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Heterogeneous Cation Exchange Membrane: Preparation, Characterization and Comparison of Transport Properties of Mono and Bivalent Cations

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Polycarbonate heterogeneous cation exchange membranes were prepared by solution casting techniques using tetrahydrofuran as solvent and cation exchange resin powder as functional groups agent. The effect of resin ratio loading on properties of prepared membranes was studied. Also, transport properties of the prepared membranes for mono and bivalent cations were evaluated. Scanning electron microscopy and scanning optical microscopy were used for the membranes structure investigation. Images showed that increase of resin ratio in casting solution results in a highly uniform phase to form. Formation and propagation of voids, cavities, and cracks were facilitated through higher resin ratio loading. The water content, surface hydrophilicity, specific surface area, ion exchange capacity, ion concentration, ionic permeability, conductivity, flux, and current efficiency of the membranes were enhanced and their energy consumption, oxidative stability, and mechanical strength were declined by increase of resin ratio loading. Moreover, membranes showed higher ionic flux, current efficiency, and lower energy consumption for sodium ions in comparison with bariums. Furthermore, with the increase of resin loading, permselectivity, membrane potential and transport number of membranes were improved for monovalent ions and diminished for bivalent ones. Also, membranes exhibited lower membrane potential, selectivity, and transport number for bivalent ions in comparison with the monovalent type.

Keywords electrochemistry; ion exchange; membranes; phase change; selectivity; separation

INTRODUCTION

In the field of separation science and technology various kinds of membranes have been studied (1,2). Nowadays, membranes have become the essential materials not only in industries but also in daily human life (3). Among the various kinds of membranes, ion exchange membranes (IEMs) are widely utilized as active separators in diverse electrically driven processes such as electro-dialysis (ED) for desalting brackish waters, reconcentrating brine from seawater, and production of table salt. ED is also used for the recovery of valuable metals from the effluents industry and food and pharmacy processing. Furthermore, it is playing an important part in treating industrial effluents, environmental protection, processing biological effluents, and many more processes (1–6). Additionally, ED can be easily scaled-up and combined with other processes; besides the fact that it requires low operating cost (7,8). In IEMs, the charged groups are attached to the polymer backbone and are freely permeable to opposite sign ions under an electrical field influence which separate the ionic species from solution and uncharged components (9–11). In such processes, ions interaction happens in a complex fashion with membrane, water, and with each other. Knowledge of the electrokinetic properties of IEMs and their structural properties is a major contributing factor behind the decision to the applicability of these membranes in a specific separation process (12,13). Energy saving, resource recovery, and pollution control are the main reasons for the development and application of ion exchange membranes (2). However, preparation of inexpensive membranes with special adapted selective characteristics such as suitable ionic conductivity and ionic selectivity for mono and bivalent ions, good thermal and electrical resistance, and appropriate mechanical and chemical stabilities is a vital step in future chemical and waste treatment applications (14–16). Variation of functional groups, selection of different polymeric matrices, alteration of cross-link density, the nature of the surface layer, and heterogeneity of the membranes are important tools to achieve superior membranes (1,16).

Ion-exchange membranes, both homogenous and heterogeneous, supersede each other (17). Usually, the homogenous ion exchange membranes have good electrochemical properties but are weak in mechanical strength whereas heterogeneous types are acceptable in mechanical properties and inadequate in electrochemical properties (18,19). Early references to heterogeneous ion-exchange membranes reveal that these membranes can be prepared

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by calendaring ion exchange particles into an inert plastic film or dry moulding of inert film forming polymers and ion-exchange particles and then milling the mould stock or in another way by dispersion of resin particles in polymeric solution and casting technique (13,17–20).

During the removal or concentration of ions from the solutions, scale formation on the membrane surface is a serious problem which affects the formation of bivalent hydroxide, membrane poisoning, and a decrease in membrane conductivity and permselectivity (7). The transport characteristic of the membrane is not adequate. It is beneficial to predict the behavior of the prepared membranes on the basis of their structural properties.

Preparation of heterogeneous cation exchange membranes with appropriate properties such as high ionic conductivity and permeability and suitable selectivity for the application in ED process for water recovery and wastewater treatment in industrial plants was the primary target of the current research. For this purpose, polycarbonate (PC) heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional group agents and tetrahydrofuran as solvent. The application of polycarbonate as membrane binder can offer special characteristics for the prepared membranes due to its interesting features. PC is a polymer with superior dimensional stability, good electrical properties, appropriate thermal stability, and outstanding impact strength. Moreover, PC has a good adsorption property due to its structure which provides high electrostatic interaction. Totally this polymer is cheap, durable, and easy to use for this purpose (21).

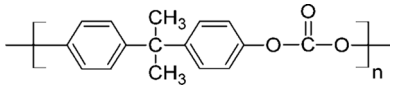
The effects of resin ratio loadings (resin to polymer binder) on morphological, electrochemical characteristics and mechanical properties of the prepared membranes were investigated and evaluated extensively. During this experiment, sodium chloride and barium chloride were employed as monovalent and bivalent ionic solutions for the membranes characterization. Moreover, the correlation between the structure and properties of home-made membranes was studied. The results are valuable for electro-membrane processes, especially electrodialysis for water recovery and wastewater treatment.

MATERIALS AND METHODS

Materials

Polycarbonate (PC), supplied by DSM (Xantar®) as binder, tetrahydrofuran (THF) as solvent and cation exchange resin (Ion exchanger Amberlyst® 15, strongly acidic cation exchanger, H^+ form), supplied by Merck, were used to prepare the membranes. All other chemicals were also supplied by Merck. Distilled water was used throughout the study. The chemical structure of the used polymer binder is shown in Table 1.

