

Characteristics of the MK-40 and MA-40 Membranes for Industrial Wastewater Treatment – A Review

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ABSTRACT

Industrial application of ion exchange membranes (IEMs) for saline water desalination is widely used. In this review, two kinds of IEMs were targeted and focused on: cation-exchange membrane (MK-40) and anion-exchange membrane (MA-40). The characteristics of ion-exchange capacity, structural water content, electrical conductivity and diffusion permeability of counter ions and co-ions, as well as the properties in diffusion of alkaline media were reviewed. IEMs are anionic or cationic fixed exchange groups; the diffusion flows of the two IEMs are scarcely impacted by the kind of an ion selective membrane, as well as of the concentration dependence. The salt diffusion coefficient increases alongside the water content in the membrane, whereas the electrical conductivity increases along with the ion exchange capacity (IEC). In addition, the permeability of the charged polymer increases along with the salt concentration, while for the uncharged polymer it decreases. Thus, the methods and formulas for determining the salt diffusion coefficient and osmotic permeability were studied. Evidently, the differences in the microstructure between membranes will significantly affect the permeability of salt transport in IEMs.

Keywords: ion exchange membrane; salt; diffusion permeability; osmotic permeability; electric conductivity

INTRODUCTION

The industrial application of ion exchange membranes (IEMs) is commonly used in many areas, such as drinking water purification, wastewater treatment, amino acid demineralization, sugar liquor demineralization, whey demineralization, organic matter purification, etc. The most important fundamental application of IEMs began with desalination of water (Tanaka, 2011). Large-scale industrial procedures prevalently utilized IEMs, for example, in electrodeionization, electrodialysis (ED), diffusion dialysis, membrane electrolysis and Donnan dialysis for water and industrial wastewater treatment (Strathmann *et al.*, 2013).

Lately, IEMs have garnered substantial attraction in membrane technologies due to their chemically stable nature, as well as favorable ion and water transport properties (Geise *et al.*, 2014b).

IEMs are considered to be the most expensive component of ED devices. Thus, the overall expenditure of IEMs in ED process ranges from 40 to 50%. Therefore, the degree of implementation of the ED process using IEMs is usually taken into account by the transport characteristics of the IEMs and its cost (Sarapulova *et al.*, 2019a). Nowadays, salt removal, especially from industrial wastewater, is known to be challenging, and is yet to be overcome by single and cost-effective treatment that can effectively remove salt. ED is

usually an economical process for desalination technology using a IEMs, especially when the saline composition of the flux is below 5 g/L (Li *et al.*, 2018). In principle, one of the advantages of electro dialysis using IEMs is a higher operating temperature (up to 50 °C) (Singh, 2016).

The ability of IEMs to exclude co-ions (inhibition their transport across the membrane) and simultaneously enabling the transportation of counter-ions, crucially impacts the efficiency of the technologies that rely on anion exchange membranes (AEMs) and cation exchange membranes (CEMs). An absolutely permselective membrane entails a membrane which allows the transfer of counter-ions (for example, cations for CEMs and anions for AEMs) (Geise *et al.*, 2014a). Moreover, it should be noted that CEMs and AEMs have higher salt permeability than water. Furthermore, CEMs usually had a higher salt permeability than AEMs (Kingsbury *et al.*, 2018). Furthermore, several factors can affect the ion exchange process, including the type of membrane, solution concentration, temperature, and pH (Chaabouni *et al.*, 2015)2015.

MK-40 and MA-40 are produced by Shchekinoazot (Russia). Heterogeneous IEMs were chosen for the current study (Pismenskaya *et al.*, 2012). In spite of the rising utilization of homogeneous ion-exchange membranes in contemporary electro dialysis process, there are various advantages of using heterogeneous membranes in the ED process. Firstly, it is inexpensive and extremely durable in relation to external factors (Melnikov *et al.*, 2018). In comparison, the composition of the cation exchange membrane (MK-40) contains fixed sulfo-groups in the form of functional groups (Sarapulova *et al.*, 2019b). In turn, the anion exchange membrane (MA-40) mainly contains secondary and tertiary amines as ion-exchange groups (Pismenskaya *et al.*, 2012). In literature, many studies indicated that MK-40 and MA-40 are effective IEMs for the desalination of water (Pismenskaya *et al.*, 2012; Vasil'eva *et al.*, 2013). Furthermore, many researchers examined the diffusion permeability of MK-40 and MA-40 for NaCl salt solution and they showed high efficiency (Izquierdo-Gil *et al.*, 2020; Sarapulova *et al.*, 2019a). Therefore, these two types of membranes have a significant advantage in the treatment of industrial wastewater with high content of salts.

There are still gaps in knowledge despite the significant progress in understanding the

response of the membrane characteristics of MK-40 and MA-40. As mentioned in the literature, most empirical research experiments along with theoretical evaluations are conducted for the transfer of different salt solutions to characterize the performance of these two types of membranes. Insufficient studies have been conducted on the utilization of the two aforementioned types of membranes to remove formed salts from industrial wastewater. Hence, it is very difficult to find any research studying the characteristics of these aforementioned membranes. Therefore, the aim of this review was to understand the characteristics of MK-40 and MA-40 for treating saline industrial wastewater. The characteristics of ion-exchange capacity, structural water content, electrical conductivity and diffusion permeability of counter ions and co-ions properties in diffusion of salt were also reviewed.

