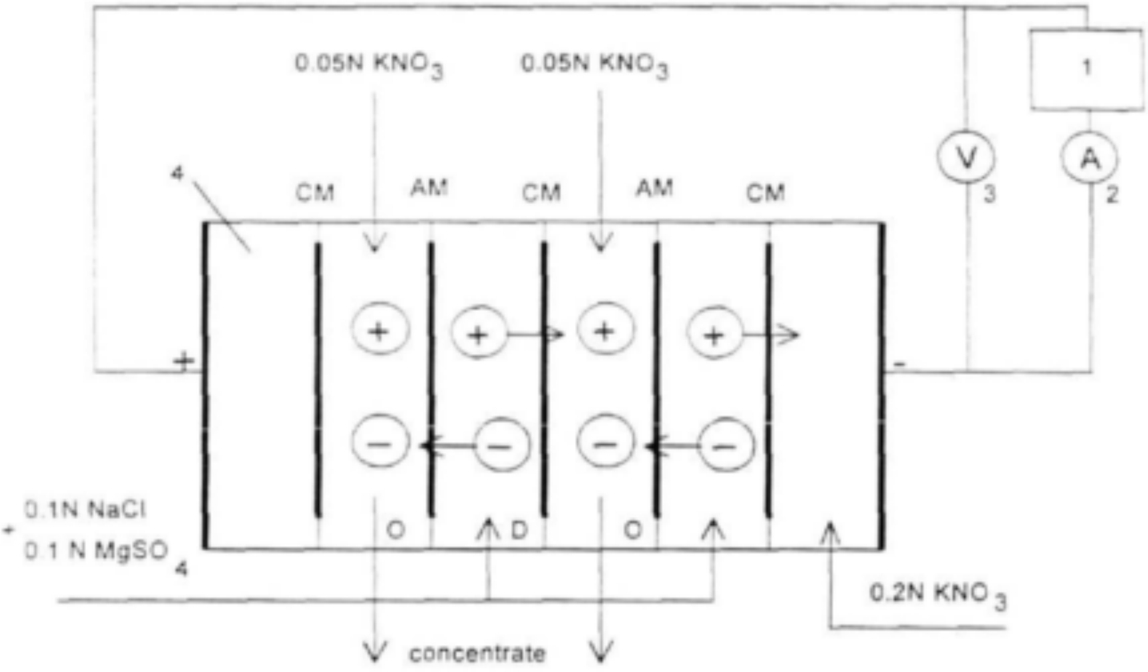


Figure 6.1: Apparatus used to study current efficiency.

1 - power supply, 2 - ammeter, 3 - high ohmic voltmeter, 4 - the six cell electrodialysis membrane stack, O - concentrate cells, D - demineralising cells, AM - anion transfer membranes and CM - cation transfer membranes.

The analysis of Na^+ ions was conducted by flame photometry, using a Flame Liquid Analyser PAZh-2. The accuracy of measurements was 2 ± 0.1 mg · l^{-1}.

The concentration of Mg^{2+} ions was determined by a complexometric titration, using Eriochrome Black T indicator in an ammonia buffer solution. The accuracy of measurement was 2 ± 0.2 mg·l^{-1}.

Analysis of the content of Cl^- ions was conducted by an argentometric method, and the accuracy of the analysis was 1 ± 0.1 mg·l^{-1}.

The content of SO_4^{2-} ions was determined by a complexometric method of reverse titration with excess $BaCl_2$; sulphate remained after bonding of the ions. The accuracy of measurement was 3 ± 0.1 mg·l^{-1}.

The concentrations of the ions in the concentrate cells were used to calculate the current efficiency, according to the formula:

$$\eta_{i\pm} = \frac{q_{ir}}{q_{theor}}, \tag{6.4}$$

where:

q_{theor}: the theoretically calculated value of current efficiency which, according to Faraday's law, under the applied experimental conditions was 0.45 mg-eq;

q_{tr}: the experimentally determined concentration of ions (mg-eq), transferred into the 50 ml volume during 1 h.

The factors P_{Na}^{Mg} for cation-transfer membranes and $P_{Cl}^{SO_4}$ for anion-transfer membranes were calculated and the permselectivity estimated.

The current density selected and applied during the experiments was chosen as Grebenyuk [51] had found that most membranes are permselective toward monovalent ions at a current density of 0.3 i_{lim}. When the current density exceeds this value then the relative transfer of divalent ions is increased, whereas the transfer of monovalent ions decreases [30]. Voltammetric curves were used to determine the limiting current density. The voltammetric data, necessary to determine the operating density of the polarising current, was measured between the electrodes of the electrodialysis apparatus. As a more concentrated 0.2 M KNO_3 solution was circulated through the electrode cells at a high velocity of 2 $cm \cdot s^{-1}$, it was assumed that the voltage drop over the membranes adjacent to the electrodes was insignificant, and would essentially not change the shape of the voltammetric curve. Taking into account that the velocity of the solution through the demineralising cell was much lower at 1.0 $cm \cdot s^{-1}$, it was possible to assume that the shape of the curve was determined by the voltammetric phenomena of membranes surrounding this cell. Based on the above, it was decided that optimal current density at a flow rate of 1 $cm.s^{-1}$ was 3.0 $mA.cm^{-2}$.

6.3. RESULTS AND DISCUSSION

The results of experimentally determined current efficiencies for Na^+, Mg^{2+}, Cl^- and SO_4^{2-} ions (η_{Na}, η_{Mg}, η_{Cl} and η_{SO_4}) and the values calculated for specific selectivities (P_{Mg}^{Na} and $P_{SO_4}^{Cl}$) are presented in Table 6.1

The initial tests for determining membrane-specific selectivities were conducted in SIMW, in which the cations and anions were present in the following ratio:

$$Na^+:Mg^{2+} = 9:1$$

$$Cl^-:SO_4^{2-} = 1:2.$$

The data in Table 6.1 shows that in the case of the unmodified (initial) Ionics membrane the current efficiency for Na^+ ions is good, reaching 88%. This is because there is an excess concentration of Na^+ cations in the solution. The specific selectivity coefficient P_{Mg}^{Na} is 1.12, indicating selectivity of the membrane towards the magnesium ion. Since the concentration of chlorides in SIMW is half that of sulphates, while the current efficiency for these ions is higher, the calculated value of $P_{SO_4}^{Cl}$ = 0.33 indicates the selectivity of the initial Ionics anion transfer membrane towards Cl^- ions.

The modification of membranes with MF581C solution, by passing 50 $mg.l^{-1}$ MF581C solution through the demineralising cell for 0.5 hours, results in an increase in the transfer of monovalent ions through the membrane. The current efficiency for Na^+ ions increases to 93 % and for Cl^- ions to 70%. The values of the specific selectivity coefficients indicate that modification of anion-transfer membranes results in an increase in selectivity toward Cl^- ions. Modification of cation-transfer membranes results in an increase in selectivity towards Na+ ions. From the tabled data it also follows that the membranes modified by MF581C show no changes in properties after electrodialysis for 20 hours.

Table 6.1: The specific selectivities of membranes modified by various polyelectrolytes.

Feed Solution	Membrane*	η_{Na}	η_{Mg}	P_{Mg}^{Na}	η_{Cl}	η_{SO_4}	$P_{SO_4}^{Cl}$
NaCl *	I	0.63	0.36	0.57	0.46	0.53	1.15
$MgSO_4$	$I_{\text{NB-8-500-6}}$	0.38	0.60	1.58	0.45	0.54	1.20
	$I_{\text{CMC-50-0}}$	0.60	0.38	0.63	0.40	0.58	1.45
	$I_{\text{CMC-50-0}}$	0.64	0.30	0.56	0.30	0.68	2.26
	$I_{\text{LT-22-100-6}}$	0.62	0.36	0.58	0.56	0.43	0.77
	$I_{\text{LT-27-100}}$	0.78	0.20	0.26	0.55	0.44	0.80
	$I_{\text{LT-27-10}}$	0.68	0.30	0.44	0.55	0.44	0.80
	$I_{\text{LT-27-10-6}}$	0.78	0.20	0.58	0.56	0.43	0.77
	$I_{\text{573C-100-6}}$	0.60	0.38	0.63	0.40	0.58	1.45
	$I_{\text{581C-10-6}}$	0.77	0.23	0.30	0.50	0.48	0.96
	As above, but after current reversal (0.5 min)	0.66	0.33	0.50	0.48	0.50	1.04
	$I_{\text{LT-27-K}}$	0.78	0.20	0.58	0.56	0.43	0.77
SIMW	I	0.88	0.11	1.12	0.64	0.43	0.33
	$I_{\text{581C-50}}$	0.93	0.06	0.06	0.70	0.30	0.21
	As above, but after 20 days in operation	0.92	0.06	0.06	0.70	0.30	0.21

*See Section 4.4.2

The results obtained indicate that, as a result of modification, the decrease in Mg^{2+} ion transfer through the membrane can be so great that the concentration remaining to be analysed is lower than the detection limit of the analytical method. It was therefore decided to discontinue the use of SIMW for the determination of the specific selectivity of membranes. Instead, solutions with equivalent concentrations of sodium and magnesium salts were used for the further testing of modified membranes.

As can be seen from Table 6.1 the specific selectivity coefficients of unmodified Ionics membranes vary, for example P_{Mg}^{Na} = 0.57 and $P_{SO_4}^{Cl}$ = 1.15. In a given solution the initial membranes are characterised by selectivity towards Na^+ and SO_4^{2-} ions. Modification of the membranes under dynamic conditions with 500 $mg{\cdot}l^{-1}$ NB-8 solution, at a current density of 6 mA·cm^{-2}, results in a decrease in Na$^+$ ion transfer (the current efficiency decreases from 0.63 to 0.38) and an increase in membrane selectivity towards Mg^{2+} (P_{Mg}^{Na} increases from 1.15 to 1.58). The influence of NB-8 on the cation-transfer membrane is related to the fact that sorption of NB-8 occurs by a hydrophobic mechanism, resulting in an increase in negative charge on the membrane surface. Increasing the charge density of a cation-transfer membrane results in an increase in selectivity towards divalent cations. Thus, chloride and sulphate ion transfers remains practically constant. It is therefore possible to conclude that the direct treatment of Ionics membranes with NB-8 in the electrodialysis apparatus leads to practically no change in the selectivity of the anion-transfer membrane, but lowers the permeability of the cation-transfer membrane towards Na$^+$ ions. This is undesirable, especially for the desalination of water with a high total-hardness value.

Results of tests to determine the specific selectivity of membranes modified by other polyelectrolytes under dynamic conditions show that all modifications result in changes in membrane permeability. In all cases the cation-transfer membrane maintains selectivity toward Na$^+$ ions. The influence of membrane modification on selectivity towards anions varies. In certain cases, eg. membranes modified by CMCell and MF 573C, an increase in permselectivity toward divalent ions is observed. The modification of membranes by other polyelectrolytes, eg. LT-27 and MF 581C, results in an increase in specific selectivity towards Cl$^-$ ions. Results show that the highest values for the specific selectivity of cation-transfer membranes are found for membranes modified with LT-27 and MF 581C.

Results of long-term tests carried out to determine the effect of membrane modification on specific selectivity showed that the modifying layer formed by the polyelectrolyte has a reasonably high stability. After twenty days of continuous operation of the electrodialysis apparatus containing modified membranes there were no appreciable changes in specific selectivity. Due to time constraints, longer testing of modified membranes was not conducted.

The durability of the polyelectrolyte layer on the membrane surface is increased by applying an electrical field during membrane modification under dynamic conditions. This, however, does not exclude the necessity to search for still newer methods by which to coat the polyelectrolytes, to increase the 'adherence' of the modifying polyelectrolyte to the membrane surface. The results of a comparative evaluation of Ionics membrane permselectivities are shown in the Table 6.1. The membrane designated as $I_{LT\text{-}27\text{-}K}$ was modified by coating with an adhesive-based polyelectrolyte layer.

The volt-ampere characteristics of several membranes modified by passing the modifier solution through the demineralising cell of the electrodialysis apparatus were measured. These measurements were conducted directly in the apparatus, by measuring the voltage drop between the electrodes. The graphs obtained have been shown in Figure 5.6 (section 5). The data shows that modification of membranes under dynamic conditions slightly alters the shape of the curve. In particular, a reduction of the limiting current is observed. This phenomena is quite possibly not connected to the change in resistance of the modified membrane in comparison with the unmodified membrane, but rather with the formation of a bipolar interface on the surface of the membrane and the deposited layer of polyelectrolyte.

6.4 CONCLUSIONS

Comparative evaluations of the influence of a number of modifying polyelectrolytes on the specific selectivities of Ionics cation- and anion- transfer membranes have shown that:

- The processing or modification of membranes under dynamic conditions, by passing the electrolyte solution through the demineralising cell of the electrodialysis apparatus whilst applying electrical current, influences the relative transfer of mono- and divalent ions through the membrane;
- The application of NB-8, a most effective modifying agents for protecting anion transfer membranes against fouling, has practically no influence on the transfer of Cl^- and SO_4^{2-} ions through the anion-transfer membrane. However, the permeability of divalent Mg^{2+} ions, in comparison to Na^+ ions, increases through the cation-transfer membrane. NB-8 modified membranes can therefore be effectively used for water softening by electrodialysis;
- The modification of membranes by LT-27 polyelectrolyte increases their permeability towards monovalent ions e.g. Cl^- through the anion-transfer membrane, and Na^+ ions through the cation-transfer membrane. Taking into account the rather high protection efficiency of this reagent, it is possible to use it for modification of membranes intended for use in the electrodialysis of highly concentrated solutions with high total-hardness values;
- Magnifloc 581C is also an effective modifier; this modifier significantly raises the specific selectivity of cation-transfer membranes in relation to monovalent ions and, to a lesser degree, of anion-transfer membranes;
- The method of depositing layers of polyelectrolyte from organic solvents onto a membrane surface using adhesives appears promising. Such a layer is stable under the applied conditions of flow, as well as current reversal.

7. COMPARATIVE STUDY OF THE ELECTROCHEMICAL CHARACTERISTICS OF SELECTED ION-EXCHANGE MEMBRANES

7.1. COMPARATIVE STUDY OF THE ELECTROCHEMICAL CHARACTERISTICS OF IONICS AND NEOSEPTA CATION MEMBRANES

In accordance with a request by Eskom, a comparative study of the electrochemical characteristics of the Ionics and Neosepta CMS (produced in Tokuyama Soda Co, Japan) membranes was conducted.

As mentioned earlier (section 4), the most objective comparison between the characteristics of various membranes may be obtained from measurement of their volt-ampere curves under identical conditions. In addition, transport characteristics in a solution consisting of equivalent concentrations of NaCl and Mg_2SO_4 salts (total salt concentration in solution is 0.2 M) provides important information pertaining to the properties of membranes.

The technique used to measure volt-ampere curves on the test installation was similar to the procedure described in Section 4 but now only cation-transfer membranes were mounted in the electrodialysis apparatus, in order to minimise concentration changes in the cells of the electrodialysis. The standard Ionics cation-transfer membranes were used as counter membranes. Two specific solution flow velocities, 0.1 and 1 cm·s^{-1}, were utilised during testing of the membranes. The most distinct volt-ampere effects on membranes can be achieved at a solution flow velocity of 0.1 cm.s^{-1}. Further, the optimum solution flow velocity for the evaluation of the specific selectivities of membranes is 1 cm·s^{-1}.

The volt-ampere curves, given in Figure 7.1, were obtained for the Ionics and Neosepta membranes at various solution-flow velocities. For the Ionics membrane, a plateau (deviation) in the curve, corresponding to the limiting current, was observed at both flow velocities. In the case of the Neosepta membrane, a deviation is observed only at a solution velocity of 0.1 cm·s^{-1}. At a solution flow velocity of 1cm·s^{-1} a smooth inclination in the volt-ampere curve was observed at a current density greater than 9 mA·cm^{-2}. This form of volt-ampere curve is characteristic for membranes with a very smooth and consistent surface. Due to the smooth surface the friction of the solution around the membrane decreases and solution convection at the membrane interface is improved. This promotes reduction in the thickness of the diffusion layer near the membrane surface. As a result, the general resistance of the system, and the voltage drop across the electrodialysis cell, is reduced.

Based on these results, an important conclusion may be derived. At a sufficiently high solution velocity the Neosepta membrane is an effective transport medium of the electrolyte over a wide range of current densities, the upper limit of which exceeds 10 mA·cm^{-2}. At reduced solution velocities, down to 0.1 cm·s^{-1}, the diffusion delivery of electrolyte becomes the limiting factor for the Neosepta membrane. This causes the distinct deviations in the volt-ampere curves at low solution velocities. It is known, however, that the feed solution velocities in industrial electrodialysis apparatus are very high. Thus, diffusion delivery of electrolyte may be disregarded as a limiting factor during industrial electrodialysis processes.

Deviations in the volt-ampere curves of the Ionics membrane were observed at both solution velocities. A smooth inclination in the volt-ampere curve of the Neosepta membrane was, however, seen at a solution velocity of 1 cm.s^{-1}. This indicates that the friction coefficient of the solution at the surface of the Ionics membrane is larger than at the surface of the Neosepta membrane. Nevertheless, the Ionics membrane may be considered to be sufficiently effective for use under industrial electrodialysis conditions, although it is slightly inferior to the Neosepta membrane.

The limiting current densities for the Ionics and Neosepta cation-transfer membranes at various solution-supply velocities, calculated from the volt-ampere curve values, are given in Table 7.1.

Table 7.1: Limiting current densities for Ionics and Neosepta cation-transfer membranes at various solution supply velocities

Membranes	Limiting current density(i_{lim}) mA·cm^{-2}	
	v=1.0 cm·s^{-1}	v=0.1 cm ·s^{-1}
Ionics	7.5	5.2
Neosepta	9.0	7.4

Based on volt-ampere data, values of membrane surface electrical resistance to applied direct current in a SIMW solution were calculated and compared with similar alternating current data obtained in a 0.6 M NaCl solution. Electrical resistance data for Ionics and Neosepta membranes is shown in Table 7.2.

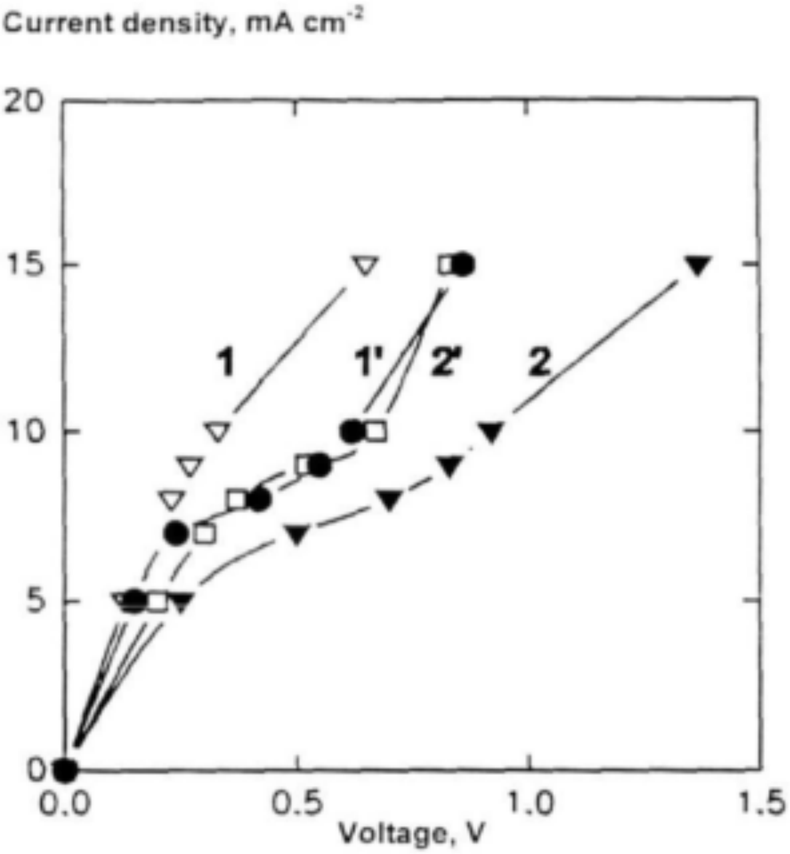


Figure 7.1: Volt-ampere characteristics of Neosepta (1) and Ionics (2) membranes in SIMW. Solution flow velocity 0.1 (1 & 2) and 1.0 (1' & 2') cm·s^{-1}.

Table 7.2: Electrical resistance (ρ) of Ionics and Neosepta membranes in SIMW and 6.0 M NaCl solutions, at various current densities (i) and solution flow velocities (v).

Membranes	Current density (i) mA·cm^{-2}	Electrical resistance (ρ) (direct) Ohm·cm^{-2}		ρ≈, (alternating) Ohm·cm^{-2}
		SIMW		0.6 M NaCl
		v=1.0 cm·s^{-1}	v=0.1 cm·s^{-1}	
Ionics	5	40	50	25.8
	10	67	91	
Neosepta	5	26	32	25.4
	10	32	62	

There is practically no difference in the resistances of the Ionics and Neosepta membranes to alternating current. The resistance values of both membranes to direct current are dependent on the current density and the solution velocity. Resistance values of the Neosepta membrane to direct current were found, however, to be 1.5 - 2 times lower than those of the Ionics membrane.

The final comparative test between the Ionics and Neosepta membranes was the determination of their relative specific selectivities toward Na^+ and Mg^{2+} cations. The main specific permeability characteristics of the Ionics cation-transfer membranes were given previously, in Table 6.1. Thus, only information pertaining to the characteristics of the Neosepta membrane is given here in Table 7.3.

Table 7.3: The current efficiencies for Na^+ (η_{Na}) and Mg^{2+} (η_{Mg}) ions and selective permeability coefficient (P_{Mg}^{Na}) values for the Neosepta membrane, obtained at various current density (i) values

	Current density (i) mA·cm^{-2}					
	1	3	6	10	15	20
η_{Na}	1.00	0.97	0.99	0.98	0.95	0.90
η_{Mg}	0	0.03	0.01	0.02	0.05	0.10
P_{Mg}^{Na}	0	0.03	0.01	0.02	0.05	0.10

Upon comparing selective permeability characteristics of the Neosepta and Ionics membranes it can be seen that the Neosepta membrane is characterised by exclusive selectivity to the single-charged Na^+ ions, and thus differs from the Ionics membrane. It should also be noted that the value of the current density has practically no influence on the selective permeability of the Neosepta membrane.