TABLE 1
Chemical structure of polymer used

Polymer	Chemical structure
Polycarbonate (PC)	

Preparation of Home-Made Membranes

Heterogeneous cation exchange membranes were prepared by the casting solution technique and phase inversion method. For membranes preparation, resin particles were dried in the oven (Behdad Co., Model: oven 5) at 30°C for 48 hrs and then pulverized into fine particles in a ball mill (Pulverisette 5, Fritisch Co.) and sieved to the desired mesh size. The ion exchange resin with the desired particles size (−200 +400 mesh) was used in the preparation of membranes. The membranes were prepared by dissolving the polymer binder in THF solvent in a glass reactor equipped with a mechanical stirrer (Model: Velp Sientifica Multi 6 stirrer) for more than 4 hrs. This was followed by dispersing a specific quantity of grinded resin particle as functional group agents in polymeric solution. The mixture was allowed to mix vigorously at room temperature for the uniform dispersion of the resin particles in the polymeric solution. The mixture was then cast onto a clean and dry glass plate at 25°C. The membranes were dried at ambient temperature and immersed in distilled water. As the final stage, the membranes were pretreated by their immersing in HCl and NaCl solutions. The membrane thickness was measured by using a digital caliper device (Electronic outside Micrometer, IP54 model OLR) in order to keep the membrane thickness around 80–120 micro meters. The composition of the casting solution is depicted in Table 2.

Test Cell

The test cell used in measuring the transport number, specific electrical resistance, ion diffusion, and other electrochemical properties is shown in Fig. 1. The cell consists of two cylindrical compartments (vessel, each 150 cm^3) made of Pyrex glass that was separated by the membrane. The membrane was fixed between rubber rings. One side of each vessel was closed by Pt electrode that was supported with a piece of Teflon (Polytetrafluoroethylene) and the other side was equipped with a piece of porous medium to support the membrane. At the top of each compartment there are two orifices for feeding and sampling purposes. In order to minimize the effect of the boundary layer on the membrane during the experiments which makes concentration polarization on the vicinity of the membrane's surface, both sections were stirred vigorously by magnetic stirrers (Model: Velp Sientifica Multi 6 stirrer). The membrane area was 13.85 cm^2.

TABLE 2
Compositions of casting solution for preparation of heterogeneous ion exchange membrane

Membrane	Polymers binder	Resin particle (Resin : polymer binder); (w/w)	Solvent (THF : (Binder + Resin)); (v/w)
Sample 1	Poly-Carbonate	40 : 60	10 : 1
Sample 2	Poly-Carbonate	50 : 50	10 : 1
Sample 3	Poly-Carbonate	60 : 40	10 : 1

Characterization of the Prepared Membranes

Morphological Studies

The structures of the prepared membranes were examined by scanning electron microscope (SEM, Philips, Model XL30, and The Netherlands) and scanning optical microscopy (SOM Olympus, model IX 70). For SEM by SEM, the samples were frozen in liquid nitrogen and then they were fractured. After sputtering with gold, they were observed by the electron microscope. Also, in these experiments, optical microscopy was used in transmission mode with light going through the membrane for scanning purposes.

Water Content

The water content was measured as the weight difference between the dried and swollen membranes. The membranes were immersed in distilled water for 24 hrs at ambient temperature ($24 \pm 2^{\circ}C$), and following discharge, its surface was wiped by filter paper and weighed (Mettler Toledo Group, Model: AL204). The wet membranes were dried at fixed temperature ($50^{\circ}C$) for 4 hrs until constant weight was obtained as dry-membrane. The following equation (4,14,18) can be used in the water content calculation:

$$Water\ content\% = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \times 100 \qquad (1)$$

Contact Angle Measurements

Water contact angle was measured to evaluate the changes in the hydrophilicity and surface wetting characteristics of the prepared membranes as a function of resin loadings. The contact angle between the water and the membrane surface was measured using a contact angle measuring instrument [G10, Kruss, Germany] in order to evaluate the membrane surface hydrophilicity. De-ionized water was used as the probe liquid in all measurements. To minimize the experimental error, the contact angle was measured in five random locations for each sample and then their average was reported (with 1–2.6% Standard division). All experiments were carried out in the ambient conditions ($23 \pm 3^{\circ}C$).

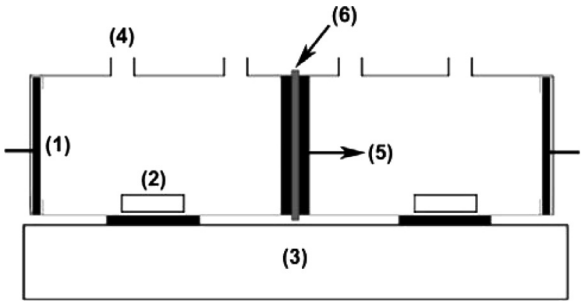


FIG. 1. Schematic diagram of test cell: **(1)** Pt electrode, **(2)** Magnetic bar, **(3)** Stirrer, **(4)** Orifice, **(5)** Rubber ring, and **(6)** Membrane.