Historical development of IEMs

The characteristics of an IEMs were first developed by Ostwald in 1890 who found that the semi-permeability of the membrane depends on the type of electrolyte, either the anion or cation, in addition to the ion type of membrane (Villenguzman *et al.*, 2019). Historical progressions of the ion exchange membrane are shown in the following Table 1 (Xu, 2005). Currently, there are numerous IEMs available with their respective positioning in the historical development and their application for several issues. According to the charge as well as the distribution of fixed ionic on the charge, IEMs are basically classified into five groups: inclusive of bipolar membranes (ion-exchange composite membranes), mosaic IEMs, CEMs, AEMs and amphoteric IEMs, as shown in Figure 1 (Luo *et al.*, 2018).

Structure of heterogeneous MK-40 and MA-40

In principle, IEMs used in the ED process can be considered as polymer matrix ion exchange resins and divided into CEMs and AEMs, as shown in Figure 2 (Warsinger *et al.*, 2018). The MK-40 composites were formed by KU-2 cation-exchange resins (polystyrene (PS) matrix cross-linked with divinylbenzene (DVB) and fixed groups), nylon and polyethylene. Meanwhile, the MA-40 composites based on the EDE-10P resin (epichlorohydrin and polycondensation of polyethylenepolyamines) are prepared by the diamine

Table 1. Ion exchange membrane development timeline and related process

Time line	Authors	Developments of ion exchange membrane
1890	Ostwald	The first electro-membrane process
1911	Donnan	Donnan potential and ion exclusion
1925	Michaelis and Fujita	First ion exchange membrane synthesis
1930	Söllner	First amphoteric membrane, mosaic membrane
1950	Juda & McRae	Initial commercial ion exchange membrane and ED process
1953	Winger et al.	The first industrial use of electro-membranes
1960	A sahi	First sea salt production
1969	Mihara & Kato	First continuous electrodeionization, first reverse electrodialysis.
1970	Dupont	First bipolar membrane, Nafion types: chlor-alkali electrolysis
1976	Chlanda	The new process of ion exchange membrane, Hybrid ion exchange membrane, Coupling / hybrid ED procedure, Integrated industrial uses etc.
1990	Haruhiko Ohya et al.	Inorganic-organic ion-exchange membranes were created for use under harsh situations

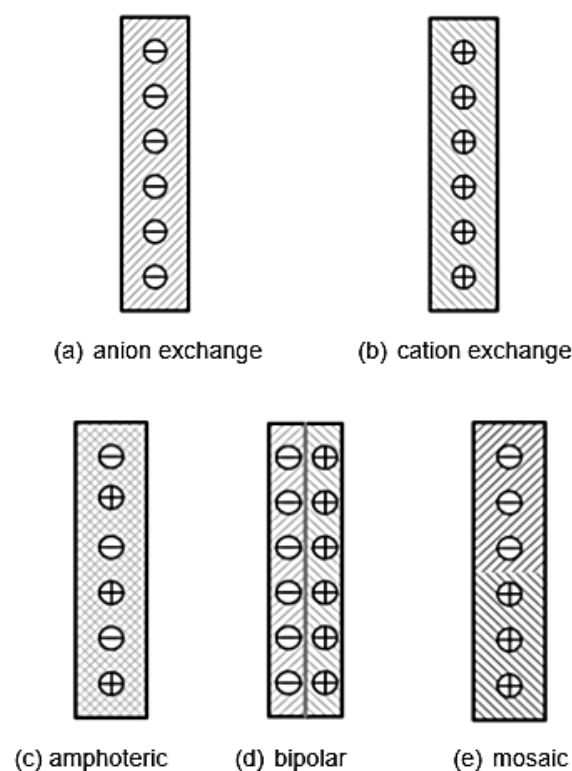


Fig. 1. Schematic illustration of different ion exchange membrane (IEM) types: (a) AEMs, (b) CEMs, (c) amphoteric IEMs, (d) bipolar IEMs, and (e) mosaic IEMs (Luo *et al.*, 2018)

condensed with epichlorohydrin, polyethylene and nylon (Berezina *et al.*, 2008). Moreover, the membrane bulk of MK-40 and MA-40 contains 35% and 45% of polyethylene, respectively. Meanwhile, approximately 80% of polyethylene coated the MK-40 and MA-40 wet membranes surface areas (Pismenskaya *et al.*, 2012). The electrical inhomogeneity of IEMs, which consists in the existence of regions with low (polyethylene phase)

conductivity and high (ion-exchanger phase), plays an important role in their electrochemical behaviour (Vasil'eva *et al.*, 2013).