Results of the comparative tests conducted on the Ionics and Neosepta cation transfer membranes reveal that:

- The electrical resistances of the Ionics and Neosepta cation membranes to alternating current are practically identical. However, the resistance of the Ionics membranes to direct current exceeds that of the Neosepta membranes by 1.5 - 2 times.
- Limiting current density values for the Neosepta membranes are approximately 1.5 times greater than those for the Ionics membranes.
- The Neosepta cation membranes are practically impermeable to divalent cations.
- The Neosepta cation membranes display high efficiency during electrodialysis. They can be used at current densities of up to 10 mA·cm^{-2} and are ideally suited for the selective concentration of Na^+ salts from multicomponent solutions.

7.2. COMPARATIVE EVALUATION OF THE CHARACTERISTICS OF IONICS AND MA-100 ANION-TRANSFER MEMBRANES

In order to select the conditions for comparative determinations for the Ionics and MA-100 membranes (Russia), volt-ampere curves in SIMW were plotted for these membranes at a flow velocity of 0.1 $cm{\cdot}s^{-1}$. From this data, limiting current density values were calculated to be 5.5 $mA{\cdot}cm^{-2}$ for the Ionics membrane, and 5.0 $mA{\cdot}cm^{-2}$ for the MA-100 membrane.

Upon analysis of the volt-ampere curve for MA-100 (shown in Figure 7.2) it can be seen that the plateau, corresponding to the limiting current, is situated in the interval between 1 and 3 V. This type of curve indicates the high degree of non-uniformity of the surface of this type of membrane. Non-uniformity of the membrane surface causes 'extreme conditions' (a decrease in electrolyte concentration near to the membrane surface down to critical values) at relatively low potentials. For the Ionics membrane the plateau indicating the limiting current is expressed rather poorly (see Figure 7.3). In over-limiting current mode, a sharp increase in current is observed with respect to an insignificant increase in the applied voltage. This type of volt-ampere curve results from the surface layer features of the membrane structure. These features enhance electrodialysis in 'over-limiting mode' by means of convection promotion or heating. In Figure 7.3 it can be seen that the characteristics of the volt-ampere curves for the Ionics membrane vary insignificantly, even after electrodialysis at a current density of 4 $mA{\cdot}cm^{-2}$ in solutions containing 50 and 100 $mg{\cdot}l^{-1}$ DBS. However, a decrease in the limiting current from 5.5 to 5.0 $mA{\cdot}cm^{-2}$ is observed. Under similar conditions, namely during electrodialysis of solutions containing DBS, an increase in the interval of potentials, corresponding to the limiting current, is observed for the MA-100 membrane. Thus, the limiting current value is reduced to 4 $mA{\cdot}cm^{-2}$.

In order to characterise the polarisation of the MA-100 membrane in the presence of DBS the fluctuations in the voltage drop across the membrane must be noted (see Figures 7.4 and 7.5). This is particularly noticeable when the limiting current density is exceeded. As can be seen in Figures 7.4 and 7.5, treatment of the MA-100 membrane with 50 $mg{\cdot}l^{-1}$ and 1.0 $g{\cdot}l^{-1}$ NB-8 solution increases the resistance of the membrane to surfactants. However, lack of resistance of the layer near the surface of the membrane is maintained.

Fluctuations in the voltage drop across the membrane during electrodialysis indicate the deposition of surfactant layer on the membrane and its periodic removal by the tangential flow of solution through the cell. It should be noted that, for the given experimental conditions, the increase in the magnitude of the voltage drop across the membrane in the presence of DBS is limited. When the solution velocity, limited by the MA-100 and Ionics membranes to 0.05 $cm{\cdot}s^{-1}$, into the desalination cells is reduced then a sharp increase in the magnitude of the voltage drop begins to appear across the MA-100 membrane. A significant yet considerably smaller increase appears in the case of the Ionics membrane (Figures 7.6-7.9). This phenomenon was used to study the influence of current reversal on the electrodialysis process.

For the initial Ionics membrane the increase in current (in the presence of 100 $mg{\cdot}l^{-1}$ DBS, at a sufficiently low flow velocity of 0.2 $cm{\cdot}s^{-1}$, and a current density of 6.0 $mA{\cdot}cm^{-2}$) is caused by the deposition of the surfactant layer onto the membrane (see Figure 7.6). This conclusion is based on the fact that almost complete restoration of the initial voltage occurs after current reversal. Other important factors are that polarisation for a period of 15 minutes does not result in deep penetration of the surfactant into the membrane and the surfactant precipitated in the surface layer is easily removed during current reversal. The result of insignificant penetration of the surfactant into the membrane is a lack of deposition onto the membrane when the flow velocity is reduced (Figure 7.6b). The absolute voltage-drop values across the MA-100 membrane are significantly higher than across the Ionics membrane. The use of reverse mode, however, results in no voltage increase across the membrane.

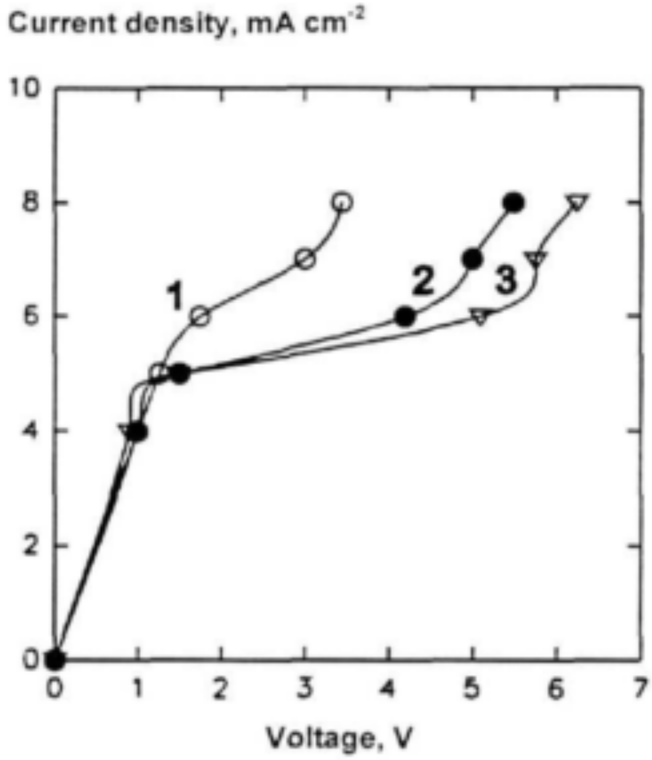


Figure 7.2: Volt-ampere characteristics of MA-100 membranes before (1) and after 4h electrodialysis of SIMW containing 50 (2) and 100 (3) mg·l^{-1} DBS.

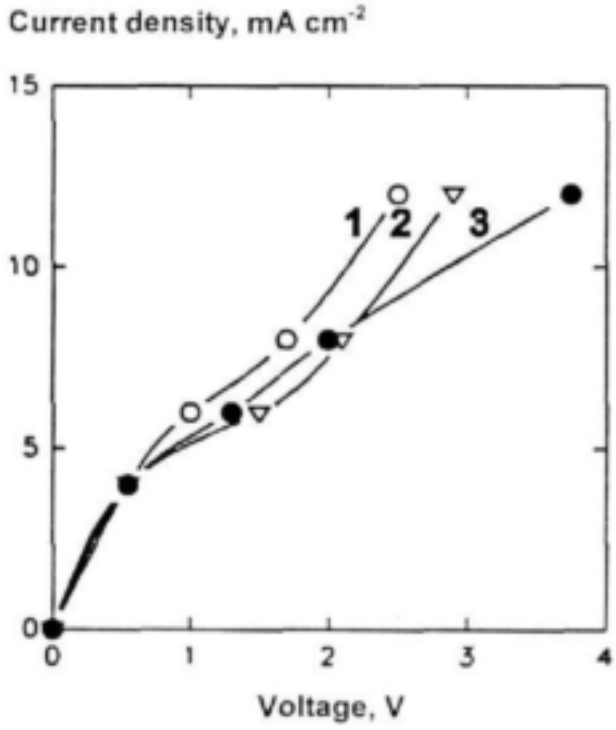


Figure 7.3: Volt-ampere characteristics of Ionics membranes before (1) and after 4 h electrodialysis of SIMW containing 50 (2) and 100 (3) mg·l^{-1} DBS.

At the time that these studies were conducted it did not seem necessary to study the resistance of the NB-8 layer on the Ionics membrane using a reverse current. After electrodialysis, in the mode of: 15 minutes direct polarisation and 15 minutes current reversal, for membranes modified with NB-8 solution (concentration of 50 and 500 $mg{\cdot}l^{-1}$) an increase in the magnitude of the voltage drop is practically absent (Figure 7.7). In the same mode, continuous testing of modified Ionics membranes was conducted for a period of 30 days. During these tests the conditions of the system remained practically unchanged. An increase in the voltage drop on the volt-ampere curve was absent. Longer tests were, however, not conducted. The results obtained confirm the stability of membranes surface-treated with NB-8 agent over a period of one month. Long term testing in an industrial apparatus is still to be done.

Thus, results of tests to compare the characteristics of Ionics and MA-100 anion transfer membranes revealed that:

- The better surface uniformity of the Ionics membrane, compared to the MA-100 membrane, allows for better convection of electrolyte along its surface and, accordingly, higher limiting current density values. The uniformity of the Ionics membrane surface also provides better resistance against fouling by DBS and HA.

- In the case of Ionics membranes, current reversal results in complete regeneration of the membrane, and restoration of the initial voltage drop across it. However, in the case of the MA-100 membrane, a gradual increase in the voltage drop, due to the irreversible adsorption of surfactants, is observed.

- It is possible to remove DBS from a membrane surface with a concentrated NaCl solution. This fact may be utilised to develop a method for defouling membranes. Since the choice of this salt was accidental, it may be possible to find more effective reagents for this purpose. (Note: it may be possible to use a mixture of NaCl and caustic soda [NaOH] for defouling of anion transfer membranes. Brine washing is utilised for cleaning of anion-exchange resins that are fouled with naturally occurring organics.)

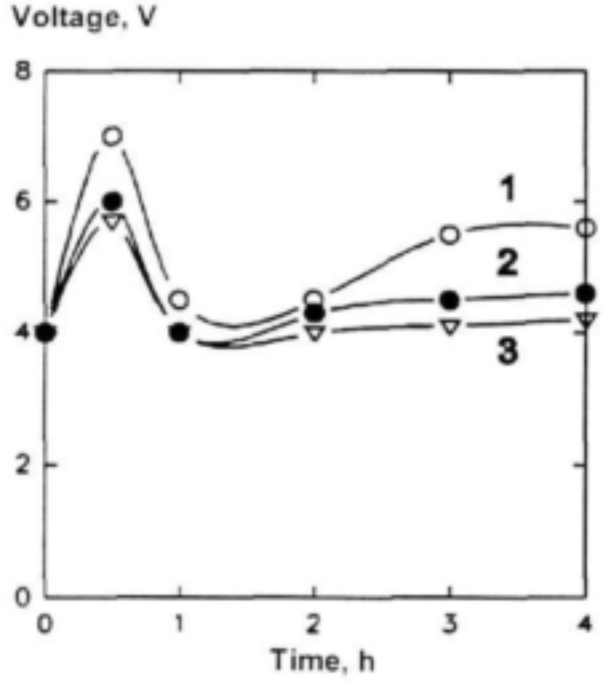


Figure 7.4: Chronopotentiometric characteristics of a standard MA-100 membrane (1), and membranes modified by 50.0 mg.l^{-1} (2) and 10.0 mg.l^{-1} (3) NB-8 solutions in SIMW containing 60.0 mg·l^{-1} DBS. Current density 3.0 mA·cm^{-2}.

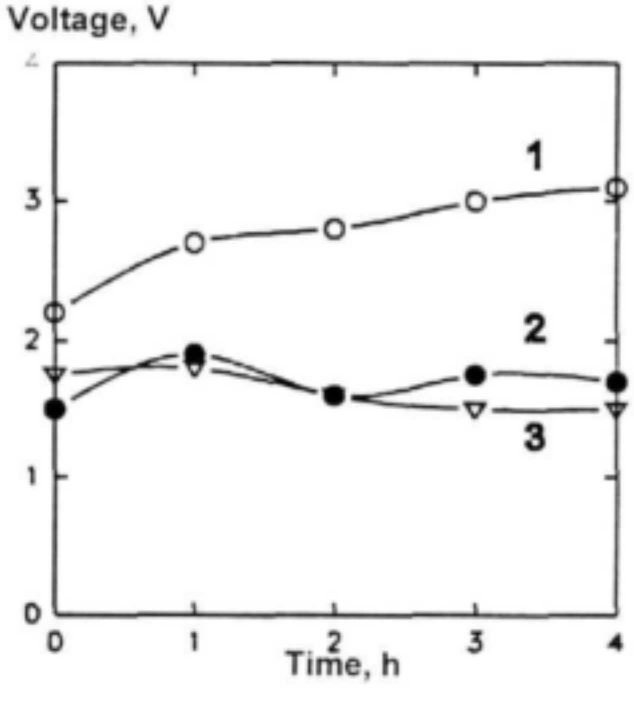


Figure 7.5: Chronopotentiometric characteristics of a standard MA-100 membrane (1), and membranes modified by 50.0 mg.l^{-1} (2) and 10.0 mg.l^{-1} (3) NB-8 solutions in SIMW containing 60.0 mg·l^{-1} DBS. Current density 6.0 mA·cm^{-2}.

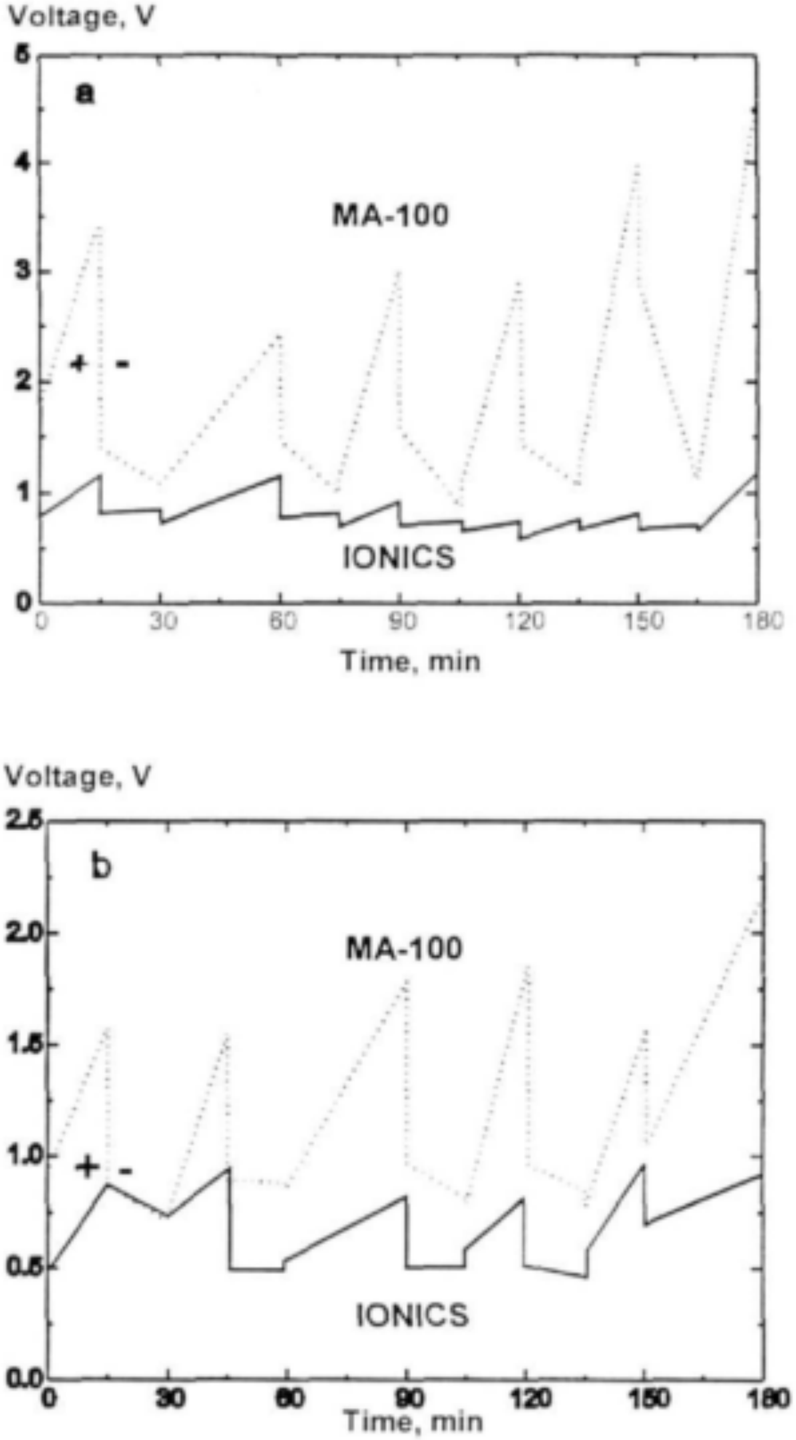
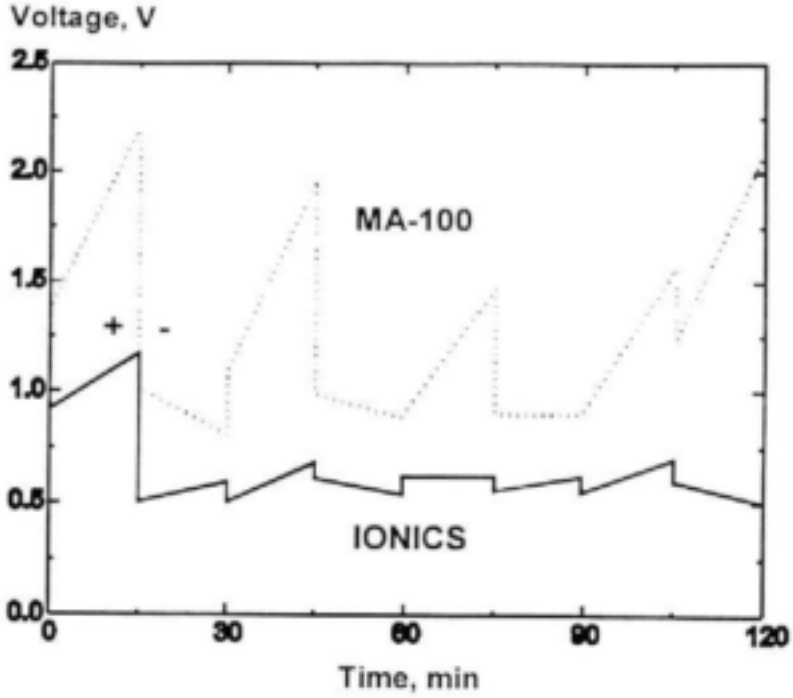


Figure 7.6: Chronopotentiometric characteristics of MA-100 and Ionics membranes during electrodialysis (+) and current reversal (-) in SIMW containing 100.0 mg·l^{-1} of DBS. Current density 6.0 mA·cm^{-2}. Solution current velocities: 0.2 (a) and 0.05 cm·s^{-1} (b).



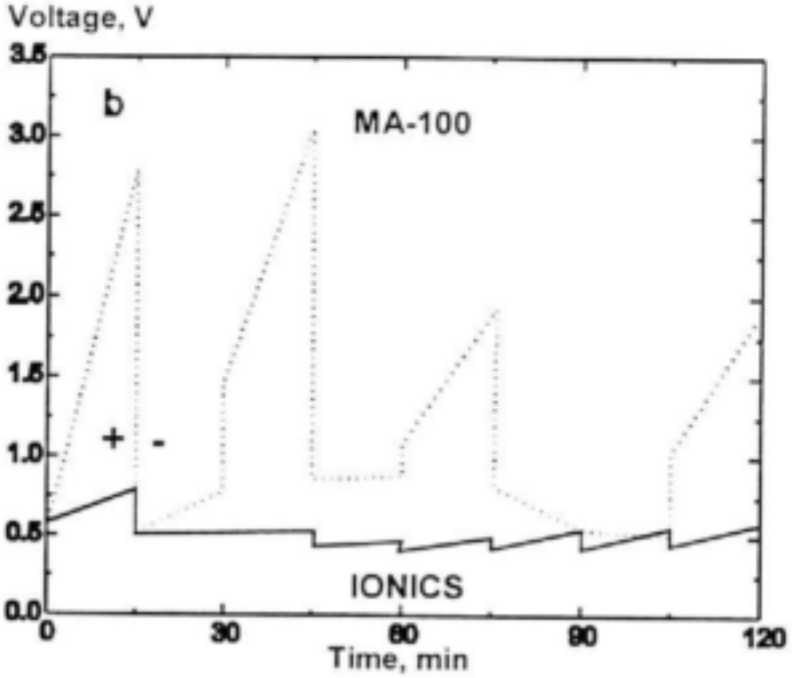


Figure 7.7: Chronopotentiometric characteristics of MA-100 and Ionics membranes modified by 50.0 (a) and 500 (b) mg·l^{-1} NB-8 solutions in SIMW containing 100.0 mg·l^{-1} of DBS. Current density 6.0 mA·cm^{-2}. Solution current velocity: 0.2 cm·s^{-1}.

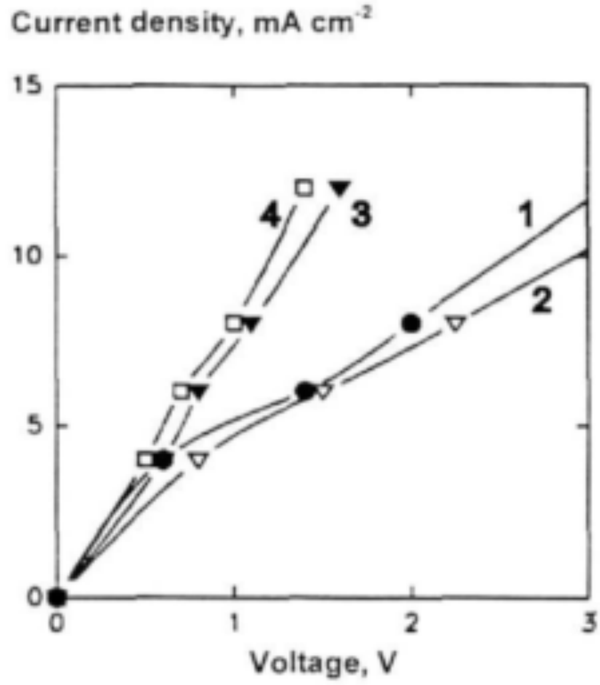


Figure 7.8: Volt-ampere characteristics of Ionics membranes modified by 500 mg·l^{-1} NB-8 solution before (1) and after (2) 4 hours electrodialysis of SIMW containing 50.0 mg·l^{-1} HA and after contact with the solution for 4 (3) and 7 days (4).