Ion Exchange Capacity (IEC)

The IEC determination was performed using the titration method. In order to measure the ion exchange capacity, membranes were initially placed in 1 M HCl solution for 24 hrs to convert the exchange group to H type, and then they were washed and kept in water for 24 hrs at ambient temperature. The sufficient washing time was obtained through not exhibiting acidity which was recognized by the reaction with methyl red. Subsequently, membranes were immersed in 1 M NaCl solution for 24 hr to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Cl^- ions). The H^+ ions in the solution were then analyzed with 0.01 M NaOH and phenolphthalein indicator (a meq). Finally, the membrane was wiped with filter paper and dried in oven at $50^{\circ}C$ for 4 hrs and then weighed (W_{dry}, gr). IEC can be calculated from the following equation (2,14,18):

$$IEC = \left(\frac{a}{W_{dry}}\right) \qquad (2)$$

The fixed ion concentration (F.I.C.) can be calculated by:

$$F.I.C. = \left(\frac{IEC}{Water\ content}\right) \qquad (3)$$

Membrane Potential, Transport Number, and Permselectivity

When both surfaces of an ion exchange membrane are in contact with a solution with different concentration, an electrical potential would be developed across the

membrane. The magnitude of this parameter depends on the electrical characteristic of the membrane along with the nature and concentration of the electrolyte solution. In fact, the membrane potential is an algebraic sum of Donnan and diffusion potentials, determined by the partition of ions into the pores as well as the mobilities of ions within the membrane phase compared to the external phase (22–24). This parameter was evaluated for the equilibrated membrane with unequal concentrations of electrolyte solution ($C_1 = 0.1$ M, $C_2 = 0.01$ M at ambient temperature) on either side of the membrane using a two-cell glassy apparatus (shown in Fig. 1). During the experiment, both sections were stirred vigorously by magnetic stirrers to minimize the effect of boundary layers on the measurement. The developed potential difference across the membrane was measured after 10 min by connecting both compartments and using a saturated calomel electrode (through KCl bridges) and digital auto multi-meter (DEC, Model: DEC 330FC, Digital Multimeter, China). The measurement was repeated for 5 min and meanwhile the potential was measured every one minute until a constant value ($E_{measure}$) was obtained. The membrane potential ($E_{Measure}$) generated is expressed using Nernst equation (7,14,15,18,22,25) as follows:

$$E_{Measure} = (2t_i^m - 1)\left(\frac{RT}{nF}\right)\ln\left(\frac{a_1}{a_2}\right) \tag{4}$$

where t_i^m is the transport number of counter ions in the membrane phase, R is the universal gases constant, T is the temperature, n is the electrovalence of counter-ion, and a_1, a_2 are solutions electrolyte activities in contact with both surfaces determined using the Debye-Huckel limiting law. The ionic permselectivity of membranes also is quantitatively expressed based on the migration of counter-ion through the ion-exchange membrane (7,22):

$$P_s = \frac{t_i^m - t_0}{1 - t_0} \tag{5}$$

Where t_0 is the transport number of the counterions in solution (26).

The ionic permselectivity (P_s) is a real quantitative measure of the characteristic difference between counter- and co-ions permeability through the membrane.

Ionic Permeability and Flux of Ions

The ionic permeability and flux of ions measurements were carried out using the test cell. A 0.1 M ($NaCl/BaCl_2$) solution was placed on one side of cell (Anodic section) and a 0.01 M solution on other side. A DC electrical potential (Dazheng, DC power supply, Model: PS-302D) with an optimal constant voltage was applied across the cell with stable platinum electrodes at the end of the compartments. During the experiment, the cations pass through the membrane (due to anodic and cathodic reactions (27)) to the concentration section and therefore the conductivity of this region increases with time.

$$2H_2O + 2e^- \Rightarrow H_2 \uparrow + 2OH^- \text{ (Cathodic reaction)} \tag{R-1}$$

$$2Cl^- \Rightarrow Cl_2 \uparrow + 2e^- \text{ (Anodic reaction)} \tag{R-2}$$

The conductivity changes versus time was measured using a digital conduct-meter (Jenway, Model: 4510). In order to ensure the equilibrium condition in two solution-membrane interfacial zones and to minimize the effect of boundary layers, both sections were stirred vigorously by magnetic stirrers.

The permeation of ions through the membrane phase can be calculated according to the variation of conductivity measurement. Based on the first Fick's law, the flux through the membrane can be express as follows (14,15):

$$N = -P\frac{dC}{dx} = P\frac{C_1 - C_2}{d} \tag{6}$$

Where P is the coefficient diffusion of ions, d is the membrane thickness, N is the ionic flux and C_1, C_2 are the cations concentration in the compartments.

The boundary conditions were:

$$C_1^0 = 0.1M,\ C_2^0 = 0.01M,\ C_1 + C_2 = C_1^0 + C_2^0 = 0.11M \tag{7}$$

Therefore:

$$N = -\frac{V_0}{A} \times \frac{dC_1}{dt} = P\frac{C_1 - C_2}{d} \tag{8}$$

Where A is the membrane surface area and V_0 is the volume of each compartment in the used test cell.

$$-\frac{V_0}{A} \times \frac{d(C_1^0 + C_2^0 - C_2)}{dt} = P\frac{(C_1^0 + C_2^0 - C_2 - C_2)}{d} \tag{9}$$

And:

$$\int_{C_2^0=0.01}^{C_2} -\frac{d(C_1^0 + C_2^0 - C_2)}{(C_1^0 + C_2^0 - C_2 - C_2)} = \int_0^t P\frac{A}{V_0 d} \times dt \tag{10}$$

$$\ln\frac{(C_1^0 + C_2^0 - 2C_2)}{(C_1^0 - C_2^0)} = -\frac{2PAt}{V_0 d} \tag{11}$$

$$\ln\left[1 - \frac{2C_2 - 2C_2^0}{C_1^0 - C_2^0}\right] = -\frac{2PAt}{V_0 d}, \quad \frac{2C_2 - 2C_2^0}{C_1^0 - C_2^0} \ll 1 \tag{12}$$

$$-\frac{2C_2 - 2C_2^0}{C_1^0 - C_2^0} = -\frac{2PAt}{V_0 d} \tag{13}$$

$$C_2 = \frac{PAt(C_1^0 - C_2^0)}{V_0 d} + C_2^0 \tag{14}$$

$$Q_2 = KC_2 \Rightarrow Q_2 = \frac{KPAt(C_1^0 - C_2^0)}{V_0 d} + KC_2^0 \tag{15}$$

Where Q is the conductivity. The diffusion coefficient of ions in the membrane phase can be determined from the slope of the straight line of Q-t.

