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CHARACTERIZATION OF PVC BASED HETEROGENEOUS CATION EXCHANGE MEMBRANES PREPARED WITH IONIC LIQUIDS

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ÖZET

İYONİK SIVILARLA PVC TEMELLİ HETEROJEN KATYON DEĞİŞTİRİCİ MEMBRAN HAZIRLANMASI VE TANIMLANMASI

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Ayırma süreçlerinde sıkça yararlanılan membran teknolojisi, birçok alanda yeni malzemeler kullanılarak yapılan gelişmeler sayesinde, geleneksel, yüksek enerji tüketen ve tehlikeli atık içeren, pahalı süreçlere kıyasla daha da yaygınlaşmıştır. Özellikle atık su arıtımı ve atık sulardan ürün eldesi, proses ve içme suyunun hazırlanmasında diğer ayırma teknikleriyle birlikte iyon değiştirici membranlar kullanılmaktadır. Katyon değiştirici membranlar ise, tuzlu sudan içme suyu eldesinden yakıt pillerine, metal kaplamacılıkta atık sudan metal tuzunun geri kazanımından klor-alkali süreçlerine kadar geniş bir kullanıma sahiptir.

Bu çalışmanın amacı, iyonik sıvılarla plastikleştirilmiş PVC bağlayıcı içeren kuvvetli asidik, heterojen yapıda katyon değiştirici membranların üretimi ve tanımlanmasıdır. Son yıllarda yapılan çalışmalarda, parlayıcı, patlayıcı olmamaları, yüksek ısıl kararlılıkları, geri dönüşümlü olmaları ve düşük buhar basınçları sebebiyle yeni bir seçenek olarak ortaya çıkan iyonik sıvıların kullanımı ümit vaat edici sonuçlar vermektedir. Bu projede izlenen heterojen yöntemde, iyonik sıvı, plastikleştirici olarak ilk defa membran üretiminde kullanılmıştır.

Bu çalışmada, membranlar heterojen yöntem izlenerek üretilmiştir. Bu yöntemde, toz haline getirilmiş iyon değiştirici reçinenin, film oluşturucu malzeme, plastikleştirici ve çözgen içeren çözeltiye dağıtılmasıyla meydana gelen karışım cam üstüne dökülür, film çekme bıçağı ile çekildikten sonra çözgen hava kurutması veya sıcaklık etkisiyle buharlaştırılır. Reçine olarak polistiren-divinilbenzen kopolimer gövde üzerinde sülfonik asit fonksiyonel grup içeren ticari iyon değiştirici reçine, membran destek malzemesi olarak süspansiyon veya emülsiyon PVC, plastikleştirici olarak dioktil ftalat veya fosfonyum bazlı bir iyonik sıvı, çözücü olarak ise siklohekzanon kullanılmıştır.

Üretilen membranların kuru ve ıslak ağırlıkları farkından yola çıkarak nem içeriğine bakılmıştır. Kuru ve ıslak yoğunlukları ölçülmüş, ıslak membrandaki su miktarının membranın birim hacmine oranından gözenekliliği hesaplanmıştır. İyon değiştirme kapasitesi membrandaki H^+ iyonlarının Na^+ iyonları ile yer değiştirme miktarından bulunmuştur. Donnan diyaliz yöntemi ile difüzyon katsayısı hesaplanmıştır. Membranın transport sayısı ise membran geriliminin ölçümü yöntemiyle belirlenmiştir.

Üretilen membranların nem içerikleri ortalama ağırlıkça %36 olarak bulunmuştur. Kuru yoğunlukları ortalama 0.93 g/cm^3, ıslak yoğunlukları ise yaklaşık 1.07 g/cm^3 bulunmuştur. Gözeneklilik değerleri ortalama 0.34, iyon değiştirme kapasitesi ise yaklaşık 1.74 meq-Na^+/cm^3-kuru membran olarak hesaplanmıştır. Transport sayıları dioktil ftalat bazlı membranlarda ortalama 0.55, iyonik sıvı bazlı membranlarda ise 1.05 civarında bulunmuştur. Membranların Na^+ iyonu yayınım katsayıları yaklaşık olarak $4.27x10^{-5}$ cm^2/s bulunmuştur.

Anahtar kelimeler: Katyon değiştirici membran, iyonik sıvı, membran tanımlama

ABSTRACT

CHARACTERIZATION OF PVC BASED HETEROGENEOUS CATION EXCHANGE MEMBRANES PREPARED WITH IONIC LIQUIDS

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Advances in membrane technology, which is used often in separation processes, especially in new materials, can make this technology more competitive with traditional, high-energy intensive, environmentally undesirable and costly processes. Ion exchange membranes are used particularly in waste water treatment and preparation of process and drinking water together with other separation techniques. Cation exchange membranes have been used in various industries such as production of drinking water from sea water, recovery of useful metal salt from waste water in metal plating, production of fuel cells, chlor-alkali processes.

The aim of this study is to produce PVC based strong acidic cation exchange membranes and to characterize them. Recent studies show hopeful results regarding ionic liquids, which are one of novel alternatives, since they have low volatility, low melting points, are high-temperature stable, nonflammable.

In this research, membranes were prepared by following a heterogeneous method, in which powdered ion exchange resin is dispersed in a solution consisted of a binder, a plasticizer and a solvent.

Resulting solution is cast on a glass surface by means of Doctor blade and is left to dry by ambient air or by heating. Suspension polymerized PVC or emulsion polymerized PVC was used as film-forming binder. Dioctyl phthalate or a phosphonium based ionic liquid was used as plasticizer. Cyclohexanone was used as solvent and commercial strong acidic styrene-divinyl benzene cation exchange resin was used as ion exchange particles.

Water content of the membranes prepared was found by the difference between their wet and dry weights. Dry and wet densities of the membranes were also measured. Membrane porosities were calculated from volume of free water within membrane per unit volume of wet membrane. Ion exchange capacity was found by the exchange amount of H^+ ions with Na^+ ions. Diffusivity values of Na^+ ions across the membrane were calculated by using Donnan dialysis method. Transport numbers were determined by membrane potential method.

Volume percent of water of the membranes prepared was approximately 36% (weight based). Dry densities were around 0.93 g/cm^3 while wet densities were about 1.07 g/cm^3. Membrane porosity was found approximately 0.34. Ion exchange capacity is around 1.74 meq-Na^+/cm^3-dry membrane. Transport numbers of DOP based membranes were calculated around 0.55 whereas that of ionic liquid based membranes about 1.05. Diffusivity values of Na^+ ions were found approximately $4.27x10^{-5}$ cm^2/s.

Key words: Cation exchange membrane, ionic liquid, membrane characterization

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Abbreviations:

AAS : Atomic Absorption Spectrophotometer
AC : Alternative current
CH : Cyclohexanone
CXR : Cation exchange resin
DC : Direct current
DOP : Dioctyl phthalate
E-PVC: Emulsion polymerized polyvinyl chloride
IL : Tetradecyl(trihexyl)phosphonium decanoate
PVC : Polyvinyl chloride
SEM : Scanning Electron Microscopy
S-PVC: Suspension polymerized polyvinyl chloride
TGA : Thermo-Gravimetric Analysis

Symbols:

A	: The mean ionic diameter	[Å]
a_i	: The activity of species i	[M]
c_i	: Concentration of species i	[M]
D	: Diffusion coefficient	[cm^2/s]
ΔE	: Membrane potential	[mV]
F	: Faraday constant	[Coulomb/mol]
I_i	: Electric current carried by ion i	[mA]
IEC	: Weight based ion exchange capacity	[meq Na^+/g-dry]
I_m	: Ionic strength	[mol/kg]
k	: Boltzmann's constant	[J/K]
m_i	: Molality of the side i	[mol/kg]

$M_{e,Na+}$	: Equilibrium concentration of Na^+	[meq Na^+]
$M_{i,Na+}$	: Initial concentration of Na^+	[meq Na^+]
N_A	: Avogadro constant	[particles/mol]
N_A	: Diffusional flux of A	[kmol/m^2s]
Q_i	: Concentration of Na^+ inside the membrane	[mg Na^+/g memb]
R	: Gas constant	[mJ/mol.K]
T	: Absolute temperature	[K]
t_i	: Transport number of solution	[-]
$\bar{t}_i$	: Transport number of ion i in the membrane	[-]
ΔV	: Volume increase of membrane	[cm^3-water/ cm^3-dry]
V_d	: Volume of dry membrane	[cm^3]
V_w	: Volume of wet membrane	[cm^3]
W_d	: Weight of dry membrane	[g]
W_w	: Weight of wet membrane	[g]
z_i	: Valence of ion i	[-]

Greek Symbols:

ε_0	: The permittivity of vacuum	[1/N.m^2]
$\varepsilon_{r,A}$	: The solvent dielectric constant	[-]
γ_i	: Activity coefficient of species i	[-]
$\gamma_\pm$	: The mean ionic activity coefficient	[-]
φ_w	: Volume fraction of water	[g-water/ g-wet membrane]
μ_i	: The chemical potential of i	[J/mol]
ρ_d	: Dry density	[g/cm^3]
ρ_w	: Wet density	[g/cm^3]
ρ_{water}	: The density of water	[g/cm^3]
τ	: Membrane porosity	[-]

1. INTRODUCTION

A membrane is defined as a film or layer with a thickness that is small in comparison with the surface (Zagorodni, 2007). Separation membranes have become important parts of the chemical technology because of their growing industrial applications in the areas of biotechnology, nanotechnology and membrane based energy devices besides different membrane based separation and purification processes. These processes are economically practical due to low energy requirements. Advances in membrane technology, especially in new materials, can make this technology more competitive with traditional, high-energy intensive, environmentally undesirable and costly processes (Nagarale et al., 2006).

Ion-exchange membranes are one of the most advanced separation membranes. An ion exchange membrane is an ion exchanger of any geometrical shape that can be used as a separation wall between two solutions (Zagorodni, 2007). They are classified into two types by preparation methods as heterogeneous and homogeneous. Homogeneous ones are prepared mostly by polymerization. Heterogeneous ion-exchange membranes may be made by mechanical incorporation of powdered ion-exchange resin into sheets of rubber, polyvinyl chloride (PVC), acrylonitrile copolymers and some other extrudable or moldable matrix. Such membranes can be prepared by different methods: (*i*) molding the mixture of ion exchange powder and dry binder polymer under the proper conditions into a sheet, (*ii*) extruding the mixture of ion exchange particles, a binder polymer and a plasticizer as a sheet, (*iii*) dispersing ion exchange particles in a partially polymerized binder polymer and casting into a film, finishing the polymerization, (*iv*)

dispersing ion exchange particles in a solution containing a binder and a plasticizer, casting the mixture into a film and evaporating the solvent.

In this study, PVC based strong acidic cation exchange membranes are prepared by following last method. Suspension polymerized PVC (S-PVC) or emulsion polymerized PVC (E-PVC) is used as film-forming binder. Dioctyl phthalate (DOP) or an ionic liquid (IL), which is tetradecyl(trihexyl)phosphonium decanoate, is used as plasticizer. Cyclohexanone is used as solvent and commercial strong acidic styrene-divinyl benzene cation exchange resin is used as ion exchange particles.

A plasticizer can be defined as a low molecular weight material added to polymeric materials to improve their flexibility by lowering glass transition temperature. Plasticizer interacts with the polymer chains on the molecular level as to speed up its viscoelastic response or increase chain mobility (Wypych, 2004). DOP, which is a phthalate ester, is the most commonly used plasticizer for PVC. However, these petroleum-derived products cause endocrine-disruption activity in laboratory rats. Extensive research is going on to find alternative plasticizers for plastic materials. Ionic liquids are one of these few novel alternatives which have shown hopeful results (Rahman and Brazel, 2004). Ionic liquids are salts that are liquid at or near room temperature. Ionic liquids exhibit extremely interesting properties (Sesto et al., 2005; Izak et al., 2007):

1. They have wide liquid range.

2. Due to their negligible vapor pressure they are not lost into the environment making possible their repeatedly use in downstream processing.

3. Ionic liquids can solubilize a large range of organic molecules and transition metal complexes, which may present reduced solubility in conventional solvents.

4. Due to selective solute-ionic liquid interactions it is possible to remove/recover defined target solutes from reaction media, while keeping other reactants or products.

5. Due to their good thermal stability, reactive processes may take place at high temperatures (up to around 250ºC), which leads to faster kinetics in the case of endothermic reactions.

Ionic liquids can be based on pyridinum, imidazolium or ammonium. There are also phosphonium based ionic liquids. Phosphonium salts are much more thermally stable than the corresponding ammonium and imidazolium salts. The imidazolium cation also contains protons which are not entirely inert. While they are somewhat acidic, phosphonium salts have no such acidic protons (CYTEC Industries).

After preparation step, ion exchange membranes were characterized by physicochemical, morphological and electrochemical ways in this thesis.

Physicochemical characterization consists of volume fraction of water, dry and wet densities of the membrane, membrane porosity, weight based ion exchange capacity and isotherm studies. Water content of a membrane determines its dimensional stability and also affects its selectivity, electrical resistance. Ion exchange capacity is a major characteristic of an ion exchange material. It is a measure of the quantity

of ions removed by an ion exchange material. Isotherm studies were carried out in order to characterize ion exchange equilibrium.

Morphological characterization is performed by Scanning Electron Microscopy (SEM). The samples were firstly coated with a gold layer under 10^{-6} atm for 120 sec. and then were examined under 20 kV. The surface images were taken x100 magnification whereas cross-sectional views were taken between x250 - x500 magnifications depending on the thicknesses of the membranes. Electrochemical characterization of the membranes prepared consists of the calculation of transport number by measuring membrane potential in two-compartment test chamber of equal volumes. The transport number can be defined as the fraction of the electric current which is carried by the ion targeted (Helfferich, 1962).

Ion exchange membrane separation processes are used today in a large variety of applications from water desalination to electrodialysis to the production of acids and bases by electrodialysis with bipolar membranes or the elimination of toxic components from industrial effluents. Figure 1-1 shows some examples of applications of ion exchange membranes used in various fields. Some processes such as electrodialysis are used on a large scale for the desalination of water or the removal of certain electrolytes from food and chemical products. Other processes such as Donnan dialysis, bipolar membrane water dissociation or the continuous electrodeionization are used on a much smaller scale for the production of ultra pure water or for purification and separation of certain food and pharmaceutical components, or for the treatment of industrial waste streams to recover toxic and valuable materials such as heavy metals or radioactive isotopes (Strathmann, 2004).

In this study, the membranes were tested by Donnan dialysis. As a result, Na^+ ion diffusivities in the membranes were found. The basic applications of the ion exchange membrane process are based on the Donnan membrane equilibrium principle and this process solve two important environmental problems, for the recovery and enrichment of valuable ions, and the removal of undesirable ions from waste water.

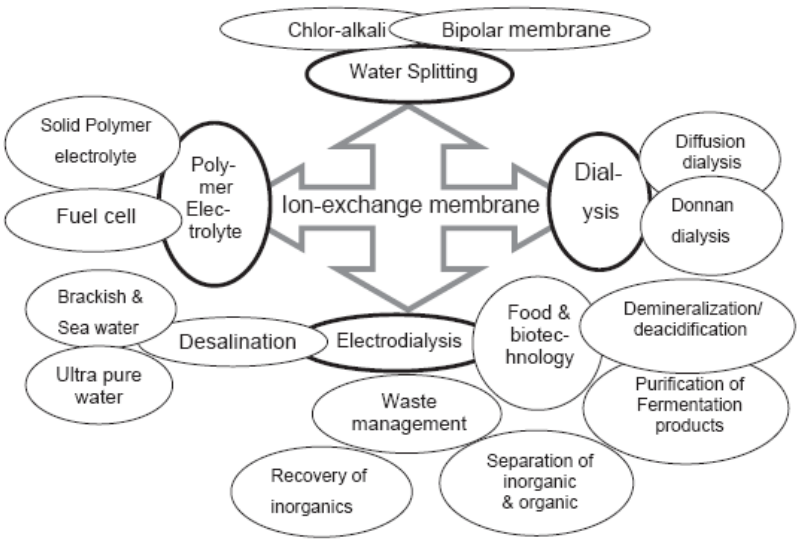


Figure 1-1 Schematic presentation for the several industrial applications of ion exchange membrane (Nagarale et al., 2006)

2. LITERATURE SURVEY

In this thesis, both preparation and characterization methods of PVC based cation exchange membranes were studied. PVC based cation exchange membranes were plasticized with either a traditional plasticizer or an ionic liquid and their physicochemical, electrochemical and morphological properties were compared.

After ion exchange resins were developed in 1930s, a heterogeneous ion exchange membrane, in which a finely powdered ion exchange resin and binding polymer were formed in a membrane, was reported. The first paper on a synthetic ion exchange membrane was published in 1950 (Sata, 2004).

Yamabe and Seno (1964) prepared cation exchange membranes heterogeneously. They mixed fine powder of PVC and dioctyl phthalate homogeneously and added cyclohexanone to plasticized PVC. This mixture was heated until it became transparent. Finely powdered cation exchange resin was added to plasticized PVC and homogeneously mixed. The mixture was kneaded between rollers and then made into a film with rollers, and dioctyl phthalate is extracted with methanol.

Gohil et al. (2004) prepared homogeneous and heterogeneous type of ion exchange membranes and compared their characteristics. They dried ion exchange resin particles in an oven at 60°C for 24 hours, powdered in a ball mill and sieved to the desired mesh size. Finely powdered ion-exchange resin was then dispersed in the solution of PVC in tetrahydrofuran and then membranes were cast on polypropylene fabric at an ambient temperature by a casting machine and were allowed

to dry for 30 minutes. They used an experimental cell made from Perspex and had two compartments separated by the membrane for membrane potential measurements. To minimize the effect of boundary layers on potential, the solutions in both compartments were vigorously stirred by magnetic stirrers. For the membrane potential measurements, the ratio of salt concentration of the higher side to that of the lower side was kept constant. The potential developed across the membrane was recorded with the help of digital voltammeter using saturated calomel electrodes.

The first ion exchange membrane separation process that was used on a large industrial scale is electrodialysis which was introduced in the late 1950s and early 1960s as an efficient and economic technique for the desalination of brackish water. The principle of the process has been known for more than 100 years. Between 1880 and 1900 Ostwald studied the properties of semipermeable membranes and discovered that a membrane is impermeable for an electrolyte if it is impermeable either for its cations or its anions. To illustrate this, he postulated the existence of the so-called "membrane potential" at the boundary between a membrane and an aqueous solution as a consequence of a difference in ion concentration. Twenty years later Donnan confirmed this postulate membrane potential between an ion exchange membrane and the surrounding solution. Simultaneously, he developed a mathematical equation describing the concentration equilibrium which resulted in the so-called "Donnan exclusion potential" (Strathmann, 2004).

Cherif et al. (1998) investigated Donnan dialysis of Ag^{+} and Zn^{2+} through a cation exchange membrane when a proton concentration difference was maintained between the two sides of the membrane. Çengeloğlu et al. (2003) studied the transport fluxes of Al^{3+}, Fe^{3+}, Ti^{4+} and Na^{+} ions from red mud through charged heterogeneous and

homogeneous cation exchange membranes as a function of H^+ ion concentration in stripping phase by applying Donnan dialysis processes. Prakash et al. (2004) applied Donnan membrane process for the recovery of alum from water treatment plant residuals or sludge. The application was studied for homogeneous and heterogeneous membranes.

In this thesis, two kinds of plasticizers were used to prepare PVC based cation exchange membranes. First one is a traditional plasticizer, which is dioctyl phthalate (DOP). The other one is an ionic liquid (IL), which is tetradecyl(trihexyl)phosphonium decanoate.

The first man-made plastic known was manufactured in 1862 by Alexander Parkes in London, but it was not until the late 19th century when the concept of plasticizers was first introduced. In the early days, manufacturers of celluloid or celluloid lacquers used natural camphor and castor oil for plasticization purposes, but those were unsatisfactory for many end uses. The discovery of triphenyl phosphate in 1912, later used as substitute for camphor oil, was a significant turning point in the era of ester plasticizers. The most important product that resulted from this early discovery was tricresyl phosphate which is still in use today. For some time, tributyl phosphate was highly regarded for cellulose derivatives, but it was eventually replaced by less volatile products. At the same time, glycerin acetates were developed but suffered the same fate due to their volatility. Phthalic acid esters found applications as plasticizers for the first time in 1920 and continue to be the largest class of plasticizers in the 21st century. Dibutyl phthalate gained a dominant position amongst plasticizers which it held for many years and continues to hold today for polyvinyl acetate dispersions. DOP was introduced in 1930 and has been the most widely used plasticizer since the 1930s (Rahman and Brazel, 2004).

Ionic liquids are a new class of compounds that have been investigated as plasticizers for some polymers such as PVC and poly(methyl methacrylate) (PMMA). They were found to be compatible with these polymers. Ionic liquids have low volatility, low melting points, a wide liquid range, are high-temperature stable, nonflammable and are compatible with a wide variety of organic and inorganic materials. It was found that a number of imidazolium-, ammonium- and phosphonium-based ionic liquids are capable of producing flexible PVC as does DOP (Rahman and Brazel, 2004).

Scott et al. (2003) used imidazolium based ionic liquids as plasticizer for PMMA. The polymer was formulated using DOP as a traditional plasticizer and properties were compared to PMMA plasticized with imidazolium based ionic liquids. Bulk and plasticized polymers were characterized for glass transition temperature, elastic modulus and the thermal stability of the plasticizers. They found that ionic liquids show technical advantages over traditional plasticizers. Ionic liquids they used were able to control glass transition temperature over wide temperature ranges. They were also able to reduce volatility for high temperature applications and elastic moduli that match those of DOP.