Additionally, the MK-40 and MA-40 membranes possess varying pore size distributions; the first one is approximately 10 nm, which corresponds to a micropore and mesopore, whereas the second one is associated with macropores having the size of approximately 1000 nm. The pores with the size belonging to first kind are situated inside the ion-exchange particles that entail sulfonated (MK-40) or aminated (MA-40) styrene divinylbenzene copolymer. Meanwhile, the pores of the second kind are the gaps between varying particles inside a membrane (Ciferri & Perico, 2012). Moreover, it was found that the distribution of ion exchange sites on the heterogeneous membranes surface areas is complex stochastic; their sizes for MK-40 are in the range of 5–30 μm , and for the MA-40 membranes are in the range of 8–40 μm (Vasil'eva *et al.*, 2013). In addition, the microstructure of the membrane controlled the transport of mobile salt in the IEMs and provides clear evidence that there is no strong interaction of the mobile salt with polymer chains in extremely swollen IEMs (Kingsbury *et al.*, 2018). The electron microphotographs of the MA-40 and MK-40 heterogeneous membrane samples after the chemical and thermal treatment in the dry states are presented in Figure 3 (Vasil'eva *et al.*, 2013). Furthermore, the amino groups in the commercial component of the AEMs, which are catalytical in nature, possess greater activeness in the water dissociation reaction in comparison to the sulfonic groups of commercial CEMs (Titorova *et al.*, 2020).

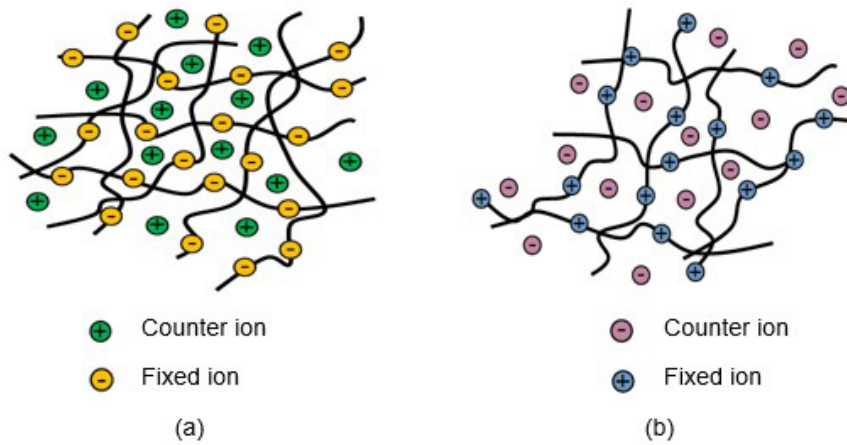


Fig. 2. Schematic diagram of the structure of a) a cation exchange membrane and b) an anion exchange membrane