Electrical Resistance

The electrical resistance is practically important due to its relation with energy consumption in the process. The membrane resistance measurement was carried out in a Pyrex cell which is schematically presented in Fig. 2. This cell consists of two platinum electrodes. The measurement was performed using 0.5 M NaCl solution. An equilibrated membrane was incorporated into the cell. A 0.5 M NaCl solution was supplied in cell compartments at 25°C. Electrical resistance (R_1) was measured by an alternating current bridge with frequency of 1500 Hz (Audio signal generator, Electronic Afzar Azma Co. P.J.S). In the next step, the membrane sample was taken away; the apparatus was re-integrated without membrane, and electrical resistance (R_2) was measured. The membrane resistance can be calculated using the difference between the cell and electrolyte solution resistances ($R_m = R_1 - R_2$) (18,28). The areal electrical resistance was expressed as follows:

$$r = (R_m A) \tag{16}$$

Where r is areal resistance and A is the surface area of the membrane.

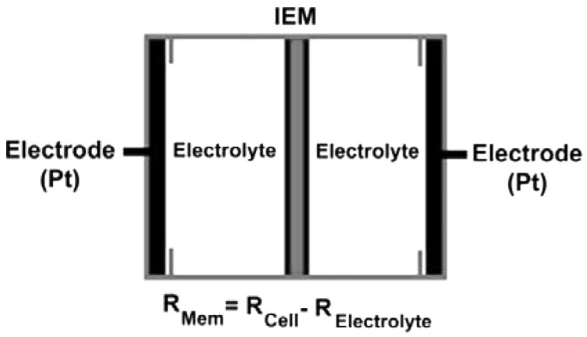


FIG. 2. Schematic diagram of the membrane resistance measurement cell.

Specific Surface Area Measurements

The membrane specific surface area is important because of its direct relation with interaction between the ions of solution and membrane and therefore has a significant effect on membrane performance. The specific surface areas of the prepared membranes were measured applying nitrogen adsorption- desorption as the Brunauer-Emmett-Teller (BET) method (29) with a Chembet 3000 Equipment. BET measurements take advantage of the low temperature adsorption of a monolayer of N_2 gas onto the surface of the sample. The N_2 gas is desorbed, and the surface area of the sample is calculated from the volume of gas desorbed and the cross-sectional area of a nitrogen molecule.

Current Efficiency and Energy Consumption

The current efficiency (C.E.) was calculated using following equation (15):

$$C.E. = \frac{F \times Z_i \times \Delta n}{\int_{t=0}^{t=t} Idt} \tag{17}$$

and for the energy consumption (E):

$$E = \frac{\int_{t=0}^{t=t} I \times V \times dt}{\Delta n \times M_w} \tag{18}$$

Where Z_i is the valance of ion, Δn is number of transported moles, V is the voltage, F is the Faraday constant, I is the current intensity, and M_w is the molecular weight of ions.

Membrane Oxidative Stability

The prepared heterogeneous membranes were immersed into 3% H_2O_2 aqueous solution containing 4 ppm Fe^{3+} at 25°C for up to 60 hr. The weights of dried samples (drying at 50°C for 4 hr) before and after the experiment were compared.

Mechanical Properties

The tear resistance as a mechanical property of the prepared membranes was tested according to ASTM1922-03. All samples were cut into the standard shape in the ambient conditions (28.6°C, relative humidity of 28%) before testing. For each test, three samples were used and their average values were reported.

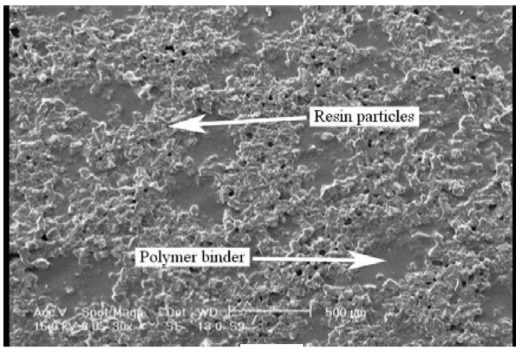
RESULTS AND DISCUSSION

Morphological Studies

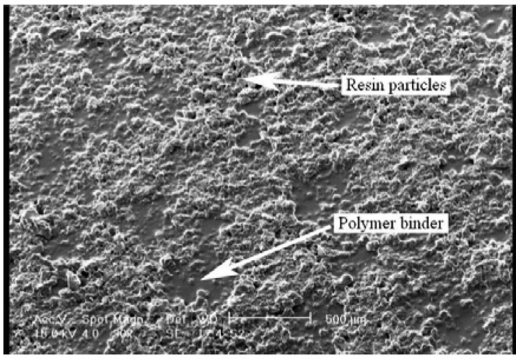
The electrochemical and mechanical behaviors of prepared membranes are closely related to their structures, especially the spatial distribution of ionic site (14). For the evaluation of morphology and ionic site condition

(resin particles) in membrane matrix, SEM and SOM studies have been carried out. The SEM images of the membranes surfaces are presented in Figs. 3 and 4 with 30 X and 250 X magnifications. Also, the cross-sections SEM images are depicted in Fig. 5. The non-conducting area (binder) and conducting ion exchange areas (resin particles) on the surface and in the bulk of the prepared membranes are clearly seen in these images.