Rahman and Brazel (2006) studied room temperature ionic liquids based on ammonium, imidazolium and phosphonium cations as novel plasticizers for PVC. All the ionic liquids tested were able to produce flexible PVC. Upon 20 wt% plasticization, some of the ionic liquids lowered the glass transition temperature of PVC more than that done by several traditional plasticizers. They showed good thermodynamic compatibility as well. Several ionic liquids showed better leaching and migration resistance than the traditional plasticizers. High temperature

and ultraviolet (UV) ray stability of ionic liquid-plasticized PVC samples were also studied (Rahman and Brazel, 2006).

Ionic liquids are used in several fields of application. Gerritsma et al. (2004) used a phosphonium salt ionic liquid, which is trihexyl(tetradecyl)phosphonium chloride, as reaction media for Heck cross-coupling of aryl iodides and bromides with olefins in excellent yields. McNulty et al. (2004) showed that another phosphonium salt ionic liquid, which is trihexyl(tetradecyl)phosphonium decanoate, was an effective promoter for the Henry nitroaldol reaction of nitromethane with aromatic aldehydes. Galinski et al. (2006) studied the physical and chemical properties of room temperature ionic liquids from the point of view of their possible application as electrolytes in electrochemical processes and devices.

3. THEORY

Membranes have gained an important place in chemical technology and are being used increasingly in a broad range of applications because they are economic and provide productive and rapid processes. A general definition for a membrane could be such as a selective barrier between two phases. The separation of substances by membranes is essential in industry and human life. Of the various separation membranes, the ion exchange membrane is one of the most advanced and is widely used in various industrial fields.

3.1. Ion Exchange Membranes

An ion exchange membrane is a thin sheet or film of ion-exchange material that may be used to separate ions by allowing the preferential transport of either cations by using cation-exchange membrane or anions by using anion exchange membrane. Ion exchange membranes are very similar to normal ion exchange resins from the chemical point of view because both are bearing functional groups. The difference between membranes and resins arises largely from mechanical requirements of the membrane process. Unfortunately, ion exchange resins are mechanically weak, cation exchange resins tend to be brittle and anion exchange resins to be soft. They are dimensionally unstable due to the variation in the amount of water imbibed into the gel under different conditions. Changes in electrolyte concentration, in the ionic form or in the temperature may cause major changes in water uptake and hence the volume of resin. The most common solution to this problem is the preparation of a membrane with a backing of a stable reinforcing

material which gives the necessary strength and dimensional stability (Strathmann, 2004).

Ion exchange membranes are classified in various ways: based on their functions, materials constituting the membranes, structure and microstructure of the membranes, etc. Classification based on the function is as follows:

- Cation exchange membranes, which have cation exchange groups (anionic charged groups) and cations selectively permeate through the membranes,

- Anion exchange membranes, which have anion exchange groups (cationic charged groups) and anions selectively permeate through the membranes,

- Amphoteric ion exchange membranes, in which there are both cation and anion exchange groups at random throughout membranes,

- Mosaic ion exchange membranes, which have domains with cation exchange groups over cross-sections of the membranes and also domains of anion exchange groups. An insulator may exist around the respective domains.

Cation exchange groups used are sulfonic acid, carboxylic acid, phosphonic acid, monosulfate ester groups, mono- and diphosphate ester groups and other groups that provide a negative fixed charge. Anion exchange groups used are positively charged groups. These exchange groups can be named as fixed ions in an ion exchange membrane. For

example, the fixed anions are in electrical equilibrium with mobile cations, which are referred to as counter-ions, in the interstices of the polymer in a cation exchange membrane (Figure 3.1-1). Mobile anions, called co-ions, are more or less completely excluded from the polymer matrix because of their electrical charge which is identical to that of the fixed ions. Due to the exclusion of the co-ions, a cation-exchange membrane permits transfer of cations only.

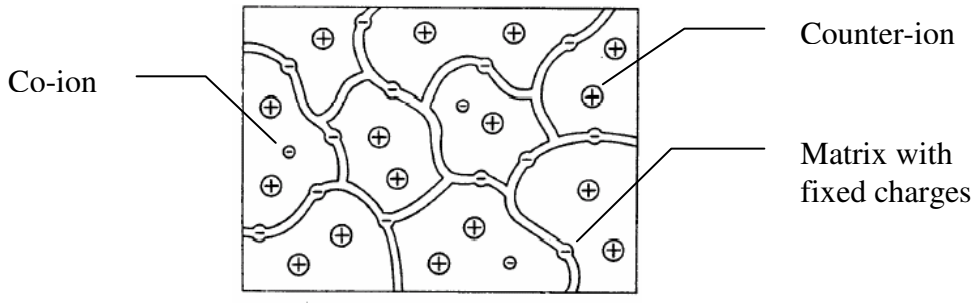


Figure 3.1-1 Schematic structure of a cation exchange membrane (Helfferich, 1962)

Ion exchange membranes are also classified into two types by their microstructure (or by preparation methods): heterogeneous and homogeneous. All preparation methods of ion exchange membranes are summarized in Table 3.1-1. The homogeneous type ion exchange membranes can be prepared by five methods: (*i*) by condensation reaction of ionic monomeric compounds, (*ii*) by polymerization of vinyl monomers, (*iii*) from conventional polymers, (*iv*) by plasma polymerization, (*v*) extrusion of thermoplastic polymers having precursor groups for cation exchange groups into a polymer film and conversion of the groups into cation exchange groups (Sata, 2004).

Table 3.1-1 Classification of preparation methods of ion exchange membranes (Sata, 2004)

Material	**Step 1**		**Step 2**	**Step 3**
Vinyl monomer	Polymerization into block		Slicing into film	Introduction of IX groups
	Polymerization into film			Introduction of IX groups
	Emulsion of polymer		Casting or coating on fabric	Introduction of IX groups
Polymer	Film	Generation of radicals (by irradiation with γ rays)	Grafting vinyl monomer	Introduction of IX groups
		Impregnation of vinyl monomers	Polymerization	Introduction of IX groups
		Introduction of IX groups		
	Introduction of IX groups into polymer			Preparation by casting method
	Coating of polymer latex on a fabric		Drying	Cross-linkage and introduction of IX groups
	Extrusion of polymer with precursor groups into film			Introduction of IX groups
Vapour of organic compounds	Plasma generation		Deposition on plate, fabric	Introduction of IX groups

Heterogeneous type ion exchange membranes consist of fine ion exchange particles embedded in an inert binder such as polyethylene, phenolic resins or polyvinylchloride (Figure 3.1-2). Heterogeneous ion exchange membranes are characterized by the discontinuous phase of the ion exchange material. The efficient transport of ions through a heterogeneous membrane requires either a contact between the ion exchange particles or an ion conducting solution between the particles. Most heterogeneous membranes that possess adequate mechanical strength generally show poor electrochemical properties. Heterogeneous ion exchange membranes can be prepared by different methods:

- An ion exchange powder is mixed with a dry binder polymer and molded under the appropriate conditions of pressure and temperature into a sheet,

- Ion exchange particles are mixed with a binder polymer which is brought into a semi-fluid state by adding a plasticizer or by heating and then extruded as a sheet,

- Ion exchange particles are dispersed in a partially polymerized binder polymer and cast into a film, then the polymerization is completed,

- Ion exchange particles are dispersed in a solution containing a film-forming binder and a plasticizer, then the mixture is cast into a film and the solvent evaporated (Strathmann, 2004).

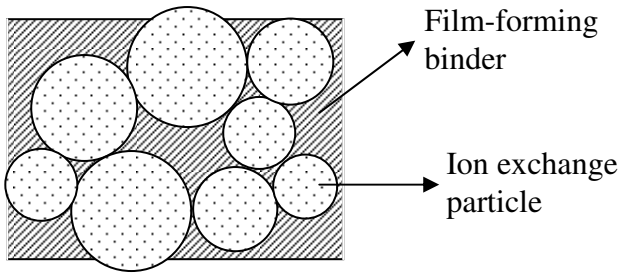


Figure 3.1-2 Schematic structure of a heterogeneous membrane

In this study, the last method was followed. S-PVC or E-PVC was used as film-forming binder, DOP or IL was used as plasticizer, cyclohexanone was used as solvent and commercial strong acidic styrene-divinyl benzene cation exchange resin was used as ion exchange materials.

3.2. Plasticizers

Plasticizers have been extensively used with polymers for producing flexible plastics to be used in commodity, engineering and medical applications. According to the council of International Union of Pure and Applied Chemistry (IUPAC), as stated in 1951, ‘‘a plasticizer is a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability or extensibility (Rahman and Brazel, 2006).

Plasticizer type is a parameter in this study. Firstly, a traditional plasticizer, which is dioctyl phthalate, was used (Figure 3.2-1a). Then, a novel plasticizer, which is an ionic liquid named as tetradecyl(trihexyl)phosphonium decanoate, was tried (Figure 3.2-1b).

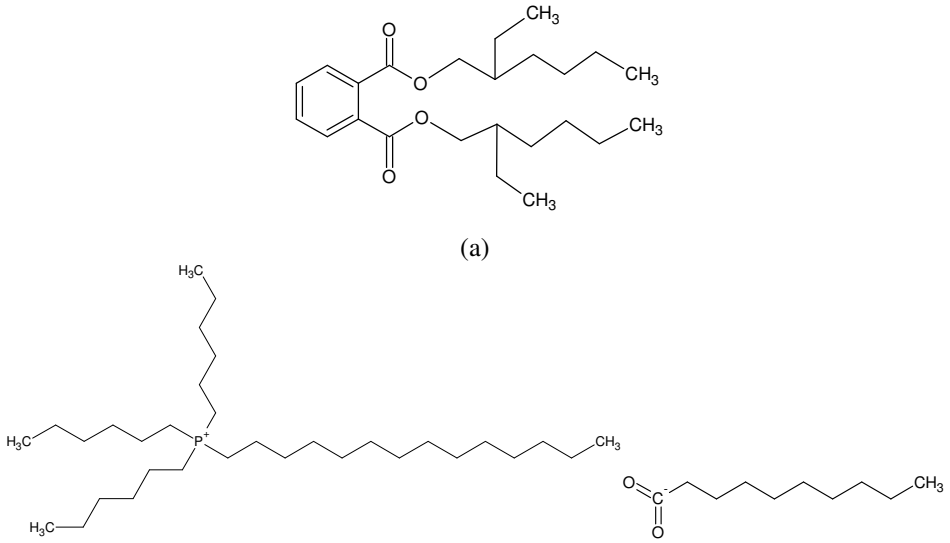


Figure 3.2-1 Structures of (a) dioctyl phthalate and (b) tetradecyl(trihexyl)phosphonium decanoate

The primary role of plasticizers is to improve the flexibility and processability of polymers by lowering the second order transition temperature. Plasticizers are actually low molecular weight resins or liquids, which form secondary bonds to polymer chains and spread them apart (Figure 3.2-2). Thus, plasticizers reduce polymer-polymer chain secondary bonding and provide more mobility for the macromolecules, resulting in a softer, more easily deformable mass.

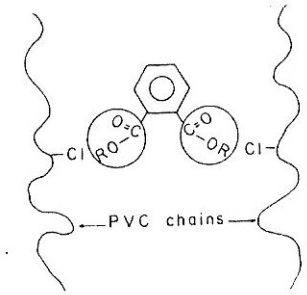


Figure 3.2-2 Action of a plasticizer on PVC chains (Stepek and Daoust, 1983)

Plasticizers are incorporated in the amorphous parts of polymers while the structure and size of any crystalline part remains unaffected. Plasticizers are expected to reduce the modulus, tensile strength, hardness, density, melt viscosity, glass transition temperature and electrostatic chargeability of a polymer, while at the same time increasing its flexibility, elongation at break, toughness and dielectric constant. Ideal plasticizers should be highly compatible with polymers, stable in both high and low temperature environments, sufficiently lubricating over a wide temperature range, insensitive to solar ultraviolet (UV) radiation, leaching and migration resistant, inexpensive and should fulfill health and safety regulations.

DOP, which is a phthalate ester, is the most commonly used plasticizer for PVC. Phthalate esters were initially found to be benign to human beings and therefore have been used in various products such as toys of children and medical plastics where they may come in close contact with the human body. However, more recent reports have criticized these petroleum-derived products because of their suspected endocrine-disruption activity in laboratory rats (Rahman and Brazel, 2004).

Extensive research is going on to find alternative plasticizers for medical and other plastic materials. Ionic liquids are one of these few novel alternatives which have shown promising results in the early stages of investigation. They are actually molten salts that melt below at about 100°C and typically consist of a bulky inorganic cation and an anion. They have attracted much attention as potential environmental solvents due to some of their unique properties. Most of the ionic liquids are liquid at room temperature and usually exhibit negligible vapor pressure, which reduces the possibility of air pollution and loss of materials at

ambient conditions. Many of them are liquid over a wide temperature range (often more than 300°C). As a class of materials, ionic liquids are highly solvating for both organic and inorganic materials. Many of them are non-flammable, non-explosive and have high thermal stability. Ionic liquids usually have high electric conductivity and possess a wide electrochemical window (commonly larger than 3.0 V). They are also recyclable, which can be helpful in reducing landfill waste (Rahman and Brazel, 2006).

The general approach to creating ionic liquids is to employ a large, unreactive, low symmetry cation with and an anion that largely controls the physical and chemical properties. The most common cations used in ionic liquids are *N*-alkylpyridinium and *N,N'*-dialkylimidazolium. Another very effective cation for the creation of them is tetraalkylphosphonium, $[PR_1R_2R_3R_4]^+$. The alkyl groups, R_n, generally are large and not all the same. Although the quaternary phosphonium ionic liquids have not received the attention and extensive resources that the more common imidazolium and other nitrogen-containing ionic liquids do, they have been used extensively in several areas of chemistry for many years, particularly catalysis and phase transfer reactions and extractions. Additionally, they have been applied to materials as well, such as liquid crystals and plasticizers (Sesto et al., 2005).

The tetraalkylphosphonium salts, $[PR_1R_2R_3R_4]^+$, were chosen for a number of features which differentiate them from other common room temperature ionic liquid cations. Phosphonium salts are much more thermally stable than the corresponding ammonium salts and even have an edge on imidazolium salts. In addition to being slightly less thermally stable, the imidazolium cation contains protons which are not entirely inert. They are some what acidic which can result in carbene formation.

Phosphonium salts, on the other hand have no such acidic protons. They are additionally attractive because the steric bulk of the large side chains around the phosphonium cation interferes with electrostatic interactions between the anions and the cation – which is generally localized on the phosphorus – allowing for greater impact of the properties of the anion itself, as compared to salts with more strongly interacting smaller cations. (Sesto et al., 2005).

Tetradecyl(trihexyl)phosphonium decanoate is prepared via the metathesis of the corresponding phosphonium chloride with sodium decanoate. It is essentially halogen-free but will contain 0.1% chloride ion. Like the majority of alkylphosphonium ionic liquids, the density is greater than 1 and is immiscible with water although it is soluble in water and can dissolve up to 21.1% water when fully saturated. When dry, it is totally miscible with a wide range of organic solvents (CYTEC Industries).

Literature reports of ionic liquid thermal stabilities using standard TGA conditions – that is heating a sample at 5 to 10 ℃ per minute under an inert atmosphere such as nitrogen or under oxidizing conditions such as under an air atmosphere will indicate high thermal stabilities – even in excess of 300 ℃. However, the true thermal stability of such salts is best determined under isothermal conditions – that is heating a sample rapidly to the test temperature and then observing the weight loss over time. It was found that safe operating temperatures for tetradecyl(trihexyl)phosphonium decanoate under air and nitrogen will be approximately 110℃ and 150℃ (CYTEC Industries).

3.3. Characterization of Ion Exchange Membranes

After preparing the ion exchange membranes, their properties and characteristics have to be evaluated according to the purpose of the experiment and their applications. A series of procedures and techniques are applied to determine ion exchange membrane properties (Sata, 2004; Nagarale et al., 2006):

- Mechanical properties of ion exchange membranes
- Chemical stability of ion exchange membranes
- Determination of membrane ion exchange capacities
- Electrochemical characterization of ion exchange membranes
- Ion exchange isotherms of membranes

3.3.1. Mechanical properties of ion exchange membranes

The mechanical characterization of ion-exchange membranes includes the determination of thickness, swelling capacity (volume fraction of water), dimensional stability, mechanical strength and hydraulic permeability.

The *thickness* of the membrane is usually measured in dry or wet state with a micrometer (Sata, 2004).

The *swelling capacity* of a membrane determines not only its dimensional stability but also affects its selectivity, electrical resistance and hydraulic permeability. It depends on the nature of the polymeric material, the ion-exchange capacity, the species of ion exchange groups, the cross-linking density, membrane pretreatment, solvents, pH of the solution, temperature of electrolyte solution. Ion exchange membranes swell with solvents, especially water, because of the ion exchange groups. Usually the swelling of a membrane is expressed in terms of *water content (volume fraction of water)* under given experimental conditions and can be defined by weight difference between the wet and dry membrane (Sata, 2004; Nagarale et al., 2006).

The *mechanical strength* of the hydrocarbon-type ion exchange membranes is expressed by the Mullen burst strength (kgf/cm^2). The strength of perfluorocarbon ion exchange membranes is expressed as tensile strength (kg/mm^2 or kg/cm^2) and tear strength (g or kg) measured in the machine direction of wet or dry membranes (Sata, 2004).

Hydraulic permeability measurements provide information on the transport of components through a membrane under a hydrostatic pressure driving forces. The presence of pinholes in ion-exchange membranes will not only lead to a drastically increased hydraulic permeability but also invalidate any application. Pinholes can be determined by placing a wet membrane sheet on a sheet of white absorbent paper. A 0.2% solution of methylene blue for an anion exchange membrane or a 0.2% solution of erythrosine-B for a cation-exchange membrane has to be spread over the entire surface. If no spot of the dye can be observed on the paper, the membrane is free of pinholes and can be tested for its hydraulic permeability. The test is carried out at room temperature using deionized water and a hydrostatic pressure

driving force. The permeability can be calculated from the volumetric flow rate (Nagarale et al., 2006).

3.3.2. Chemical stability of ion exchange membranes

The economics of electro-membrane processes is determined basically by the chemical stability and the life of the ion-exchange membranes under applied conditions. Deterioration in polymer matrix or functionality of the ion exchange membranes after exposure for certain time periods to various test solutions containing acids, bases, or oxidizing agents is estimated by comparison with new, unexposed samples and by determining changes in their mechanical, dimensional and electrical properties (Nagarale et al., 2006).

3.3.3. Determination of ion exchange capacities

Ion exchange capacity is a major characteristic of ion exchange materials. From a practical point of view, an ion exchanger can be considered as a “reservoir” containing exchangeable counter-ions. The counter-ion content in a given amount of material is defined essentially by the amount of fixed charges which must be compensated by the counter-ions, and thus is essentially constant. According to this fact, ion exchangers are quantitatively characterized by their capacity which is defined as the number of counter-ion equivalents in a specified amount of the material (Zagorodni, 2007).

3.3.4. Electrochemical characterization of ion exchange membranes

The performance of ion exchange membranes in the various electro-membrane processes is determined to a very large extent by their electrochemical properties. Therefore, a major task in characterizing ion exchange membranes is the determination of their electrochemical properties such as electrical resistance and transport number.

3.3.4.1. Electrical resistance of ion exchange membranes

The electrical resistance of ion-exchange membranes is one of the factors that determine the energy requirements of electrodialysis processes. The specific membrane resistance is given as Ωcm. From the engineering point of view, the membrane area resistance in Ωcm^2 is more convenient. The electrical resistance of a membrane is determined by the ion exchange capacity and the mobility of the ion within the membrane matrix. The area resistance of ion exchange membranes can be measured by direct current (DC), by alternative current (AC) or by impedance spectroscopy.

In *DC measurements*, the membrane is installed in a cell (Figure 3.3.4.1-1) which consists of two chambers containing the test solution separated by the test membrane. The two electrodes (E_1, E_2) are used to provide the electrical potential driving force to obtain a certain current. The actual potential drop across the membrane is determined with calomel (probe) electrodes (P_1, P_2) placed close to the membrane surface. The potential drop is measured with and without the membrane in the test cell as a function of the current density passing through the cell. The

resistance is given by the slope of the current versus the voltage drop curve. To obtain the membrane resistance, the resistance of the cell without the membrane is subtracted from the resistance of the cell with the membrane (Strathmann, 2004).

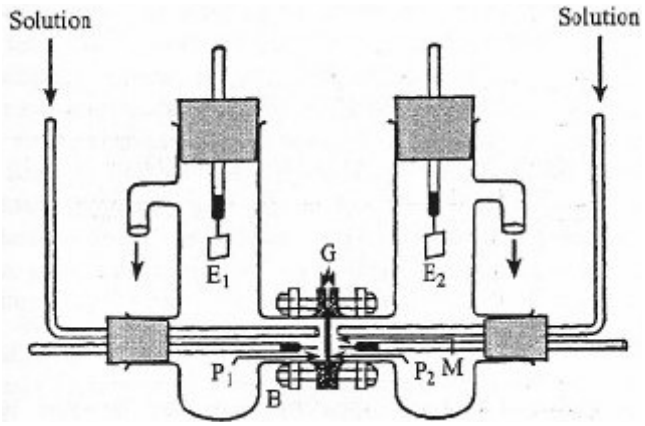


Figure 3.3.4.1-1 Cell used to measure electrical resistance of an ion exchange membrane by DC. M: Ion exchange membrane, E_1, E_2: Ag-AgCl electrodes for current supply, P_1, P_2: Ag-AgCl probe electrodes, G: Gasket, B: Bolt (Sata, 2004)

Electrical resistance can also be determined by *AC measurements* using a two-compartment cell with platinized platinum electrodes (Figure 3.3.4.1-2). After a salt solution of a given concentration is poured into the two compartments of the cell, the electrical resistance of the cell is measured with and without the membrane at a constant temperature. The difference between the electrical resistances is the resistance of the membrane (Sata, 2004).