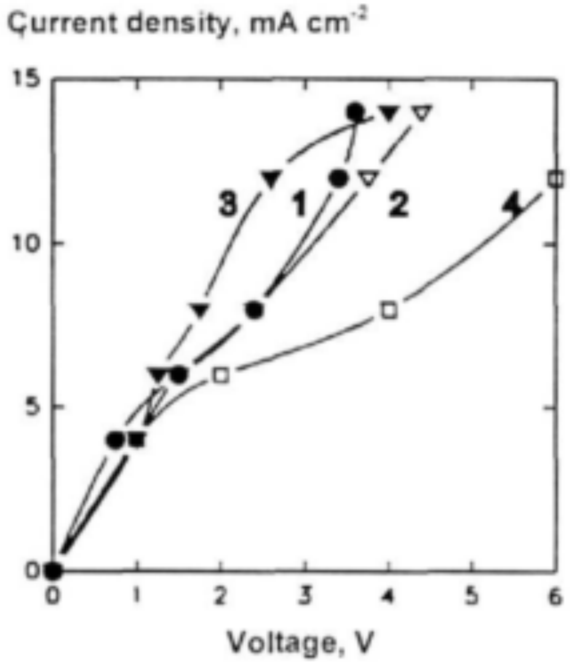


Figure 7.9: Volt-ampere characteristics of MA-100 membranes modified by 500 mg·l^{-1} NB-8 solution before (1) and after (2) 4 hours electrodialysis of SIMW containing 50.0 mg·l^{-1} HA and after contact with the solution for 4 (3) and 7 days (4).

8. USE OF A PULSING MODE OF ELECTRODIALYSIS FOR WATER DEMINERALISATION

8.1. INTRODUCTION

By using periodic current interruption or supply pulsing during electrodialysis it is possible to considerably reduce, or even prevent, the harmful effect of concentration polarisation. The interruption of current during electrodialysis has at least two major advantages over current reversal. Firstly, it is technically easier to execute than current reversal. Secondly, reverse-mode electrodialysis during current reversal, which results in a part of the demineralised water (dialysate) mixing with the concentrate, no longer occurs. Historically, difficulties associated with the design and development of membrane technologies were related to the effects of concentration polarisation [52]. The phenomenon of concentration polarisation occurs for all finite cell currents and involves salt depletions and enrichments in the membrane boundary layers. It includes all processes occurring in the layer near to the membrane surface, imposed by the electrical field. These processes include the demineralisation of electrolyte, fouling of the receiving side of the membrane by large particles and macromolecules, and the concentration of salts and formation of poorly-soluble precipitates on the recovery side of the membranes in the concentrate cells.

The major element of this struggle, that is the reduction of the negative influence of concentration polarisation on the efficiency of the separation process during electrodialysis, is the establishment of an optimum ratio between the polarising current density and the tangential flow velocity of liquid in the intermembrane spaces. One of the most effective methods by which to reduce precipitate formation on the membrane is the utilisation of a pulsing mode during the electrodialysis process [53 - 57]. Thus, with time, the mode of current pulsing reaches steady state conditions, necessary for the formation of concentration gradients of salts at the receiving and recovery sides of the membrane. This time is determined by the dynamic characteristics of the specific electrodialysis apparatus. It is also dependent on the concentration of precipitate-forming impurities and the density of the polarising current. Unfortunately, it is not possible to formulate a model of all of these parameters under laboratory conditions. It is known that the distribution of the solutions, flowing along the surface of the membranes, is dependent on the length and form of the intermembrane intervals. This is determined by the design of the electrodialysis apparatus. If optimisation of the current pulsing mode of electrodialysis was conducted in a test apparatus under laboratory conditions then the same conditions may not be best for electrolysis in an industrial electrodialysis apparatus.

There is a further condition that must be considered when determining the parameters for the achievement of electrodialysis in the pulsing mode. It is possible that the time required to form deposits of weakly soluble salts, or to achieve saturation concentrations of $CaSO_4$, $MgCO_3$ and other salts at the recovery surface of the membrane, will not correspond to the time and conditions for the deposition of organic substances on the receiving surface. Therefore, the parameters of the pulsing mode of electrodialysis, used to reduce scaling or to prevent deposition of organics onto the membrane surface, should be different.

Inferometry has shown that for 0.05 - 0.1 M Na_2SO_4 solutions at a current density of 100-400 $mA{\cdot}cm^{-2}$ and flow velocity of 0.5-4.0 $cm{\cdot}s^{-1}$, the concentration of the solution at the recovery surface of the membrane reaches a limiting value 15-20 minutes after the time of current application [54, 57].

Approximately the same time period is necessary for the concentration of electrolyte in the diffusion layer to reach equilibrium with that of the electrolyte outside this layer, by means of diffusion when no current is applied. Due to the low mobility of large organic anions the time required to remove the surfactant layer formed on the surface of the membrane is significantly (approximately 5 minutes) [58]. It is also known that the optimum pause-duration between current pulses should not exceed 1/4 of the current supply-duration when operating in the pulsing mode [54]. Information gained from literature provides a basis for the experimental determination of optimum pulse duration and periodicity during development of the pulsing electrodialysis process.

In the present work the use of a pulsing DC potential (by current interruption) during electrodialysis, for reducing the negative impact of organic substances on anion membranes, was investigated. A solution to the problem of precipitate formation in the concentrate cells by utilising pulsing mode electrodialysis was, however, not provided - it was considered beyond the objectives of the present project.

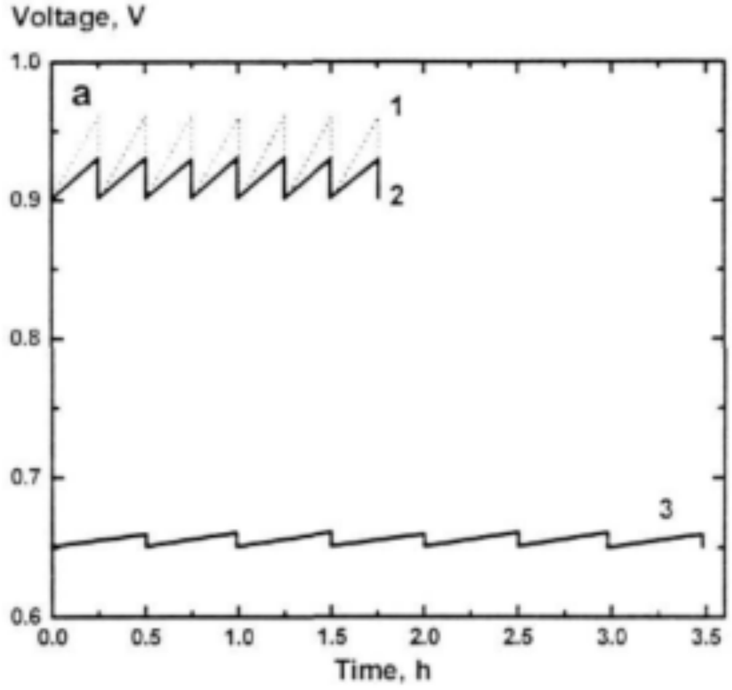
8.2. EXPERIMENTAL

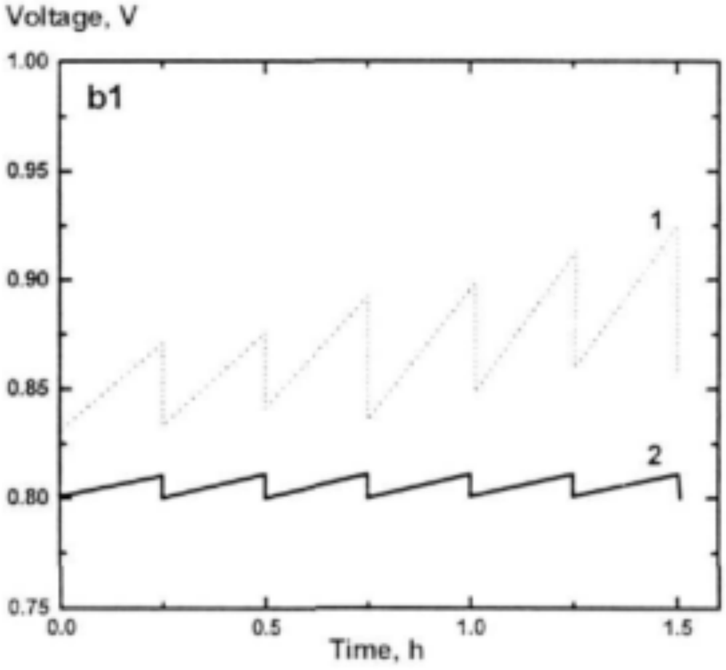
An electrodialysis apparatus consisting of 6 cells (shown in Figure 4.1 and described in Section 4.2) was used to study electrodialysis processes in the current reversal and pulsing modes. The supply of solutions to the electrodialysis apparatus used differed from that in Figure 4.1. 0.05 M Na_2SO_4 solution was supplied to electrode cells1and 6 at a velocity of $1 cm.s^{-1}$. The SIMW was supplied, at an equivalent velocity, into concentrate cells 2 and 4. The SIMW, containing DBS at a concentration 50 $mg{\cdot}l^{-1}$, was passed through demineralising cells 3 and 5 at a velocity of 0.01 $cm{\cdot}s^{-1}$. Polarising current was supplied to the electrodialysis apparatus at a density of 10 $mA{\cdot}cm^{-2}$. The pause duration between current supply was set at 1 and 3 minutes.

8.3. RESULTS AND DISCUSSION

The low solution velocity in the demineralisation cells and the high current density were selected because it was necessary to monitor deposit formation on the membranes. The thickness of the deposit layer, formed in the layer near to the surface of the membrane, should be approximately 0.5 mm under these conditions [58]. That is, the layer of liquid that is not removed by solution flow comes into close proximity to the measuring capillaries. These conditions do not coincide with typical electrodialysis conditions. However, the selected experimental conditions enabled observation of the formation and removal of deposits over short time intervals of 15 - 30 minutes (see Figure 8.1). During preliminary experiments it was found that a layer of organic substances could not be deposited over a short time interval at higher flow velocities and with a foulant concentration of less than 50 $mg{\cdot}l^{-1}$. The influence of a pulsing current supply on the process of membrane fouling was evaluated from the chronopotentiometric data, according to the change in the voltage drop across the membranes.

In Figure 8.1 it can be seen that the increase in voltage drop across the Ionics membrane, after polarisation for 15 minutes, was insignificant (value of 10 ± 5 mV). Therefore in order to increase the effect of fouling substances on the membrane the polarisation time was increased to 30 minutes before current interruption. The measurement of membrane characteristics after 7 hours in a pulse mode of 30 minutes polarisation and 3 minutes current interruption showed that the voltage drop across the membrane remained constant and equivalent to the initial value, for the duration of the procedure. The effect of current pulsing on the electrochemical characteristics of membranes is clearly demonstrated with MA-100 membranes which are more susceptible to fouling by organic substances than the Ionics anion-transfer membrane (Figure 8.1). The sharp increase in voltage drop, which corresponds to the formation of a deposit layer on the membrane surface during a 15 minute polarisation cycle, is characteristic of this membrane. A 3-minute current interruption results in almost complete removal of the deposit layer.





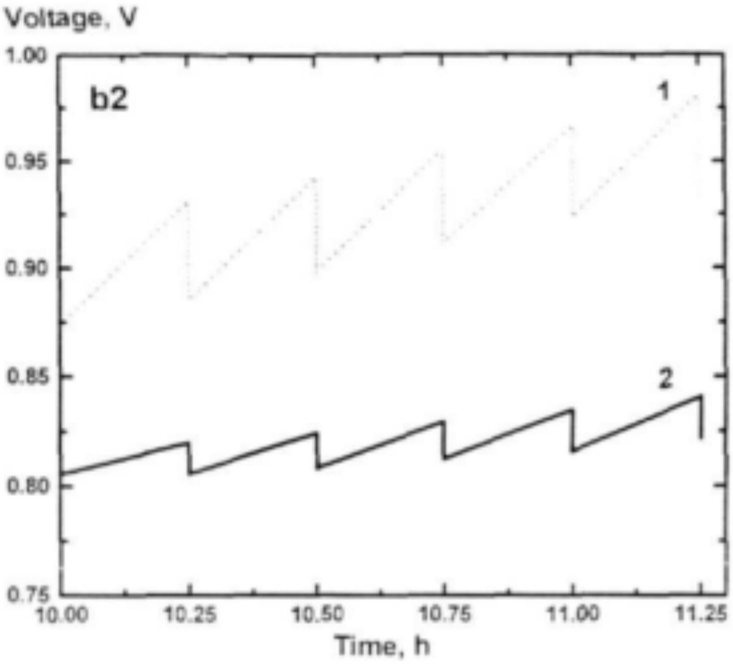


Figure 8.1: Potential drop across MA-100 (1) and Ionics (2, 3) anion membranes during 15 (1, 2) and 30 (3) minutes polarisation in SIMW with 3 (a) and 1 (b 1 and 2) minute current interruptions. Current density 10.0 mA·cm^{-2}.

In order to increase the efficiency of the electrodialysis process an attempt was made to reduce the interruption of current supply to 1 minute. This pause duration appeared, however, to be insufficient for the complete removal of the deposit. As a result a gradual deposit accumulation on the surface of the membrane (Figure 8.1 b) was observed.

Data pertaining to the increase in electrical resistance of the membranes to alternating current is given in Table 8.1. This data describes the process of membrane fouling by organic substances over a period of 15 hours, using a pulse mode of 30 minutes polarisation and 1 minute current interruption. Information pertaining to the influence on the electrical resistance values of membranes after current reversal for a period of 1 hour and chemical regeneration (processing in 0.5 M NaCl solution for 7 hours) is also given.

Table 8.1: Electrical resistances of the Ionics and MA-100 membranes to alternating current before and after operation and regeneration

Membrane	Resistance, Ohm cm^{-2}			
	Initial	After 15 h run	After current reversal	After chemical regeneration
MA-100	3.5	12.5	10.1	3.5
Ionics	2.5	2.8	2.6	2.5

Results show that operation in the pulse mode of electrodialysis over a period of 15 hours results in an increase in the electrical resistance of the membranes. It indicates that the organic substances, accumulated on the surface of the membrane, are not completely removed during current pulses. Application of current reversal for a period of 1 hour, for electrodesorption of precipitated surfactants, results in the partial reduction of electrical resistance. However, initial resistance values are not reached.

Results of further experiments revealed that processing of fouled membranes in a 0.5 M NaCl for a period of 7 hours results in essentially the complete restoration of membrane properties and initial electrical resistance. The action of the NaCl solution is most clearly demonstrated when using MA-100 membranes, because a substantial change in the electrical resistance (due to fouling) occurs. The regenerating action of NaCl solution is probably related to the fact that expansion of the membrane pore volume occurs when the membrane is in contact with NaCl. This may enhance the diffusion of organic substances existing in the membrane volume. Ion exchange of organic anions present on the surface and in the volume of the membranes, for Cl^- anions, is also probable.

8.4. CONCLUSIONS

- In the study of the change in electrochemical characteristics of anion membranes in the pulsing electrodialysis mode it was shown that the use of current pulsing to minimise membrane fouling resulted in reduction of electrical resistance of the membranes, the effect comparable to that of chemical regeneration.
- In the case of the Ionics membranes, optimum conditions of pulsing electrodialysis were determined to be: polarisation for a period of 15 minutes and current interruption for 3 minutes.
- An effective method for regenerating the above membranes that are fouled with organics is by processing in NaCl solutions.

Only preliminary experiments on the chemical regeneration of membranes with NaCl solution were conducted. Further studies should be conducted in the future. In particular, the influences of salt solution concentrations, and the processing time on the degree of regeneration, require investigation. In addition, it may be possible to find more effective salts, or mixtures of salts, for this purpose. The development of an effective and economically justified method for the chemical regeneration of fouled membranes would be of great benefit to industry.

9. APPLYING ANODIC OXIDATION TO ORGANIC COMPONENTS TO REDUCE THEIR EFFECT ON ION-EXCHANGE MEMBRANES

9.1. INTRODUCTION

The electrochemical oxidation of organic compounds is well documented and widely applied in practice [59]. For example, alcohols and aldehydes in contact with an anode can be oxidised to carbonic acids and CO_2. Galvanocoagulation is a method used to remove organic substances from natural waters. This method combines the principle of anodic oxidation of organics with coagulation of dissolved by-products formed at the anode [60]. The possible use of anodic oxidation for removing a number of organic compounds, such as alcohols, aldehydes, ethers and carbonic acids has been investigated [61-63]. Anodic oxidation products are usually deposited onto the membrane in the anode cell, or are transferred into the concentrate cell of the electrolysis apparatus. Removal efficiencies as high as 100 % for carbonic acids and amines, and 55 - 60 % for lower ethers and aldehydes, have been achieved by this method.

9.2. EXPERIMENTAL

An experimental electrodialysis installation as described in Section 4 and Figure 4.1 was used. The following three Ionics anion-transfer test membranes were mounted into the installation:

AM_1 – unmodified Ionics membrane,

AM_2 – Ionics membrane modified with 50 $mg{\cdot}l^{-1}$ NB-8 solution, and

AM_3 – Ionics membrane modified with 500 $mg{\cdot}l^{-1}$ NB-8 solution.

Membrane treatment was carried out using the static method. An imitation mine water solution (SIMW) was supplied to all cells of the electrodialysis apparatus at a velocity of 1.0 $cm{\cdot}s^{-1}$. HA and DBS were added to the SIMW solution as membrane foulants. Membrane polarisation was conducted at various current densities, namely 3.0, 6.0 and 10.0 $mA{\cdot}cm^{-2}$.

Evaluation of the influence of organic substances on the electrodialysis process, in various modes of operation, was based on changes in voltage drop across the membrane. In order to increase oxidation efficiency a platinum-plated carbon catalyst [62] was inserted into the anode compartment of the electrodialysis cell. Enhancement of the oxidation process was indeed observed. However, destruction of the carbon during the process resulted in the release of small carbon particles into the water, and these precipitated onto the membranes. Naturally, this made the demineralisation process more complicated. The catalytic oxidation of organic substances during electrodialysis of water is, however, a new idea and should be further investigated.

During the study of the demineralisation process of SIMW containing saturated hydrocarbons no changes in the membranes' transport characteristics were observed (section 5). However, the addition of HA and DBS to SIMW resulted in the deterioration of membrane permeability, causing the electrical resistance of the membrane to increase. Thus, in order to reduce their negative impact on membrane permeability, the anodic oxidation of organic substances was investigated. This research was conducted in parallel with the development of modifying agents and techniques to effectively protect these membranes against organic fouling.

9.3. RESULTS AND DISCUSSION

The initial part of the work entailed a study of the influence of preliminary anodic oxidation on the electrochemical characteristics of the membranes, using SIMW containing organic additives. The SIMW was first supplied to the anodic cell, prior to all the consecutive cells of the electrodialysis apparatus. Since SIMW is acidified when passing through the anodic cell, the feed-solution velocity was increased to reduce the acid concentration. The current density selected for polarisation was below the limiting value.

In order to determine the limiting current density at a selected solution velocity of 1.0 $cm{\cdot}s^{-1}$ the volt-ampere characteristics of membranes in SIMW, and SIMW containing 100 $mg{\cdot}l^{-1}$ each of HA and DBS, were measured. High concentrations of organic additives were chosen because it was necessary to produce quantifiable volt-ampere changes in the system with high solution velocity. From Figure 9.1 it can be seen that the limiting current density for the pure SIMW-membrane-solution system is equal to 8.0 mA·cm^{-2}. With the addition of HA and DBS the values decreased to 6.5 and 6.0 mA·cm^{-2} respectively. Based on the results obtained, the operating current density values selected for the study were 3.0, 6.0 and 10.0 mA·cm^{-2}. The range of current density values selected included values equivalent to, and exceeding, the limiting current density.

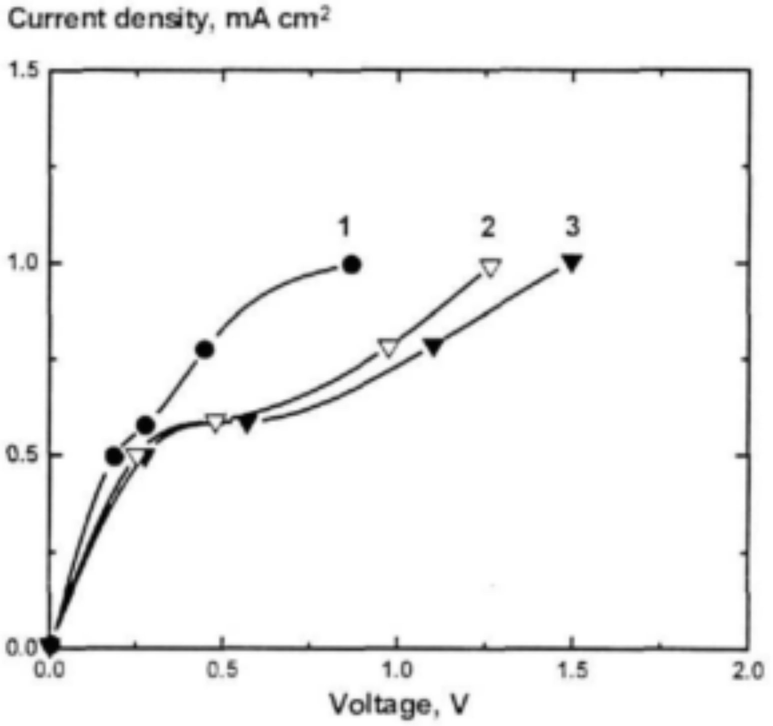


Figure 9.1: Volt-ampere characteristics of Ionics anion-transfer membrane in SIMW (1), and SIMW containing 100.0 mg·l^{-1} HA (2) and DBS (3) respectively.

The results shown in Figure 9.1 were obtained without pumping the solution through the anodic cell of the electrodialysis apparatus. The decrease in the limiting current density in the presence of substances which form a charged hydrogel layer on the receiving surface of the membrane appears to be caused by the formation of a bipolar layer at the interface between the positively charged membrane and the negatively charged modifying layer. The degree of dissociation of DBS's sulfo-groups was greater than that of HA's carboxyl groups, under the experimental conditions. More intensive electrolyte demineralisation therefore occurs beyond the membrane/DBS interface. This results in an increase in the electrical resistance of the solution-membrane-solution system, and a greater decrease in the limiting current.