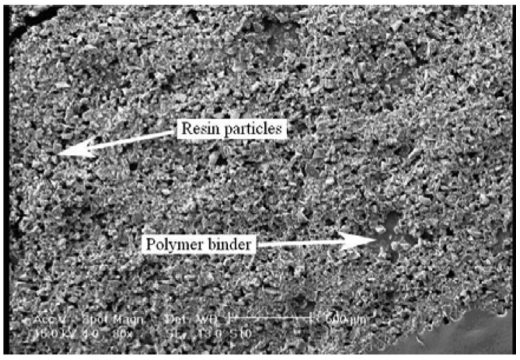
According to SEM images, resin particles are uniformly distributed in the prepared membranes. Moreover, the increase in resin content results in a more uniform distribution of resin particles in the prepared membranes. This



(a)

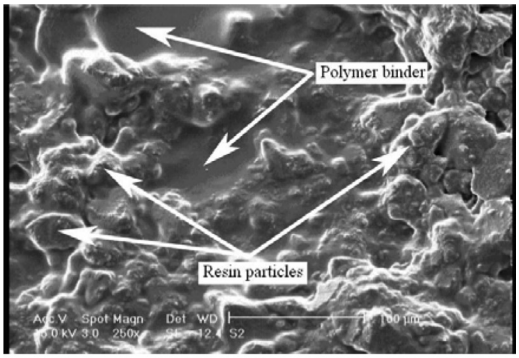


(b)

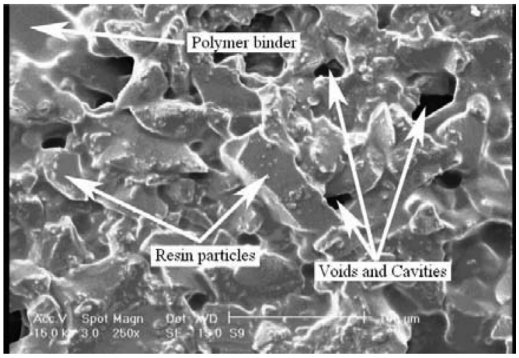


(c)

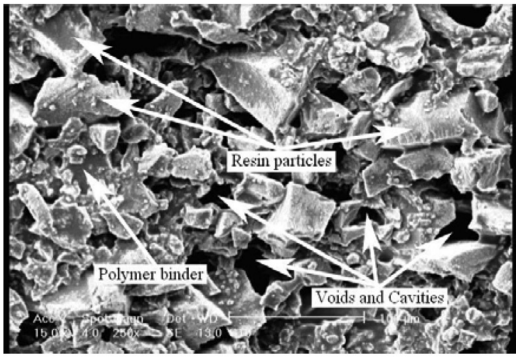
FIG. 3. SEM surface images (30X magnification) of the prepared membranes with different resin ratio content: (a) 40% resin loading, (b) 50% resin loading, and (c) 60% resin loading.



(a)



(b)



(c)

FIG. 4. SEM surface images (250X magnification) of poly carbonate membrane with different resin ratio loading: (a) 40% resin loading, (b) 50% resin loading, and (c) 60% resin loading.

may be attributed to higher resin particles density in the casting solution and lower random distribution possibility of these particles in polymeric film with the increment of resin loading. Also, as it can be seen in these pictures, with the increase of resin content, phase inversion occurs and the polymer binder tends to form the discrete phase. Insoluble and infusible ion exchange particles are incapable of forming a film. Therefore, the formation and propagation of voids, cavities, and cracks will be facilitated and increased with the increment of resin loading (as shown in SEM images). When these heterogeneous membranes swell in water, the cracks and fissures (Fig. 6) open more

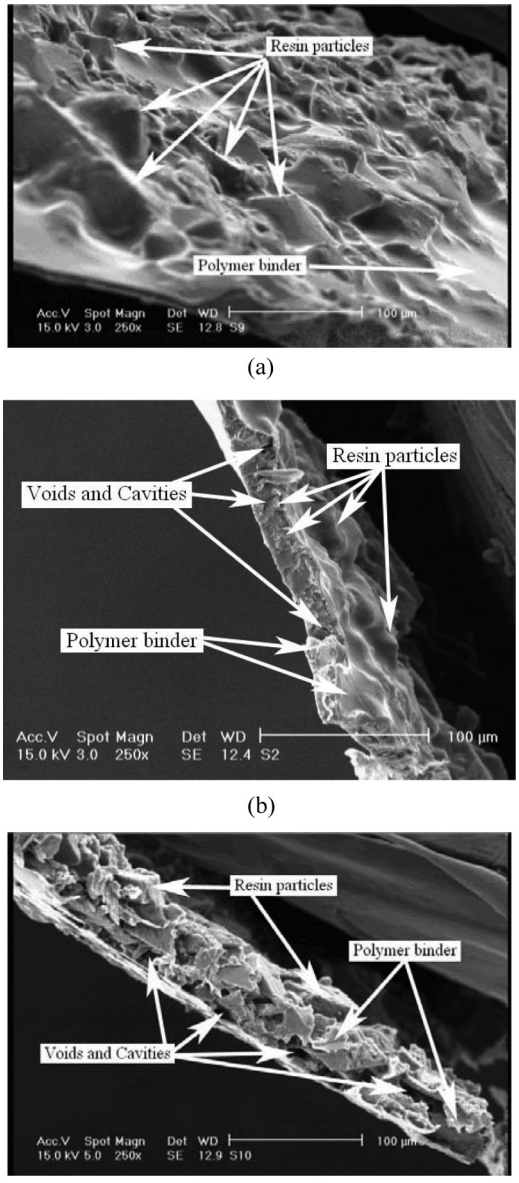


FIG. 5. SEM cross section images (250X magnification) of prepared PC membranes with various resin content: (a) 40% resin loading, (b) 50% resin loading, and (c) 60% resin loading.