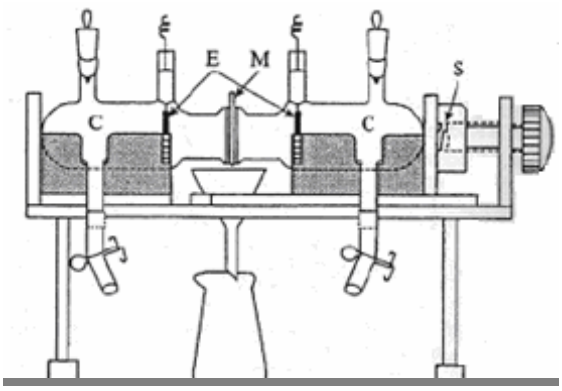


Figure 3.3.4.1-2 Cell used to measure electrical resistance of an ion exchange membrane by AC. C: Half cell, E: Platinized platinum electrodes, M: Ion exchange membrane, S: Spring (Sata, 2004)

Impedance spectroscopy has been also used extensively to determine the electrical resistances of ion-exchange membranes by applying AC across the membrane under operating conditions. The difference between the alternating current resistance measurements and the impedance spectroscopy is that in the first case the frequency of AC is kept constant while in latter case the frequency is changed and the response to the changing frequency is determined by a spectrometer. To determine membrane resistances by impedance spectroscopy, the entire system, which consists of the membrane, the electrolyte and the electrodes, treated as a “black box”. An alternating sinusoidal voltage of a given frequency and amplitude is applied to the system. The resulting current is measured and then the phase shift compared to the input signal is determined. The procedure is repeated at different frequencies (Strathmann, 2004).

3.3.4.2. Transport number

When an ion exchange membrane is placed in an electrolyte solution, concentration ratio of counter-ions in the membrane is extremely larger than that of co-ions, so that the greater part of an electric current is carried across the membrane by counter-ions. The transport number of an ion exchange membrane $\bar{t}_i$ is defined as a ratio of an electric current I_i carried by specific ions i against total electric current I (Zagorodni, 2007):

$$\bar{t}_i = \frac{I_i}{I} \qquad \text{(Eqn. 3.3.4.2-1)}$$

There are three methods to measure the transport number: Its calculation from the membrane potential, by Hittorf's method (electrodialysis) and by chronopotentiometry.

The transport number during *electrodialysis (Hittorf's method)* may be measured using a two-compartment cell with reversible electrodes such as Ag-AgCl electrodes (Figure 3.3.4.2-1). The transport number is calculated from the ions transported and the amount of electricity passed through the membrane (Sata, 2004).

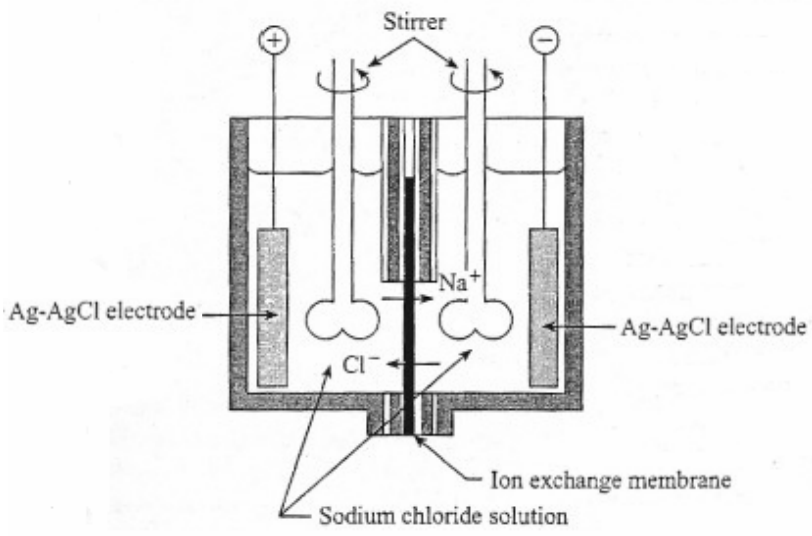


Figure 3.3.4.2-1 Cell used to measure transport number by Hittorf's method (Sata, 2004)

Counter-ion transport number in the membrane phase also can be determined by the *chronopotentiometry* by using a chronopotentiometric cell shown in Figure 3.3.4.2-2. The chronopotentiometric method is the variation of potential versus time for the variation in concentration of an electroactive species. The resultant potential time data obtained give more important information regarding polarization phenomena, electrical conductance, ion specificity, surface fouling, heterogeneity, and value of permselectivity and transport number of ion-exchange membrane under investigation. In a chronopotentiometric study of ion-exchange membrane, the transition time (τ) at which the concentration of electrolyte at the membrane surfaces reaches zero is expressed by Eqn. 3.3.4.2-2:

$$I\tau^{1/2} = \frac{z_i F(\pi D)^{1/2}}{2(\bar{t}_i - t_i)} C_i \qquad \text{(Eqn. 3.3.4.2-2)}$$

where I is current density, z_i valence of counter-ion, F Faraday constant, D diffusion coefficient, C_i concentration of electrolyte, t_i transport number in solution and $\bar{t}_i$ transport number in membrane.

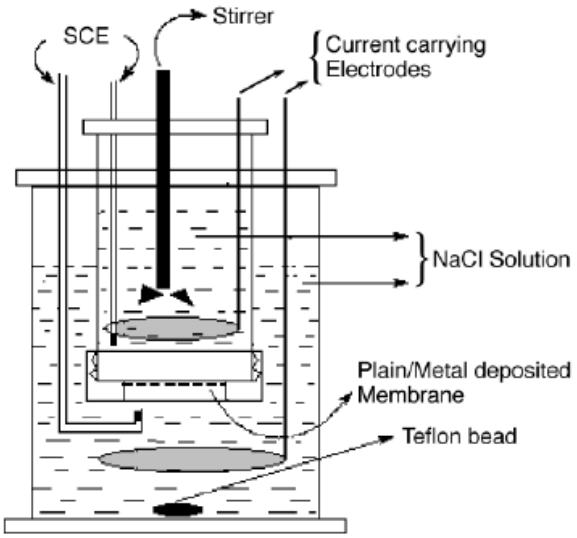


Figure 3.3.4.2-2 Chronopotentiometric cell (Shahi et al., 1999)

In this study, transport number of an ion in cation exchange membranes prepared was calculated by using *Membrane Potential* method.

When an ion exchange membrane separates solutions containing different concentrations of the same counter-ions, an electrical potential is generated across the membrane named as the membrane concentration potential. Because a cation exchange membrane is permeable to cations, and anions can not pass through the membrane, a difference of

electrochemical potential occurs across the membrane, which causes the membrane concentration potential (Sata, 2004).

A liquid junction represents a boundary between two dissimilar solutions across which ions migrate. The differences in the mobilities of positive and negative ions result in the liquid junction potential (Figure 3.3.4.2-3).

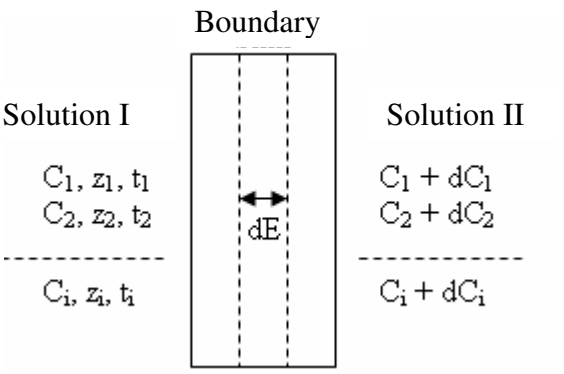


Figure 3.3.4.2-3 Liquid junction between two different solutions

Solution I and II contain several ions 1, 2,…, *i*,… at concentrations C_1, C_2,…, C_i,… and they form a liquid junction. The values of z are valences and the values of t are transport numbers. A potential dE will arise from the process occurring in the thin boundary indicated by the dashed line.

If a Faraday current is passed reversibly from Solution I to Solution II, the change in free energy is given by,

$$dG_i = \frac{t_i}{z_i}\left[\left(\mu_i + d\mu_i\right) - \mu_i\right] = \frac{t_i}{z_i} d\mu_i \qquad \text{(Eqn. 3.3.4.2-1)}$$

where dG_i is the change in free energy, t_i is transport number, z_i is valence of i ve μ_i is the chemical potential of i.

For the transfer of all the ions, the total free energy change is;

$$\Delta G = \sum_i \frac{t_i}{z_i} d\mu_i = \sum_i \frac{t_i}{z_i} RTd \ln a_i \qquad \text{(Eqn. 3.3.4.2-2)}$$

$$\Delta G = -FdE \qquad \text{(Eqn. 3.3.4.2-3)}$$

$$dE = -\frac{RT}{F} \sum_i \frac{t_i}{z_i} d \ln a_i \qquad \text{(Eqn. 3.3.4.2-4)}$$

where a_i, the activity of i, F is Faraday constant and dE is the potential when 1 Faraday current passes through the solutions. Membrane potential is calculated as follows (Lakshminarayanaiah, 1969);

$$\Delta E = -\frac{RT}{F} \int_I^{II} \sum_i \frac{t_i}{z_i} d \ln a_i \qquad \text{(Eqn. 3.3.4.2-5)}$$

Eqn. 3.3.4.2-5 is the general formula of the Nernst equation for the membrane concentration potential.

When an ion exchange membrane separates solution having an activity of a_1 from solution having an activity of a_2 of the same electrolyte ($a_1 > a_2$), the membrane potential is given by,

$$\Delta E = -\frac{\bar{t}_+}{z_+}\frac{RT}{F}\ln\frac{(a_+)_2}{(a_+)_1} - \frac{\bar{t}_-}{z_-}\frac{RT}{F}\ln\frac{(a_-)_2}{(a_-)_1} \qquad \text{(Eqn. 3.3.4.2-6)}$$

For 1:1 electrolyte;

$$\frac{(a_+)_2}{(a_+)_1} = \frac{(a_-)_2}{(a_-)_1} = \frac{a_2}{a_1} \qquad \text{(Eqn. 3.3.4.2-7)}$$

$$\Delta E = -(\bar{t}_+ - \bar{t}_-)\frac{RT}{F}\ln\left(\frac{a_2}{a_1}\right) \qquad \text{(Eqn. 3.3.4.2-8)}$$

$$\Delta E = (1 - 2\bar{t}_+)\frac{RT}{F}\ln\left(\frac{a_2}{a_1}\right) \qquad \text{(Eqn. 3.3.4.2-9)}$$

where ΔE is the potential for 1:1 electrolytes, $\bar{t}_+$ and $\bar{t}_-$ are transport numbers of cations and anions in the membrane phase, a_1 and a_2 are the activities of electrolytes, R is gas constant and T is absolute temperature (Sata, 2004). The activities (a_i) are calculated by activity coefficients by using Eqn. A-10. The calculation procedure is explained in *Appendix*. From the slope of the graph (E versus $\ln(a_2/a_1)$) transport numbers are calculated.

The concept of transport number can be explained in the following aspect:

Consider a galvanic cell operating under reversible conditions at constant temperature;

$$H_2\ (1\ atm)\ |\ HCl\ |\ AgCl\text{-}Ag \qquad \text{(Eqn. 3.3.4.2-10)}$$

Two cells of this type containing HCl at concentrations m_1 and m_2 and having potentials E_1 and E_2 can be connected in opposition;

H_2 (1 atm) | HCl (m_1) || AgCl | Ag | AgCl || HCl (m_2) | H_2 (1 atm)
(Eqn. 3.3.4.2-11)

This is an illustration of a concentration cell without transference. This type of connection brings about the following equation;

$$\Delta E = \frac{RT}{F} \ln\left(\frac{a_2}{a_1}\right) \qquad \text{(Eqn. 3.3.4.2-12)}$$

where ΔE is the potential, a_1 and a_2 are the activities of solutions, R is gas constant and T is absolute temperature. In this equation, there is no term regarding transport number. In other words transport numbers tend to go to 1.

If Ag-AgCl bridge is removed from the cell (3.3.4.2-11), one solution actually contacts the other and the direct transfer of HCl from the more concentrated m_2 to more diluted m_1 takes place;

$$H_2 \text{ (1 atm)} \mid \text{HCl } (m_1) \,\vdots\, \text{HCl } (m_2) \mid H_2 \text{ (1 atm)} \qquad \text{(Eqn. 3.3.4.2-13)}$$

This is an example of a concentration cell with transference and results in the following equation;

$$\Delta E = \left(1 - 2\bar{t}_+\right)\frac{RT}{F} \ln\left(\frac{a_2}{a_1}\right) \qquad \text{(Eqn. 3.3.4.2-14)}$$

where $\bar{t}_+$ and $\bar{t}_-$ are transport numbers of cations and anions in the membrane phase (Lakshminarayanaiah, 1969).

3.3.5. Ion exchange isotherms of membranes

Similar to other chemical processes, the ion exchange equilibrium can be characterized by the corresponding equilibrium isotherm. Generally, the isotherm is a graphical representation of the relationship between the equilibrium and all possible experimental conditions at constant temperature. The most common ion exchange isotherm represents interdependence between ionic compositions of two phases: the ion exchange material and surrounding solution (Zagorodni, 2007).

3.4. Ion Exchange Membrane Processes

Ion exchange membranes have been used in various industrial fields and have great potential for use in new fields. Table 3.4-1 shows reported examples of applications of ion exchange membranes and membrane species used in various fields.

Table 3.4-1 Examples of applications of ion exchange membranes (Sata, 2004)

Process	**Purpose**	**Membrane to be used**
Electrodialysis	Concentration or desalination of electrolyte solution, separation of non-electrolyte from electrolyte, recovery of valuable materials, continuous fermentation.	Cation and/or anion exchange membrane
	Continouous electrodialytic ion exchange across the membrane	Bipolar ion exchange membrane and cation and/or anion exchange membrane
	Double decomposition ($AX + BY \leftrightarrow AY + BX$)	Cation and anion exchange membrane
	Water splitting ($H_2O \rightarrow H^+ + OH^-$)	Bipolar ion exchange membrane and cation and/or anion exchange membrane
Electrolysis	Electro-synthesis of inorganic and organic chemicals (chlor-alkali process, organic synthesis)	Cation exchange membrane, or cation and anion exchange membrane
Electrodeionization (EDI, CDI)	Continous production of ultra pure water, removal of trace metal ions.	Cation and anion exchange membrane and cation and anion exchange resins
Diffusion dialysis	Recovery of acid or alkali from waste acid or alkali	Anion or cation exchange membrane
Donnan dialysis	Recovery of removal of trace ions	Anion or cation exchange membrane
Neutralization dialysis	Separation of electrolyte from non-electrolyte	Anion and cation exchange membrane
Pervaporation	Dehydration of water-miscible organic solvents	Cation, anion or amphoteric exchange membrane
Battery	Alkali battery, redox flow battery, fuel cell	Anion or cation exchange membrane

Electrolysis is one method of synthesizing chemicals, on the basis of oxidation at anode and reduction at cathode. Ion exchange membranes are used in electrolysis as ion selective separators not only to synthesize inorganic and organic chemicals, but also for other purposes such as treating waste solutions (Sata, 2004).

Electrodialysis is a process by which ionic substances permeate through a membrane in the presence of an electrochemical potential in order to concentrate salt from dilute solution, to desalinate electrolytic solutions, to separate ionic form non-ionic substances.

In the production of deionized water the conventionally used mixed bed ion exchange resin is replaced by continuous *electrodeionization*. The process is similar to electrodialysis. Anion and cation exchange membranes are arranged in alternating series and from individual cells between two electrodes. One of two adjacent cells is filled with a mixed bed ion exchange resin which absorbs the ions from a feed stream and enhances their migration into the adjacent cell (Strathmann, 2004).

Donnan dialysis can be defined as a pretreatment technique in wastewater and drinking water treatment, and in hydrometallurgical operations. In most of these applications ionic contaminants (heavy metal ions and anions) have been concentrated from a low concentration feed solution to a high concentration sweep solution, for further handling (Prakash et al., 2004).

Diffusion dialysis is used to recover acids or alkalis from waste acids and alkalis using ion exchange membrane. In this process, the membranes are arranged in parallel in a cell system. There are also two

flow systems, one containing the feed solution and the other is so-called dialysate, which often consists of pure water. In this application, solutes pass through ion-exchange membrane when driven by a concentration difference (Sata, 2004; Nagarale et al., 2006).

Neutralization dialysis is one of Donnan dialysis for de-ionization. The solution is to be de-ionized is fed into a compartment between a cation and anion exchange membrane. Acid is fed into the compartment adjacent to the cation exchange membrane and alkali to that adjacent to the anion exchange membrane. Neutralization occurs across the membrane and the solution in the middle compartment is de-ionized (Sata, 2004).

Pervaporation is the separation of solvents on the basis of their different affinities for the ion exchange membrane and different permeation speeds through the membrane phase. It is based on the hydrophilicity of the ion exchange membrane, which shows excellent performance for dehydration of organic solvents (Sata, 2004).

Ion exchange membranes have been used in various *batteries* and cells such as dialysis battery, redox flow battery and fuel cell. Dialysis battery is a technology to generate electricity using salt concentration difference across an ion exchange membrane placed in salt solutions. In redox flow batteries, oxidation–reduction reaction occurs between two chemical species on inactive electrode surfaces in the battery and chemical species stored outside the battery are supplied by pumps to the battery. Fuel cells are a power-generation technology. They are classified into phosphoric acid fuel cell, molten carbonate fuel cell, solid oxide fuel cell and polymer electrolyte fuel cell, which only includes an ion exchange membrane (Tanaka, 2007).

Donnan dialysis is an ion exchange process in which an ion exchange membrane is placed between two solutions. The membrane is permeable to counter-ions and excludes co-ions. This process is explained by Donnan potential principle (Figure 3.4-1): Suppose a cation exchanger is placed in a dilute solution of strong electrolyte. There are concentration differences between two phases; the cation (counter-ion) concentration is larger in the ion exchanger, but the anion (co-ion) concentration is larger in solution. If the ions carried no electric charges, this concentration difference is leveled out by diffusion. However, in the case of ion exchange system, such a process would disturb electroneutrality since the ions are charged. Migration both of cations into the solution and anions into ion exchanger results in an accumulation of positive charge in the solution and negative charge in the ion exchanger. The first few ions which diffuse build up an electric potential difference between the two phases. This so-called *Donnan Potential* pulls cation back into the negatively charged ion exchanger and anions back into the positively charged solution. Equilibrium is established in which the tendency of ions to level out the concentration differences is balanced by the action of the electric field (Helfferich, 1962).

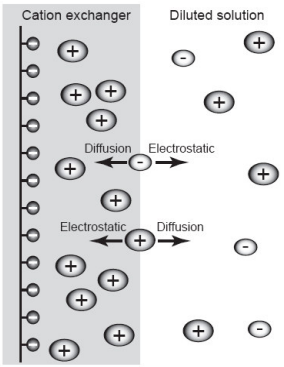


Figure 3.4-1 Donnan exclusion in strong cation exchangers (Zagorodni, 2007)

In this study, the performance of cation exchange membrane prepared is tested by using Donnan dialytic method. For this reason, two-compartment cell of equal volumes is used and membrane is placed between these compartments (Figure 3.4-2).

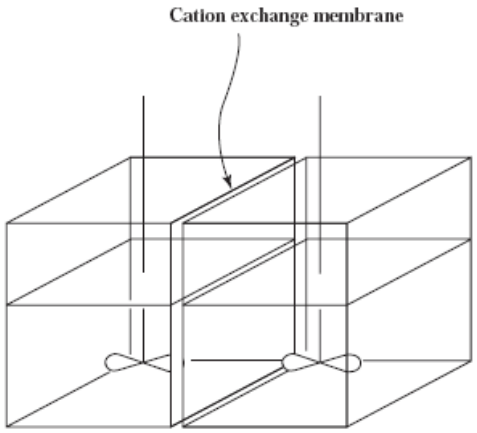


Figure 3.4-2 An illustration of Donnan dialysis experimental unit

Compared to other ion exchange processes, Donnan dialysis has advantages and disadvantages. For example, Donnan dialysis process does not use an electric current, so it is energy saving compared to electrodialysis. It does not need regeneration and is operated continuously. However, the system is not economical because the effect of the driving force (concentration difference) is weak and it becomes necessary to use larger membrane area to maintain the output of a process (Tanaka, 2007).

3.4.1. Diffusion test

The performance of cation exchange membranes prepared is analyzed by diffusion test with the process of Donnan dialysis. Two-compartment cell of equal volumes is used in diffusion tests. Between these compartments, cation exchange membrane is placed.