Using the usual solution supply scheme (without flow through the anodic cells), at a solution flow velocity of 1 cm·s^{-1} and a current density of 6.0 mA·cm^{-2}, increases in the chronopotentiometric curves for modified membranes are less than for the initial membrane (see Figure 9.2). A more abrupt increase is observed in the chronopotentiometric curve in the presence of HA (Figure 9.2 a) than in the presence of DBS (Figure 9.2 b). From the curves in Figure 9.2 it can be seen that preliminary pumping of the solution through the anodic cell is accompanied by a reduction in the fouling effect of the organic substances.

It may be assumed that preliminary processing of electrolyte solutions in the anodic cell of the electrodialysis apparatus results in the destruction of organic substances present in them. This is indicated by the reduced inclination in the chronopotentiometric curve (Figure 9.2). The oxygen and chlorine produced at the anode as a result of electrode reactions may act as oxidising agents. The destruction of some organic compounds as a result of electrode reactions, with the participation of these anodic reaction products, is also probable. From the form of the curves in Figure 9.2 it is possible to deduce that DBS molecules are more stable toward oxidation than HA. Inclinations in the curves for solutions containing DBS are less prominent than for solutions containing HA. It must be noted that the increase in potential across the membranes in the presence of HA is less than 10 % and may be regarded as insignificant (Figure 9.2 c).

When the current density is reduced to 3.0 mA·cm^{-2} the degree of oxidation of organic substances by anodic reactions decreases. A confirmation of this is the increase in the voltage drop across the membranes (Figure 9.3). Increasing the current density to 10.0 mA· cm^{-2} results in fluctuations in the voltage drop across the membrane. This is related to the instability of the system, resulting from the occurrence of additional convection currents at a current density significantly greater than the limiting value.

9.4. CONCLUSIONS

- Preliminary pumping of the electrodialysis feed solution through the anode compartment reduces the negative influence of fouling organic substances, HA and DBS, on the Ionics anion-transfer membranes.
- Reduction of the negative effect of HA and DBS is due to the destruction of these foulants in the anode compartment of the electrodialysis cell by anode reaction-products, such as chlorine and oxygen.
- An increase in current density results in an increase in the efficiency of anodic oxidation of organic substances present in solution.
- The application of preliminary anodic oxidation is more effective for the destruction of HA than for DBS.

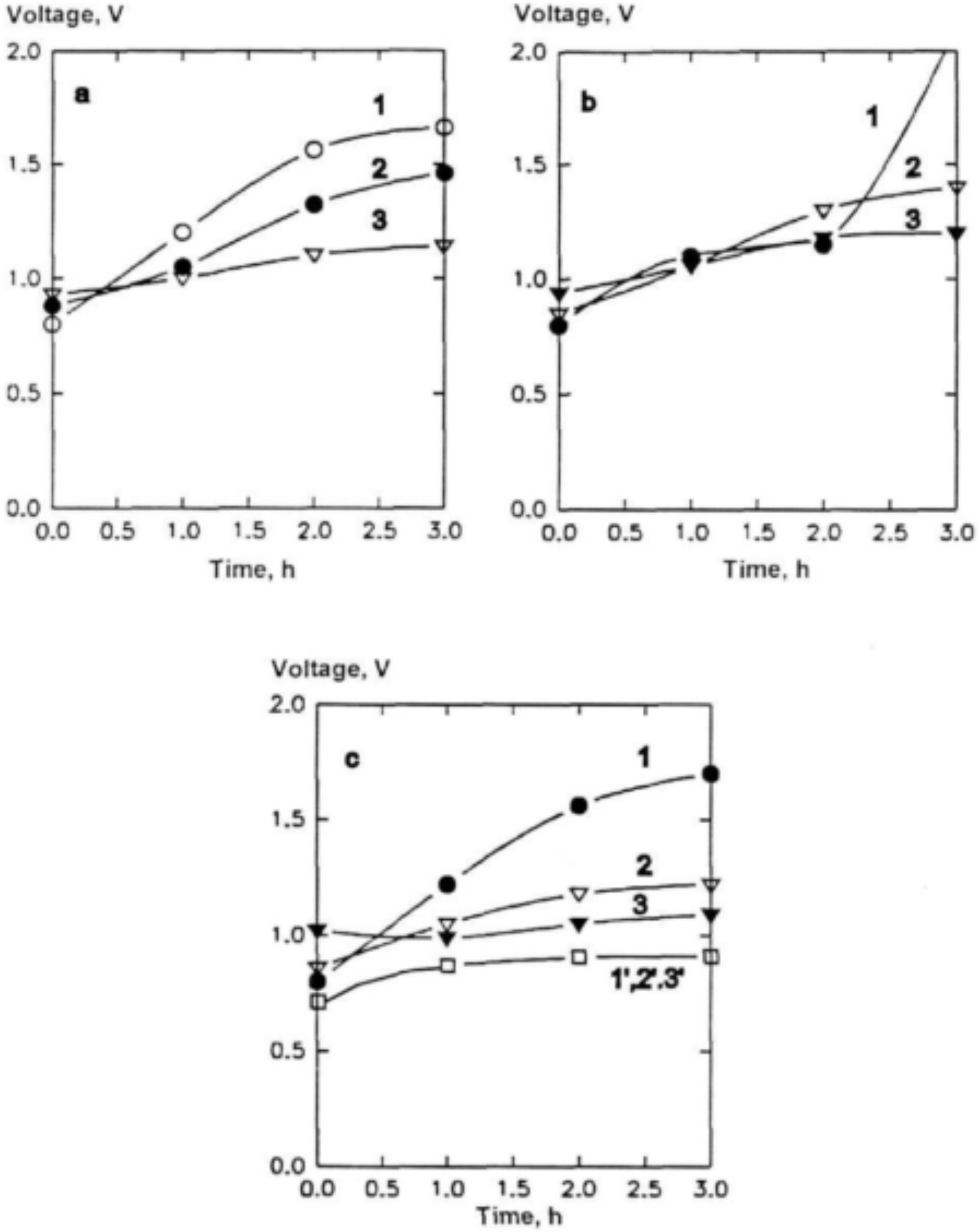
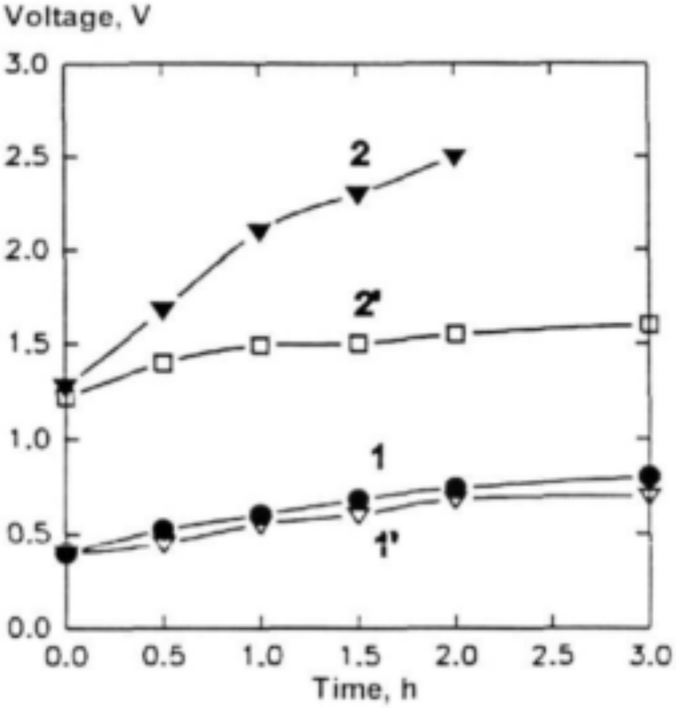


Figure 9.2: Chronopotentiometric characteristics of I (1), $I_{NIB-8-50}$ (2) and $I_{NIB-8-500}$ (3) membranes in SIMW solutions containing 100.0 mg·l^{-1} DBS (a) and 100.0 mg·l^{-1} HA (b). Current density 6.0 mA·cm^{-2}.

The same membrane characteristics obtained after passing SIMW through the anodic cell (SIMW containing DBS [1,2,3] and SIMW containing HA [1',2',3']) are also shown.



Figures 9.3: Chronopotentiometric characteristics of Ionics anion-transfer membrane in SIMW containing 100.0 mg·l^{-1} HA. Current density 3.0 (1) and 10.0 (2) mA·cm^{-2}.

The same characteristics of the Ionics membrane obtained after passing SIMW through the anodic cell (1' and 2') are also given.

10. OVERALL CONCLUSIONS – PART A

Anti-fouling treatment

Research focused on the study of the influence of organic impurities, present in water, on the process of water desalination using electrodialysis technology. It was shown that from a wide spectrum organic impurities HA and DBS had the most significant effects. The presence of these substances in electrodialysis feed water results in fouling of the anion membranes, by the formation of HA or DBS layers on the membrane surfaces. As a consequence, the increase in the electrical resistance of the membrane and in the voltage drop across it, results in an increase in power consumption during electrodialysis and reduces the efficiency of the process.

In an attempt to minimise fouling of anion-transfer membranes by organic substances, a method of surface treating these membranes with a polyelectrolyte coating was explored. The results of a study, conducted on a large number of prospective polyelectrolyte modifiers, indicated that NB-8 and LT-27 have the greatest efficiencies for the protection of anion-transfer membranes against fouling. Based on the results obtained, a method of ion-transfer membrane treatment, by simple processing in dilute aqueous solutions of modifier substances, was developed. This method allows for membrane processing under both static and dynamic conditions.

Static treatment involves simply immersing the membrane in a solution, containing a given concentration of the modifying agent. Treatment of membranes under dynamic conditions is also a simple operation; modifier solution is pumped through the concentrate and demineralisation chambers of the electrodialysis apparatus. It was found that by applying an electrical current during treatment of the membranes under dynamic conditions improved bonding of the modifying substance onto the membrane surface is achieved. In the case of modified membranes operating in the electrodialysis cell the polyelectrolyte layer, electroprecipitated onto the membrane surface, provides effective protection against organic substances for at least 20 days. It was found that there was practically no difference in the properties of anion-transfer membranes modified under static or dynamic conditions. In particular, no difference between the increases in operating periods prior to fouling with organic substances was found for membranes modified under static and dynamic conditions.

Ion selectivity

The specific selectivity of anion-transfer membranes modified with NB-8 solution does not change with respect to mono- and divalent anions. Treatment of anion transfer- membranes with LT-27 increases their permeability to monovalent anions, such as Cl^- anions. This effect can be potentially suitable for the production of potable water from a feed source with a sufficiently high total hardness content, using standard electrodialysis apparatus.

During membrane treatment under dynamic conditions, both the anion- and cation-transfer membranes were exposed to the modifying agent. It was shown that treatment of the standard Ionics cation-transfer membrane results in changes in its transport properties. Application of NB-8 results in an increase in the membrane permeability to divalent cations, whereas LT-27 increases the permeability to monovalent cations. In addition to the protective action with respect to fouling by organic substances, the distinct influence of the modifier on membrane transport characteristics can successfully be used to control the composition of demineralised water, produced by the method of electrodialysis.

Current reversal and pulsing mode

Research was not limited to only the application of membrane treatment for the purpose of increasing the efficiency of the electrodialysis process. A comparative study of the electrochemical characteristics of the modified and unmodified Ionics membranes was also conducted. It was determined that the use of current reversal results in complete membrane regeneration and restoration of its initial electrical resistance and voltage drop.

The results of a study to determine changes in the electrochemical characteristics of anion-transfer membranes during operation in the pulsing mode of electrodialysis have shown that the pulsing mode can effectively reduce membrane fouling in the presence of organic substances. For the Ionics membranes, optimum conditions of pulsing electrodialysis were determined to be: polarisation for a period of 15 minutes, and current interruption for 3 minutes.

Anodic oxidation

Results of the present research have indicated that a significant decrease in organic fouling of anion-transfer membranes can be achieved by initially pumping feed water through the anodic cell of the electrodialysis apparatus. The destruction of organic substances present in the anodic chamber, with the aid of anode reaction products, significantly reduces their concentrations in the water and, thus, reduces organic fouling of the membrane. The efficiency of this process is dependent on the current density, and maximum anodic oxidation of organics is observed at high current density values. It should be noted that a simple yet effective method for the regeneration of membranes fouled with organic compounds, was found to be by chemical processing in sodium chloride solutions.

Membrane comparison

Comparative research between the electrochemical characteristics of a number of cation and anion transfer membranes, produced by various companies, was conducted. Properties of the standard Ionics membranes greatly surpass those of the MA-100 and MK-100) membranes (produced in USSR). However, the Neosepta cation-transfer membrane (produced in Japan) display high efficiency during electrodialysis, maintaining a current density of up to 10 mA·cm^{-2}, and is ideally suited for the selective concentration of sodium salts from multicomponent solutions.

11. RECOMMENDATIONS FOR FUTURE RESEARCH

Results of the research conducted revealed that significant opportunities exist to increase the efficiency of the electrodialysis process for water desalination by reducing the organic fouling of smooth surface styrene-divinylbenzene membranes (e.g. Ionics). To date, these opportunities have only been investigated under laboratory conditions. Further research should be focused on the appropriate testing of recent research findings and developments in industrial electrodialysis apparatus, and improvements in the efficiency of the electrodialysis process should be monitored.

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PART B – CERAMIC MEMBRANES

13 INTRODUCTION

13.1 INORGANIC MEMBRANES

Inorganic materials generally possess superior chemical and thermal stability to polymeric materials. Although to date their use as membrane material has been limited there has recently been a growing interest, especially in the fields of microfiltration and ultrafiltration.

Four different types of inorganic membranes frequently used may be distinguished: ceramic membranes, glass membranes; metallic membranes and zeolitic membranes.

13.2 CERAMIC MEMBRANES [1]

Ceramics are formed by the combination of a metal (eg. aluminium, titanium or zirconium) with a non-metal in the form of an oxide, nitride or carbide. Ceramic membranes prepared from such materials form the main class of inorganic membranes, with aluminium oxide or alumina (Al_20_3) and zirconium oxide or zirconia (ZrO_2) as the most important representatives. These membranes are usually prepared by sintering or sol-gel processes. The following material properties of ceramics are considered important: thermal stability, chemical stability and mechanical stability

13.2.1 Thermal stability

The thermal stability of polymers has been discussed by Mulder [1]. Polymers can generally be applied over temperatures ranging from 100-300°C. Ceramics have very specific properties, originating from their electronic behaviour. The valence electrons of the metal part are retained by the non-metal atoms resulting in a highly stable bond and, consequently, these materials are highly thermally and chemically resistant. The melting points are very high and can reach values above 4000°C. This high temperature resistance makes these materials very attractive (for example for gas separation at high temperatures), especially in combination with a chemical reaction where the membrane is used as a catalyst as well as a selective barrier to remove one of the components which has been formed.

13.2.2 Chemical stability

The chemical stability of existing polymeric membranes is limited with respect to pH and organic liquids. The chemical stability of inorganic materials is superior and they can generally be applied at any pH and in any organic solvent. Thus, in the field of ultrafiltration and microfiltration the number of applications of inorganic membranes can be expected to increase, especially in harsh environments. Another important factor is the ease of cleaning, especially in high fouling applications. Fouling leads to a drastic decrease of flux through the membranes and periodic cleaning is necessary. For inorganic membranes all kinds of cleaning agents can be used, allowing strong acid and alkali treatment. Another point to consider is that the lifetime of inorganic membranes is greater than that of organic polymeric membranes.

13.2.3 Mechanical Stability

Mechanical stability is not a very high priority in membrane separations and only in some applications, for instance those involving high pressures or self-supporting materials, must this parameter be considered. Ceramics are characterised as hard materials.

13.3 BACKGROUND TO PROJECT

To date it is generally only polymeric membranes with functional groupings in their structure that have been successfully used in commercial electrodialysis apparatus. The dissociation of the functional groups in aqueous solutions, according to an acid or base mechanism, creates the membrane charge and determines the selectivity of membrane. It is known, however, that there are potential disadvantages associated with using polymers for the preparation of membranes for electrodialysis [2], resulting in limited potential applications of electrodialysis for the removal of ionic impurities from different types of solutions.

The first disadvantage is that the chemical, thermal and radiation stability of polymeric membranes is not always adequate for a potential electrodialysis application. For example, their inferior stability in strong solutions of acids and alkalis is not conducive to their use in the preparation of chlorine and caustic by electrodialysis. Polymers are also unstable to the action of oxidising agents, for example, to the action of chlorine. The poor thermal stability of polymeric ion-exchange membranes, widely used for electrodialysis, not only limits the possibilities of their use in the electrodialysis for hot solution processing but also excludes their use in electrodialysis at high current load. The degree of separation is reduced. Further, the low radiation stability of polymers results in the exclusion of electrodialysis for the purification of wastewaters containing radioactive isotopes. Secondly, polymer membranes are sensitive to the presence of even small quantities of organic compounds in the feed solution (to be dialysed). Some such compounds incorporate themselves into the membrane volume, causing membrane fouling and, as a result, the energy characteristics of electrodialysis are decreased.

Whilst continuing with the development of new methods of synthesis for the preparation of novel and improved polymeric membranes for electrodialysis (Part A), intensive investigations have been carried out into another class of membranes - membranes based on inorganic materials. During the past few years significant success has been achieved in this field, as reported in the literature [3,4]. Such membranes are generally formed on ceramic bases prepared from multivalent metal oxides. The oxide bases of ceramic membranes are far more stable than polymers. They have much greater chemical, thermal and radiation stabilities [1]. It can also be expected that the inorganic membrane matrix will be significantly less sensitive to organic compounds.

Notwithstanding the apparent good suitability of inorganic membranes for use in electrodialysis it does not mean that the inorganic membranes will always supersede polymer ones in the electrodialysis apparatus. But they can/may be useful in cases or situations where polymeric membranes cannot be used or when their effectiveness is low. The cost of self supporting inorganic (ceramic) membranes is not much higher than the best polymeric ones. Results of one study [5] have shown that an inorganic electrodialysis membrane prepared by the precipitation of its components on a paper base can be cheaper than a polymeric one. Several authors [5-9] have recently demonstrated the possibility of effectively using ceramic membranes for the electrodialysis of solutions with radioactive isotopes. An increasing number of patents have been published recently, describing methods of inorganic membrane preparation for the processes in which the electric current is a moving force: electrolysis [10-15] and electrodialysis [16].

The current study is aimed at determining the possibility, and suitability, of using selected inorganic membranes for separation by electrodialysis. The main task is to investigate the porous structure, transport and electrochemical characteristics and, on the basis of obtained data, draw conclusions regarding the advisability of more goal-oriented further investigations.

14 MATERIALS AND METHODS

14.1 MATERIALS

Plate-and-frame and tube elements made from porous oxide ceramics, according to South African patent No. 977639, were selected as initial membrane materials. The main characteristics of the initial ceramic elements are listed in Table 14.1.

Table 14.1: Main characteristics of the initial plate and tube porous ceramic elements.

Thickness, mm	1
Composition	70% Al_2O_3 + 30% ZrO_2
Total porosity, %	45
Average diameter of pores, µm	0.19
Specific surface area, m^2/g	4.5 - 5.0

The initial ceramic membranes were modified by pyrolytic carbon, manganese dioxide and zirconium phosphate. The modification by pyrolytic carbon, as carbon deposition, was carried out by the pyrolysis of methane at 800-1000 °C. The modification by manganese dioxide was carried out by treating the initial membrane with a 1M solution of $MnNO_3$, air-drying and then heating to 220 °C for 2 hours. The impregnation of zirconium phosphate into porous structures of ceramic materials was carried out according to an original, newly developed method. It involved the preparation of a crystalline sol of zirconium dioxide, immersion of ceramics into the sol, treatment by phosphoric acid and drying. In order to completely fill the ceramics the operation was repeated several times.

14.2 INVESTIGATION INTO THE TRANSPORT PROPERTIES OF INORGANIC MEMBRANES

14.2.1 Background

All membrane separation processes entail the mass transfer of substances through the membrane. The driving force of these processes is the presence of concentration, pressure, temperature or electric field gradients over the membrane. In describing the mechanism of mass transfer through membranes it is the diffusion or osmotic processes (their moving force is only the concentration gradient) that are of great importance. The membrane-separation of substances is based on the establishment of different concentrations of substances in the volumes separated by the membrane. This naturally results in a concentration gradient and osmotic processes, which are the result of mass transfer in the opposite direction, that also significantly influence the separation characteristics. This is also applicable to the removal of ionic impurities from water by electrodialysis, for which the main driving force is created by an electric field. Taking into consideration that the goal of the current study is to investigate membrane application in electrodialysis, it is appropriate to study the transport characteristics of those membranes.

Among the several different characteristics that can be used to estimate membrane transport properties of separation membranes the most methodologically simple and generally used are determinations of their diffusion and osmotic characteristics. The electro-osmotic permeability is also important for membranes used in processes with an applied electric field (eg. electrodialysis). Once the value of the electro-osmotic membrane permeability has been determined it is possible to make conclusions regarding the concentration ability of a membrane during the electromembrane separation of electrolyte solutions and make preliminary estimations about the effectiveness of using such a membrane in these processes. The results of investigations into the inorganic membranes selected for the current study and their transport properties will be presented in the following sections.

14.2.1 Investigation of the diffusion permeability of inorganic membranes

The diffusion and osmotic permeabilities of membranes were measured by means of a simply constructed device, shown in Figure 14.1. The device consisted of a vessel (1) with selected test solution (feed solution) in which the tubular membrane with corked ends (2), and solution, were placed. To measure the volume of product solution a calibrating capillary (3) was inserted in the upper cork. The solution in the inner volume was constantly mixed by a magnetic stirrer (4). To increase the accuracy of measurements we maintained a minimal level difference.

It is known that the diffusion of electrolyte through a membrane is accompanied by an immediate osmotic water-flow, in an opposite direction to the diffusion flow. Therefore, if distilled water was inside the tubular membrane and the membrane was placed in a sodium chloride salt solution (with a different concentration) the diffusion salt flow would be directed to the inside of the membrane and the osmotic water flow to the outside. To compensate for the outflow of liquid a graduated dropper containing water was attached to the capillary, exiting from the membrane (see Figure 14.1.). The diffusion permeability of the membrane was estimated according to the change in electrolyte concentration inside the membrane. Taking into consideration that the electrolyte volume outside the membrane was rather high (it was 100 - 200 times as much as the volume of liquid inside the membrane) we assumed that the electrolyte concentration outside the membrane would remain constant throughout the entire experiment.