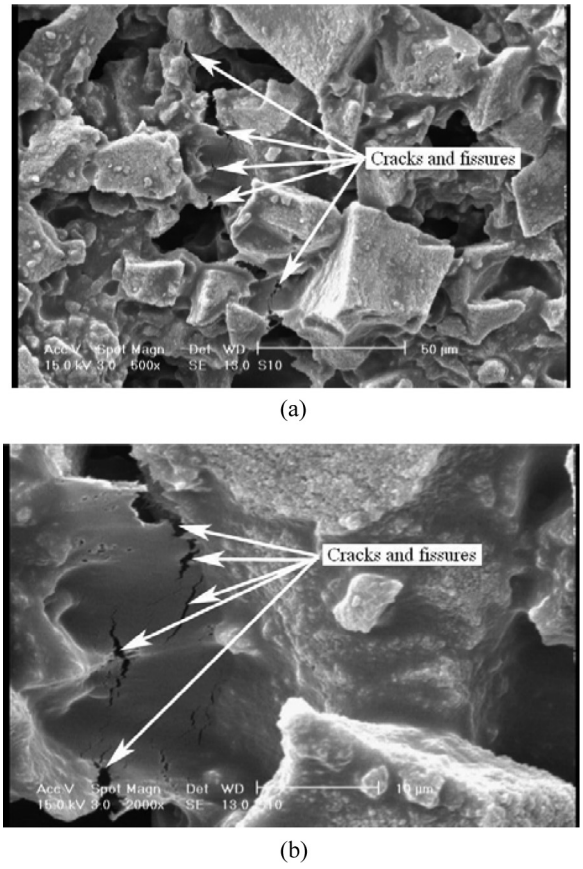


FIG. 6. SEM images of the home-made membranes: Formation of cracks and fissures on the surface of prepared membranes: (a) 500X magnification, and (b) 2000X magnification.

and the fraction of the conductive area is increased (30). In addition, as it appeared in SEM cross sections, with lower amount of resin ratio loading, particles of resin are more covered and isolated by the polymer binder in the membrane matrix and therefore they are not partially accessible to ion exchanges which lead to the decreasing of membrane performance.

Also, SOM was used for the evaluation of a more extended area of prepared membranes. The SOM images in transmission mode with light going through the membrane are depicted in Fig. 7 with 4X and 10X magnifications. The resin particles are seen as dark spots. The images show a relatively uniform surface for the prepared membranes. Moreover, resin particles are distributed uniformly. The uniform distribution of resin particles i.e., functional groups, can provide more conducting regions on the membrane surface and therefore will improve their electrochemical properties. The images confirm that the increase of resin content causes more uniform phase distribution. Moreover, as shown in these images, with the increase of resin ratio loading, particles of resin may be aggregated similar to ionic hydrophilic clusters and this will lead to the loose structure of the prepared membranes (14).

Water Content

The results (Fig. 8) revealed that the increment of resin ratio in the casting solution led to increasing of water content from 20.50 to 28% in the prepared membranes. The enhancement of the water content by increasing the resin ratio is attributed to the increment of hydrophilic functional groups which are hydrated by water molecules and therefore enhance the amount of absorbed water. Also,