When a salt dissociates in solution, it is ions rather than the molecules which diffuse. In the absence of an applied electrical potential, the diffusion of a single salt may be treated as molecular diffusion (Sherwood et al., 1975). As a result of the determination of cation concentration, molecular diffusivities are calculated by two-cell method (Geankoplis, 1993):

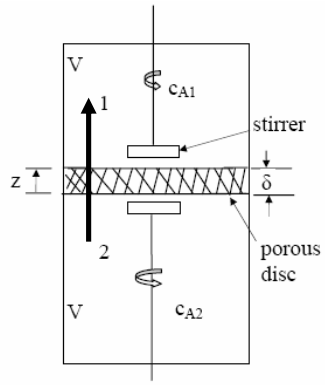


Figure 3.4.1-1 Experimental set-up for two-cell method

A relatively dilute solution and a slightly more concentrated solution are placed in cells on opposite sides of a porous glass membrane as shown in Figure 3.4.1-1. Molecular diffusion takes place through the

pores in the glass while two compartments are stirred. The effective diffusion length is $K\delta$, where $K > 1$ is a constant and corrects for the fact the path is actually greater than δ cm.

To derive the equation, quasi-steady-state diffusion in the membrane is assumed.

$$N_A = \varepsilon D_{AB} \frac{c_{A2} - c_{A1}}{K\delta} \qquad \text{(Eqn. 3.4.1-1)}$$

where c_{A2} is the concentration in the lower chamber at a time t, c_{A1} is the concentration in the upper ($c_{A2} > c_{A1}$), and ε shows the fraction of the area which is open to mass transfer in the porous disc. Making a balance on solute A in the upper chamber, where the rate in = rate out + rate of accumulation, making similar balance on the lower chamber, using equal volumes (V), and combining and integrating the final equation is,

$$D_{AB} = \frac{K\delta V}{2\varepsilon S t} \ln \frac{c_{A2}^0 - c_{A1}^0}{c_{A2}^t - c_{A1}^t} \qquad \text{(Eqn. 3.4.1-2)}$$

where S is cross-sectional area of the disc and $c_{A1}^0, c_{A2}^0, c_{A1}^t, c_{A2}^t$ are molar concentrations of component A in the cells at $t = 0$ and at $t = t$.

The constants of the experimental set-up can be collected under one constant $\alpha = (K\delta V / 2\varepsilon S)$, and this constant can easily be determined by conducting an experiment with a liquid pair whose molecular diffusivity is already known. Experimental procedure is explained in *Experimental Study*.

4. EXPERIMENTAL STUDY

In this study, PVC based strong acidic cation exchange membranes were prepared using different polymers and plasticizers with same cation exchange resin and organic solvent. Ion exchange membranes were prepared by heterogeneous method and then characterized by physicochemical, morphological and electrochemical ways.

4.1. Materials

Two kinds of polymers were used as binder for the cast solution of membrane. First material used is suspension polymerized polyvinyl chloride (S-PVC) whereas the second one is emulsion polymerized polyvinyl chloride (E-PVC). Dioctyl phthalate (DOP) or an ionic liquid, which is tetradecyl(trihexyl)phosphonium decanoate (IL), were used as plasticizer. For all types of membranes prepared, polystyrene crosslinked with divinyl benzene, macroporous, and strongly acidic cation exchange resins (CXR) was used as resin and cyclohexanone (CH) was used as solvent.

S-PVC was supplied from PETKIM and E-PVC was supplied from SOLVIN. CH was supplied from Lab-Scan. DOP was supplied from Akdeniz Kimya and IL was supplied from CYTEC. CXR was supplied from PUROLITE. The properties of the materials are given in Table 4.1-1.

Table 4.1-1 Properties of materials used for the preparation of membranes

Material	Properties	Unit	Range/Value
CXR	Polymer structure		Polystyrene crosslinked with DVB
	Physical form and appearance		Opaque spherical beads
	Functional groups		$R\text{-}SO_3^-$
	Particle size	mm	0.3-1.2 mm
	Total exchange capacity	eq/L	1.8 eq/L
	Moisture retention		48-53%
	Specific gravity, Na^+ form		1.25
	Maximum operating temperature	°C	130
	pH range, stability		0-14
S-PVC	K-number		69-72
E-PVC	K-number		73
DOP	Molecular weight	kg/kmol	390.56
	Boiling point	°C	385
	Density	kg/L	0.986
CH	Molecular weight	kg/kmol	98
	Boiling point	°C	156
	Density	kg/L	0.945
IL	Appearance		Paste
	Molecular weight	kg/kmol	655.11
	Melting point	°C	20
	Boiling point	°C	>180
	Density	kg/L	0.887

Doctor blade was used to cast the solution over the glass manually (Figure 4.1-1). Two-compartment Plexiglass cell of equal volumes was used for performance tests (Figure 4.1-2). Two-compartment glass test chamber of equal volumes (Figure 4.1-3) and Ag/AgCl electrodes (saturated KCl) were used for electrochemical characterization.

The concentration of the cations was determined by means of Atomic Absorption Spectrophotometer (AAS, *Varian 10 Plus A*). Thicknesses of the membranes prepared were measured by micrometer (*Chuan Brand, 0-25 mm - 0.01 mm*).

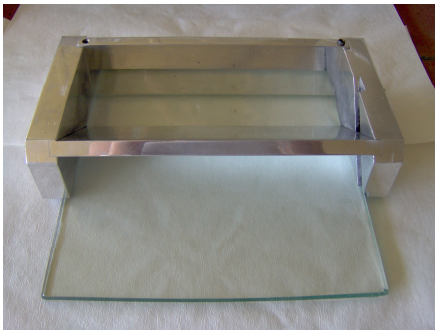
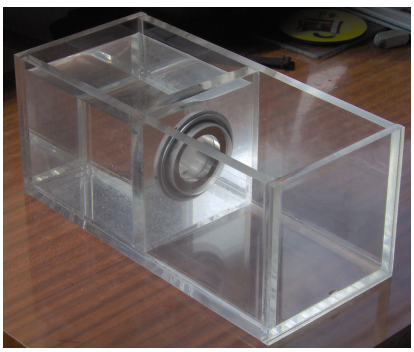


Figure 4.1-1 Figure illustrating doctor blade over glass where membrane cast



(a)

(b)

Figure 4.1-2 Two-compartment Plexiglas test cell used for Donnan dialysis

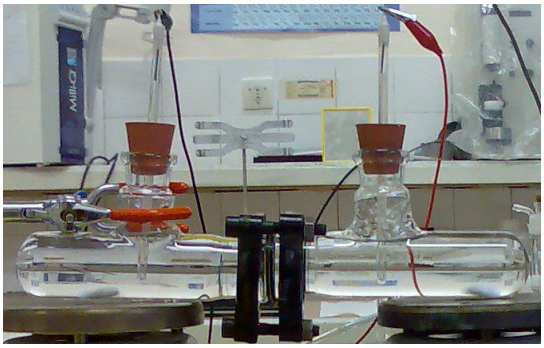


Figure 4.1-3 Two-compartment glass test cell used for electrochemical characterization

4.2. Method

Cation exchange membranes were prepared, characterized by physicochemical, morphological and electrochemical ways and tested by means of Donnan dialysis.

4.2.1. Preparation method

The membranes were prepared by a heterogeneous method. In this method, ion exchange particles are dispersed in a mixture which contains a film forming binder (polymer), a solvent and a suitable plasticizer. Then, the mixture is cast on a glass surface by means of doctor blade manually and solvent is evaporated (Sata, 2004; Gohil et al., 2004).

Two different polymers with a traditional (DOP) or an alternative (IL) plasticizer were used to form the membrane. The ratio of plasticizer

to polymer is a parameter of preparation process. Another parameter is the drying method.

The common step for the preparation of the all types of membranes was to grind the cation exchange resins to a particle size around 45 μm. The resins powdered were dried at 60°C in an atmospheric oven for 24 hours.

4.2.1.1. Preparation of cation exchange membrane with DOP

Two kinds of formulations were used in the preparation of membranes with DOP. In the first formulation, the ratio of DOP amount to PVC amount was chosen as 1:1 (*RLow*), while in the second 2:1 (*RHigh*), where *low* and *high* refer to the relative amount of plasticizer per unit amount of polymer. In both formulations, the ratios for solvent CH and resin CXR were kept constant as 6 and 3, respectively. The ratios chosen and the membrane names assigned are shown in Table 4.2.1.1-1.

In the drying of membranes cast, two different methods were applied. In the first method, the solution cast on the glass surface was left to dry by ambient air while in the second by heating at 75°C in an oven.

Table 4.2.1.1-1 Membranes plasticized with DOP

S-PVC *(S)* **E-PVC** *(E)*			**Drying**	
			Ambient air	**Heating at 75°C**
Ratios	**Low *(RLow)*** DOP:PVC = 1:1	*(S)*	MSA11	MSH11
		(E)	MEA11	MEH11
	High *(RHigh)* DOP:PVC = 2:1	*(S)*	MSA21	MSH21
		(E)	MEA21	MEH21

The preparation procedures of membranes with DOP are shown in Table 4.2.1.1-2, where eight membranes are given with their ratios and preparation procedures.

Table 4.2.1.1-2 Materials and preparation procedures of cation exchange membranes with DOP

Membrane Name	Ratios	Preparation Procedures
MSA11	*RLow*	• The mixture of S-PVC+DOP+CH was prepared. • CXR was added and was heated to 45°C during mixing. • The final mixture was cast on the glass surface and was left one day to dry by ambient air.
MSA21	*RHigh*	
MSH11	*RLow*	• The mixture of S-PVC+DOP+CH was prepared. • CXR was added and was heated to 45°C during mixing. • The final mixture was cast on the glass surface and was dried at 75°C in an oven for 10 minutes.
MSH21	*RHigh*	
MEA11	*RLow*	• The mixture of E-PVC+DOP+CH was prepared. • CXR was added and was not heated during mixing. • The final mixture was cast on the glass surface and was left one day to dry by ambient air.
MEA21	*RHigh*	
MEH11	*RLow*	• The mixture of E-PVC+DOP+CH was prepared. • CXR was added and was not heated during mixing. • The final mixture was cast on the glass surface and was dried at 75°C in an oven for 10 minutes.
MEH21	*RHigh*	

4.2.1.2. Preparation of cation exchange membrane with IL

Two ratios were used in the preparation of membranes with IL and PVC. The first ratio of IL amount to PVC amount was chosen as 1:1 (*RLow*), while the second as 2:1 (*RHigh*). In both cases, the ratios for solvent CH and resin CXR were kept constant as 8 and 3, respectively.

The ratios and the membrane names are shown in Table 4.2.1.2-1. In the drying of membranes cast, only air drying way was followed.

Table 4.2.1.2-1 Membranes plasticized with IL

S-PVC *(S)* **E-PVC** *(E)*			**Drying** **Ambient air**
Ratios	**Low *(RLow)*** IL:PVC = 1:1	*(S)* *(E)*	ILSA11 ILEA11
	High *(RHigh)* IL:PVC = 2:1	*(S)* *(E)*	ILSA21 ILEA21

The preparation procedures of membranes with IL are shown in Table 4.2.1.2-2, where four membranes are given with their ratios and preparation procedures.

Table 4.2.1.2-2 Materials and preparation procedures of cation exchange membranes with IL

Membrane Name	**Ratios**	**Preparation Procedures**
ILSA11	*RLow*	• IL and S-PVC were mixed. CH was added and mixed. CXR was added on this mixture. • The mixture was heated to 45°C. • The final mixture was cast on the glass surface and was left one day to dry by ambient air.
ILSA21	*RHigh*	
ILEA11	*RLow*	• IL and E-PVC were mixed. CH was added and mixed. CXR was added on this mixture. • The final mixture was cast on the glass surface and was left one day to dry by ambient air.
ILEA21	*RHigh*	

4.3. Characterization

Characterization of membranes was performed in three ways: Physicochemical, morphological and electrochemical.

4.3.1. Physicochemical characterization

Physicochemical characterization was performed including volume fraction of water, density of the membrane, membrane porosity, ion exchange capacity and isotherm studies.

4.3.1.1. Volume fraction of water

Water content of a membrane determines its dimensional stability and also affects its selectivity, electrical resistance, and hydraulic permeability. The procedure is as follows (Fang et al., 2004):

- Membrane was immersed in 50 mL of distilled water for 24 hours.
- Its surface was wiped and the wet membrane was weighed.
- Wet membrane was dried at 60°C for 30 min and was weighed.
- The volume fraction of water was;

$$\varphi_w = \frac{W_w - W_d}{W_w} \times 100 \qquad \text{(Eqn. 4.3.1.1-1)}$$

where φ_w is volume fraction of water in g-water/g-wet membrane, W_w is weight of wet membrane in g, W_d is weight of dry membrane in g.

4.3.1.2. Density of membrane

Dry membrane of known area and thickness was weighed for dry density, wet membrane of known area and thickness was weighed for wet density.

$$\rho_d = \frac{W_d}{V_d} \qquad \text{(Eqn. 4.3.1.2-1)}$$

$$\rho_w = \frac{W_w}{V_w} \qquad \text{(Eqn. 4.3.1.2-2)}$$

where ρ_d and ρ_w are dry and wet densities in g/cm^3, respectively and V_d and V_w are volumes of dry and wet membrane in cm^3, respectively.

4.3.1.3. Membrane porosity

Membrane porosity is defined as the volume of free water within membrane per unit volume of wet membrane. It is calculated in the way below (Nagarale et al., 2006):

$$\Delta V = \frac{(W_w - W_d)\rho_d}{\rho_{water} W_d}$$
$$\tau = \frac{\Delta V}{1 + \Delta V} \qquad \text{(Eqn. 4.3.1.3-1)}$$

where ΔV means the volume increase of the membrane upon absorption of the water per unit volume of dry membrane in cm^3-water/cm^3-dry membrane, ρ_{water} is the density of water in g/cm^3, ρ_d is the density of dry membrane in g/cm^3 and τ is membrane porosity.

4.3.1.4. Ion exchange capacity

Ion exchange capacity (*IEC*) is a measure of the quantity of ions removed (adsorbed) by an ion exchange material. The experimental procedure for the determination of *IEC* is in the following way (Vyas et al., 2002):

- The membrane was cut into three pieces of size 3 cm x 3 cm.
- They were immersed in 100 mL of 1 M HCl for 24 hours.
- They were washed with distilled water for 4 hours.
- They were equilibrated with 100 mL of 0.01 M NaCl for 24 hours.
- *IEC* (meq Na^+/g) was calculated by the decrease of Na^+ concentration in NaCl solution with AAS.

$$IEC = \frac{M_{i,Na^+} - M_{e,Na^+}}{W_d} \qquad \text{(Eqn. 4.3.1.4-1)}$$

where $M_{i,Na+}$ and $M_{e,Na+}$ are the initial and equilibrium concentration of Na^+ in meq Na^+, respectively. W_d is the weight of dry membrane in g and *IEC* is weight based ion exchange capacity in meq Na^+/g.

4.3.1.5. Isotherm Studies

In these studies, the relation between the concentration of ions in membrane and in solution at constant temperature was found by using six different concentrations.

When a membrane of A^{m+} form is equilibrated with a solution containing B^{n+} ions in solution, the ion exchange equilibrium occurs between membrane and solution as shown below:

$$nR_mA + mB^{n+} \leftrightarrow mR_nB + nA^{m+}$$

where R is a fixed-ion of the membrane, m and n are valences of ions A^{m+} and B^{n+}, respectively (Miyoshi, 1993a).

The procedure followed for the collection of isothermal data is in the way below:

- The membrane was cut of size 3 cm x 3 cm.
- They were immersed in 100 mL of 1 M HCl for 24 hours.
- Its surface was washed with distilled water and wiped with filter paper.
- 100 mL of 25, 50, 75, 100, 300 and 500 ppm Na^+ solutions were prepared and blank samples (C_{0i}) were taken for AAS.

- The membranes were put in erlenmeyer flasks with solutions and the flasks were placed in a bath at 30°C for 24 hours.

- The solutions were taken after 24 hours and the metal ion concentration was measured by AAS.

- The concentration of Na^+ inside the membrane (Q_i) versus the concentration of Na^+ in the bulk solution (C_i) was plotted.

4.3.2. Electrochemical characterization

The transport number is a measure of the permselectivity of counter-ions through the ion exchange membrane. It can be also defined as the fraction of the electric current which is carried by the ion. Transport number is related to the ratio of the concentration of ion exchange groups in the membrane, which is called fixed ion concentration, to the concentration of the outer solution (Sata, 2004, Helfferich, 1962).

The transport number of Na^+ in cation exchange membrane prepared is found by measuring membrane potential in two-compartment test chamber of equal volumes (Figure 4.3.2-1). Cation exchange membrane is placed tightly between these compartments. The measurement method is as follows (Canas and Benavente, 2002):

- The membrane was cut with diameter of 4 cm and was immersed in 100 mL of 1 M HCl for 1 hour.

- One half of the test chamber was filled with 150 mL of 0.01 M NaCl (C_1) solution.

- Magnetic stirrer bars were put

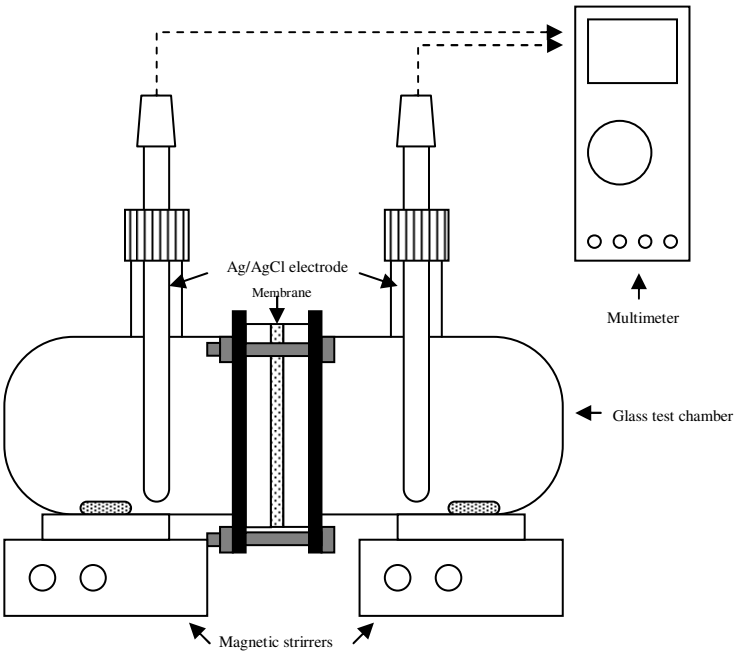
- Other half of the test chamber was filled with 145 mL of 0.001 M NaCl (C_2) solution.

- The electrode in the 0.01 M solution was connected to the ground socket of the multimeter.

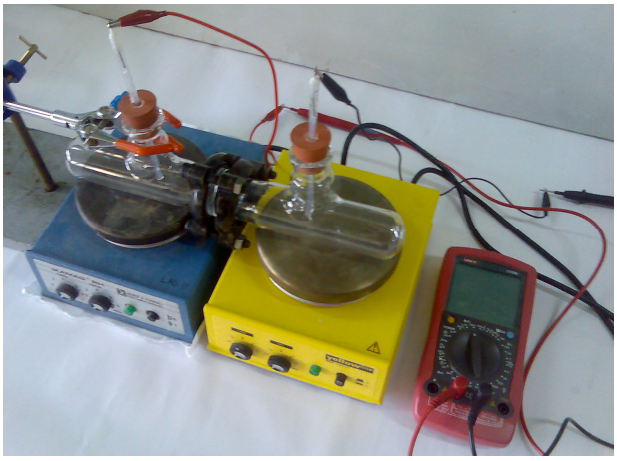
- The concentration in the chamber half which was filled with 0.001 M NaCl solution was increased by adding the volumes of 1 M NaCl solution and temperature was measured.

- The membrane potential values were read after each addition of 1 M NaCl solution.

- Membrane potential (E) versus $\ln(a_2/a_1)$ was plotted. Transport number was calculated from these data with the method explained in section *Theory*.



(a)



(b)

Figure 4.3.2-1 Two-compartment test chamber used for membrane potential measurements (a) Test Cell (b) Experimental setup

4.3.3. Morphological characterization

Morphological characterization is performed by Scanning Electron Microscopy (SEM).

4.3.3.1. SEM Analysis

For SEM analysis, the samples should be dry and electrically conductive. The membrane samples were coated with a gold layer under 10^{-6} atm for 120 sec. in order to make them conductive and were examined in SEM (*JEOL JSM-6060*) under 20 kV potential difference.

Surface and cross-sectional views were examined in SEM analysis. To study the cross sectional view of the membranes, samples are cut and then attached to sample holders by one sided conductive silver tapes (Figure 4.3.3.1-1). The surface images were taken x100 magnification whereas cross-sectional views were taken between x250 - x500 magnifications depending on the thicknesses of the membranes.

(a) (b)

Figure 4.3.3.1-1 (a) Sample holders and silver conductive tape, (b) Samples attached to sample holder

4.4. Performance Study

The performance of cation exchange membrane prepared is analyzed by Donnan dialysis (See Figure 4.1-2). For this purpose, two-compartment cell of equal volumes is used. Cation exchange membrane is placed between these compartments. The method in step by step is given below:

- Membrane was equilibrated with 1 M HCl solution.
- It was placed between two compartments of the diffusion cell
- Concentrate part was filled with Na^+ solution and permeate part was filled with pure water or dilute Na^+ solution.
- While both of the parts were continuously being mixed with magnetic stirrers, samples were taken at specified time intervals.
- Cation concentrations were determined by AAS.
- The concentration of concentrate and permeate part versus time was plotted and diffusivities were determined from these data as explained in section *Theory*.