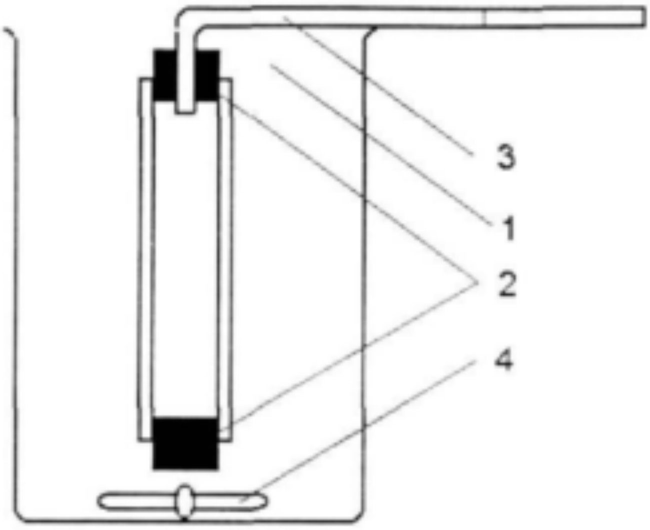


Figure 14.1: Schematic representation of the device used for measuring the diffusion and osmotic permeability of a tubular inorganic membrane

Once the concentration profile in the membrane was established and diffusion had proceeded in steady state conditions we could determine the kinetic dependency of the electrolyte diffusion flow through the membrane (by sampling electrolyte from the inner membrane volume at the equal time intervals) and calculate the coefficients of diffusion and osmotic permeability.

The calculations of diffusion (β_d) and osmotic (β_o) membrane permeability have been performed according to the following formulae:

$$\beta_d = q \cdot \sigma / C \cdot S \cdot t \qquad (14.1)$$

$$\beta_o = \Delta V \cdot \sigma / 18 \cdot t \cdot C \cdot S \qquad (14.2)$$

where:

ΔV - volume of liquid (cm^3) transferred during the time t (s) through the membrane with cross-section area S (cm^2) and wall thickness σ (cm);

18 - molecular mass of water;

C - concentration of electrolyte solution (g-eqv·l^{-3}) which was transferred into distilled water during the time t (s);

q - quantity of the transferred substance (g-eqv).

14.2.3 Determination of the electro-osmotic permeability of inorganic membranes

A schematic representation of the cell that was used to determine the electro-osmotic permeability (EOP) of a tubular inorganic membrane is shown in Figure 14.2. It is similar to that in Figure 14.1 except that it has two electrodes. The first electrode (cathode) was placed inside the membrane and the other electrode (anode) was placed outside. A measuring cylinder was used to measure the volume of liquid that passed through the membrane.

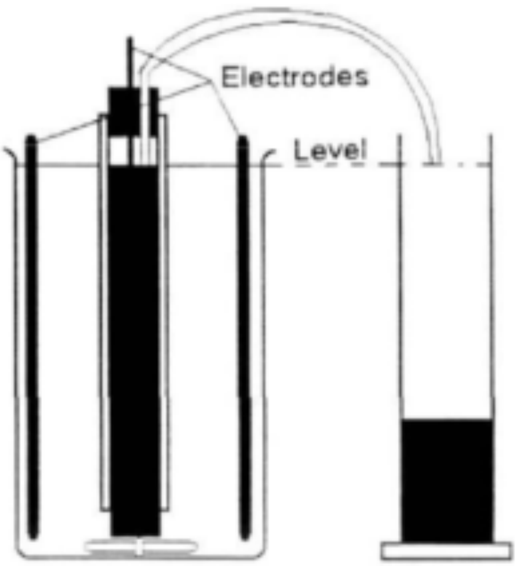


Figure 14.2: Schematic representation of the device used to investigate the electro-osmotic permeability of inorganic membranes.

Use of the device meant that we could measure the EOP over a wide range of current densities, including the over-limiting currents. As mentioned, one of the conditions required to obtain valid EOP results for tubular membranes was that the levels of solution in the capillary and the solution around the membrane were kept the same. The problem of gas generation was addressed by experimental adjustments. The electrodes were prepared from platinum wire (2 mm in diameter).

Calculation of electro-osmotic permeability was performed according to the following equation:

$$\beta=\Delta V/Q \qquad (14.3)$$

where:

ΔV - volume of liquid passing through the membrane during a determined period of time (1h) under the current flow,

Q- quantity of transferred electricity (A·h).

14.3 DETERMINATION OF THE ELECTRIC RESISTANCE OF A MEMBRANE

To measure the electric resistance of tubular membranes to alternating current a special cell that contained two platinum rings was pressed into to the membrane tube, with application of constant force from the both sides. Prior to any measurements being made the membrane was wet and conditioned with a solution of pre-determined content and concentration. The measuring of cell resistance was done using a resistance bridge E 7-12, at an alternating current frequency $1.0 \cdot 10^3$ Hz. The final value of cell resistance was determined as the average of three subsequently obtained results.

The value of specific membrane resistance (ρ_{sp}) was determined according the following formula:

$$\rho_{sp} = R / l \; (\mathrm{Ohm} \cdot \mathrm{cm}^{-1}) \qquad (14.4)$$

where:

R - resistance of the wet membrane after conditioning with a solution of predetermined concentration;

l - length of membrane (cm) between two measuring electrodes.

The surface electrical resistance (ρ_s) was determined according the following formula:

$$\rho_s = R \cdot S \; (\mathrm{Ohm} \cdot \mathrm{cm}^2) \qquad (14.5),$$

where:

S - area of outer membrane surface (cm^2).

14.4 STUDY OF THE VOLTAMMETRIC AND CHRONOPOTENTIOMETRIC CHARACTERISTICS OF MEMBRANES

(These membrane characteristics have been mentioned to earlier – see Polymeric membranes, section 4)

The hydraulic and electrical circuits of the apparatus used for studying the voltammetric and chronopotentiometric characteristics of membranes are shown in Figure 14.3. A stabilised NIIRIT B5-49 power supply was used to provide current. A high-resistance NIIRIT SC-4313 voltammeter was used to measure the voltage drop.

The electrodialyser (ED) used during experiments consisted of varying number of cells. In Figure 14.3 six cells are shown, two of which contained electrodes. The remaining four cells contained the probes, mounted for measuring a voltage drop across the membranes AM_1, AM_2 and AM_3. The working area (cross-section) of the cells was 2 x 5 cm^2, and the width was 0.5 cm. A platinum wire (2 mm thick) was used as electrode.

The measuring probes were glass capillaries, centrally positioned into the intermembrane spaces, through an outer wall of the cell. The capillaries were supported by flexible tubing, closed by dense filters, and placed in a saturated potassium chloride (KCl) solution, into which silver/silver chloride (Ag/AgCl) reference electrodes have been placed. Earlier the capillaries had been filled with a freshly prepared saturated KCl solution that provided low electrical resistance for the measuring system. Electrical resistance is an important parameter for estimating the voltage drop across a membrane during the electrodialysis of dilute solutions.

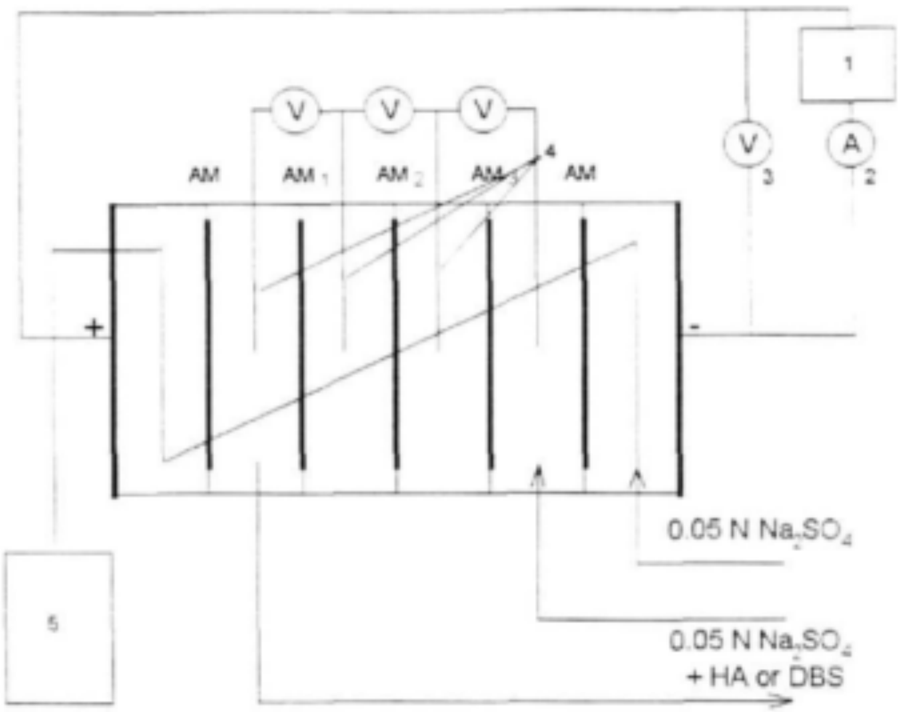


Figure 14.3: Electrical and hydraulic circuits of the apparatus used to study the volt-ampere and chronopotentiometric characteristics of membranes.

1 - power supply, 2 - ammeter, 3 - high resistance voltmeter, 4 - measuring probe, 5 - vessel containing electrode solution, AM – anion-transfer membranes, AM_1, AM_2 and AM_3 - test membranes.

15 RESULTS AND DISCUSSION

15.1 THE POROUS STRUCTURE OF INORGANIC MEMBRANES

The main properties of the inorganic membrane materials that were investigated in the current study are described in Table15.1. The investigation of the porous structure of membrane samples was performed by two independent methods: low-temperature adsorption of nitrogen and mercury porosimetry. (Similar results were obtained from both methods.)

The pore size distributions of inorganic membranes (according to their radii), as determined by mercury porosimetry, are shown in Figure 15.1. The initial ceramic sample had a uniform macroporous structure with average pore diameter of 0.11 μm (curve 1, Figure 15.1) and the almost complete absence of micropores. The main structural properties of the macropores of the initial sample are the same, both before and after the pyrolytic carbon precipitation. The pyrolytic precipitation of carbon does, however, result in the formation of a secondary mesoporous structure. Pores 0.05 μm in size can be seen in the membrane. According to analytical data recorded by electron microscopy one can conclude that the formation of pores takes place only in the thin near-surface membrane layer. Having analysed the curves in Figure 15.1 it is noticed that an increase in the temperature of pyrolytic carbon precipitation significantly decreases the porosity of the prepared samples (curves #2 and #3). An increase in pyrolysis time has a similar effect (curve #4). The incorporation of manganese dioxide in the porous structure of initial ceramic material results in almost no change in the position of the pore-distribution maximum and a decrease in the total porosity of the material (curve #5).

Table 15.1: Main characteristics of inorganic membranes investigated.

Number of sample	Description of the inorganic membrane material
1	Total porosity of membrane samples 45%; specific surface area (determined by nitrogen absorption) 5 m^2/g; average pore size 0.11 μm
2	The membrane was prepared by the precipitation of carbon on membrane #1 in the process of natural gas pyrolysis at 800 °C*
3	The membrane was prepared by the precipitation of carbon on membrane #1 in the process of natural gas pyrolysis at 900°C under the conditions of formation of surface carbides
4	The membrane was prepared by coating with manganese nitrate and its further conversion to manganese dioxide by heating in a thermal oven at 220°C
5	The membrane was prepared in the same way sample #3 was, but the quantity of precipitated carbon was 2 times greater than that used for sample #3

*The time of pyrolysis was 8h for the modification of all membranes.

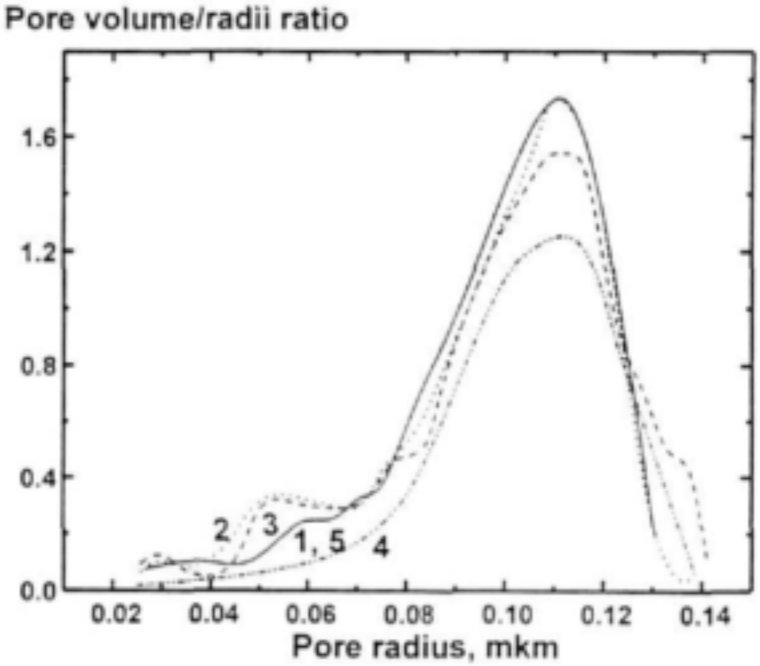


Figure 15.1: Pore size distributions of samples of inorganic membranes as determined by mercury porosimetry. (The figures on the curves correspond to the membrane numbers as indicated in Table 15.1.)

15.2 AN INVESTIGATION INTO THE EFFECTS OF MEMBRANE MODIFICATION ON DIFFUSION, OSMOTIC AND ELECTRO-OSMOTIC MEMBRANE CHARACTERISTICS

The results of investigations into the diffusion and osmotic characteristics of modified inorganic membranes are presented in Figures 15.2 and 15.3. Decreasing membrane porosity upon pyrolytic coating with carbon in the near-surface layer results in decreasing permeability of both electrolyte (Figure 15.2) and water (Figure 15.3).

The increase in pyrolytic precipitation of carbon also results in a decrease in membrane permeability. As has already been mentioned, the mass increase of thermally precipitated carbon (sample #5) results in an abrupt drop in membrane permeability (see Figure 15.3, curve #5). In this regard there are two important factors that are relevant: decreases in pore size and total porosity and also the hydrophobic ability of the surface accepting membrane's layer (which largely determines the membrane's permeability). Modification of a membrane with manganese dioxide (sample #4), which changes the porosity and surface charge (see Figures 15.2 and 15.3, curve #4), changes the character of the concentration dependence of diffusion and the osmotic membrane permeability, in principle. This is because the composition of the electrolyte passing through the membrane is formed in this layer. Although the permeability of the modified membrane is lower than the permeability of the initial one, it increases when the electrolyte concentration increases. Charged polymeric membranes show the same behaviour.

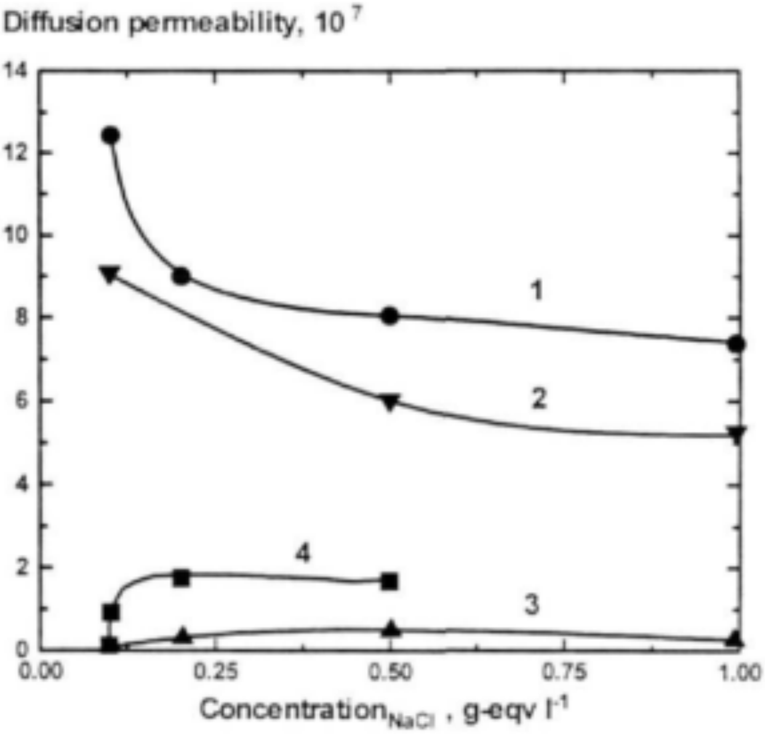


Figure 15.2: Dependence of the diffusion permeability of inorganic membranes on the concentration of a NaCl solution. (The figures on curves correspond to numbers of the membranes as indicated in Table 15.1.)

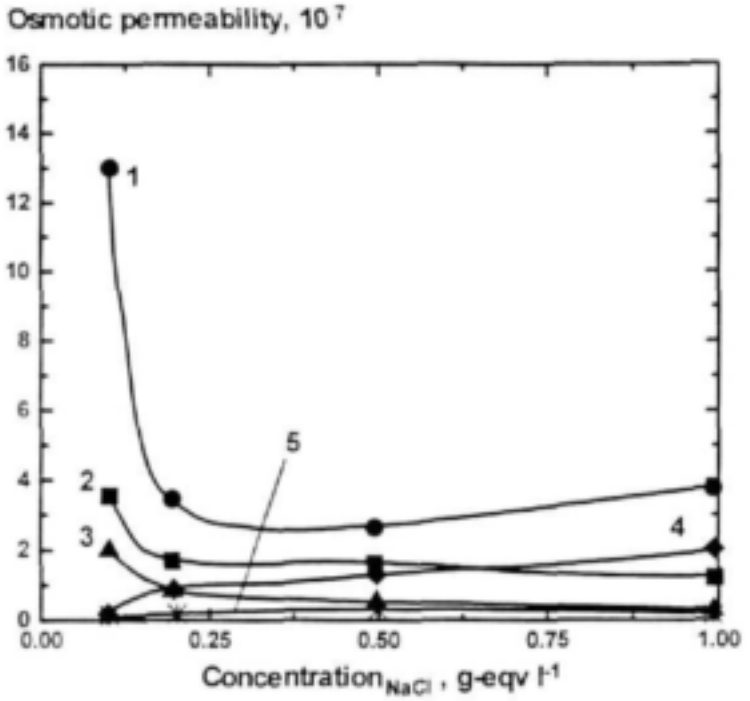


Figure 15.3: Dependence of the osmotic permeability of inorganic membranes on the concentration of a NaCl solution. (The figures on curves correspond to the numbers of the membranes as indicated in Table 15.1.)

The concentration dependencies of the electro-osmotic permeability coefficients resembles the analogous dependencies of the osmotic water permeability (Fig.15.3 and 15.4). It can be observed, that they decrease if the modification, that decreases the membrane porosity, takes place and the electrolyte concentration increases. If the membrane porosity increases, the concentration dependency of both osmotic and electro-osmotic permeability becomes less prominent. The influence of concentration in the area of concentrated solutions (0.5-1.0 g-eqv·l^{-1}) is very slight. It can be connected seemingly with the significant decrease of diffusion layers thickness in the pore membrane space. But it should be also mentioned that if the current density decreases, the electro-osmotic membrane density increases.

15.3. THE ELECTRIC RESISTANCE OF MEMBRANES TO ALTERNATING AND DIRECT CURRENTS

The main characteristic of separation membranes used under the application of an electric field is their electric resistance; resistance to either direct or alternating current. When a stationary electrical field is applied then the process of electro migration takes place and concentration profiles in the membrane and the diffusion layers, in solutions on the accepting and rejecting sides of the membrane, are formed. Hence, the measurement of resistance to direct current includes the error connected with the diffusion layers. Taking this into consideration one can conclude that a more accurate characteristic of the membrane is its resistance to alternating current (which is measured at the rather high frequency).

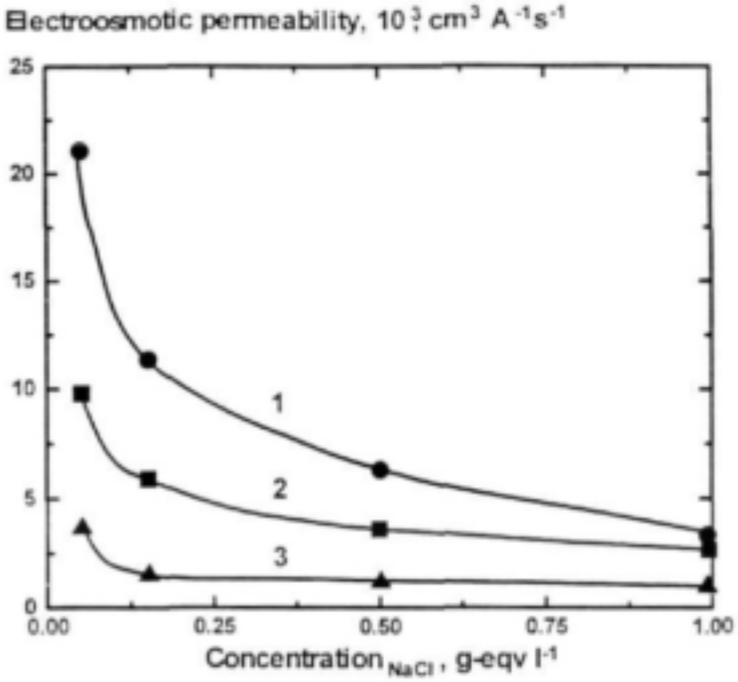


Figure 15.4: Dependence of the electroosmotic permeability of inorganic membranes on the concentration of an equilibrium NaCl solution at current density 15 mA cm^{-2}. (The figures on the curves correspond to the membrane numbers in Table 15.1.)

Results of an investigation into determining the electric resistance of modified membranes has shown that the modification of membranes by pyrolytic precipitated carbon, by the pyrolysis of natural gas, results in an increase in electrical conductivity (Figure 15.5). The membrane becomes electrically conductive, but the value of electrical conductivity is not higher than 4 ohm^{-1} cm^{-1}. The maximum value of membrane conductivity (200 ohm^{-1}·cm^{-1}) can be obtained after pyrolysis at 900 - 1000°C. An increase in pyrolysis time of more than 5 h is not efficient as it results in an abrupt decrease in porosity and therefore in the membrane's permeability.

The membranes coated with manganese dioxide (see Figure 15.5 b, curve 4) have much higher electrical resistance. If the thickness of the coating increases (i.e. the number of manganese dioxide layers) then the membrane's electric conductivity increases significantly. Despite the rather high electrical conductivity of the precipitated manganese dioxide layer it covers only the surface membrane layer, and the membrane's resistance depends on the conductivity of whole cross-section. Therefore it is possible to conclude that to use an inorganic membrane (for example, as an anode) it is necessary to preliminarily modify it to increase its conductivity through the entire volume and only then to coat the outer membrane surface with manganese dioxide.