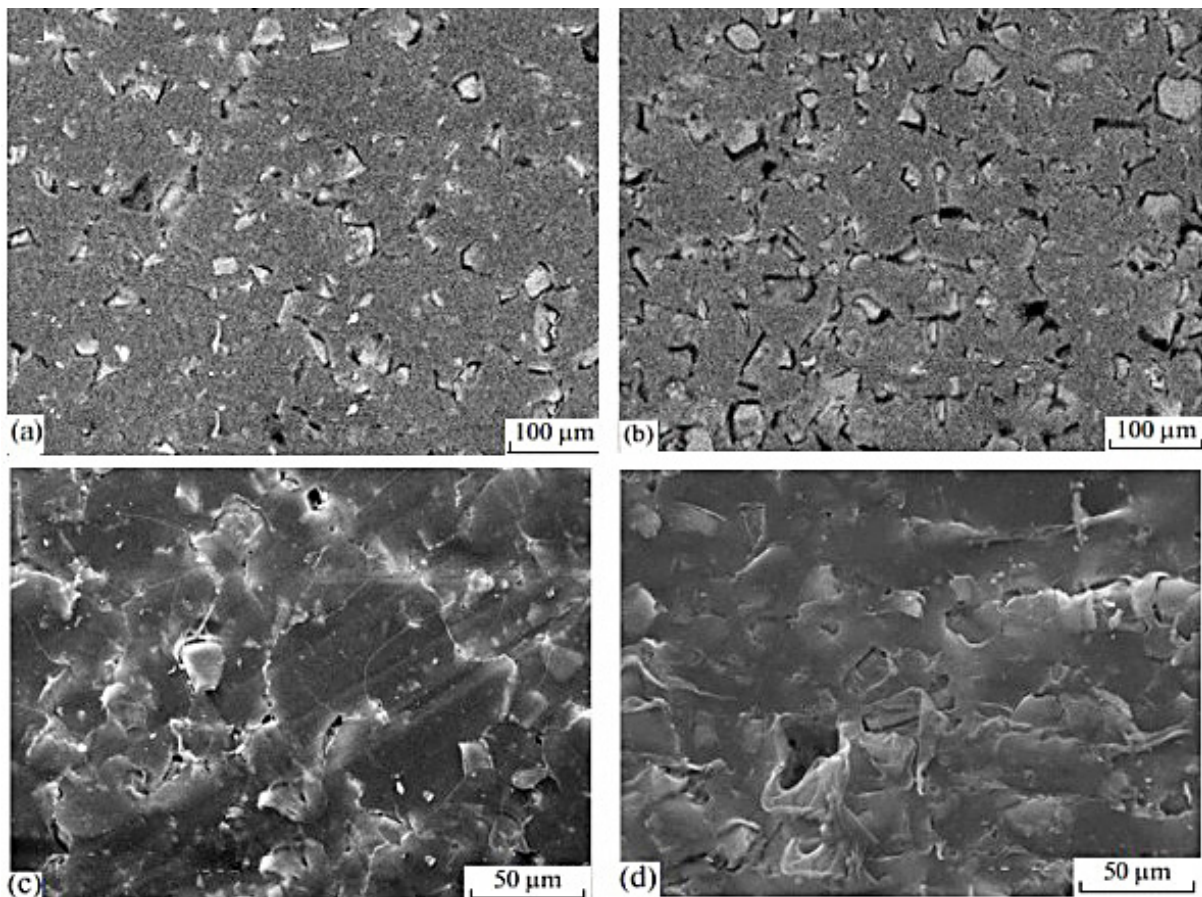


Fig. 3. Scanning Electron Microscope images of the surface of (a, b) dry samples of MA-40 and (c, d) dry samples of MK-40 after (a, c) chemical and (b, d) thermal treatment in water at a temperature of 100 °C for 50 h

Advantages and disadvantages of MK-40 and MA-40

The advantages of the heterogeneous MK-40 membrane are chemical stability, high mechanical and high counterion transport numbers. In turn, the high electric resistance due to the polyethylene

content of more than 30 percent and low current of salt counterions, was one of the disadvantages of MK-40 (Titorova *et al.*, 2020). On the other hand, the MA-40 membrane surface has a high hydrophilicity due to the high exchange capacity of the resin in the membrane (Pismenskaya *et al.*, 2012). Lopatkova *et al.* (Lopatkova *et al.*, 2006)

concluded that the main drawback of MA-40 is the rate of water dissociation at the interface between the membrane and the solution has a significant effect on the characteristics of the electrodiagnosis desalination of dilute solutions. In addition, the rate of water dissociation on the AEMs was typically higher than on the CEMs.

Characterization of heterogeneous MK-40 and MA-40

The efficiency of membranes decreases when transporting large amounts of water and salts through the IEMs, which in turn increases their energy consumption, and this is one of the most important ways to characterize the properties of IEMs (Tedesco *et al.*, 2017; Yip & Elimelech, 2014). Generally, some studies investigated the characterization of MK-40 and MA-40 membranes using the standard NaCl solution salt (Kozmai *et al.*, 2019; Nikonenko *et al.*, 2020; Sarapulova *et al.*, 2019b). Cation exchange MK-40 and anion exchange MA-40 are heterogeneous ion-exchange membranes which are in the form of flat sheets (Vasil'eva *et al.*, 2013). The main properties of commercial membranes MA-40 and MK-40 are collected in Table 2 (Pismenskaya *et al.*, 2012).

Vasil'eva *et al.* (2013) noted that the porosity of the chemically treated MK-40 and MA-40 membranes increased by more than three fold after being heated in water at 100°C. Such changes in the structure are accompanied by a noticeable increase in the average radius of the pores. The maximum increase in the pore magnitude was 1.5 times for the MK-40 membrane and twice the magnitude for the MA-40 membrane. Moreover, during the desalination process using the MK-40 and MA-40 membranes, the desalinated solution becomes more acidic as the result of the extensive formation of H⁺ and OH⁻ ions on the topside of the AEM in comparison to the CEM.

In order to reduce water splitting, the quaternary amines replace the secondary and tertiary amines on the surface of MA-40 that are marked by poor catalytic activity. In order to achieve this objective, the modification of commercial MA-40 membrane was conducted with a dimethyldiallyl-ammonium chloride copolymer (Pismenskaya *et al.*, 2012). Modification of the MK-40 membrane by slightly increasing the number of mesopores or reducing the number of mesopores does not change the water content in MK-40 (Zabolotskii *et al.*, 2010). Basically, IEMs are characterized by their properties of hydrophilicity, ion exchange capacity (IEC), electrical resistance, ion transport number, solute permeability coefficient, electro-osmotic coefficient, swelling ratio, mechanical strength, and water permeation coefficient (Tanaka *et al.*, 2007). Some of these properties are presented in this review.

Structural water content

The percentage of MK-40 and MA-40 membranes was attained via air heat dehydration [34] water content (W) can be found by Eq. (1) (Sarapulova *et al.*, 2019b):

$$W, \% = \frac{m_s - m_{dry}}{m_{dry}} \times 100\% \quad (1)$$

where: m_{dry} and m_s are the masses of dry and wet membrane samples, respectively.