5. RESULTS AND DISCUSSION

In this research, preparation and characterization methods of PVC based strong acidic heterogeneous cation exchange membranes were investigated. Membranes were plasticized with a traditional plasticizer and an ionic liquid. Their properties were compared in physicochemical, electrochemical and morphological ways.

The preparation conditions for both types of cation exchange membranes were given in Table 4.1-1. For the preparation of membranes, plasticizer was added on the PVC, firstly. Then, solvent was added and mixed. At the end, cation exchange resins were added and mixed until the appearance of the cast mixture became homogeneous. The commercial cation exchange resin which has the particle size of 0.3-1.2 mm was ground to 45 μm before adding to the mixture. As resin becomes finer, is distributed more uniformly through the mixture resulting in a more homogenous membrane product (Vyas et al., 2000).

After preparation step, the mixture was cast on the glass surface and dried by ambient air or by heating at 75°C, which is glass transition temperature of PVC.

Thicknesses of membranes were varied with respect to materials used for preparation. Membranes prepared with E-PVC and DOP had a thickness of around 170 μm while membranes prepared with S-PVC and DOP had a thickness of about 200 μm. The thickness of membranes plasticized with S-PVC and IL was approximately 210 μm, whereas that with E-PVC and IL was around 155 μm.

5.1. Physicochemical Characterization

Physicochemical characterization consists of volume fraction of water (ϕ_w), dry (ρ_d) and wet (ρ_w) densities of the membrane, membrane porosity (τ), weight based ion exchange capacity (*IEC*) and isotherm studies. The results of the experiments are listed in Table 5.1-1.

Table 5.1-1 Physicochemical characteristics of membranes cast*

Membrane		*IEC* (meq Na^+/g-dry)	ϕ_w	ρ_d (g/cm^3)	ρ_w (g/cm^3)	τ
Name	**No**					
MSA11	1	2.085 ± 0.055	0.3859 ± 0.0002	0.94 ± 0.03	1.05 ± 0.03	0.37 ± 0.01
MSA21	2	1.662 ± 0.055	0.3810 ± 0.0003	0.85 ± 0.03	0.94 ± 0.03	0.34 ± 0.01
MSH11	3	2.108 ± 0.055	0.3991 ± 0.0003	0.82 ± 0.03	0.94 ± 0.03	0.35 ± 0.01
MSH21	4	1.520 ± 0.043	0.3435 ± 0.0003	0.97 ± 0.03	1.08 ± 0.03	0.34 ± 0.01
MEA11	5	1.589 ± 0.067	0.4094 ± 0.0003	1.06 ± 0.04	1.20 ± 0.04	0.42 ± 0.01
MEA21	6	1.656 ± 0.060	0.3912 ± 0.0003	1.02 ± 0.04	1.18 ± 0.04	0.40 ± 0.01
MEH11	7	1.401 ± 0.053	0.3986 ± 0.0003	1.13 ± 0.04	1.24 ± 0.04	0.43 ± 0.01
MEH21	8	1.692 ± 0.065	0.3290 ± 0.0003	1.01 ± 0.04	1.09 ± 0.04	0.33 ± 0.01
ILSA11	9	2.802 ± 0.053	0.3470 ± 0.0003	0.85 ± 0.03	1.05 ± 0.04	0.31 ± 0.01
ILSA21	10	1.674 ± 0.051	0.3116 ± 0.0004	0.93 ± 0.09	1.16 ± 0.05	0.30 ± 0.02
ILEA11	11	2.019 ± 0.072	0.3048 ± 0.0004	0.86 ± 0.04	1.02 ± 0.04	0.27 ± 0.01
ILEA21	12	1.269 ± 0.132	0.3018 ± 0.0005	0.71 ± 0.03	0.86 ± 0.03	0.24 ± 0.01

*The determination of uncertainties and significant figures of the results are given in *Appendix*.

Volume fraction of water, dry density and ion exchange capacity values of the membranes prepared were compared with commercial ones. The properties of commercial cation exchange membranes, which are copolymers of sulfonated styrene-divinyl benzene, are shown in Table 5.1-2.

Table 5.1-2 The properties of commercial cation exchange membranes (ASTOM Corporation*, AGC Engineering Co. **)

Membrane	ρ_d (g/cm^3)	**IEC** (meq/g-dry)	ϕ_w
Neosepta C66-5T*	1.14	2.48	0.41
Neosepta CL-25T*	1.20	1.66	0.29
Neosepta CM-1*	1.18	2.32	0.32
Neosepta CM-2*	1.23	1.76	0.23
Neosepta CMX*	1.25	1.57	0.26
Selemion CMV**	1.08	2.08	0.27

The volume fractions of water estimated by using Eqn. 4.3.1.1-1 are shown for different cation exchange membranes in Figure 5.1-1. Mean volume fraction of water for S-PVC based membranes prepared with DOP was found as 0.3774 ± 0.0001, while that for membranes E-PVC based as 0.3821 ± 0.0002. Negligible difference in volume fraction of water can be explained by the resin ratio of membranes which was kept constant at 3:1 (CXR:PVC) for all types of membranes studied.

Average water contents of membranes prepared with IL were found as 0.3293 ± 0.0003 and 0.3033 ± 0.0004 for S-PVC and E-PVC based membranes, respectively. There is no remarkable difference regarding water content between S-PVC and E-PVC based membranes prepared with IL.

Same arguments can be proposed for both DOP and IL plasticized membranes by taking into consideration corresponding average values of water contents, 0.3797 ± 0.0001 and 0.3163 ± 0.0002.

Water content of CXR is 0.5, which is greater than all types of membranes prepared. This reduction in water content of the membranes can be explained by the decrease in particle size and porosity of resin after grinding.

Average water content of commercial cation exchange membranes was around 0.2962, which is less than that of prepared ones, 0.3586 ± 0.0001, respectively.

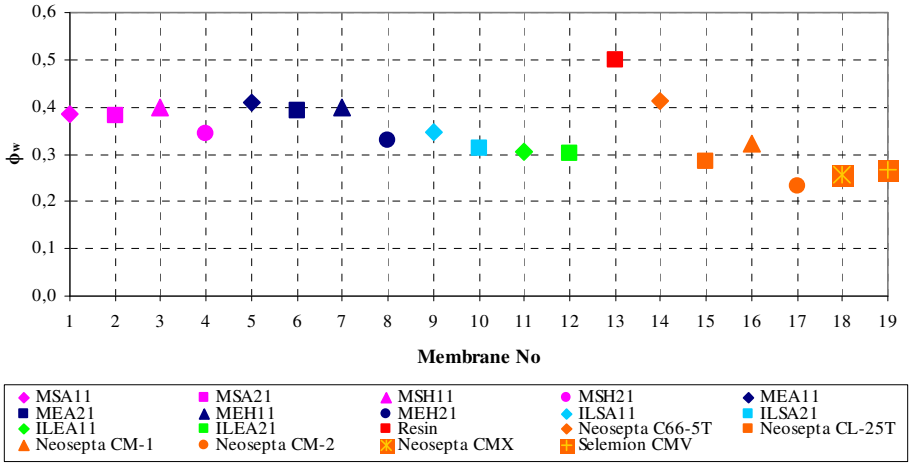


Figure 5.1-1 Chart illustrating the values of volume fraction of water (ϕ_w) in cation exchange membranes

Densities of the membranes prepared were estimated by using Eqn. 4.3.1.2-1 and Eqn. 4.3.1.2-2. The values of dry and wet densities are illustrated in Figure 5.1.-2 and 5.1-3.

Average dry density value for S-PVC based membranes prepared with DOP was found as 0.90 ± 0.02 g/cm^3, while those for membranes E-PVC based as 1.05 ± 0.02 g/cm^3. E-PVC based membranes had greater

values with respect to S-PVC based membranes because E-PVC based membranes had more regular and stiff structure than S-PVC based ones.

Mean dry density values prepared with IL were found as 0.89 ± 0.05 g/cm^3 and 0.79 ± 0.03 g/cm^3 for S-PVC and E-PVC based membranes, respectively.

Commercial cation exchange membranes had an average dry density of around 1.18 g/cm^3, which was higher than that of prepared ones, 0.93 ± 0.01 g/cm^3.

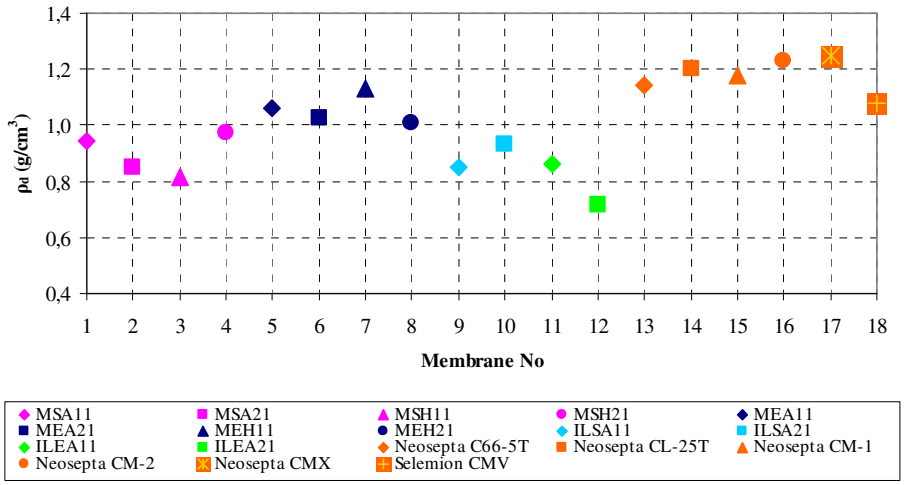


Figure 5.1-2 Chart illustrating the dry density values (ρ_d) of cation exchange membranes.

S-PVC based membranes prepared with DOP had a mean wet density value about 1.00 ± 0.02 g/cm^3, while E-PVC based ones had around 1.18 ± 0.02 g/cm^3. E-PVC based membranes had greater density

values with respect to S-PVC based membranes because E-PVC based membranes had more rigid structure than S-PVC based ones.

Mean wet density values prepared with IL were found as 1.10 ± 0.03 g/cm^3 and 0.94 ± 0.03 g/cm^3 for S-PVC and E-PVC based membranes, respectively.

All types of membranes having same plasticizer (DOP or IL) to PVC ratio had similar trend of decrease or increase in dry and wet density values.

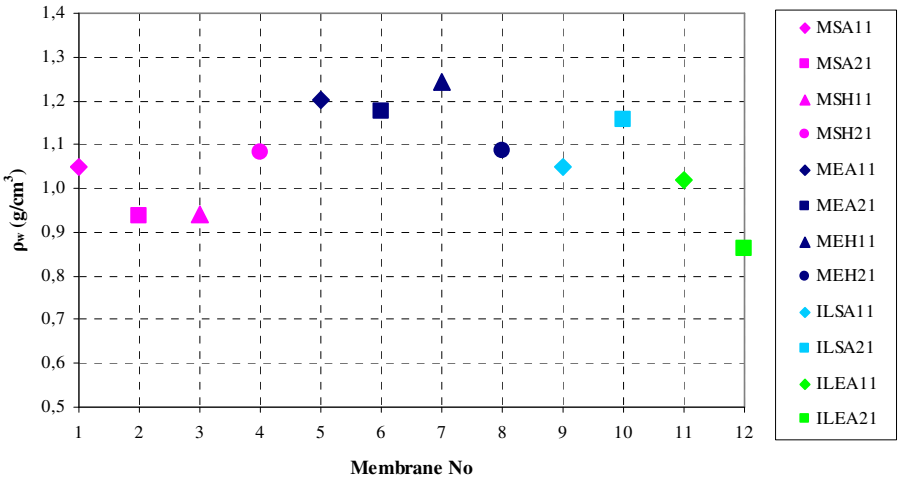


Figure 5.1-3 Chart illustrating the wet density values (ρ_w) of cation exchange membranes.

Membrane porosity values, which were shown in Figure 5.1-4, calculated as the volume of free water within membrane per unit volume of wet membrane (Eqn. 4.3.1.3-1). The values of the membranes

prepared with DOP and S-PVC was around 0.35 ± 0.01, while that of the membranes prepared DOP and E-PVC was about 0.39 ± 0.01.

Average porosity of the membranes with IL and S-PVC is 0.30 ± 0.01 and with IL and E-PVC was 0.26 ± 0.01. Porosities of the membranes contained IL were lower than that of the membranes contained DOP regarding as the average values, 0.28 ± 0.01 and 0.37 ± 0.00, respectively.

Molecular size of IL is greater than that of DOP (Figure 3.2-1). Free volume of IL and thus porosity of the membranes prepared with IL is expected to be larger than DOP regarding molecular sizes of them. However, density values of the membranes prepared with IL was not so different from that with DOP and porosity values of this type of membranes were lower than the membranes prepared with DOP. This situation can be explained by strong interactive forces in IL, which has an ionic structure, and resin particles in the membrane draw each other resulting in a decrease of porosity.

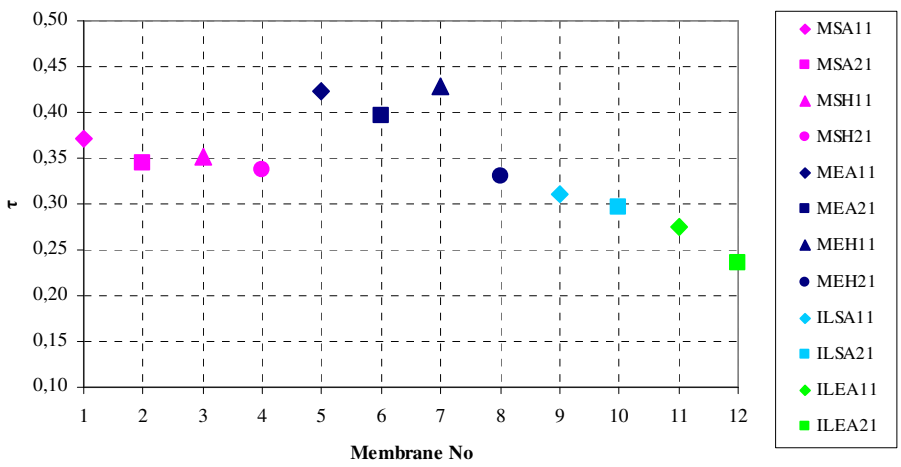


Figure 5.1-4 Chart illustrating the porosity values (τ) of cation exchange membranes.

The determination of ion exchange capacity is an important step in characterizing an ion exchange membrane because the amount and species of ion exchange groups determine the properties of an ion exchange membrane. It depends basically on the content of ion exchange resin in heterogeneous ion exchange membranes. In this study, the amount of ion exchange resins was kept constant in all formulations.

Ion exchange capacity was calculated as in Eqn. 4.3.1.4-1. It had an average value of 1.844 ± 0.026 meq Na^+/g-dry for the membranes prepared with DOP and S-PVC while prepared with DOP and E-PVC was 1.585 ± 0.031 meq Na^+/g-dry.

Average ion exchange capacities of membranes prepared with IL were found as 1.920 ± 0.037 meq Na^+/g-dry and 1.644 ± 0.075 meq Na^+/g-dry for S-PVC and E-PVC based membranes, respectively. For membranes prepared with IL, ion exchange capacity decreased with increasing IL amount because the resins in the membrane having the formulation with RHigh ratio were covered by plasticizer more than that with RLow ratio.

When the mean ion exchange capacities of both DOP and IL plasticized membranes were considered, it was seen that the average value of the membranes prepared with IL, 1.782 ± 0.042 meq Na^+/g-dry, was higher than that with DOP, 1.714 ± 0.020 meq Na^+/g-dry, since IL has an ionic structure while DOP has a molecular and nonconductive structure.

It can be said that the ion exchange capacity value of ion exchange resins increases by grinding (Figure 5.1-5). The raise in ion exchange capacity of cation exchange resin ground can be explained by

the decrease in particle size and porosity of resin after grinding. The resin ground had an ion exchange capacity of 2.324 meq Na^+/g-dry.

Average ion exchange capacity of commercial cation exchange membranes was around 1.978 meq Na^+/g-dry, which was higher than prepared ones, 1.737 ± 0.019 meq Na^+/g-dry.

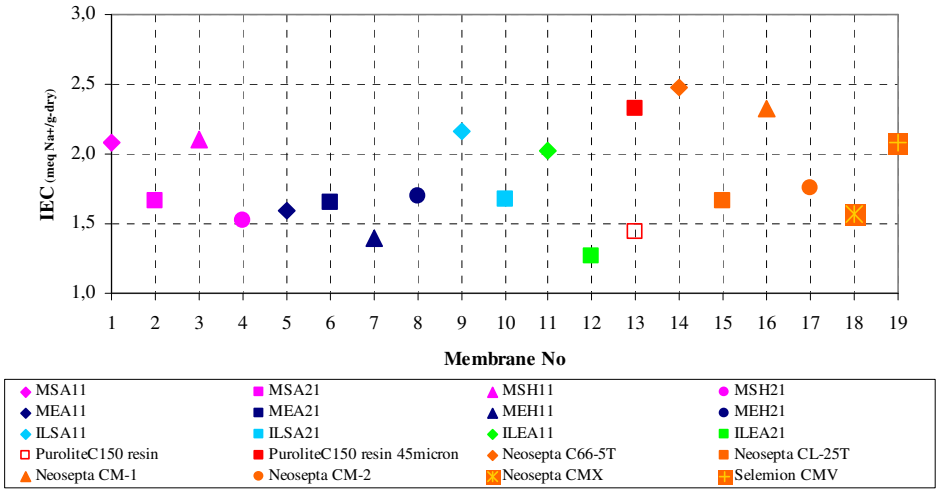


Figure 5.1-5 Chart illustrating the ion exchange capacity values (*IEC*) of cation exchange membranes

In isotherm studies, the relation between the concentration of ions in membrane and in solution at constant temperature was investigated by using six different Na^+ concentrations. The ion-exchange equilibrium is reached when an ion-exchanger of A^{m+} form is soaked in an electrolyte solution with counter-ions (B^{n+}) which are different from that in the ion-exchanger.

The relation between the concentration of Na^+ in membrane phase prepared with S-PVC and DOP and in solution phase at 30°C is shown in Figure 5.1-6. A steep change in all the isotherms is clearly seen up to the solution concentration of 50 ppm Na^+. Although there is a separation among isotherms in richer concentrations of solutions than 50 ppm Na^+, membranes having low DOP:PVC ratio (MSA11, MSH11) have similar behavior with the maximum concentrations in membrane 55 and 53 ppm Na^+, respectively.

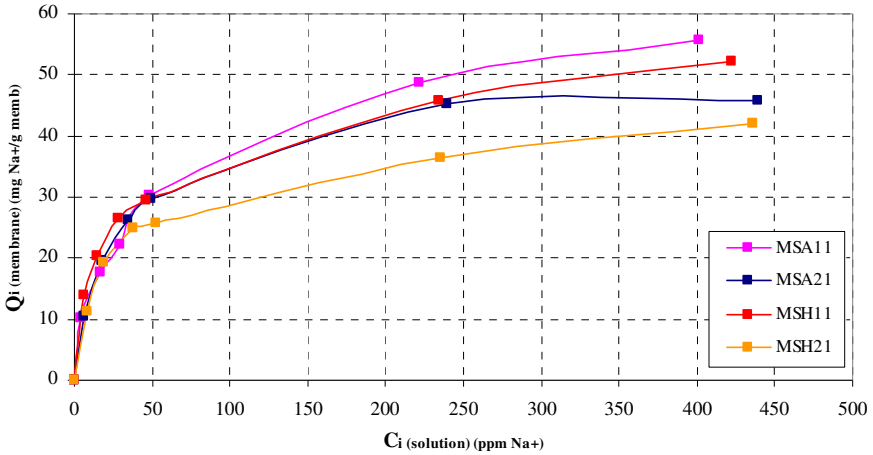


Figure 5.1-6 Chart illustrating equilibrium concentration of Na^+ in membrane phase prepared with S-PVC and DOP versus that of solution phase at 30°C

Sorption behavior of membrane phase prepared with E-PVC and DOP at 30°C is shown in Figure 5.1-7. Initial profile has a sharp increase up to solution concentration of 50 ppm Na^+ for all types of membranes. Around solution concentration of 250 ppm Na^+, all the isotherms reach a plateau levels between 40 and 45 ppm Na^+.

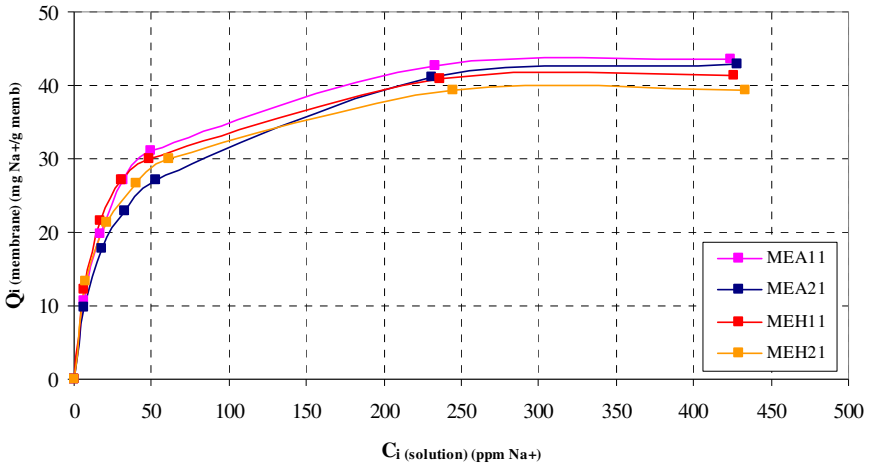


Figure 5.1-7 Chart illustrating equilibrium concentration of Na^+ in membrane phase prepared with E-PVC and DOP versus that of solution phase at 30°C

Equilibrium concentration of Na^+ in membrane phase prepared with S-PVC and IL and that of solution phase at 30°C is shown in Figure 5.1-8. Sorption equilibrium curves for membranes prepared with ionic liquids remarkably differ from each other. Initial steep changes in sorption capacities of membranes are around 6 and 16 ppm Na^+ for S-PVC based membranes ILSA11 and ILSA21, respectively.