Inorganic membranes with the highest electrical conductivity values and which have similar characteristics to polymeric membranes are those membranes modified with zirconium phosphate (Figure 15.5 b, curve 5). Coating with zirconium phosphate (4-5 layers) increases the membrane conductivity, up to 50 ohm^{-1}·cm^{-1}.

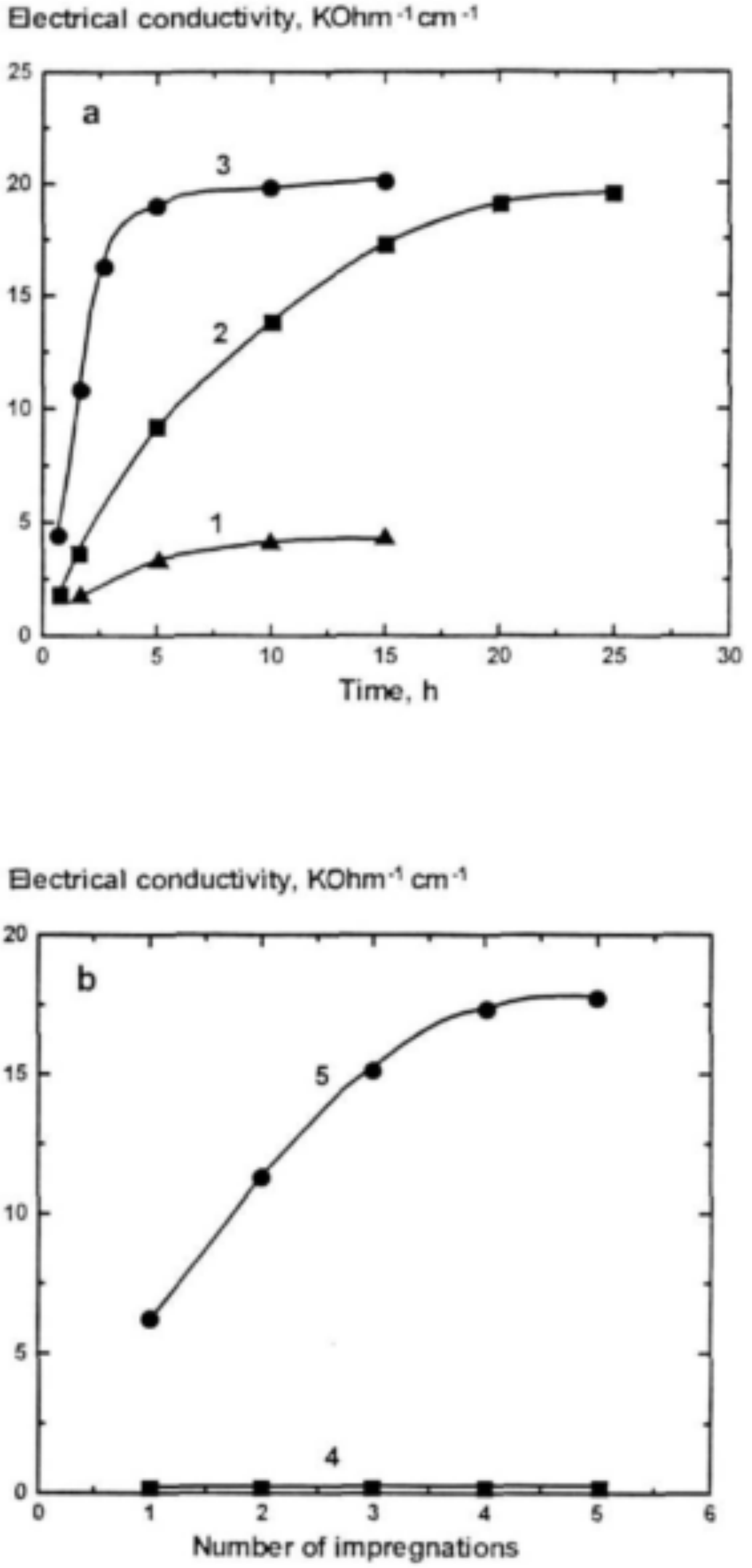


Figure 15.5: The influence of membrane modification on the electrical conductivity of inorganic membranes. (a) The influence of time and temperature of pyrolytical coating with carbon (1 - 800; 2 - 900; 3 - 1000 °C). (b) The influence of a number of sequential impregnations of manganese dioxide (4) and zirconium phosphate (5).

Results of studies of the porosities, permeabilities and electrical conductivities indicated that it was the membranes modified by zirconium phosphate that had the best properties, for use in electrodialysis processes. Hence, further research was conducted with this type of membrane only.

The electrical resistance of the membrane was calculated on the basis of current-voltage characteristics (see Figure 15.6), determined by means of probing devices, and included the near-membrane layers of solution. This means that it is not possible to determine the true value of resistance, but merely to provide information for the comparison of membrane characteristics over a wide range of current densities.

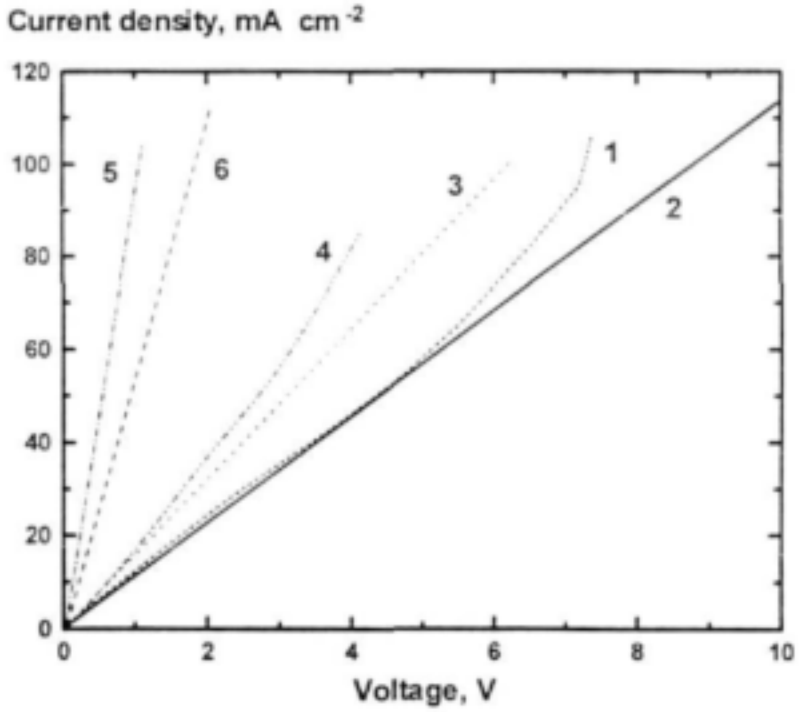


Figure15.6: Volt-amperic curves for an initial membrane (1,2) impregnated with zirconium phosphate (3,4) and for a solution without membrane (5,6) with stirring (1,3,5) and without stirring (2,4,6). Solutions used: 0.5N Na_2SO_4.

Analysis of the volt-amperic curves presented in Figure 15.6 and similar curves obtained for more diluted solutions, with concentrations 0.1 M and 0.01 Na_2SO_4, allows us to make the following conclusions:

1. The resistance of balanced solutions between the probing devices is higher than the resistance of a solution-membrane-solution system at current densities lower than 5mA·cm^{-2}.

2. The volt-amperic curves of the initial unmodified membrane in the concentrated solutions have slightly marked intervals of limiting current density at current densities greater than 7mA·cm^{-2}. The limiting current decreases down to 3-4 mA·cm^{-2} in the less concentrated solution (0.01 M solution Na_2SO_4). Stirring of the electrolyte solution is very important for establishing steady current density – limiting current equilibrium in those initial membranes.

3. In the volt-amperic curves of a membrane modified by the zirconium phosphate there are no intervals which correspond to limiting current density. The resistance of

the membrane is significantly lower than the resistance of solutions and it almost does not depend on the solution content (in the concentration range investigated).

The mode of electrolyte stirring does therefore not affect the character of the volt-amperic dependence of the modified membrane. It can be considered that the resistance of the membrane is primarily determined by the resistance of its inner matrix. In the 0.5 and 0.1 M Na_2SO_4 solutions the resistance is 60 $ohm^{-1} \cdot cm^{-1}$ and if there is a significant decrease in electrolyte concentration (0.01 M solution Na_2SO_4) then it increases to 70 $ohm^{-1} \cdot cm^{-1}$. (Calculations were performed at a current density equal to 5 $mA \cdot cm^{-2}$). It can be expected that in this case the formation of a solution film on the membrane surface has an influence on the membrane resistance.

Hence, on the basis of the analysis of volt-amperic curves, it is concluded that modified membrane should be stable in the processes of desalination over a wide range of current densities. It is proposed that if the electrolyte is stirred sufficiently then the membranes might be suitable for use in the desalination of diluted solutions.

15.4 ELECTRODIALYSIS OF MODEL SOLUTIONS

With reference to the data pertaining to the diffusion characteristics of modified membranes, as described in Section 15.2, the diffusion coefficients of neutral salts through the pores of inorganic membranes are much higher than analogous parameters of polymeric membranes. It is well known that due to their flexible chain structure and charge, as a result of the dissociation of incorporated functional groups, polymeric membranes are rather permeable to not only counterions but also to neutral electrolyte molecules. This characteristic is a shortcoming of polymeric membranes because it restricts the degree of concentration of saline solutions due to electrolyte reverse diffusion.

It is also known that, unlike polymeric membranes, the inorganic membranes based on ceramic oxides, and in particular the membranes with aluminum and zirconium matrices (as used in our investigation), are almost uncharged in neutral, weak acidic and weak alkaline solutions. It was therefore appropriate to estimate both cation and anion permeabilities in an electric field. The influence of modification on transport properties had also to be estimated.

The electrodialysis of solution through the inorganic membranes was studied in a five-chamber electrodialysis apparatus (similar to the one shown in Figure 14.3), containing flat-sheet membranes. The central desalination chamber was separated from two other concentration chambers by two inorganic membranes (1±0.02 mm thickness). The other membranes in the apparatus were polymeric cation- and anion-exchange membranes. The permeabilities of both cations and anions were determined.

First, the characteristics of the initial unmodified ceramic membrane were experimentally investigated. As seen in Figure 15.7, the electro-migration streams of Na^+ and SO_4^{2-} ions through this membrane are almost equal, at about 55-65%. If the current density increases then the productivity of cation transfer processes abruptly decreases. This is related to an increase in the parallel competing stream of hydrogen ions (H^+) formed upon water dissociation.

The decrease in membrane permeability for anions is less apparent. It is probably due to the lower mobility of the hydroxyl (OH^-) ions than the H^+ ions being transported through the membrane. The competing stream of hydroxyl anions is not as great as that of the hydrogen ions. The yield of SO_4^{2-} ions does therefore not drop below 45% (Figure 15.7).

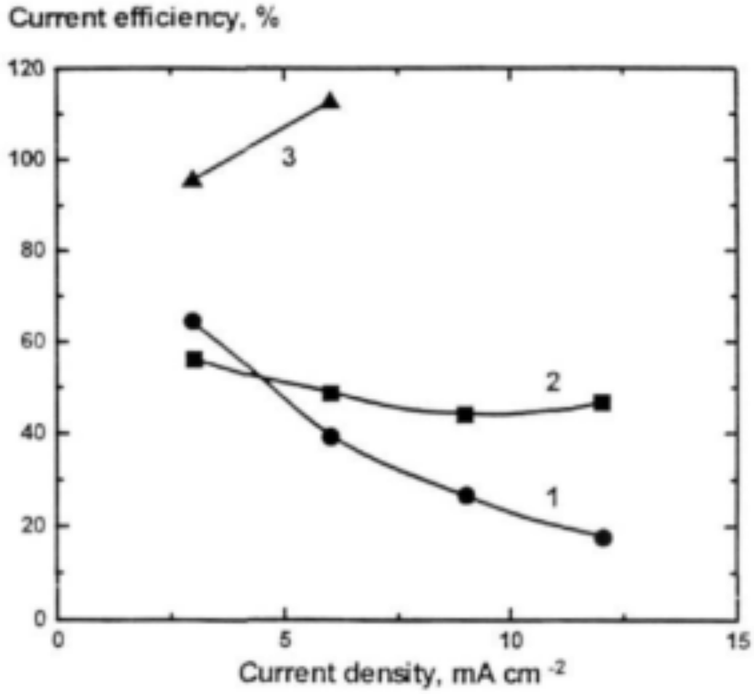


Figure 15.7: Dependence of the current efficiency on current density (i) for the transport of Na^+(1) and SO_4^{2-}(2) ions through the initial ceramic membrane and current efficiency for the Na^+ (3) ions coming through the membrane modified by zirconium phosphate. (A solution of Na_2SO_4 containing 0.1 g-eqv·l^{-1} salt was used for dialysis.)

The modification of a membrane by zirconium phosphate results in the formation of negatively charged functional groups and changes in the membrane's electrotransport. The transfer of SO_4^{2-} ion through such a membrane decreases to zero and the output of Na^+ ions increases to 100%, as described by the curve #3 in Figure 15.7. Having analysed this curve one can observe that the increase in current density results in an increase in the current efficiency of Na^+ ions to over 100%. The electro-osmotic stream of solution through the membrane is a possible reason for the excessive transport of cations passing through the membrane.

It is important to mention here that the effectiveness of the modification can be observed only after membranes have been coated with 5 or more subsequent modification layers. The characteristics of membranes coated with 2 or 3 layers of modifier differ only slightly from the initial unmodified membrane. They are not shown in Figure 15.7. Figure 15.8 shows changes in the porous structure of an initial ceramic carrier membrane upon filling with zirconium phosphate. It is only with 4-5 layers that the filling of the main transport pores takes place in the membrane. It is therefore concluded that the optimum preparation method for such membranes requires the incorporation of zirconium phosphate 4-5 times.

The initial ceramic membrane and a membrane modified by means of a five-time incorporation of zirconium phosphate were also tested in the electrodialysis of a model solution containing 0.1 M sodium sulfate with 0.01-0.05 g-eqv·l^{-1} nickel sulfate. Figure 15.9 shows the dependence of the current efficiency of Ni^{2+} and Na^+ ions on their concentrations in the solution after electrodialysis through the initial ceramic membrane. From the curves it can be deduced that if the current is lower than the limiting value for the unmodified membrane then an insignificant decrease in current efficiency is observed for the Na^+ ions. This decrease becomes more marked if the concentration of Ni^{2+} ions increases. This is possibly connected with a competing stream of nickel ions through the membrane. The current efficiency for Ni^{2+} ions in the area of diluted solutions increases proportionally to its concentration in the dialysis solution.

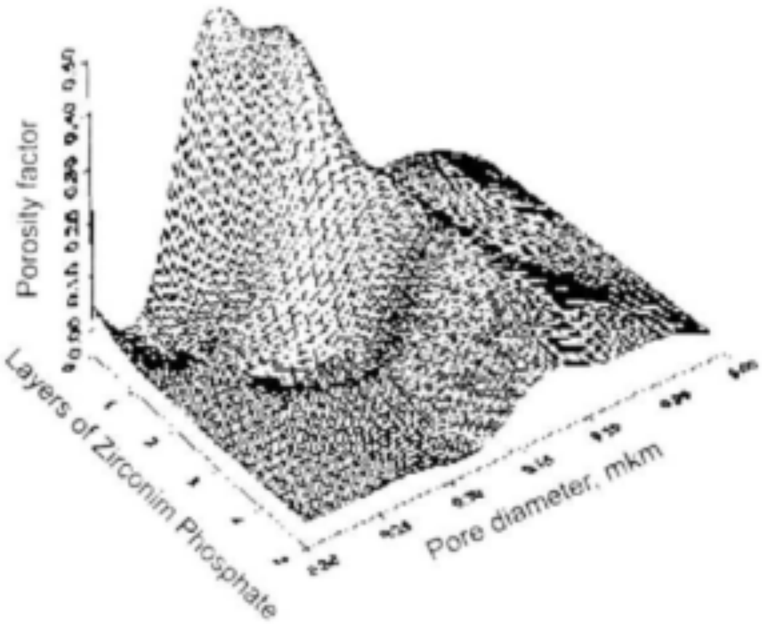


Figure 15.8: Change in the porous structure of an initial ceramic carrier upon the incorporation of zirconium phosphate (1-5 layers).

Having analysed the dependence of the current efficiencies of Ni^{2+} and Na^{+} on the ratio of their concentrations in solution it can be seen that at low current densities the electromigration transfer of nickel is proportional to its mobility in the solution. If the current increases to higher than the limiting value then this can be visually described by the curves in Figure 15.10, i.e. the transfer of Na^{+} and Ni^{2+} ions decreases. This can, under the experimental conditions used, be ascribed to the formation of hydroxy-complex nickel compounds both in the pores and on the accepting membrane surface, resulting in the loss of membrane selectivity.

To restore the selectivity of such a membrane to monovalent sodium ions during electrodialysis it is necessary to periodically either use current reversal or wash the dialysis chambers with acid solution. But it can be considered in general that such behaviour of inorganic membrane in the electrodialysis can be efficient. The formation of hydroxides of multivalent metals in the membrane allows to concentrate and separate them from the salts of monovalent ions.

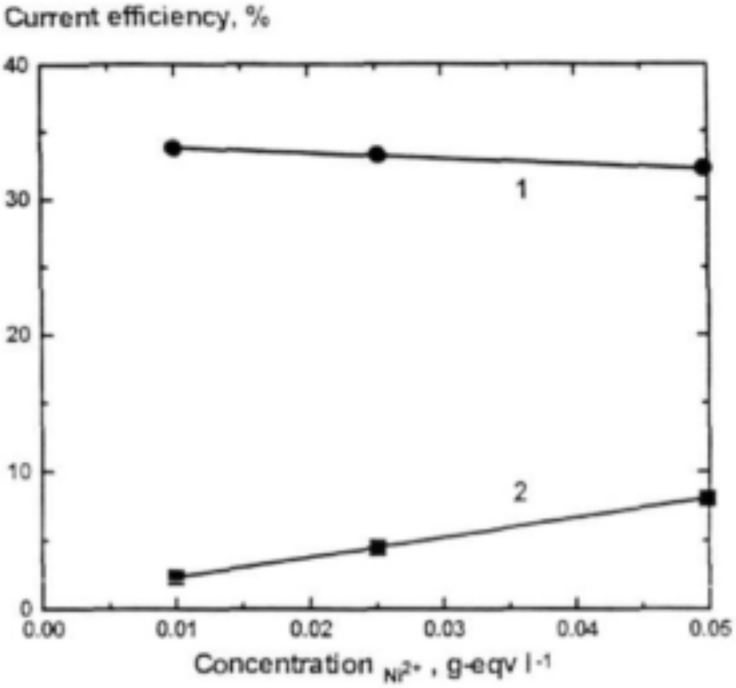


Figure 15.9: Dependence of current efficiency for Na^{+}(1) and Ni^{2+} (2) ions on their concentrations in the ionic solution after electrodialysis through the initial ceramic membrane. The solution contains $NiSO_4$ and 0.1 g-eqv·l^{-1} Na_2SO_4. Current density 6.2 mA cm^{-2}.

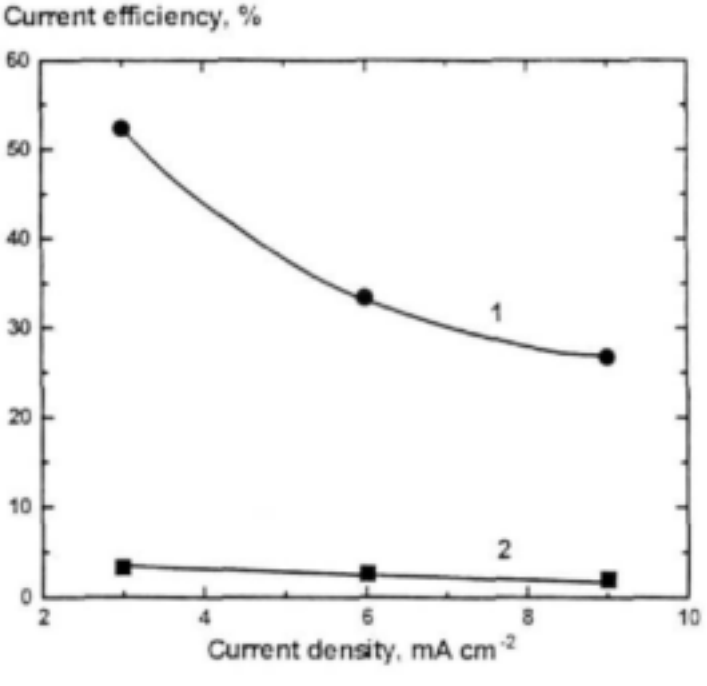


Figure 15.10: Dependence of the current efficiency for Na^{+} (1) and Ni^{2+} (2) ions on the current density of the electrodialysis solution through the initial ceramic membrane. The solution contains 0.01 g-eqv·l^{-1} $NiSO_4$ and 0.1g-eqv·l^{-1} Na_2SO_4.

The dependence of the current efficiency for sodium and nickel ions on the current density, obtained upon the electrodialysis of a solution of sodium sulphate and nickel sulfate by a ceramic membrane modified by the 5x incorporation of zirconium phosphate is shown in Figure 15.11. Analysis of the curves shows that the current efficiency for nickel ions does not increase over 80% and if the concentration of nickel ions and the density of the polarising current in the solution increases then the membrane selectivity decreases.

It was considered to be of interest to investigate the process of nickel ion transfer through the modified membrane at a much higher concentration of nickel ions in the solution. During the experimental investigation the ions of another bivalent metal - magnesium, which forms hydroxyl compounds less intensively than nickel ions, were added to the dialysis solution. The introduction of magnesium ions to the solution was prompted by the necessity to determine the reason for the hindered transfer of nickel ions through the membrane. If the increased ionic charge (+2) is the reason, then the transfer of magnesium ions will be analogously hindered. Alternatively, the reason would be the formation of hydroxyl nickel compounds.

Experimental data from the electrodialysis of a solution containing equal quantities of sodium, magnesium and nickel sulfates (0.2 g-eqv·l^{-1}) are presented in Figure 15.12. There is no increase in the current efficiency of nickel, even at its rather high concentration in the solution. A precipitate of nickel hydroxyl is formed on the membrane, even at rather low current density. The relative transfer of sodium and magnesium ions are not very high but exceeds that of the nickel ions. This demonstrates some decrease in membrane permeability in the presence of nickel ions.