The water content is crucial in ascertaining the characteristics of a polymer. With increasing water sorption in uncharged and charged polymers, there is a tendency to increase the diffusion and permeability coefficients, and materials typically possess lower selectivity (Geise *et al.*, 2014b). Kamcev *et al.* (2018b) showed that a membrane with higher water volume fraction exhibited faster ion transfer than a membrane with lower water volume fraction. The water volume fraction was relatively

Table 2. Certain properties of commercial MA-40 and MK-40 membranes (Pismenskaya *et al.*, 2012)

Membranes properties	Anion exchange (MA-40)	Cation exchange (MK-40)
Ion exchange groups, bulk	=NH, ≡N	-SO ₃ ⁻
Idem, surface	=NH, ≡N	-SO ₃ ⁻
Thickness, μm	470 ± 20	480 ± 10
Ion exchange capacity, mM cm ⁻³ wet	3.2 ± 0.08	1.7 ± 0.1
Ion exchange material surface fraction of, %	19 ± 4	22 ± 3
Contact angle, degrees	50 ± 2	55 ± 3
Particular electrical conductivity in 0.5M NaCl solution, mS · cm ⁻¹	7.5 ± 0.3	7.7 ± 0.3
Diffusion permeability, 10 ⁻⁹ cm ² · s ⁻¹	7.0 ± 0.4	6.7 ± 0.4

constant at low concentrations of NaCl (< 0.1 M) and is reduced at heightened concentrations of NaCl (> 0.1 M) as the result of osmotic deswelling.

According to Kozmai *et al.* (2019), when studying the characteristics of the MA-40 and MA-41 membrane as shown in Figure 4, they illustrated that when the pH value increased from 3 to 6 at different NaCl concentrations, the water content was increased as well. At this pH range, tertiary amino groups are deprotonated. The swelling transformation was caused by a relatively significant amount of deprotonated tertiary amino groups hydration compared to their protonated compositions. However, in the case of MA-40 membrane, when the pH value increases from 6 to 10, the water content passes through the maximum level and then decreases due to the deprotonation of secondary amino groups. Furthermore, when the pH is greater than 6, there was a change in the water content of the MA-40 and MA-40 membranes, depending on their pH. The water content of the MA-40 membrane undergoes a noticeable decrease, while the MA-41 membrane shows only a slight decrease in the water content. This is due to deprotonation of relatively highly hydrated secondary amino groups (Kozmai *et al.*, 2019). Sarapulova *et al.* (2019a), observed that macropore types (>100 nm) contain up to 25 percent of water in the MK-40 membrane. These voids appear when the membrane dries.

Ion-exchange capacity

The total static MK-40 and MA-40 membranes exchange capacity was ascertained by

means of acid–base titration (Vasil’eva *et al.*, 2014). The total ion-exchange capacity Q_{sw} , mmol g_{sw}^{-1} of the membrane was computed by Eq. (2) (Sarapulova *et al.*, 2019b):

$$Q_{sw} = \frac{(100 - 4V_1)}{10m_{sw}} \quad (2)$$

where: V_1 is the volume of titrant utilized for titration, cm^3 , m_{sw} is the mass of swollen membrane.

Moreover, the total ion-exchange capacity of the ion-exchange membranes Q_{dry} in mmol g_{sw}^{-1} calculation considered the water content of the membrane W (Sarapulova *et al.*, 2019b):

$$Q_{dry} = \frac{(100 - 4V_1)}{10m_{sw}(1 - W)} \quad (3)$$

The IEC of AEM was estimated through the titration with silver nitrate solution ($AgNO_3$). Meanwhile, the use of acid-base titration established the IEC of CEM (Zhang *et al.*, 2016). According to study Hosseini *et al.* (2012), they worked on a modified membrane surface by emulsion polymerization to produce polymethylmethacrylate (PMMA) in order to improve the selectivity of the membrane and anti-fouling properties. They found that the modified membranes have a lower IEC in comparison to the unmodified ones. This may be due to reduced availability of ion exchange functional groups. In addition, increasing the density and rigidity of the membrane due to the PMMA coating on the membrane surface makes it difficult to transfer ions between the solution and the membrane phase and, consequently, reduces the possibility of ion exchange.

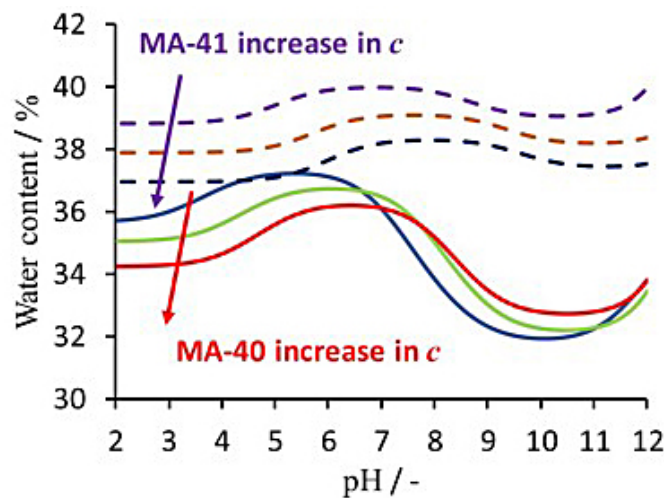


Fig. 4. Calculated pH dependence of water content in the MA-40 (solid lines) and MA-41 (dashed lines) membranes at different concentrations of NaCl in the bathing solution: $c_{NaCl} = 0.1, 0.5$ and 1 M