The sorption behavior of the membrane ILSA11 is highly interesting since there is continuous rise in equilibrium curve, whereas the increase in sorption capacity for ILSA21 is around 10 ppm Na^+ within the same range of solution concentration.

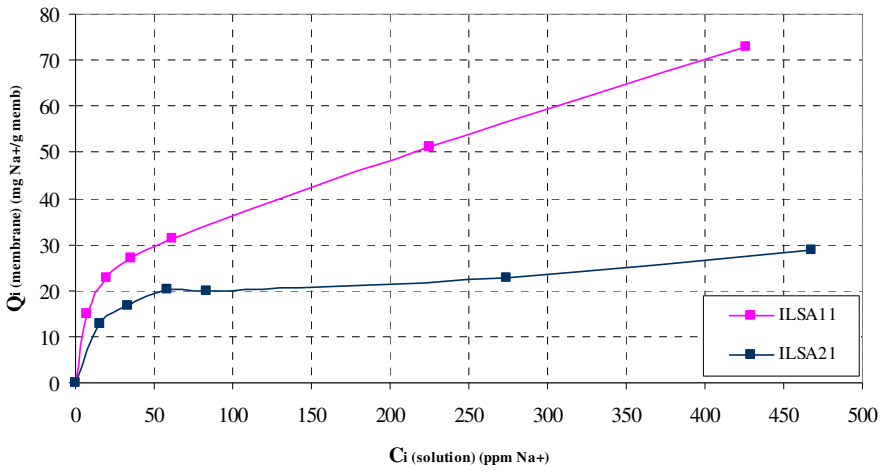


Figure 5.1-8 Chart illustrating equilibrium concentration of Na^+ in membrane phase prepared with S-PVC and IL versus that of solution phase at 30°C

Equilibrium concentration of Na^+ in membrane phase prepared with E-PVC and IL and that of solution phase at 30°C is shown in Figure 5.1-9. Membranes based on E-PVC and IL (ILEA11, ILEA21) have a sharp change in sorption capacity reaching 15 ppm Na^+ with the solution concentration of 9 ppm Na^+. The plateau value reached by ILEA21 is 32 ppm Na^+ but ILEA11 shows an increase like ILSA11 at a solution concentration of 236 ppm Na^+.

Larger sorption capacities with the membranes having low PVC:IL ratio (ILSA11, ILEA11) is in accordance with the ion exchange capacities for same membranes (Figure 5.1-5).

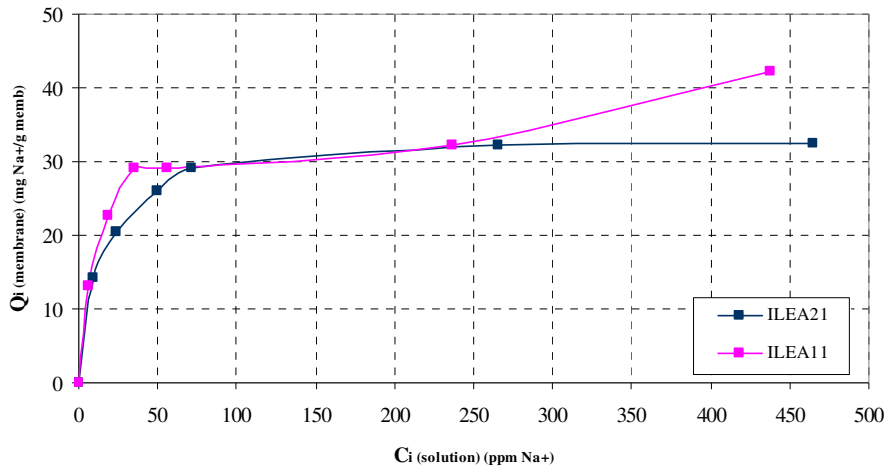


Figure 5.1-9 Chart illustrating equilibrium concentration of Na^+ in membrane phase prepared with E-PVC and IL versus that of solution phase at 30°C

5.2. Electrochemical Characterization

In an electrolyte solution the current is carried by both cations and anions. However, they usually carry different portions of the overall current. In ion exchange membranes the current is carried preferentially by the counter-ions. The fraction of the current that is carried by a certain ion is expressed by transport number of that ion (Strathmann, 2004).

A method to measure transport number is its calculation from the membrane potential. In this thesis, this method was followed to find the transport number of Na^+ in cation exchange membrane prepared. For each membrane, potential (E) versus $\ln(a_2/a_1)$ was plotted. The calculation procedure of transport number was explained in section *Theory*.

For membranes plasticized with DOP, the graphs illustrating membrane potential versus $\ln(a_2/a_1)$ values for the membranes prepared with PVC and DOP are shown in Figure 5.2-1 and Figure 5.2-2 with the linear trend lines. In these figures, as slope decreases, transport number of Na^+ in cation exchange membrane prepared increases.

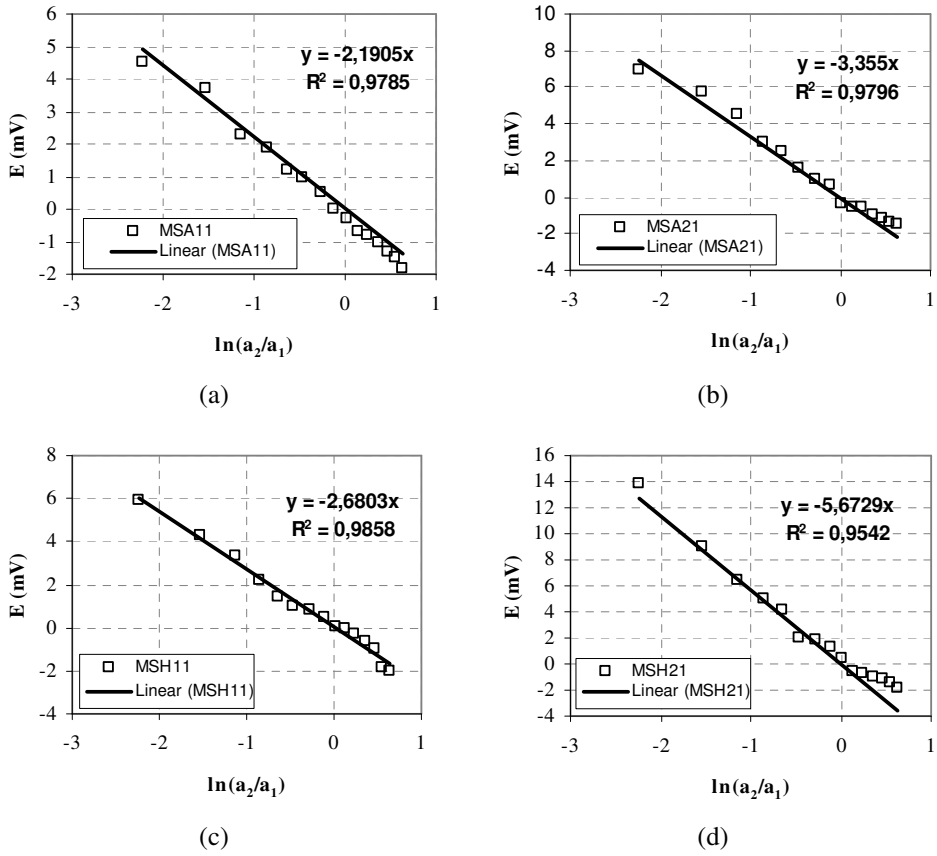


Figure 5.2-1 Charts illustrating the membrane potential versus $\ln(a_2/a_1)$ for the membranes prepared with S-PVC and DOP (MSA and MSH types)

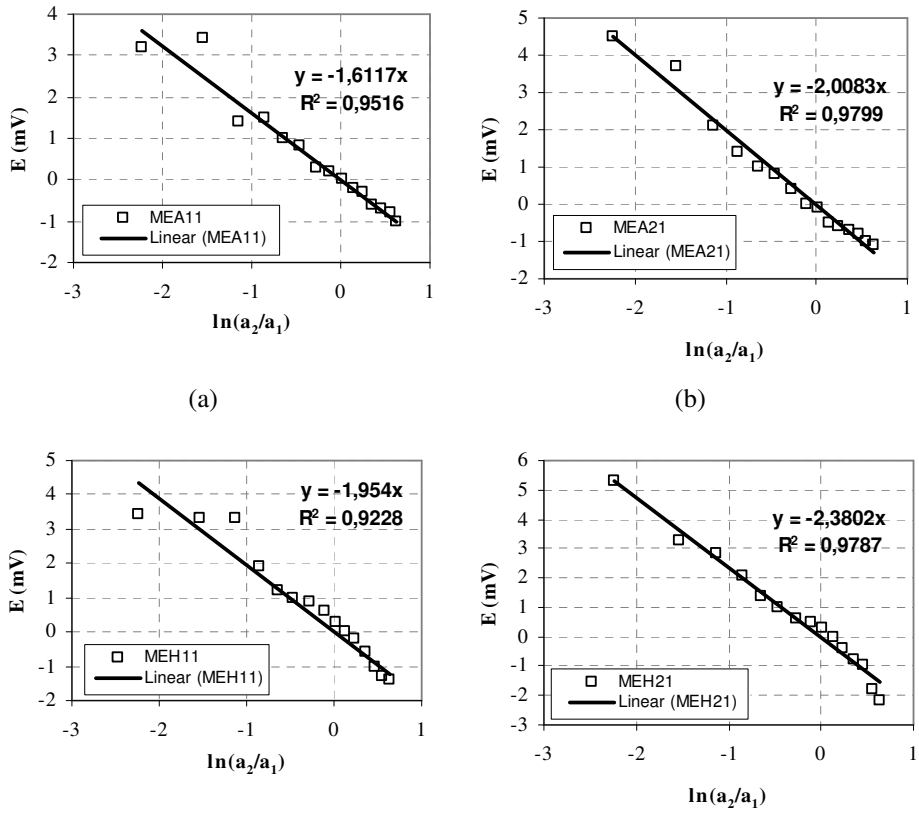


Figure 5.2-2 Charts illustrating the membrane potential versus $\ln(a_2/a_1)$ for the membranes prepared with E-PVC and DOP (MEA and MEH types)

The graphs illustrating membrane potential versus $\ln(a_2/a_1)$ values for membranes plasticized with IL are shown in Figure 5.2-3 with the linear trend lines. In these charts, as slope decreases, transport number of Na^+ in membrane prepared increases also.

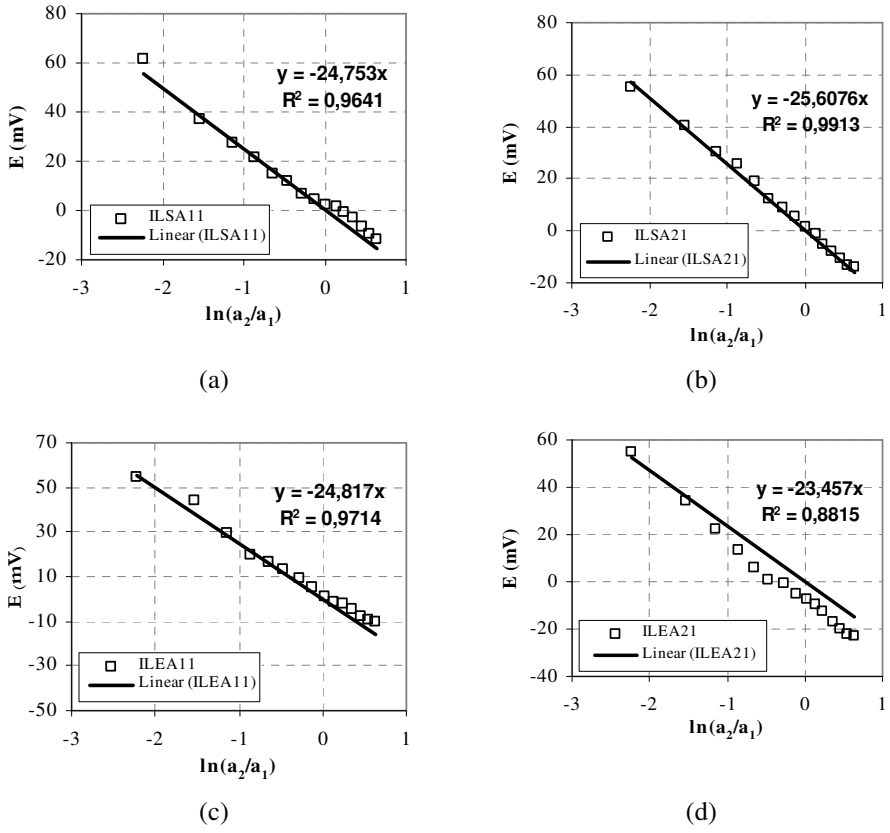


Figure 5.2-3 Charts illustrating the membrane potential versus $\ln(a_2/a_1)$ for the membranes prepared with IL (ILSA and ILEA types)

The calculation procedure of transport numbers were explained in section *Theory*. Transport numbers of cation Na^+ in cation exchange membranes prepared with DOP and IL are given in Table 5.2-1.

Table 5.2-1 Transport numbers of membranes prepared with DOP

Membrane Name	**MSA11**	**MSA21**	**MSH11**	**MSH21**
t_{Na+}	0.54	0.56	0.55	0.61
Membrane Name	**MEA11**	**MEA21**	**MEH11**	**MEH21**
t_{Na+}	0.53	0.54	0.54	0.55
Membrane Name	**ILSA11**	**ILSA21**	**ILEA11**	**ILEA21**
t_{Na+}	0.97	0.99	0.98	0.95

It is clearly seen from the Table 5.2-1 that the transport numbers of the membranes prepared with IL was larger than that with DOP since IL, which is a conductive material, is combined with cation exchange resin, which is a selective material, resulting in an increased mobility of ions passing through the membrane.

5.3. Morphological Characterization

Morphological characterization includes SEM analysis of the membranes prepared.

5.3.1. SEM Analysis

In SEM analysis, surface and cross-sectional views of the cation exchange membranes prepared were investigated. The samples were

coated with a thin gold layer before scanning because they must be conductive for analyses. Samples that are nonconductive or that have nonconductive portions may cause severe problems during the imaging and photographic processes because of the accumulation of static electric fields at the specimen due to the electron irradiation required during imaging (Flegler et al., 1993).

In this study, membranes were prepared with several formulations by using different polymer and plasticizer. They were cast and dried by heating or by ambient air. Results will be handled in the following structure:

- SEM analysis of the membrane prepared with DOP
  - Surface views of the membranes prepared with DOP and S-PVC
  - Surface views of the membranes prepared with DOP and E-PVC
  - Cross-sectional views of the membranes prepared with DOP and S-PVC
  - Cross-sectional views of the membranes prepared with DOP and E-PVC
- SEM analysis of the membrane prepared with IL
  - Surface views of the membranes prepared with IL and S-PVC
  - Surface views of the membranes prepared with IL and E-PVC
  - Cross-sectional views of the membranes prepared with IL and S-PVC
  - Cross-sectional views of the membranes prepared with IL and E-PVC

5.3.1.1. SEM analysis of the membranes prepared with DOP

Surface views of cation exchange membranes prepared with DOP and S-PVC and dried by ambient air are shown in Figure 5.3.1.1-1. In these images, the surfaces facing the glass, on which the membranes were cast, and the surfaces open to air were illustrated. On the glass side of MSA11, membrane has an organized structure with very small pores. However, it has large cavities on the air side of the same membrane. It may be because of solvent evaporation during drying. Same manner can be said for MSA21. When MSA11 and MSA21 are compared, the pore size on the air side of MSA21 is smaller than that of MSA11. The reason can be the plasticizer ratio doubled of MSA21.

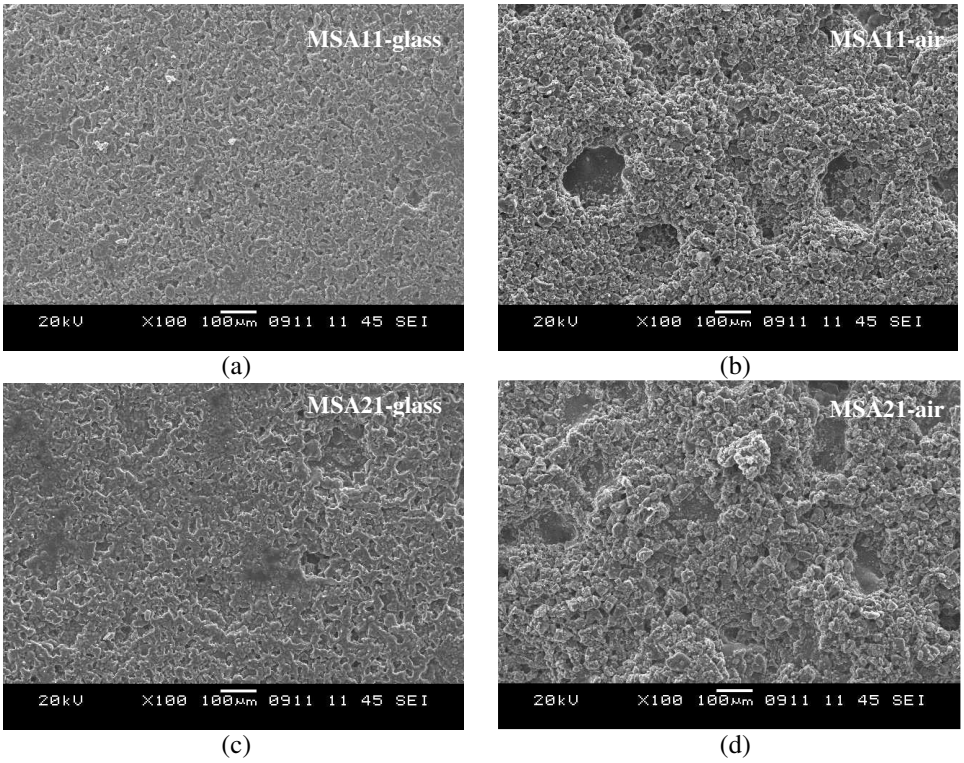


Figure 5.3.1.1-1 SEM images of cation exchange membranes prepared with DOP and S-PVC and dried by ambient air

Surface views of membranes prepared with DOP and S-PVC and dried by heating in an oven are shown in Figure 5.3.1.1-2. On the glass side of both of MSH11 and MSH21, membranes have an ordered structure, but they have large cavities on the air sides of the same membranes. When the plasticizer ratio is doubled (MSH21), the pores on the glass side are closed.

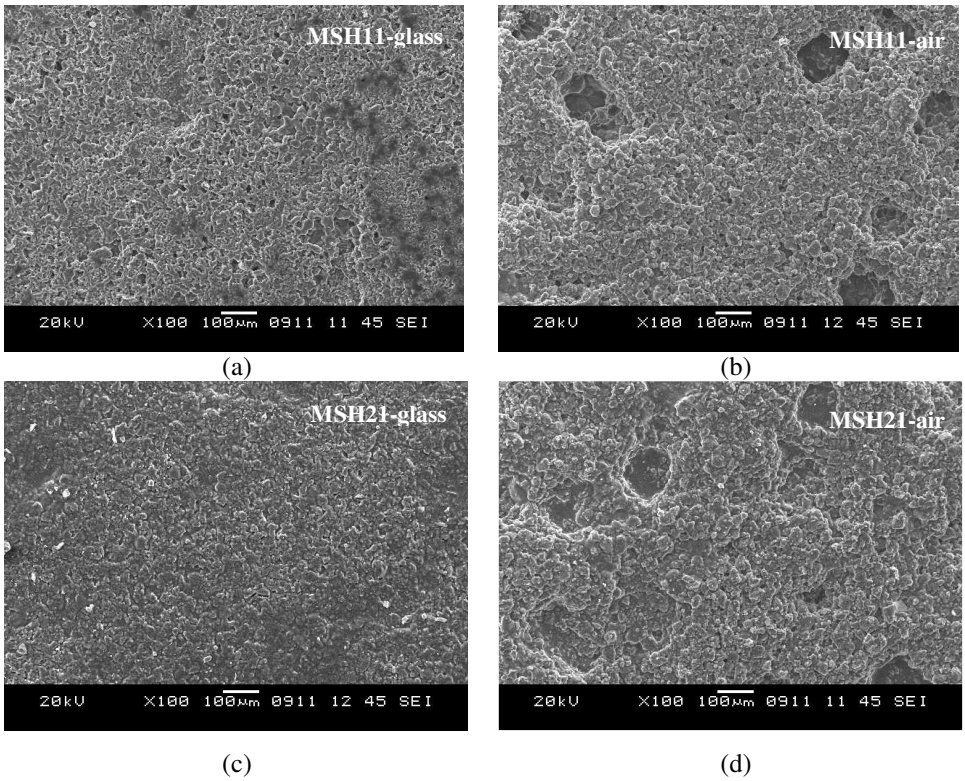


Figure 5.3.1.1-2 SEM images of cation exchange membranes prepared with DOP and S-PVC and dried by heating

Surface views of cation exchange membranes prepared with DOP and E-PVC are shown in Figure 5.3.1.1-3. On the glass sides of both

MEA11 and MEA21, membranes have more regular structure than on the air sides of them. While the air side of MEA11 has some pores, that of MEA21 does not have pores.