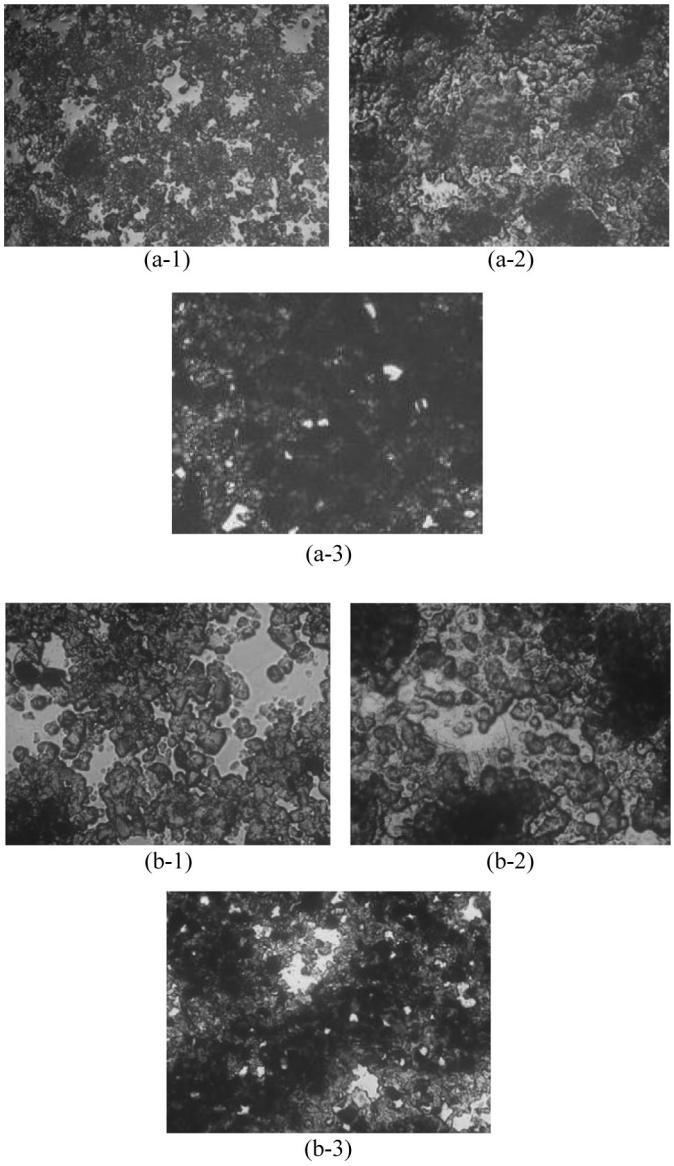


FIG. 7. SOM images of the membrane with (a-1, 2, 3) 4X and (b-1, 2, 3) 10X magnifications; (a-1), (b-1) 40% resin loading; (a-2), (b-2) 50% resin loading; (a-3), (b-3) 60% resin loading.

the increase of voids and cavities in the bulk of prepared membranes with the increment of resin ratio (SEM images), will increase the water content. Furthermore, at higher resin ratio loading, discontinuity of polymer chains binder causes higher water content for the prepared membranes.

The suitable amount of membrane water content can have better control on the pathways of ions traffic and improves the membrane permselectivity.

Additionally, high water content can provide more and wider transfer channels for co- and counter-ions transportation and decrease the ion selectivity and leads to a loose structure for the membranes.

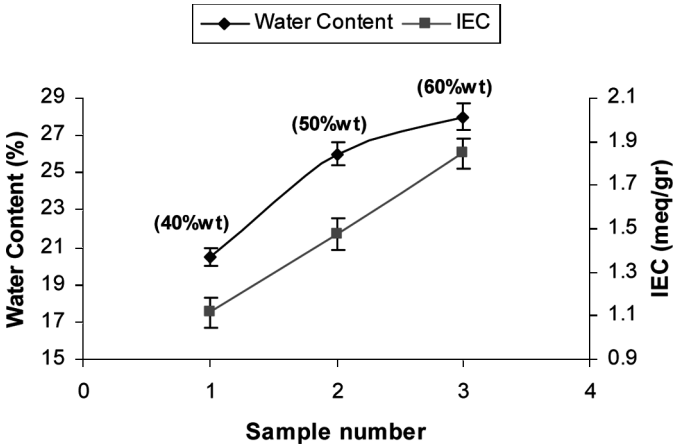


FIG. 8. The effect of resin ratio loading (%wt) on the water content and ion exchange capacity (IEC) of home-made cation exchange membranes.

Contact Angle Measurements

The contact angles were measured to evaluate the changes in the hydrophilicity and surface properties of the prepared membranes. Table 3 shows the effect of resin ratio loading in the casting solution on contact angle and wettability of the surface of the membranes. The increment of the resin ratio in the casting solution leads to lower contact angle for the prepared membranes. This indicates that a more hydrophilic surface is produced by increasing the percentage of resin ratio in the casting solution. This can be attributed to more uniform phase distribution of resin particles with the increment of resin loading and due to the increase in hydrophilic functional groups on the membrane surface which are hydrated by water molecules and therefore enhance the membrane surface hydrophilicity.

Ion Exchange Capacity (IEC) and F.I.C.

The results (Fig. 8) indicated that the increment of resin loading in the casting solution led to ion exchange capacity improvement (1.117 versus 1.846 $meq \cdot gr^{-1}$) in the prepared membranes due to the excessive functional groups.

Also, with the increment of resin ratio loading, formation of cavities and voids in the bulk of prepared membranes increases the free spaces in the membrane matrix

TABLE 3
Contact angle of prepared heterogeneous membranes with various ratios of resin loading (With 1–2.6% Standard division)

Membrane	Degree (°)
PC based with 40% resin loading	96.90
PC based with 50% resin loading	92.90
PC based with 60% resin loading	88.00

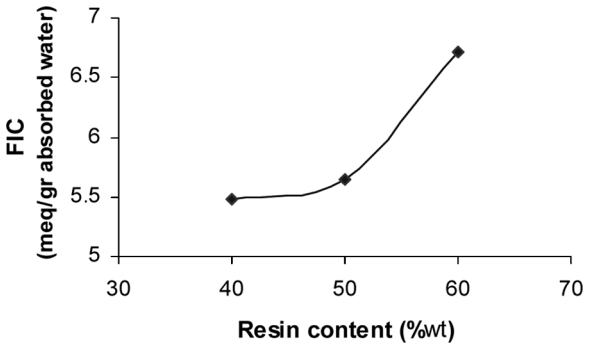


FIG. 9. The effect of resin ratio loading on fixed ion concentration (F.I.C.) of prepared cation exchange membranes.

(as was shown before in SEM images). These free spaces can prevent the isolation of functional groups by the polymer binder and therefore leads to improvement in ion exchange capacity. At a low amount of the resin content, functional groups can be covered and more isolated with the binder (see SEM cross section images) and so they are not partially accessible to ion exchanges.

A relationship exists between the IEC and water content (Eq. 3) and accordingly the effects between these parameters during the process can be optimized. The fixed ion concentration (F.I.C.) or the equivalent of the functional group per absorbed water content can be used for the purpose. The results for F.I.C. are presented in Fig. 9. The appropriate fixed ion concentration for the prepared membranes can have better control on the pathways for counterions traffic in the membrane matrix and increases the ion selectivity.