Electric conductivity

Many authors have investigated the electrical conductivity of membranes following various methods, including – but not limited to – the utilization of a tweezers-type cell (Lopatkova *et al.*, 2006). There are significant of varying methods of measuring the electrical resistances of a membrane within a solution, and a membrane without a solution. The membrane conductivity was then calculated using Eq. (4) (Titorova *et al.*, 2020).

$$K_m = \frac{d_m}{R_{m+s} - R_s} \quad (4)$$

where: K_m is membrane conductivity, d_m is membrane thickness, R_{m+s} is the membrane resistance in solution, and R_s is the membrane without solution resistance.

According to the study by Sarapulova *et al.* (2019b), a significant decrease in the electrical conductivity of the IEMs was observed when a single-charge (NaCl) counterion replaced by a doubly-charged single CaC₁₂/CEM and Na₂SO₄/AEM systems. The authors observed a reduction in conductivity by a factor of 2.5 (MK-40) in comparison to the NaCl solutions. This reduction in electric conductivity is due to the slackening of the doubly-charged counterions resulting from the simultaneous ion-to-ion interactions with two fixed collectives, in contrast to the NaCl solution, which interacts with only one group.

Golubenko *et al.* (Golubenko *et al.*, 2018) showed that the permeability of membranes decreases with an increase in the water content, while the conductivity of membranes increases along with the water content and pore size. Furthermore, the electric conductivity of IEMs simultaneously rises with their exchange capacity, and reduces with a rise in the ionic strength of the external solution (Fontananova *et al.*, 2017; Zhang *et al.*, 2016). Vasil'eva *et al.* (2019) reported that the transport properties of the MA-40 membrane in electro dialysis stack, the specific electrical conductivity was increased by 40% due to the loss of exchange capacity and an increase in the water content. The probable reason for the enhanced electrical conductivity was an increase in the pore size due to the degradation of the ion exchanger and the inert binder polyethylene due to long-term operation.

Fontananova *et al.* (2017) explained how the constricting of the conductive channels leads to a

decrease in the water content of membranes. According to their study, the specific electrical conductivity of the MK-40 membrane significantly depends on the concentration of the external equilibrium NaCl solution. As illustrated by Kozaderova *et al.* (2020), the conductivity of the ion exchange membrane is relatively high when the external solution has low concentrations. According to Lopatkova *et al.* (2006), when the MA-40 membrane is modified with a strong polyelectrolyte, it leads to an almost two-fold increase in its electrical conductivity.

Ion transport mechanisms

The processes of moving ions in a membrane are complex and happen close to each other. It can be clearly explained by transporting the H⁺ ions in proton exchange membranes, since proton transport is considered the most complex ion (Saito *et al.*, 2004). Diffusion convection, electromigration, and surface site are four potential mechanisms for specific ion transport of membrane process. The extended Nernst-Planck equation explains the ion flux J_i as the sum of three terms for quantitative theoretical understanding of ion transport in IEMs, as shown in Eq. (5) (Strathmann, 2004):

$$J_i = vC_i - D_i \frac{dC_i}{dx} - \frac{z_i F C_i D_i}{RT} \frac{d\phi}{dx} \quad (5)$$

where: v is convective velocity of the solvent (water); C_i is concentration, D_i is diffusion, and z_i is valence of ion i , R is the universal gas constant; T is the absolute temperature; F is the Faraday constant, is the electrical potential, and x is the distance coordinate across the membrane.

Although the driving force of electric potential can contribute to the diffusion and convection of ion transport in the membrane, their effect is small compared to electromigration. This is due to the fact that IEMs are dense and the electrolyte diffusion coefficient in the membrane is three times less than in the bulk solution (Nikonenko *et al.*, 2010). Despite the restrictions on the traditional Nernst-Planck equation (without the convective term) in describing the transport of ions in heterogeneous media, the suitability of this equation for application has been proven (Buck, 1984). Currently, the extended Nernst-Planck equation is important for quantitative processing.

Diffusion permeability

The permeability of IEMs for counter ions was first clarified by Donnan; thus, this mechanism is called the Donnan exclusion (Luo *et al.*, 2018). In electro dialysis, a decrease in selective ion transport across the membrane is the result of the diffusion permeability of IEMs. This is due to the substance transported through the membrane, rather than the transfer of individual ions, as in the case of electromigration. The diffusion permeability is clearly related to the study of co-ion transport through the gel and intergel-phase stages of the membrane. It is emphasized that the flow of co-ions in the gel phase is significantly lower compared to the flow of counterions due to their significantly lower concentration (Melnikov *et al.*, 2018).

According to the study by Kamcev *et al.* (2017), the partition salt coefficients increase similarly along with the external salt concentration, indicating that the diffusion permeability coefficients are increased with the external NaCl concentration. Furthermore, a rise in the total salinity of a solution and a reduction in its temperature results in a decrease in the osmotic coefficient permeability (Alekseeva, 2012). Moreover, the diffusion permeability increases along with temperature (Luo *et al.*, 2010). In addition, it is illustrated that when the pH of the solution increases, the diffusion permeability of the membrane passes through the maximum rate (Kozmai *et al.*, 2019).