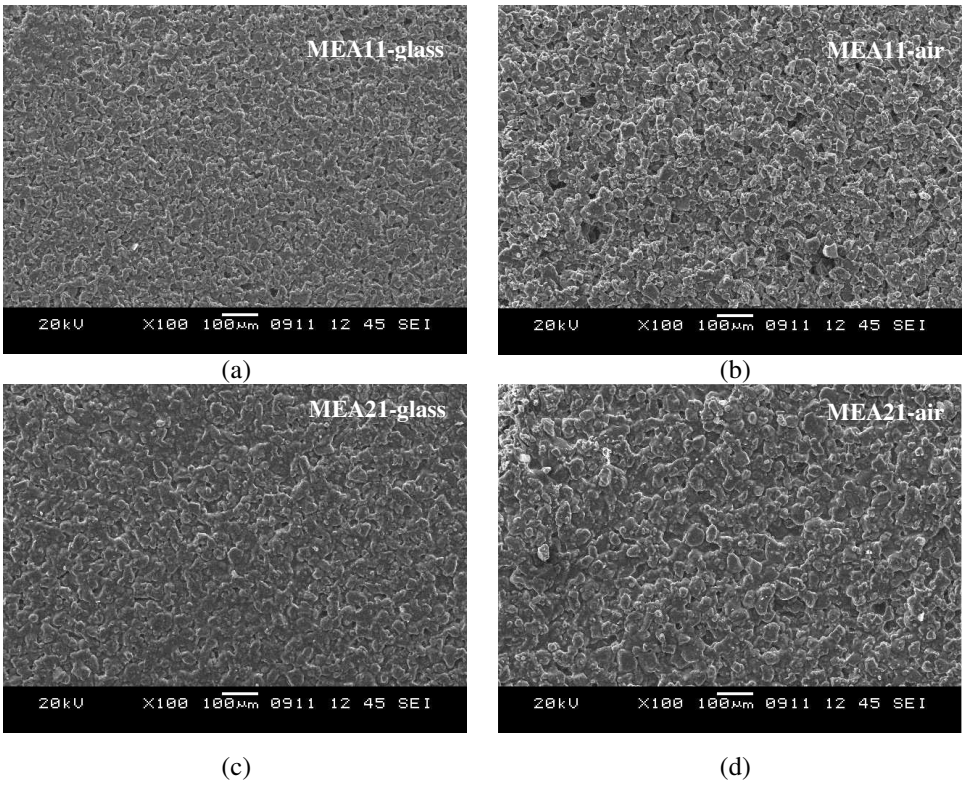


Figure 5.3.1.1-3 SEM images of cation exchange membranes prepared with DOP and E-PVC and dried by ambient air

Surface views of cation exchange membranes prepared with DOP and E-PVC and dried by heating in an oven are shown in Figure 5.3.1.1-4. There is not so much difference between glass side and air side for both of MEH11 and MEH21.

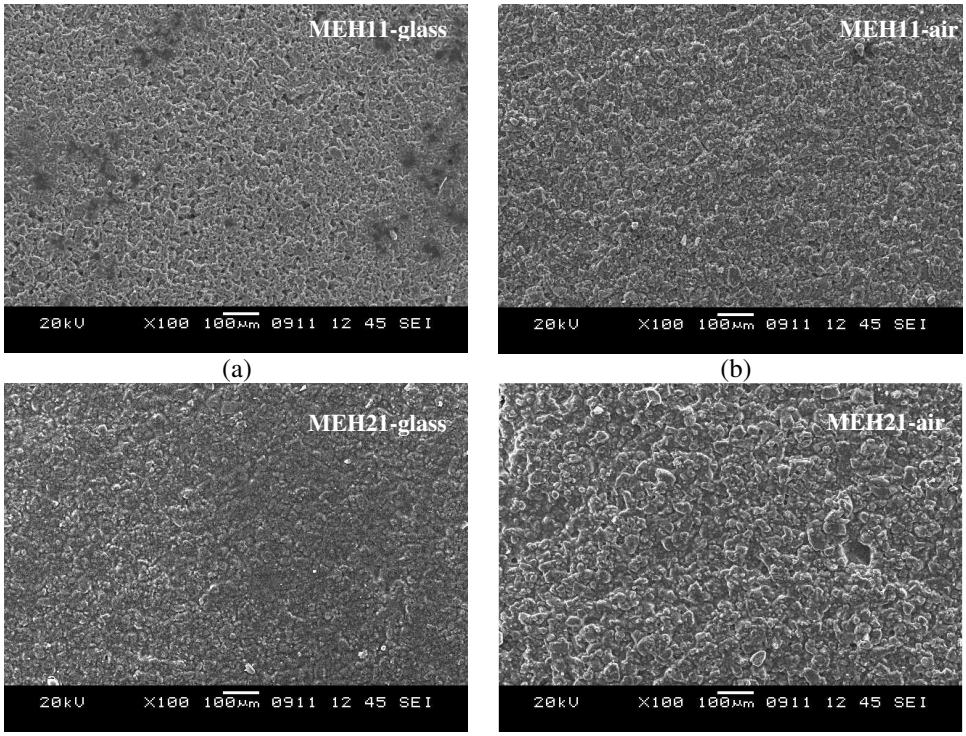


Figure 5.3.1.1-4 SEM images of cation exchange membranes prepared with DOP and E-PVC and dried by heating

The surfaces facing the glass of the E-PVC membranes are similar to S-PVC membranes. However, the surfaces open to air of E-PVC membranes have no cavities and they are smoother than S-PVC membranes.

Cross-sectional views of cation exchange membranes prepared with DOP and S-PVC are shown in Figure 5.3.1.1-5. The cation exchange resin particles were attached to each other and to PVC particles by means of DOP. As a result, the membranes prepared with lower amount of DOP were more brittle than those with higher one. Please note that different

views of membranes are coming from the difference in their thicknesses, since scaling was kept same in all images.

At the first glance, thickness of the membrane MSA11 is less than that of MSA21. The distribution of the resins is more balanced in MSA21 than MSA11 due to the larger amount of plasticizer. Similar structural views, namely lumped versus organized structures, are easily seen from the SEM images of the membranes MSH11 and MSH21. In the comparison of the drying condition, it can be stated that more regular structure is obtained in drying by heating.

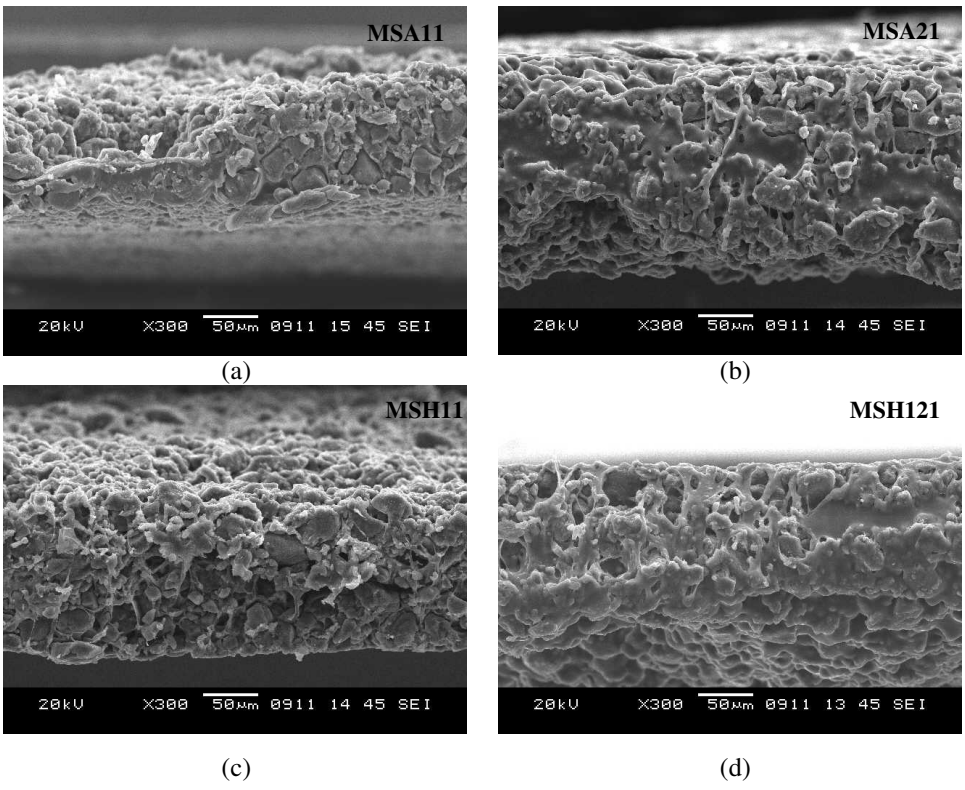


Figure 5.3.1.1-5 Cross-sectional views of membranes prepared with DOP and S-PVC

Cross-sectional views of cation exchange membranes prepared with DOP and E-PVC are shown in Figure 5.3.1.1-6. Similar arguments can be developed for this type of membranes.

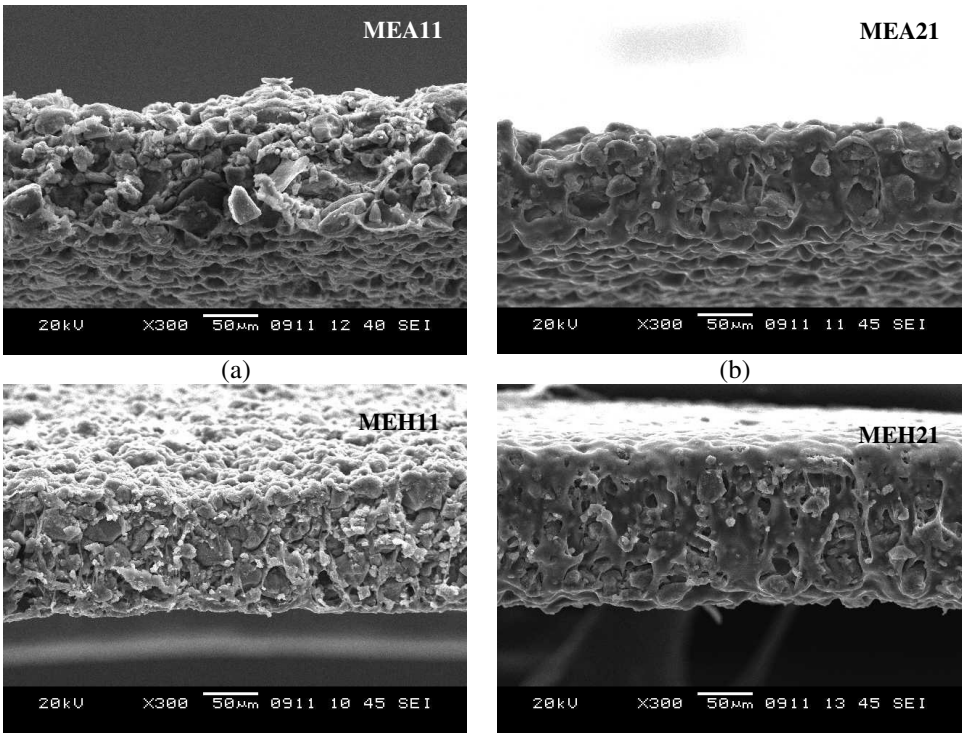


Figure 5.3.1.1-6 Cross-sectional views of membranes prepared with DOP and E-PVC

5.3.1.2. SEM analysis of the membranes prepared with IL

Surface views of cation exchange membranes prepared with IL and S-PVC are shown in Figure 5.3.1.2-1. On the glass side of ILSA11, membrane has an organized structure with small pores. Nevertheless, it

has larger pores on the air side of the same membrane. Same approach can be made for ILSA21. When ILSA11 and ILSA21 are compared, there are fewer pores on the air side of ILSA21 than that of ILSA11. The cause can be higher plasticizer amount of ILSA21.

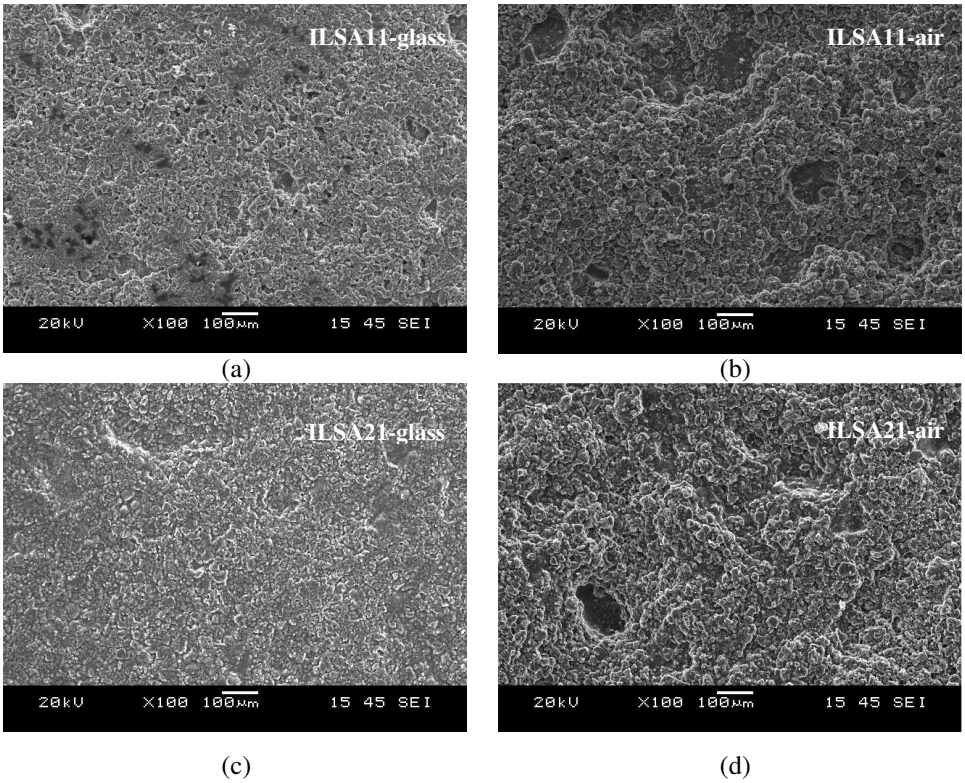


Figure 5.3.1.2-1 SEM images of cation exchange membranes prepared with IL and S-PVC

Surface views of cation exchange membranes prepared with IL and E-PVC are shown in Figure 5.3.1.2-2. In the case of glass sides of ILEA11 and ILEA21, membranes have more regular structure than on the air sides of them. At the air side, ILEA11 has very small pores, whereas ILEA21 does not have pores.

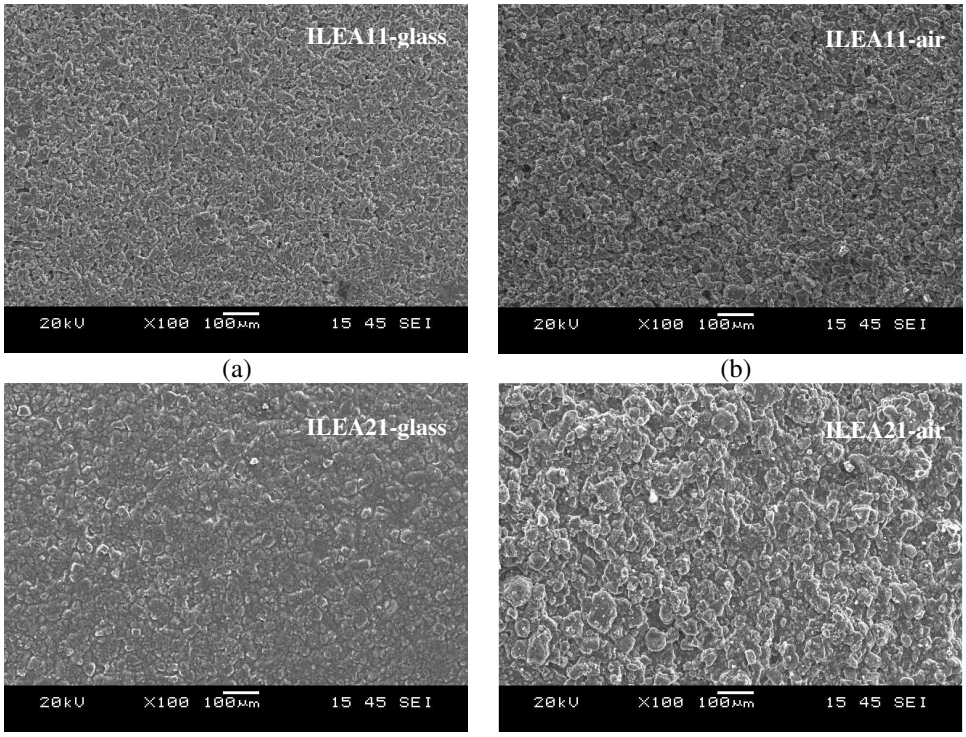


Figure 5.3.1.2-2 SEM images of cation exchange membranes prepared with IL and E-PVC

The surfaces facing the glass of the S-PVC membranes prepared with IL are rougher than of the E-PVC membranes. The surfaces open to air of S-PVC membranes have cavities while E-PVC membranes are more uniform.

Cross-sectional views of the membranes prepared with IL and both S-PVC and E-PVC are shown in Figure 5.3.1.2-3. In these images, resin particles were attached to each other and to PVC particles by means of IL. They are more disordered than the membranes prepared with DOP. Moreover, the membranes prepared with E-PVC and IL have more uniform view with respect to S-PVC and IL.

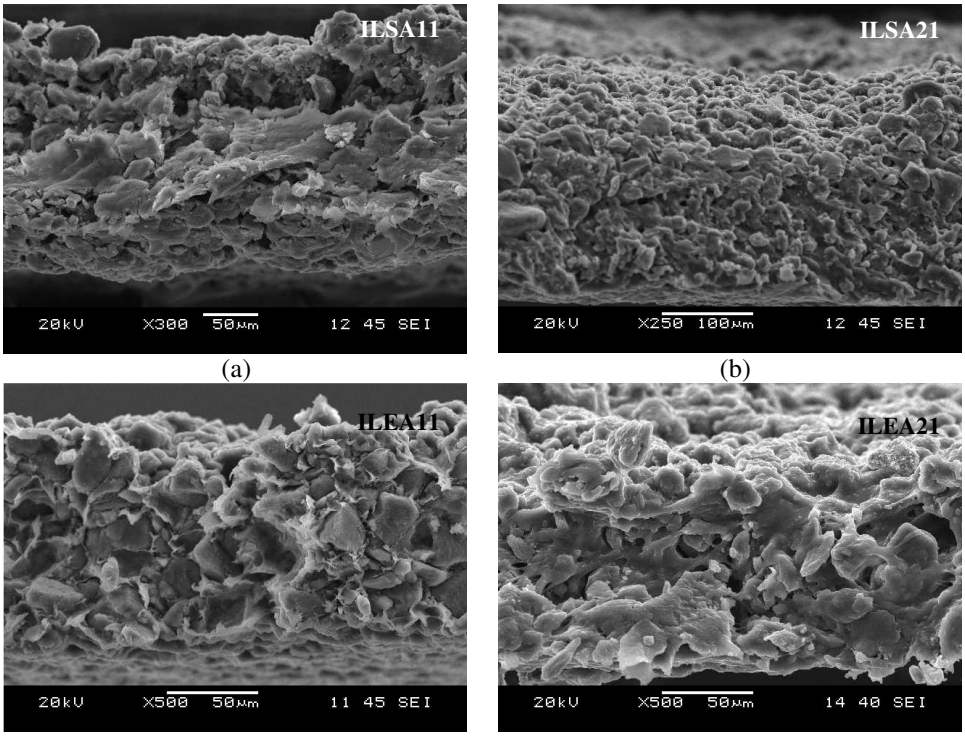


Figure 5.3.1.2-3 Cross-sectional views of the membranes prepared with IL

5.4. Performance Study

The performance of cation exchange membrane prepared is analyzed by Donnan dialysis with two-compartment cell, which are named as concentrate and permeate sides (Figure 4.4-1). Cation exchange membrane is placed between these compartments tightly. Initial Na^+ concentration in concentrate part was 50 ppm, while permeate part was filled with pure water, for all experiments of Donnan dialysis.

The change in Na^+ concentration of concentrate and permeate part with respect to time is illustrated in Figure 5.4-1 for the membranes based on S-PVC and DOP and in Figure 5.4-2 for those on E-PVC and

DOP. The concentration of concentrate part decreases approximately by 6 ppm Na^+ for MSA21, MSH21 and MSH11, but it decreases nearly by 10 ppm Na^+ for MSA11. Likewise, the concentration reduces about by 5.5 ppm Na^+ for MEA21, MEH21 and MEH11, but it decreases around by 15 ppm Na^+ for MEA11.