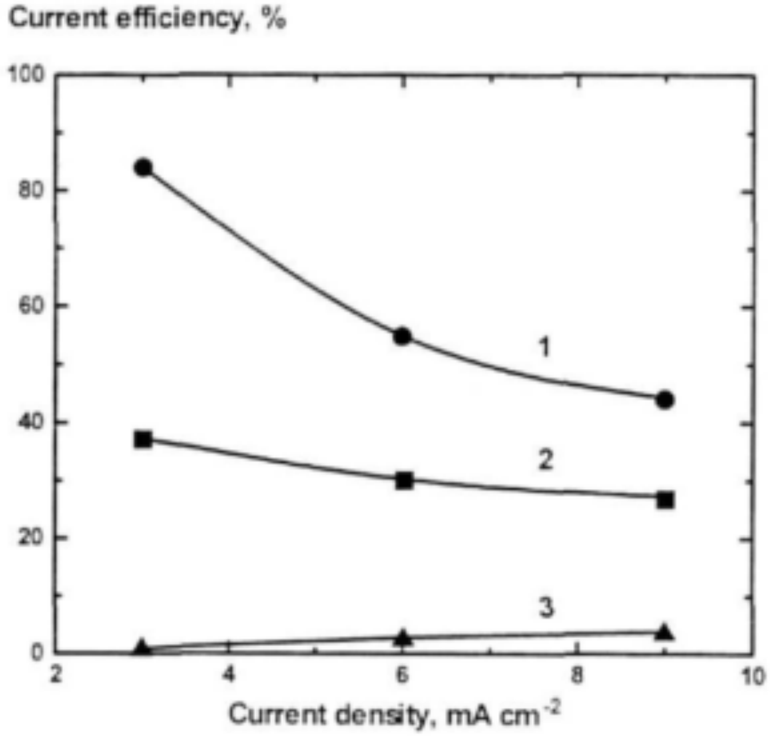


Figure 15.11: Dependence of current efficiency for Na$^+$(1,2) and Ni^{2+} (3,4) ions on the current density during electrodialysis through a zirconium phosphate modified ceramic membrane. The solution contains 0.01 (1,3) and 0.05 (2,4) g-eqv·l^{-1} $NiSO_4$ and 0.1g-eqv·l^{-1} Na_2SO_4.

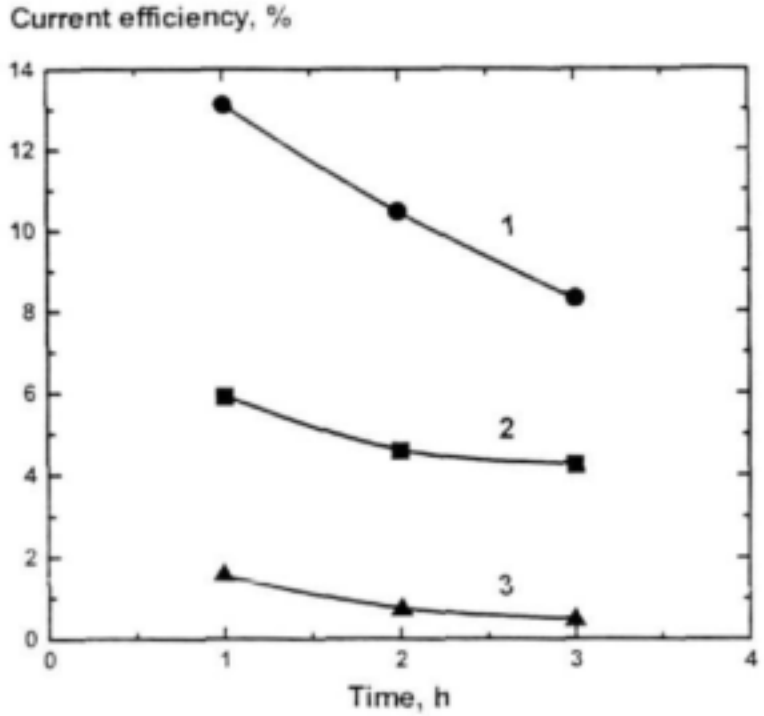


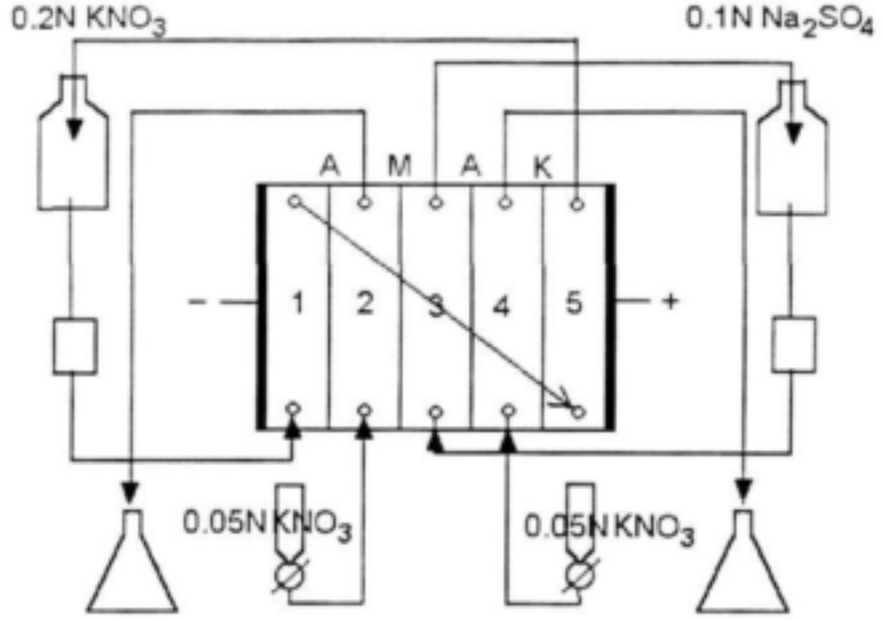
Figure 15.12: The kinetic dependencies of current efficiency for Na^+(1), Mg^{2+} (2) and Ni^{2+}(3) ions upon electrodialysis through the initial membrane modified by zirconium phosphate. The solution contains 0.2 g-eqv·l^{-1} Na_2SO_4, $MgSO_4$ and $NiSO_4$.

Results of our investigations performed with model solutions have shown some interesting and potentially useful results. There was almost no transfer of nickel ions through the inorganic membranes. The concentration of nickel compounds on the surface of the inorganic membranes can be useful for the selective separation of nickel ions from multicomponent solutions. Similar dependencies could possibly be obtained for other metal ions which can form hydroxides (for example, cooper, cobalt cadmium, etc.), but this will only be ascertained if future studies are undertaken.

15.5 INVESTIGATION OF THE INFLUENCE OF ORGANIC CONTENT IN THE DIALYSIS SOLUTION ON THE ELECTROCHEMICAL CHARACTERISTICS OF INORGANIC MEMBRANES

It is well known that the presence of organic compounds in aqueous solutions with rather high molecular mass results in the fouling of polymer membranes in the electrodialysis. One of the goals of the current study was the investigation of the influence of some organic compounds such as humic acid (HA) and dodecyl benzene sulfonate (DBS) in the dialysis solution on electrochemical characteristics of inorganic membranes. (A very similar study had also been done with polymeric membranes in Part A)

These investigations were carried out with a 4-chamber electrodialysis apparatus, shown in Figure 15.13. The membrane to be tested, an inorganic membrane with the incorporated zirconium phosphate (treated 5x), (surface area 2 cm^2), was placed between two anion-exchange membranes. A 0.2 M solution of sodium sulphate was used as a model solution in the investigations. Mixtures of the organic compounds were added to the solution in concentrations of 50-200 mg·l^{-1}.



A - anion exchange membrane MA 40
K - cation exchange membrane MK 40
M - testing inorganic membrane

Figure 15.13: Schematic representation of the 4-chamber electrodialysis apparatus used to study electrodialysis in the presence of organic compounds.

Results of the investigation are presented in Figures 15.14 and 15.15. Figure 15.14 shows the volt-amperic curves obtained under the conditions of solution circulation and that the addition of HA and DBS, in various concentrations, has almost no effect on the character of the obtained dependencies. Irrespective of whether there are organic compounds in the solution or not, the investigated dependencies do not contain the intervals which correspond to the limiting current density. Further, it is only under the conditions of natural convection of the solution, without stirring (curve 6), that an insignificant increase in voltage is observed in the overlimiting mode. This is probably due to the formation of a bipolar border membrane-layer of organic compound/s. When stirring of the solution recommenced, the current-voltage curve changed its shape (from its initial pattern). This confirms the fact that there is no interaction between the membrane with HA nor with DBS.

The absence of interaction of organic compounds with the inorganic membrane is also confirmed by the chronopotentiometric curves, shown in Figure 15.15. They reveal that addition of organic compounds changes the characteristics of electrodialysis with the inorganic membrane in some way. This change does, however, not depend on the concentrations of the added compounds. Further, no poisoning of the membrane by HA and DBS has taken place.

It is considered that the absence of the influence of organic compounds on the electrochemical characteristics of inorganic membranes is of great importance and this fact can be used in the technological design of the purification of complex solutions by electrodialysis.

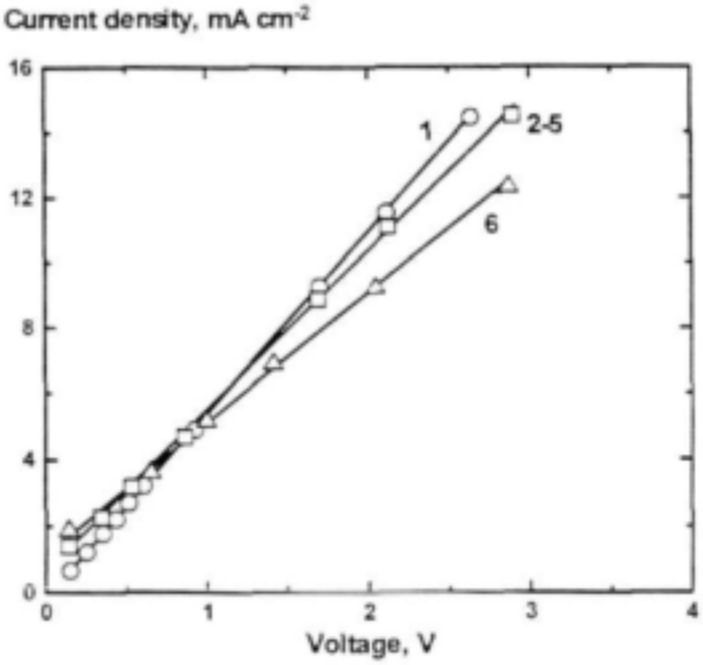


Figure15.14: Current-voltage curves of the solution-membrane system without the addition of fouling compounds (1), with the addition of HA 100 (2), 200 (3) and DBS 100 (4), 200 (5) mg·l^{-1}. Solution pumping rate: 100 ml·min^{-1}. The curve 6 is similar to the curve 5 under the condition of no stirring of solution.

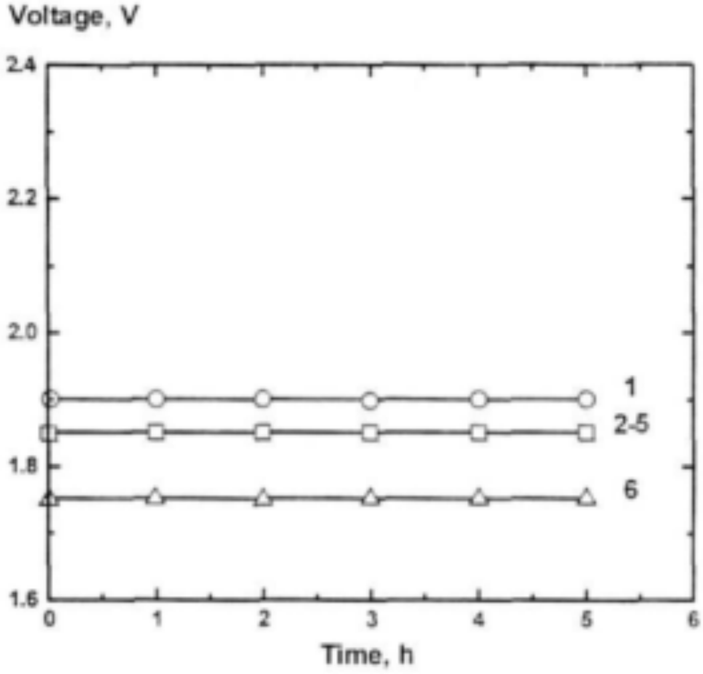


Figure 15.15: The chronopotentiometric curves of the solution-membrane system. The solution does not contain fouling compounds (1), it contains HA 100 (2), 200 (3) and DBS 100 (4), 200 (5) mg·l^{-1}. Pumping rate of solution:100ml·min^{-1}. The curve 6 is similar to the curve 5 under the condition of no stirring of solution.

15.6. ELECTRODIALYSIS OF MINE WATERS USING MODIFIED INORGANIC MEMBRANES

It has been reported that the modification of aluminium and zirconium oxide based inorganic membranes with zirconium phosphate results in the creation of functional charges on the membranes and cation conductivity with selective permeability towards monovalent ions. It was also found that the modified membranes are not affected by the presence of humic acids and surface-active compounds such as DBS. Based on the above findings it was possible to assume that the newly developed membranes would be useful in desalination, by means of electrodialysis, of natural waters containing significant quantities of organic substances.

It was of special interest to study the performance of the inorganic membranes in the electrodialysis of model solutions closely imitating the mine water composition used for similar tests of polymeric based membranes, described in Section 4. The composition of such a solution, termed SIMW, is given in Tables 4.2 and 4.3. The total organic content of the model solutions used was higher than that found in actual mine waters. This was in order to establish the maximum possible influence of organic compounds on the long-term performance of inorganic membranes in electrodialysis process.

The study was carried out using the testing unit shown in Figure 14.3. During the experiments the electrochemical properties of the membranes were constantly monitored by means of the probes connected to silver/silver chloride electrodes. An increase in the voltage drop over the membranes was used as the main characteristic of any fouling. The electrodialysis process was carried out at a current density of 6 mA cm^{-2} and a solution flow rate of 2 $cm.s^{-1}$.

It is clear from Figure 15.16, in which the chronopotentiometric curves for the average for all experiments are given, that when inorganic membranes are used for electrodialysis at a predetermined current density the establishment of a steady state condition takes place after approximately 2 h of operation. Under such conditions the process continues without significant voltage increase both over the membrane and across the electrodialysis cell. This fact testifies to the absence of the fouling effect of organic compounds present in SIMW solutions on the inorganic membranes. In around-the-clock experiments (see Figure 15.17) it was found that a certain increase in voltage does take place (curve #1) but this disappears after the current was switched off (curve 2). In the periodic switching off mode (pulse mode) the operating period was 8 h.

An increase in the voltage drop over the electrodialysis cell under the condition of continuous power supply is related not to fouling by organic compounds but to the formation of a thin layer of low-soluble salts on the membrane surface. Such deposits were found to contain calcium sulfate ($CaSO_4$) and magnesium carbonate ($MgCO_3$). After switching the power off, the solution concentration in the concentration chamber drops because of salt diffusion into the desalination chamber. Due to the porous nature of the inorganic membrane this process, and the resulting dissolution of the thin layer deposits, takes place even in the absence of current reversal. After deposition, dissolution voltage decreases to initial levels. Based on these experimental results it is possible to conclude that the use of inorganic cation exchange membrane containing zirconium phosphate requires operation either in the pulse or current-reversal modes.

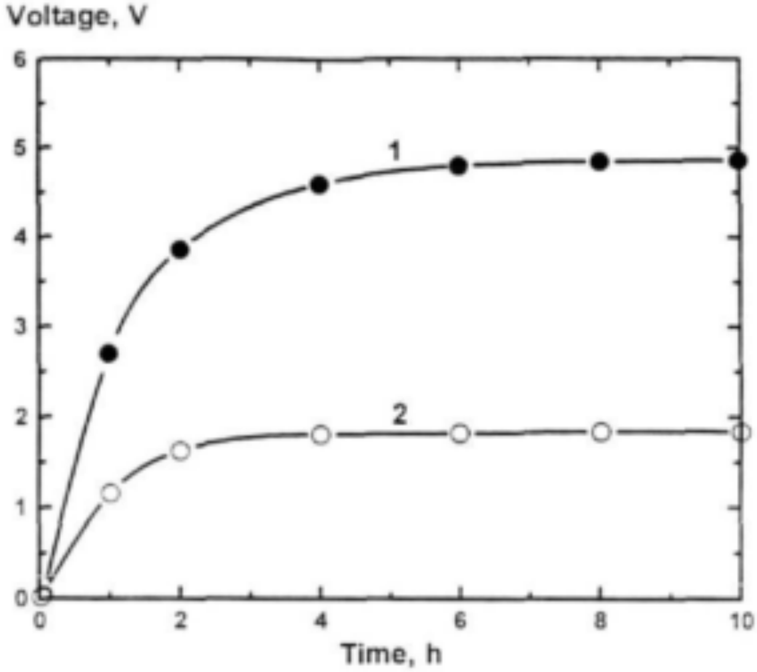


Figure 15.16: Experiment-average chronopotentiometric curves for the electrodialysis of simulated mine waters containing organic compounds. Voltage-drop over the electrode cell (1) and over the inorganic membrane (2).

15.7 COMPARING POLYMERIC AND INORGANIC MEMBRANES

A comparison of the main anti-fouling characteristics of polymeric membranes (Ionics) with and without modification with those of inorganic phosphate-containing membranes, developed in the course of this WRC project, has been carried out. First of all it was established that inorganic membranes have specific properties that make them superior to polymeric membranes, such as the absence of fouling by organic compounds and the lack of limiting current even at significant voltage drops across the membrane. Furthermore, the transport characteristics of monovalent ions through inorganic membranes are similar to those through polymeric based ones (Na^+ current efficiency not less than 95%). As far as the transport of divalent ions (Ca^{2+} and Mg^{2+}) is concerned, it takes place to a lesser extent through the inorganic membranes than through the polymeric ones. This results in another important characteristic of inorganic electrodialysis membranes, namely their selectivity for monovalent ions.

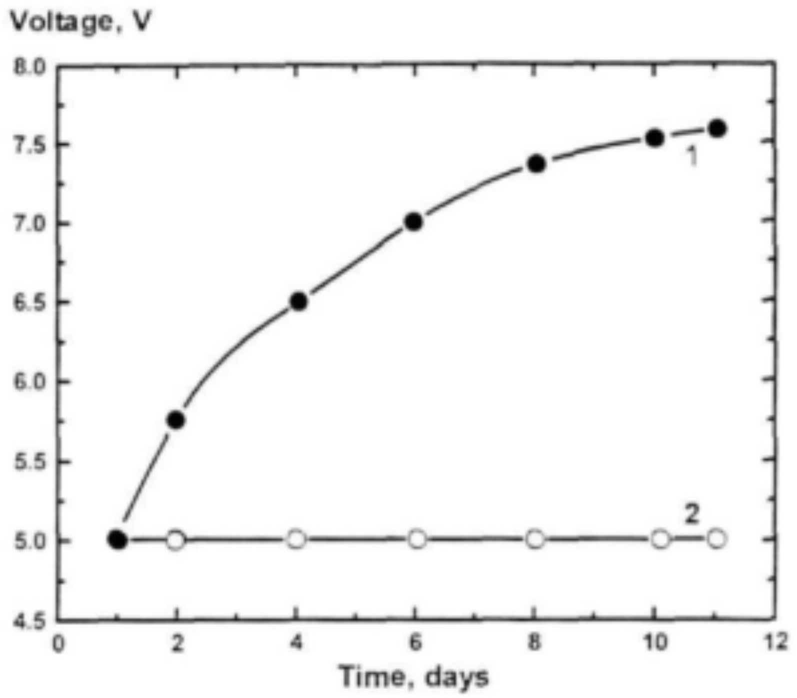


Figure 15.17. Voltage-drop over the electrodialysis cell under continuous power supply (1) and in the pulse mode (2).

16. CONCLUSIONS

The current study entailed investigations into the distinct features of porous structure, transport and electrochemical characteristics of a range of inorganic ceramic membranes. Results of investigations into the preparation of these inorganic ceramic membranes based on the oxides of multivalent metals include the following:

- Ceramic inorganic membranes prepared on the basis of zirconium dioxide and aluminum oxide have similar osmotic permeabilities to the polymeric Ionics membranes.
- It was found that the diffusion permeability of low-molecular electrolytes through the ceramic membranes is 100-1000 times less than that of polymeric ones.
- Modification of ceramic membranes by the incorporation of zirconium phosphate, pyrolytic precipitated carbon and manganese dioxide results in decreases in membrane permeability for water and electrolyte solutions.
- The modification of ceramic membranes by manganese dioxide results in a decrease in their electrical resistance in the electrolyte solutions. This fact can be useful for the application of these membranes in the wide range of electrochemical processes, as electrodes.
- The modification of a ceramic membrane by zirconium phosphate increases its selectivity for cation transfer, making them suitable for use in electrolyte desalination and solution electrolysis.

According to results of investigations in which model solutions were used it was found that the inorganic membranes have a high stability to fouling by HA and surface active compounds. This was confirmed during the electrodialysis of simulated mine water solutions; the potential drop across the membranes remained unchanged after more than 10 days operation. The effective operation of inorganic membranes in electrodialysis installations requires the use of current pulsing and the reversal of power supply.

Hence the following general conclusion is made. As a result of the high stability of inorganic membranes in aggressive media, including oxidizing environments, and their insensitivity to the presence of high-molecular mass electrolytes, they can potentially be used in the following water-related fields: utilisation of effluents of galvanic manufacturers or extraction of non-ferrous metals by electrodialysis, electrodialysis of mine waters, electrochemical synthesis of acids and alkalis, preparation of disinfecting solutions, etc.

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18 CONCLUSIONS TO THE PROJECT AS A WHOLE

It is well known that the presence of organic substances in ED feed waters results in the fouling of anion-exchange membranes by the formation of layers on the membrane surfaces. There is an increase in the electrical resistance of the membrane and in the voltage drop across it, leading to an increase in the power consumption and reduction in the efficiency of the process (an increase in its cost).

The following (18.1 – 18.5) are the main conclusions drawn from the results of our research, according to the original objectives (set out in Section 1.2). The section is concluded with a brief comparison between polymeric and ceramic membranes.