Basically, the size of the system and the dilute and concentrate concentrations affect the values of diffusion and osmosis permeability in the IEMs, which are set by the system operation of the electro dialysis process (Chehayeb & Lienhard, 2019). Additionally, for the respective IEMs series, the apparent salt diffusion coefficients experience an average decrease with increasing concentration of the fixed charge group. Specifically, with an increase in the concentrations of fixed charge groups, the apparent salt diffusion coefficients of the AEMs on average experienced a greater decrease compared to CEMs (Kamcev *et al.*, 2018a). Furthermore, greater water

permeability was correlated with higher salt permeability (Kingsbury *et al.*, 2018).

Geise *et al.* (2013) observed that the permeability of sodium chloride of an uncharged hydrogel decreases simultaneously with an increase in the salt concentration in the upstream from 0.01 to 1 mol/L. The transformation of salt permeability occurs as a result of a decrease in the water content in the polymer with an increase in the salt concentration. Conversely, it was found that the sodium chloride permeability of charged polymers increases along with salt concentration in the upstream from 0.01 to 1 mol/L. This increase in salt permeability is due to the raised diffusion and sorption coefficients of salts transported with an increase in salt concentration, regardless of the decrease in the water content in the polymer membrane with a heightened salt concentration.

CHEMICAL PROPERTIES OF NaCl SOLUTION

According to numerous experiments conducted to describe the properties of an ion-exchange membrane (Kingsbury *et al.*, 2018; Melnikov *et al.*, 2018; Shutkina, 2015), the most important chemicals utilized to characterize the efficiency of MK-40 and MA-40 is solid NaCl with distilled water. Fundamentally, the pH of the solution increased along with the salt concentration. Table 3 illustrates certain properties of the ions found in NaCl solutions (Sarapulova *et al.*, 2019b).

Membrane diffusion permeability methods

Several methods have been used to determine the effect of operational parameters on the diffusion permeability of membranes, such as concentration, temperature, flow, pH, time, etc. Shutkina (2015) investigated the diffusion characteristics of membranes measured in a flow cell with special input-output devices that provide a laminar hydrodynamic system of the pumped solution. In their study, the cell consists of two compartments separated by IEMs, as illustrated in Table 4. The cell was connected to

Table 3. Certain properties of ions (at 25°C) included in the NaCl solution under study (Sarapulova *et al.*, 2019)

Ion	Crystallographic radius, Å	Stokes radius, Å	Hydration energy, kJ·mol ⁻¹	Hydration number	Diffusion coefficient at infinite dilution $D_0 \times 10^9, \text{m}^2 \cdot \text{s}^{-1}$
N ⁺	0.95	1.84	407	5	1.334
Cl ⁻	1.81	1.21	376	2	2.032

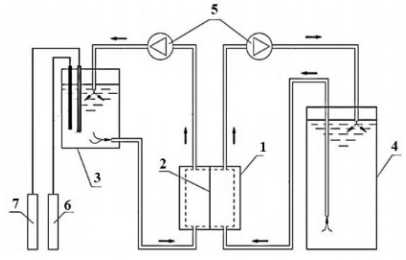
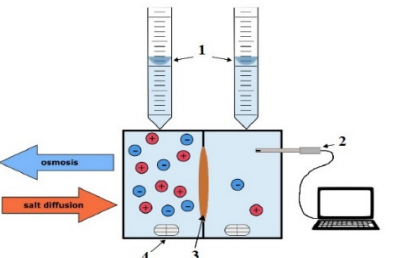
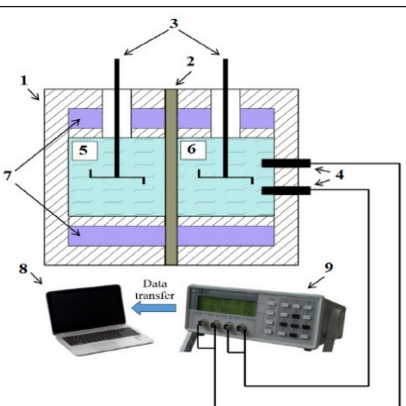
two containers, one containing distilled water and the other containing an electrolyte solution of a given concentration, using flexible tubes to connect it. In this method, an “Expert 002” type ionometer was used to control the pH and temperature. In addition, the conductometer was used to measure the electrical conductivity and it was found that diffusion permeability of IEMs increases along with the concentration of such salts in the compartment.

Kingsbury *et al.* (2018) studied water and salt permeability concurrently by utilizing a two-chamber cell, shown in Table 4. In this method, one half of the cells contains a NaCl solution, while the other half contains distilled water. Moreover, concentrated NaCl solution was chosen to maximize the osmosis rate, and to assist in the water transfer measurements. An ion exchange membrane was stabilized in the cell between two compartments. Furthermore, both compartments were stirred using a magnetic stir bar. However, each compartment of the cell was

sealed and connected to a burette, which made it possible to measure the change in volume in the compartment with high accuracy. Thus, the conductivity probe was positioned in a distilled water compartment to gauge the quantity of conductivity changes over a duration of time.