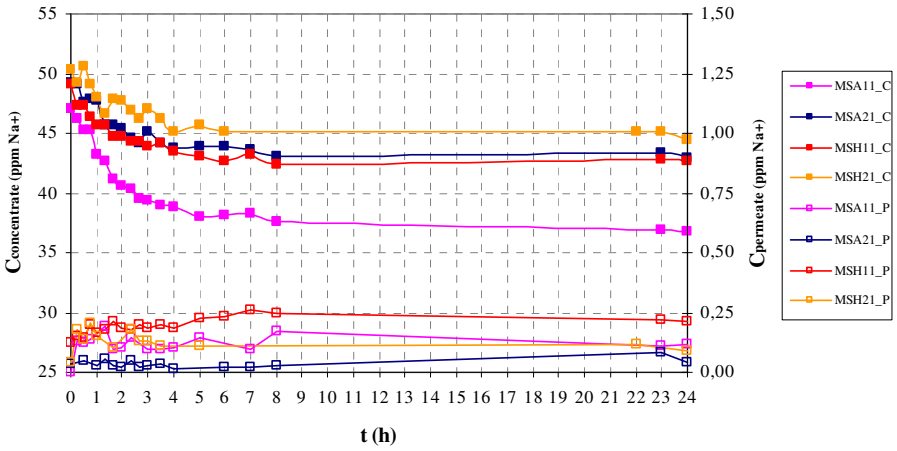


Figure 5.4-1 Chart illustrating the change in Na^+ concentration of concentrate and permeate part using different S-PVC and DOP based cation exchange membranes

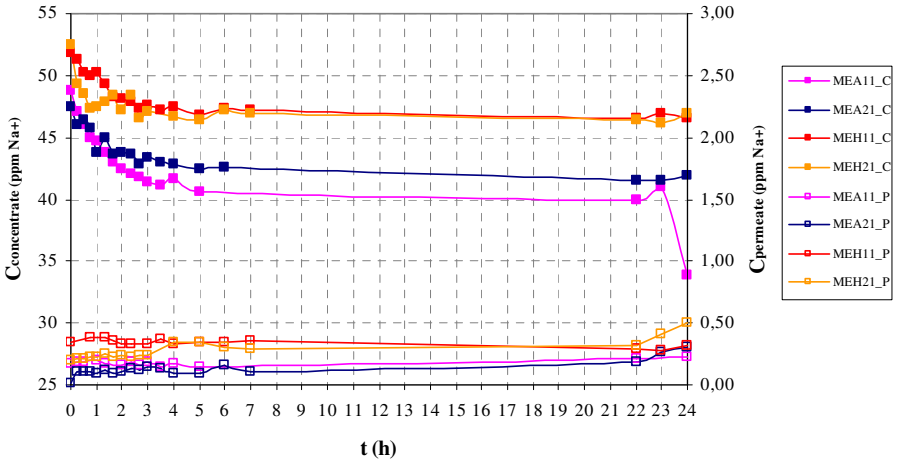


Figure 5.4-2 Chart illustrating the change in Na^+ concentration of concentrate and permeate part using different E-PVC and DOP based cation exchange membranes

The change in Na^+ concentration with respect to time is illustrated in Figure 5.4-3 for the membranes based on S-PVC and IL and in Figure 5.4-4 for that on E-PVC and IL. The concentration of concentrate part decreases approximately by 5 ppm Na^+ for ILSA11, but it decreases by 1 ppm Na^+ for ILSA21. The reason can be higher ion exchange capacity of ILSA11 than ILSA21 and also higher transport number of ILSA11 than ILSA21. The concentration reduces about by 3.85 ppm Na^+ for both of ILEA11 and ILEA21 since their transport numbers are also almost equal.

For all types of membranes, the concentrations of concentrate and permeate parts reach a plateau after 24 hours.

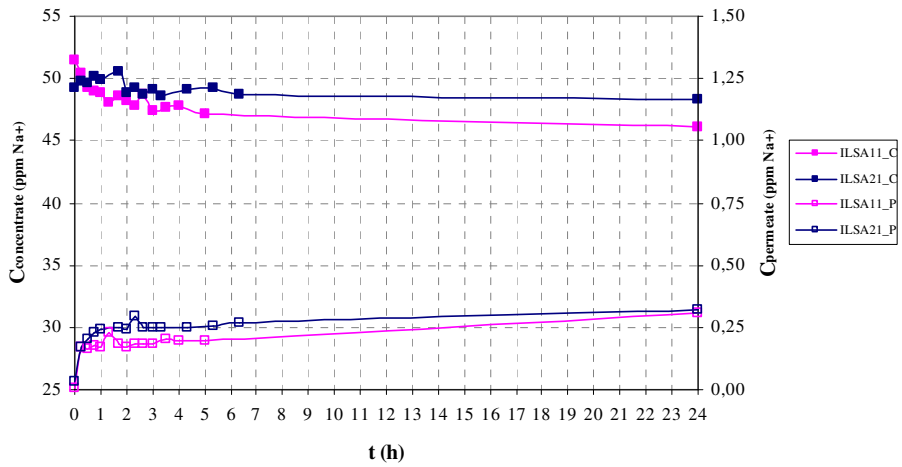


Figure 5.4-3 Chart illustrating the change in Na^+ concentration of concentrate and permeate part using different S-PVC and IL based cation exchange membranes

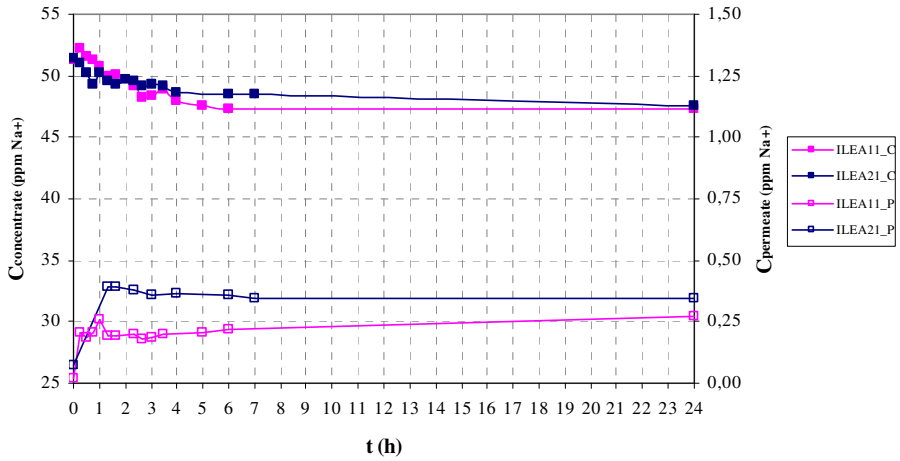


Figure 5.4-4 Chart illustrating the change in Na^+ concentration of concentrate and permeate part using different E-PVC and IL based cation exchange membranes

After getting the graphs of concentration versus time, the diffusivity values were calculated by using Donnan dialytic method. In calculations, there is a constant (α) (Geankoplis, 1993) for each membrane and this constant can easily be determined by conducting an experiment with a liquid pair whose molecular diffusivity is already known. The molecular diffusivity taken is D = 1.17 x 10^{-5} cm^2/s at the concentration of NaCl, C = 0.4 M (Sherwood et al., 1975). The calculation procedure was explained at pages 40-41 in section *Theory*. The resulting diffusivity values are shown in Table 5.4-1.

All diffusivity values are around 3.5 x 10^{-5} except ILEA11, which has a value of 13.05 x 10^{-5}. Ion exchange capacity of this membrane is also high. The values are in the range of molecular diffusivities in liquids, which has a level of 10^{-5} cm^2/s.

Table 5.4-1 Diffusivity values of membranes prepared

Membrane Name	**Membrane No**	**Diffusivity** (cm^2/s) ($x10^5$)
MSA11	1	4.36
MSA21	2	1.97
MSH11	3	3.49
MSH21	4	2.62
MEA11	5	5.68
MEA21	6	4.11
MEH11	7	1.59
MEH21	8	3.17
ILSA11	9	4.19
ILSA21	10	1.31
ILEA11	11	13.05
ILEA21	12	5.70

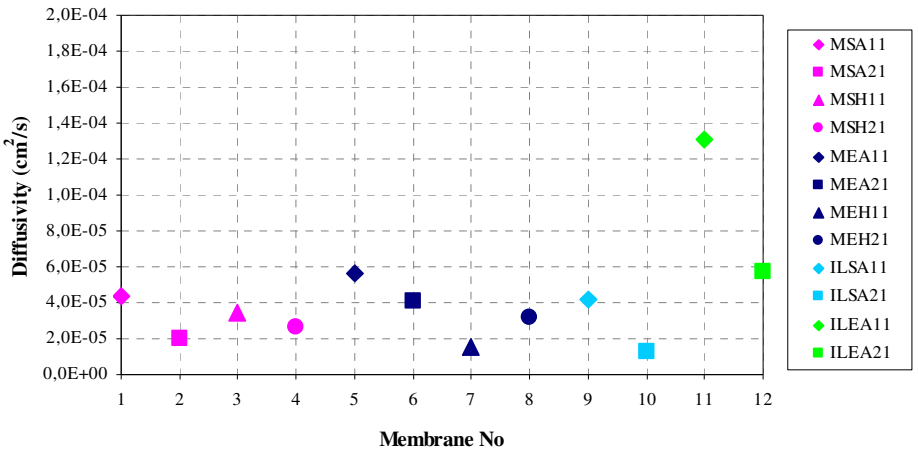


Figure 5.4-5 Chart illustrating the diffusivity values of the membranes prepared.

6. CONCLUSION

In this research, PVC based strong acidic cation exchange membranes were prepared by heterogeneous method and then characterized by physicochemical, morphological and electrochemical ways.

First parameter studied in the preparation step was the type of polymeric binder. Two kinds of PVC, S-PVC and E-PVC, were used to prepare cation exchange membranes. Second parameter was the kind of plasticizer from DOP and IL. Third one was drying procedure after casting the solution as air drying and drying by heating in an oven at 75ºC. Polystyrene crosslinked with divinyl benzene, macroporous, and strongly acidic cation exchange resins (CXR) were same for all types of membranes prepared. Cyclohexanone (CH) was used as solvent.

For the preparation of membranes, commercial CXR was ground to 45 μm before adding to the mixture. As resin becomes finer, is distributed more uniformly through the mixture resulting in a more homogenous membrane. Thicknesses of membranes were varied with respect to polymers used for preparation. Membranes prepared with E-PVC had a thickness lower than that with S-PVC.

Physicochemical characterization included volume fraction of water, dry and wet densities of the membrane, membrane porosity, ion exchange capacity and isotherm studies.

There was no notable difference in volume fraction of water among all types of membranes. Average water content of commercial cation exchange membranes was less than that of prepared ones.

E-PVC based membranes had greater density values with respect to S-PVC based membranes because E-PVC based membranes had more stiff structure than S-PVC based ones. Average dry density values of commercial cation exchange membranes were higher than that of prepared ones.

Porosities of the membranes containing IL were lower than that of the membranes containing DOP.

Ion exchange capacity (IEC) depends essentially on the content of ion exchange resin in heterogeneous ion exchange membranes. In this study, the amount of ion exchange resins remained constant in all formulations. For membranes prepared with IL, IEC decreased with increasing IL amount. It was seen that the average value of the membranes prepared with IL was higher than that with DOP.

Isotherm studies were performed to characterize ion exchange equilibrium. A sharp change in all the isotherms for the membranes were seen at dilute concentrations. There was a separation among isotherms for the membranes prepared with S-PVC and DOP in richer concentrations. At richer concentrations, all the isotherms for the membranes prepared with E-PVC and DOP reached plateau levels. Sorption equilibrium curves for membranes prepared with ionic liquids differed remarkably from each other.

Membranes were characterized in morphological ways by SEM. Surface and cross-sectional views of the cation exchange membranes prepared were investigated. In the surface images, the surfaces facing the glass, on which the membranes were cast, and the surfaces open to air were investigated.

The surfaces facing the glass of the membranes prepared with DOP and E-PVC were similar to those with S-PVC. However, the surfaces open to air of E-PVC membranes had no cavities and they were smoother than S-PVC membranes. Glass sides of the S-PVC membranes prepared with IL were rougher than those of the E-PVC membranes. Air sides of S-PVC membranes had cavities while E-PVC membranes were more uniform. In cross-sectional views of the IL-based membranes, they were more disordered than the membranes prepared with DOP.

Electrochemical characterization of the membranes prepared comprised of the calculation of transport number by measuring membrane potential. The transport numbers of the membranes prepared with IL was larger than that with DOP because IL having a conductive structure was combined with selective CXR causing an increased mobility of ions passing through the membrane.

The performance of cation exchange membrane prepared was tested by Donnan dialysis. For all types of membranes, the concentrations of concentrate and permeate parts reached a plateau after 24 hours. As a result of the graphs of concentration versus time, the diffusivity values were calculated by using Donnan dialytic method. All diffusivity values were similar except ILEA11, which had a higher value. Ion exchange capacity of this membrane was also high. The values were in the range of molecular diffusivities in liquids.

By looking at the experimental results, a strongly acidic heterogeneous cation exchange membranes can be prepared with tetradecyl(trihexyl)phosphonium decanoate, which is a phosphonium based ionic liquid. The membranes based on IL prepared had similar physicochemical and morphological properties and they had also better electrochemical properties than the membranes prepared with dioctyl phthalate, which is a traditional plasticizer. Hence, ion exchange membranes with higher conductivity and higher electrochemical properties can be produced by using ionic liquids.

APPENDIX

Calculation of activity coefficients

Debye-Hückel Theory of Electrolyte Solutions

In this model, the ions are taken to be uniformly charged hard spheres of diameter *a*. The difference in size between positive and negative ions is ignored, and *a* is interpreted as the mean ionic diameter. Debye and Hückel's final result is;

$$\ln \gamma_+ = -\frac{z^2 + AI_m^{1/2}}{1 + BaI_m^{1/2}} \quad and \quad \ln \gamma_- = -\frac{z^2 - AI_m^{1/2}}{1 + BaI_m^{1/2}} \qquad \text{(Eqn. A-1)}$$

where A, B and I_m are defined as;

$$A \equiv (2\pi N_A \rho_A)^{1/2} \left(\frac{e^2}{4\pi \varepsilon_0 \varepsilon_{r,A} kT} \right)^{3/2} \quad and \quad B \equiv e \left(\frac{2N_A \rho_A}{\varepsilon_0 \varepsilon_{r,A} kT} \right)^{1/2} \qquad \text{(Eqn. A-2)}$$

$$I_m \equiv \frac{1}{2} \sum_j z_j^2 m_j \qquad \text{(Eqn. A-3)}$$

In these equations, a is the mean ionic diameter, γ_+ and γ_- are the activity coefficients for cations and anions, respectively, N_A is the Avogadro constant, k is the Boltzmann's constant, e is the proton charge, ε_0 is the permittivity of vacuum, ρ_A is the solvent density, $\varepsilon_{r,A}$ is the solvent dielectric constant, and T is the absolute temperature, I_m is called ionic

strength; the sum in Eqn. A-3 goes over all ions in solution, m_j being the molality of ion j with charge z_j.

Although the Debye-Hückel theory gives γ of each ion, γ_+ or γ_- cannot be measured individually. Hence, The Debye-Hückel result is expressed in terms of the mean ionic activity coefficient $\gamma_\pm$;

$$(\gamma_\pm)^{\upsilon_+ + \upsilon_-} \equiv (\gamma_+)^{\upsilon_+} (\gamma_-)^{\upsilon_-} \qquad \text{(Eqn. A-4)}$$

$$\ln \gamma_\pm = \frac{\upsilon_+ \ln \gamma_+ + \upsilon_- \ln \gamma_-}{\upsilon_+ + \upsilon_-} \qquad \text{(Eqn. A-5)}$$

Since the electrolyte is electrically neutral;

$$\upsilon_+ z_+ + \upsilon_- z_- = 0 \qquad \text{(Eqn. A-6)}$$

Multiplication of Eqn. A-6 by z_+ yields $\upsilon_+ z_+^2 = -\upsilon_- z_+ z_-$; multiplication of Eqn. A-6 by z_- yields $\upsilon_+ z_-^2 = -\upsilon_+ z_+ z_-$. Addition of these two equations gives;

$$\upsilon_+ z_+^2 + \upsilon_- z_-^2 = -z_+ z_- (\upsilon_+ + \upsilon_-) = z_+ |z_-| (\upsilon_+ + \upsilon_-) \qquad \text{(Eqn. A-7)}$$

Substitution of Debye-Hückel equations (Eqn. A-1) into Eqn. A-5 followed by use of Eqn. A-7 gives;

$$\ln \gamma_\pm = -z_+ |z_-| \frac{A I_m^{1/2}}{1 + B a I_m^{1/2}} \qquad \text{(Eqn. A-8)}$$

By replacing the values of N_A, k, e and ε_0, ε_r and ρ;

$$A = 1.1744\ (kg/mol)^{1/2} \qquad B = 3.285\times10^{9}\ (kg/mol)^{1/2}\, m^{-1}$$

Substituting these values into Eqn. A-8;

$$\log \gamma_{\pm} = -0.510 z_{+} |z_{-}| \frac{(I_m / m^0)^{1/2}}{1 + 0.328(a/\text{Å})(I_m / m^0)^{1/2}} \qquad \text{(Eqn. A-9)}$$

where 1 Å = 10^{-10} m and m^0 = 1 mol/kg. A complete equation (Eqn. A-9) is reasonably accurate for aqueous solutions with $I_m \leq 0.1$ mol/kg if the ionic diameter a is chosen as good fit to the data. Values of a range from 3 to 9 Å for common inorganic salts. To eliminate the empirically determined ionic diameter a from Eqn. A-9, for a $\approx$ 3 Å, $0.328(a/\text{Å}) \approx 1$ (Levine, 1995);

$$\log_{10} \gamma_{\pm} = -0.510 z_{+} |z_{-}| \frac{(I_m / m^0)^{1/2}}{1 + (I_m / m^0)^{1/2}} \qquad \text{(Eqn. A-10)}$$

Uncertainty analysis and significant figures

Measurements involve errors and uncertainties. Every measurement is influenced by many uncertainties. Because measurement uncertainties can never be completely eliminated, measurement data can give us only an estimate of the "true" value. However, the probable magnitude of error in a measurement can often be evaluated. It is then possible to define limits within which the true value of a measured quantity lies (Skoog et al., 2004).

A precise method of estimating uncertainty in experimental results has been presented by Kline and McClintock. The method is based on a careful specification of the uncertainties in the various experimental measurements. For example, a certain pressure reading might be expressed as;

$$p = 100 \pm 1 \; kPa$$

Suppose a set of measurements is made and the uncertainty in each measurement may be expressed with the same odds. These measurements are then used to calculate some desired result of the experiments. The goal is to estimate the uncertainty in the calculated result on the basis of the uncertainties in the primary measurements. The result R is a given function of the independent variables x_1, x_2, x_3,…, x_n. Thus,

$$R = R(x_1, x_2, x_3, ..., x_n) \qquad \text{(Eqn. A-11)}$$

Let w_R be the uncertainty in the result and w_1, w_2,…,w_n be the uncertainties in the variables. The uncertainty in the result is given by (Holman, 2001),

$$w_R = \left[\left(\frac{\partial R}{\partial x_1} w_1 \right)^2 + \left(\frac{\partial R}{\partial x_2} w_2 \right)^2 + ... + \left(\frac{\partial R}{\partial x_n} w_n \right)^2 \right]^{1/2} \qquad \text{(Eqn. A-12)}$$

If this relation is applied to the volume fraction of water measurements of physicochemical characterization steps, the calculation is as follows;

For the membrane MSA11, wet and dry weights of three samples were measured on a balance having an uncertainty value $w_{R(balance)}$ = 0.0001 g and volume fractions of water of these samples were calculated;

	Sample-1	***Sample-2***	***Sample-3***
W_w (g)	0.2884	0.2777	0.2692
W_d (g)	0.1769	0.1663	0.1696
ϕ_w	0.3866	0.4012	0.3700

From Eqn. 4.3.1.1-1, the derivatives of the variables are given by;

$$\frac{\partial \phi_w}{\partial W_w} = \frac{W_d}{W_w^2} \qquad \frac{\partial \phi_w}{\partial W_d} = -\frac{1}{W_w}$$

Hence, w_R values were calculated by Eqn. A-12;

	Sample-1	***Sample-2***	***Sample-3***
W_w (g)	0.2884	0.2777	0.2692
W_d (g)	0.1769	0.1663	0.1696
ϕ_w	0.3866	0.4012	0.3700
w_R	0.0004	0.0004	0.0004

Average value of water content values was calculated as 0.3859. The derivatives of the three average values were calculated as 0.3333, which is same for all samples. Therefore, w_R value of the average water content of MSA11 was calculated by Eqn. A-12 as 0.0002.

The probable uncertainty associated with an experimental measurement was often indicated by rounding the result so that it contains only significant figures. By definition, the significant figures in a number are all of the digits known with certainty plus the first uncertain

digit. As a general rule, mathematical operations involving addition and subtraction are carried out to the last digit that is significant for all numbers included in the calculation. For example (Skoog et al., 2004 and Harvey, 2000),

$$135.6\underline{2}1 + 0.3\underline{3} + 21.2\underline{1}63 = 157.1673 = 157.1\underline{7}$$

When multiplying and dividing, the general rule is that the answer contains the same number of significant figures as that number in the calculation having the fewest significant figures. For example (Skoog et al., 2004 and Harvey, 2000),

$$\frac{22.91 \times 0.\underline{152}}{16.302} = 0.21361 = 0.\underline{214}$$

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