18.1 Polymeric anion-exchange membranes with improved fouling characteristics

In efforts to minimise the fouling of existing anion-transfer membranes by organic substances, methods of chemically treating (modifying) the membranes were explored. Flat-sheet homogenous Ionics anion-exchange membranes were selected. They were successfully modified with various aqueous polyelectrolyte solutions, by both static and dynamic methods. Static treatment entailed simply immersing the membrane in a solution containing a given concentration of modifying agent (generally a polyelectrolyte). Dynamic treatment comprised pumping a solution of the modifier through the concentrate and demineralisation chambers of the ED apparatus. Very good bonding of the modifier to the membrane was achieved under dynamic conditions.

The following conclusions were reached:

- Saturated hydrocarbons in mine drainage water in concentrations of up to 20 mg per litre have no influence on the power consumption of the ED process when Ionics membranes and NB-8-modified Ionics membranes were used.

- Modification of Ionics membranes with NB-8 led to membranes with the greatest resistance coefficient to fouling by organic substances, followed by LT-27. NB-8 is a double charged, high molecular mass, sulfo-containing, surface-active substance. T-27 is an anionic polyacrylamide flocculant of the "Magnafloc" range.

- Membranes modified with LT-27 had lower resistance coefficients than the membranes modified with NB-8 but could also be used as an effective membrane-modifier, especially in terms of costs as it could be used in a lower concentration than NB-8 (5-10 times less).

- Anion-transfer membranes modified under static and dynamic conditions had practically the same measured properties.

- The layer of polyelectrolyte, electroprecipitated under dynamic conditions is quite stable and effectively protects the membrane against fouling for at least 20 days.

Research was not limited to only the chemical treatment of membranes to increase the efficiency of the ED process, electrochemical pre-treatment methods were also used. Current reversal was used and found to result in complete membrane regeneration and restoration of its electrical resistance and voltage drop.

Changes in the electrochemical characteristics of anion-transfer membranes during the pulsing mode of ED have revealed that the pulsing mode can effectively reduce membrane fouling by organics. Optimum conditions of pulsing electrodialysis were determined to be: polarisation for a period of 15 min and current interruption for 3 min. It should be noted, however, that use of the pulsing mode can result in the loss of productivity of the ED process.

There was a significant decrease in organic fouling of anion-transfer membranes when the feed water was initially pumped through the anodic cell of the ED apparatus. Organic substances present in the anodic chamber were destroyed by anode reaction-products and as their concentrations were reduced so the organic fouling of the membrane was reduced.

A further simple, and effective, method for the regeneration of membranes fouled by organic substances was chemical processing in a NaCl solution.

18.2 The preparation of novel non-fouling ceramic membranes

Ceramics were selected for their excellent thermal, chemical and mechanical stabilities.

The following conclusions were drawn from results of investigations into the preparation of the inorganic ceramic membranes based on the oxides of multivalent metals.

- Inorganic ceramic membranes prepared on the basis of zirconium dioxide and aluminum oxide have similar osmotic properties to the polymeric Ionics membranes, but the diffusion permeability of the ceramic membranes for low-molecular electrolytes is 100-1000 times less.
- Modification of ceramic membranes by the incorporation of zirconium phosphate, pyrolytic precipitated carbon and manganese dioxide results in decreased membrane permeabilities for water and electrolyte solutions.
- The modification of ceramic membranes by manganese dioxide results in a decrease in their electrical resistance in the electrolyte solutions. This fact can be useful for the application of these membranes in the wide range of electrochemical processes, as electrodes.
- The modification of a ceramic membrane by zirconium phosphate increases its selectivity for cation transfer, making them suitable for use in electrolyte desalination and solution electrolysis.

Results of the electrodialysis of model solutions of mine water showed that the inorganic membranes have a high stability to fouling by HA and surface active compounds. The potential drop across the membranes remained unchanged after more than 10 days operation. The effective operation of inorganic membranes in electrodialysis installations requires the use of current pulsing and the reversal of power supply.

18.3 Cation-exchange membranes with increased transfer for monovalent ions.

Results of research into the modification of cation-exchange membranes to enhance their transport of monovalent ions have shown that:

- The processing or modification of membranes under dynamic conditions influences the relative transfer of mono- and divalent ions through the membranes. The application of the NB-8 modifier, a most effective anti-fouling modifying agent, has practically no influence on the transfer of chloride and sulfate through the NB-8-modified anion-transfer membrane. The permeability of divalent magnesium ions, compared to monovalent sodium ions, does however increase through the modified cation-transfer membrane. This reagent can therefore be used to modify membranes for use in water softening by ED.

- Modification of membranes by the polyelectrolyte LT-27 increases their permeability to monovalent ions, eg. chloride, through the anion-transfer membrane and Na^+ through the cation-transfer membrane. This reagent has a high protection efficiency and could be suitable for modifying membranes intended for use in the ED of concentrated solutions with high total-hardness values.

18.4 Production of ceramic ion-exchange membranes with increased chemical stability

As a result of the high stability of inorganic membranes in aggressive media, including oxidizing environments, and their insensitivity to the presence of high-molecular mass electrolytes, they can potentially be used in the following water-related fields: utilisation of effluents of galvanic manufacturers or extraction of non-ferrous metals by electrodialysis, electrodialysis of mine waters, electrochemical synthesis of acids and alkalis, preparation of disinfecting solutions, etc.

18.5 Incorporation of the novel membranes into reactor units

The novel membranes developed by us have been successfully incorporated into ED units/installations. The experimental apparatus used by us during the course of our investigations was similar to that used in industry, only on bench-scale.

18.6 Brief comparison of polymeric and inorganic membranes

Polymeric membranes (Ionics), unmodified and modified, and phosphate-containing inorganic membranes, developed during the course of the study were compared for their main anti-fouling characteristics. Inorganic membranes have specific properties that make them superior to polymeric membranes. First, they are not fouled by organic compounds, and they have a lack of limiting current even at significant voltage drops across the membrane. The transport characteristics of monovalent ions through inorganic membranes are similar to those through polymeric based ones (Na^+ current efficiency not less than 95%). The transport of divalent ions (Ca^{2+} and Mg^{2+}), however, takes place to a lesser extent through the inorganic membranes than through the polymeric ones. This results in another important characteristic of inorganic electrodialysis membranes, namely their selectivity for monovalent ions.

18.7 Recommendations for future research

Results of our extensive investigations, carried out under laboratory and bench-scale conditions have revealed that significant opportunities exist by which to increase the efficiency of the ED process for water desalination, by reducing the organic-fouling of Ionics membranes. Future research should be focused on the appropriate testing of our research findings in industrial-scale ED apparatus. Improvements in the ED process should be monitored.

APPENDIX A1

TECHNIQUE USED FOR THE TREATMENT OF IONICS MEMBRANES BY NB-8

A1.1 Preparation of matrix solution of NB-8 modifier

NB-8, in an amount required to produce a solution concentration of 10 $g \cdot l^{-1}$, was dissolved in water with agitation for 2 - 3 hours. The prepared solution should be slightly opalescent and consistent in appearance. The use of demonised water for the preparation of the matrix solution is preferable. However, water with a mineral content of no more than 3 $g \cdot l^{-1}$ may be used. If deionised water is not used then it is necessary to test the available water in the laboratory prior to the preparation of a large volume of matrix solution. For this purpose, a 1 litre matrix solution should be prepared and kept for 3 hours in order to evaluate its quality. If turbidity or deposit formation is observed in the prepared solution then the quality of the water used is not suitable. In such a case, it would be necessary to first purify this water.

The matrix solution storage period, at a temperature of 10 (± 5) ^{0}C, should not exceed 3 days. It is also necessary to store the matrix solution in a dark place.

A1.2 Preparation of a modifier working solution of NB-8

Demineralised water, or other suitable water, is used for the preparation of a modifier working solution. The modifier working solution is prepared by diluting the matrix solution in water with careful agitation. To prepare 1 litre of the working solution, 50 ml of a matrix solution is diluted with 950 ml of water. The concentration of NB-8 in the working solution should be 500 ml per litre. The volume of working solution, required for treatment of the membrane is 0.4 litres per 1 m^2 of the membrane's surface area.

A1.3 Membrane modification by the static method

Membranes are treated under static conditions by immersing the membranes in the NB-8 working solution, with constant agitation for 10 minutes. The minimum solution to membrane volume ratio should be 3:1. It is, however, possible to increase this ratio by increasing the volume of the modifying solution. After treatment, the NB-8 solution is removed and the excess modifying agent is washed off the membranes with water, in a volume ratio of 100:1 - with respect to the membranes. At this point, the membranes are ready to be mounted into the electrodialysis cells.

A1.4 Membrane modification by the dynamic method in an electrodialysis apparatus

Membrane treatment in the electrodialysis cells is carried out by pumping a NB-8 working solution through the cells of the apparatus. The working solution is passed through both the demineralisation and concentration compartments. The velocity of the feed solution, circulating through the electrodialysis cells, has no essential significance, but should not exceed 1 $cm \cdot s^{-1}$. During primary treatment of anion transfer membranes, circulation of the modifier working solution is conducted with an electrical current imposed between the electrodes of the electrodialysis apparatus. The density of the applied current should exceed the limiting value during membrane treatment. In the case of the Ionics anion transfer membranes this value is 1.0 $A \cdot m^{-2}$ of the membrane surface. The treatment time required for the polarisation mode is

15 minutes. After current interruption, the electrodialysis cells are washed out with deionised water, produced during solution dialysis, in circulation mode. For this purpose, the water supply is maintained at the usual feed velocity experienced during electrodialysis. The time required for washing is 20 minutes. The dialysis cell should then be filled with fresh water. Washing is repeated for a further 10 minutes, with current applied in the opposite direction. Upon termination of the washing procedure, the rinse water is expelled from the electrodialysis apparatus.

APPENDIX A2

CRITERIA FOR ESTIMATING MEMBRANE RESISTANCE TO FOULING

Evidence of membrane fouling is usually seen in a decrease of selectivity with respect to counter-ion transfer, and in an acceleration of the voltage drop during electrodialysis, i.e. in a decrease of electrical conductivity of the membrane surface. Sometimes both effects occur simultaneously. However, often only a decrease in the electrical conductivity of the membrane is observed during fouling.

Several methods by which the stability of membranes to fouling can be estimated are known. The most common methods are the following:

- from a change in the static exchange capacity of membranes after contact with foulants
- from a decrease in membrane selectivity
- from the electrical conductivity of the membranes,
- from an acceleration in the voltage drop across the membrane stack , and
- from an acceleration in the voltage drop directly at the membrane surface (including diffusion layers).

Often the static exchange capacity of a membrane is practically unaffected, but its selectivity and/or electrical conductivity decreases substantially, i.e. membrane fouling has occurred. The change in selectivity of a membrane reflects only one side of the process, namely ion transfer. The other side, namely the energetics of the process, cannot be determined. It is inconvenient to estimate membrane resistance to fouling from the change in electrical conductivity because, in order for this parameter to be measured, the electrodialyser must be dismantled. In-situ probes allow only for the estimation of the combined resistance of the membrane and pre-membrane layers.

Detection of an increase in the rate of voltage drop across a membrane stack can only serve as a sign of membrane fouling; it cannot be used for a quantitative estimation of fouling. Acceleration in the voltage drop at the membrane surface, including the pre-membrane layers, is most frequently used for the estimation of membrane stability against fouling. However, this value is firstly an actual measurement (i.e. $V.h^{-1}$), and cannot therefore be used in the capacity of a criterion (a concept which, by definition, cannot be measured). Secondly, different membranes already have different degrees of specific resistance before the fouling process begins. This situation prohibits comparison between the stabilities of different membranes against fouling from the outset. As a result, it is difficult to develop a criterion for the estimation of the stabilities of different membranes towards fouling.

For a suitable estimation, two criteria were used, namely K_f and K_s.

K_f is a criterion that shows the relative increase in power consumption required for ion transfer through a membrane during the process of fouling, in relation to an ideally non-fouled membrane.

An ideally non-fouled membrane is understood to be a membrane that has an equivalent initial selectivity compared to the membrane under consideration. The voltage drop and current efficiency of a test membrane and an ideally non-fouled membrane are shown in Figure A2.1.

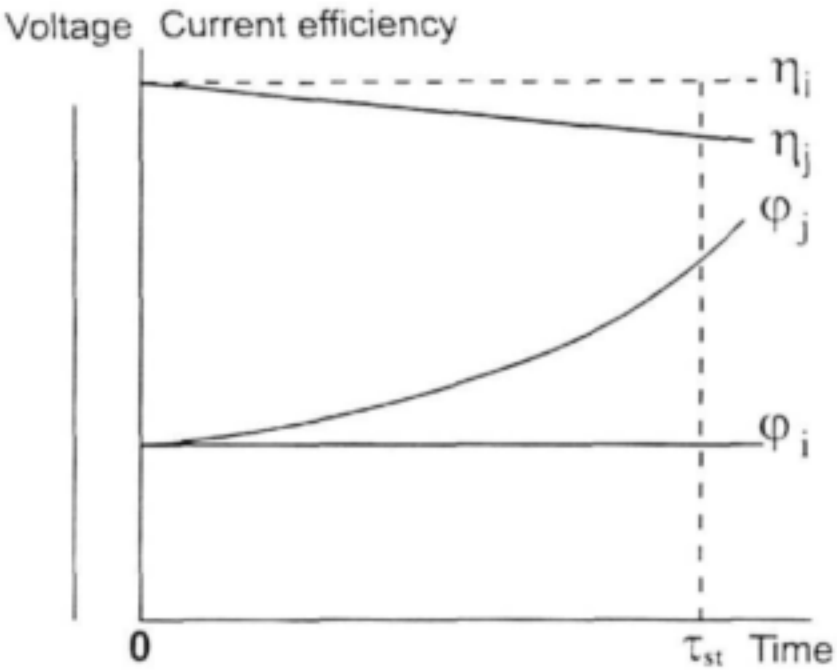

Figure A2.1: Voltage drop (V) and current efficiency (η) of membrane to be studied (j) and ideally non-fouled membrane (i) versus time of electrodialysis (t). τ_{st}: standardised time.

After examination of the given functions in Figure A2.1, it follows that the value of K_f is a function of the time selected for electrodialysis. This value must, therefore, be standardised. Thus, criterion K_f can be determined by the following equation:

$$K_f = \left[\frac{\int_0^{\tau} \varphi(\tau)\, d\tau}{\int_0^{\tau} \eta(\tau)\, d\tau} \right]_j \left[\frac{\eta}{\varphi\tau} \right]_i \qquad (A.1)$$

where:

φ - voltage drop at the membrane

τ - time elapsed during electrodialysis

η - counter-ion current efficiency

The indices "j" and "i" represent the examined membrane and the same membrane if it were ideally non-fouled, respectively.

The physical meaning of criterion K_f is the relative increase in power consumption during the process of electrodialysis, for real membranes subjected to modification, in comparison with ideally non-fouled membranes. For the modification of membranes, with the objective of increasing their stability against fouling, it is more convenient to use criterion K_s.

Criterion K_s gives an indication of how many times the power consumption is reduced when the initial unmodified membranes are substituted with modified membranes.

Upon modification of the initial membrane, it is possible that its surface resistance may increase. However, because the rate of voltage increase at modified membranes is lower than at the initially unmodified ones, the power consumption required for electrodialysis with modified membranes may be reduced.

Coefficient K_s can be quantitatively expressed as follows:

$$K_s = \left[\frac{\int_0^{\tau} \varphi(\tau)\,d\tau}{\int_0^{\tau} \eta(\tau)\,d\tau}\right]_{in} \left[\frac{\int_0^{\tau} \eta(\tau)\,d\tau}{\int_0^{\tau} \varphi(\tau)\,d\tau}\right]_{m} \qquad (A.2)$$

In the above equation, indices "in" and "m" describe the initial and modified membranes respectively. If $K_s > 1$, then membrane modification is beneficial. If $K_s \leq 1$, membrane modification does not result in a reduction in power consumption. The above effect is illustrated in Figure A2.2.

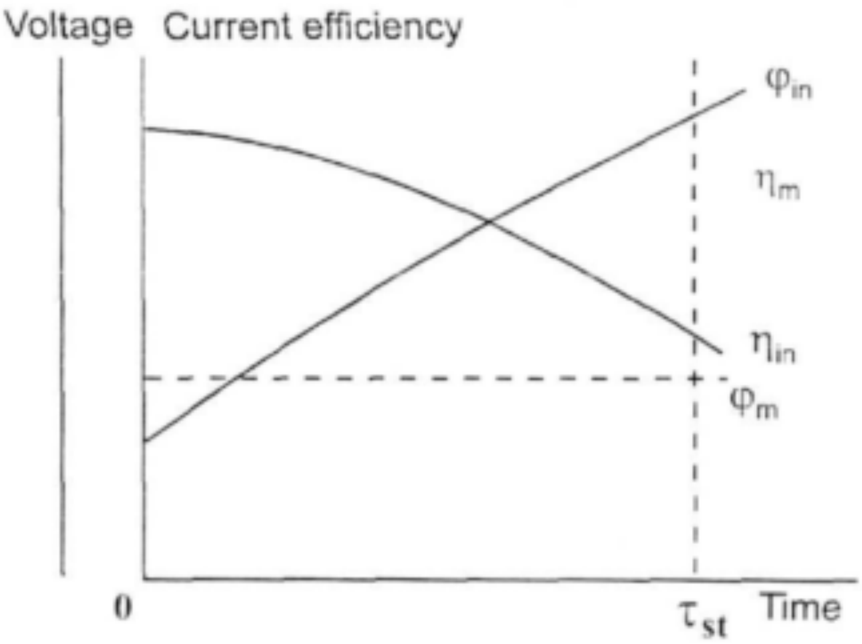

Figure A2.2: Voltage drop (V) and current efficiency (η) of initial unmodified (in) and modified (m) membranes versus time (t). τ_{st}: standardised time.

In Figure A2.2 it is shown that the areas of curves $\varphi_m = f_1(\tau)$ and $\eta_{in} = f_2(\tau)$ are smaller than the areas of curves $\varphi_{in} = f_3(\tau)$ and $\eta_m = f_4(\tau)$, i.e. $Ks > 1$ and membrane modification is beneficial in terms of a reduction in power consumption required during electrodialysis.

APPENDIX 3 (A3)

TECHNOLOGY TRANSFER ACTIONS

PATENTS

1. V.M. Linkov, V.N. Belyakov "Ceramic membranes", RSA patent 97/7639.

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4. V.M. Linkov, V.N. Belyakov, "Composite inorganic membranes for desalination reactors", *IDA World Congress on Desalination and Water Reuse*, Madrid, Spain, 6-9 October, 1997, 487.
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INDUSTRIAL MEETINGS

ESKOM-TRI	7 meetings
Tutuka power station	2 meetings

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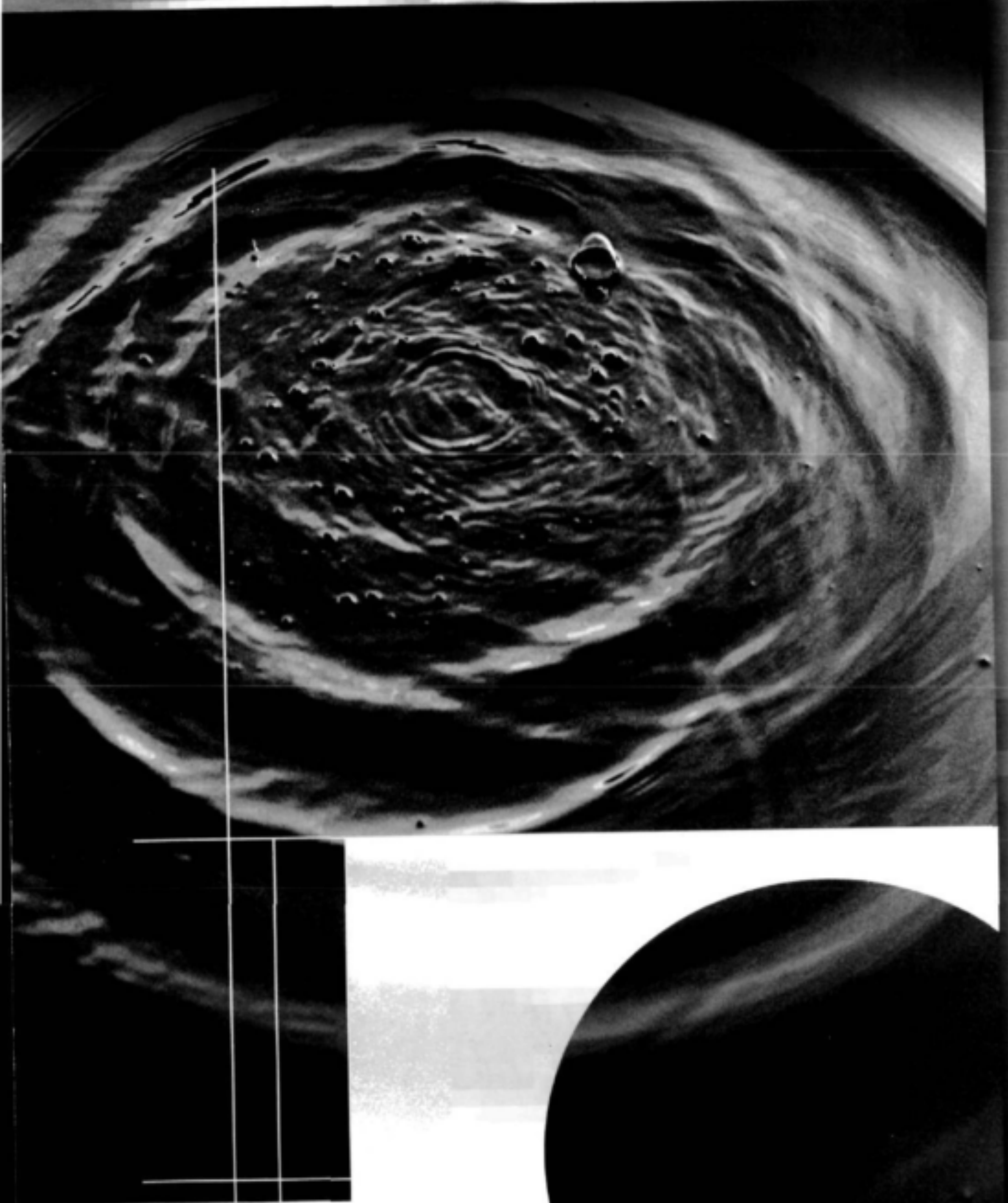

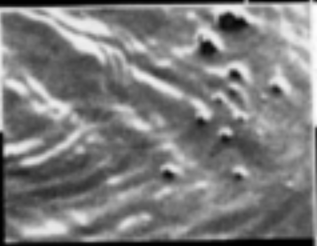

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