Melnikov *et al.* (2018) used a non-flowing two-chamber cell to study the diffusion permeability, one half of the cell consisted of an equilibrium solution of salt or acid, while the other half consisted of distilled water. An ion-exchange membrane separated the half-cells from each other. The water jacket was used to maintain the temperature of solution and distilled water in the cell using a thermostat outside the cell. A vertical mechanical glass mixer was utilized to mix the solutions strongly in a non-flow cell and eliminate the concentration polarization close the membrane, which lowers the formation layer and increases the transport of ions crossing the membrane. All of these methods were used to test the membranes shown in Table 4.

Table 4. Schematic drawing of the experimental set-up

Cell schematic	Definition of parts	References
	<ol style="list-style-type: none"> 1. Chamber cell 2. Ion exchange membrane 3. Distillation water 4. Electrolyte solution 5. Pump 6. Ionometer 7. Conductometer 	Shutkina <i>et al.</i> , 2015
	<ol style="list-style-type: none"> 1. Burette 2. Conductivity 3. Membrane 4. Stirring 	Kingsbury <i>et al.</i> , 2018
	<ol style="list-style-type: none"> 1. Diffusion cell 2. Studied membrane 3. Mechanical mixers 4. Platinum electrodes 5. Semi-cell containing salt solution 6. Semi-cell containing distilled water 7. Water cooling jacket 8. Notebook 9. E7-21 admittance meter 	Melnikov <i>et al.</i> , 2018

Most of current semipermeable membranes are designed specifically for the pressure-controlled membrane processes, rather than the osmotically controlled membrane processes. In addition, to transfer water through the membrane, it is necessary to establish an osmotic pressure gradient on the selective part of the membrane. The osmotic pressure gradient is established between a relatively dilute feed solution and concentrated solution.

Calculation of salt and water permeability

One of the important factors in determining the characteristics of new composite and hybrid ion-exchange materials of charged membranes obtained by surface or bulk modification of polymers is the diffusion permeability coefficients (Filippov *et al.*, 2017). The calculation of salt diffusion coefficients is based on the self-diffusion measurements. The dilute effect of osmosis on the salt concentration gradient must be taken into account. Therefore, the flow of water from the pure water chamber dilutes the salt concentration in the other chamber, thus reducing the driving force of diffusion and osmosis (Kingsbury *et al.*, 2018). Diffusion permeability was determined by the amount of substance transferred through the membrane per unit of time through a unit of surface. In addition, the osmotic permeability was determined by the change in the volume of solutions in the chambers over a certain period of time, measured by capillaries (Alekseeva, 2012). Overtime, the flow of water from the distilled water chamber leads to a decrease in the concentration of the solution in the other chamber. Thus, the water permeability (P_w) was obtained from the diffusion coefficient of water (D_w) and the water partition coefficient (K_w) in accordance with Eq. (6) (Kingsbury *et al.*, 2018):

$$P_w = D_w \cdot K_w \quad (6)$$

Similar to water permeability, the solute diffusion data can be analyzed in order to obtain solute permeability (P_s), solute diffusion coefficient (D_s) and solute partition coefficients (K_s) according to Eq. (7):

$$P_s = D_s \cdot K_s \quad (7)$$

P_s can be determined directly from the observed solute concentration over operational time. In addition, volume change of diluted cell chamber can be observed due to the influence of diffusion and osmosis on solute concentration (Kingsbury *et al.*, 2018).

Basically, the separation coefficient is obtained by dividing the concentration of a substance inside the membrane by its concentration in a bulk solution. Meanwhile, the diffusion coefficient is a measure of how rapidly a substance is transported across the membrane. Eventually, it can be concluded that MK-40 and MA-40 can be used for industrial wastewater, specifically for pigmented industrial wastewater, due to the large amount of salts mixed with the pigment in the production process.

CONCLUSION

The MK-40 and MA-40 membranes are heterogeneous IEMs, which are considered efficient method in the small-scale desalination process due to its long lifetime usage capability and low cost. They have high selectivity capacity for the transportation of single charge ions and high electrical conductivity. The properties affecting the diffusion permeability were found to be the chemical structure of membrane, membrane water content and system operating conditions. Electrical conductivity was one of the most important characteristics of the MK-40 and MA-40 membranes that define their practical suitability. Although the conductivity and permselectivity of heterogeneous IEMs is generally lower than a homogeneous IEMs membrane, the creation of novel and modified heterogeneous IEMs is of high research interest. The salt diffusion coefficient and the water diffusion coefficient are the main factors used to analyze the differences in the permeability of the MK-40 and MA-40 membranes. The salt concentration gradients should practically be low in order to reduce the flow of the solvent due to osmosis. To conclude, an efficient and cost-effective way to resolve this issue is to modify either the bulk or the surface of membranes.

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