Membrane Potential, Permselectivity, and Transport Number

Characterization in Monovalent Ionic Solution (NaCl)

The potentials of the prepared membranes were between 47 to 49 mV (Table 4) in NaCl solution. The membrane potential of the prepared membranes increases with the increment of resin loading in NaCl solution. This may be attributed to the increment of fixed ion concentration and membrane surface charge density due to increase in functional groups by more resin loading. The increase of resin content provides further uniform distribution of resin particles in the bulk and on the membrane surface (shown in SEM and SOM images). This leads to enhanced Donnan exclusion that is responsible for the increment of membrane potential. Furthermore, the homogeneity and uniform distribution of functional groups can provide additional conducting regions on the membrane surface and improve the electrochemical properties of the membranes by the generation of appropriate flow channels for the easy passage of counterions.

Also, the ionic selectivity and transport number for Na^+ ions are presented in Table 4. Both of them will increase with increment of resin loading. This can be explained by the increment of fixed ion concentration with improved control of pathways for ions traffic due to the existence of adequate ionic functional groups and appropriate quantity of water content.

Characterization in Bivalent Ionic Solution ($BaCl_2$)

The results (Table 5) revealed that the increment of resin ratio loading led to the decrease in membrane potential, transport number, and selectivity for the prepared membranes in $BaCl_2$ solution (bi-valent ions).

Also, prepared membranes exhibited lower potential, selectivity, and transport number for the bivalent ions in comparison with monovalent ones. These lower electrochemical properties of membranes for bivalent ions compared to the monovalent type can be explained by the stronger bonds of bivalent cations with ion exchange functional groups (24) which poison the membranes and decrease the membranes transport number and selectivity. In fact, bivalent cations have stronger electrostatic attraction with the oppositely fixed charge sites (functional groups) and therefore they prevent functional groups' dissociation. This attraction, which enhances with the increase of the resin ratio content due to increment of fixed ion

TABLE 4
Membrane potential, transport number and permselectivity of the home-made membranes with various ratios of resins loading in NaCl ionic solution (Monovalent ions-Na^+)

Membrane	Membrane potential (mV)	Transport number	Permselectivity
Sample 1	47	0.9022	0.8409
Sample 2	48	0.9093	0.8525
Sample 3	49	0.9148	0.8614

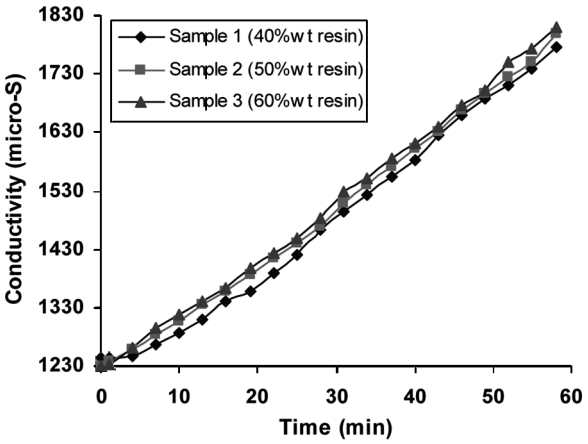
TABLE 5
The effect of resin ratio loading on membrane potential, transport number and permselectivity of prepared membranes in $BaCl_2$ ionic solution (Bivalent ions-Ba^{2+})

Membrane	Membrane potential (mV)	Transport number	Permselectivity
Sample 1	15	0.757	0.555
Sample 2	14	0.740	0.524
Sample 3	11	0.689	0.430

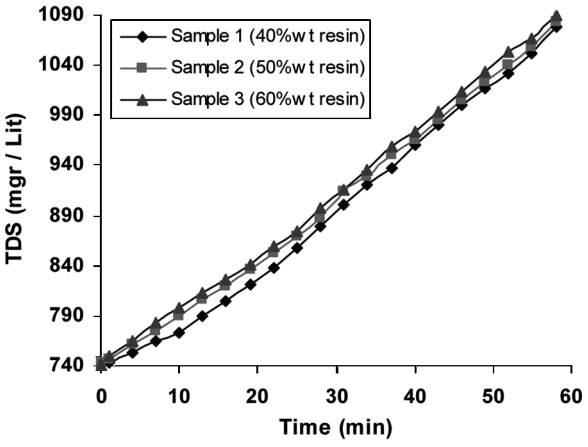
concentration (31), has a strong influence on Ba^{2+} transportation through the membrane and reduces the membranes transport number and selectivity with poisoning of functional groups. Furthermore, the larger radius of barium ions and their hydrated size in comparison with sodium ions make lower membrane potential, transport number, and permselectivity (7,13,14).

Conductivity and Permeability

During the experiment, ions cross through the membrane to the concentration section. Hence, conductivity and the total dissolved solid (TDS) of this section which are indicators of the passage of ions through the membrane were increased over time for all of the prepared membranes. The variation of conductivity and TDS in the concentration section with time are depicted in Figs. 10 and 11 for mono and bivalent ionic solutions. Moreover, ion permeability and flux of ions (Table 6) through the membranes

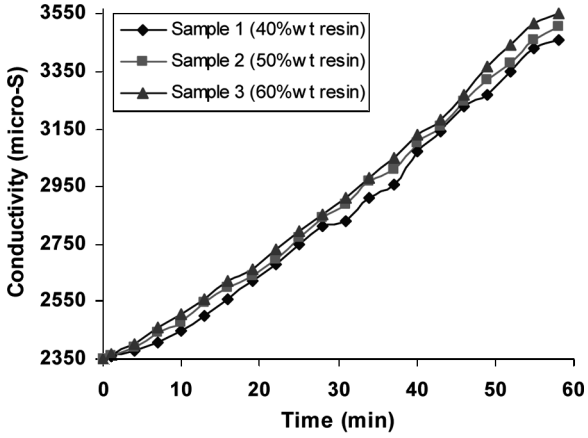


(a)

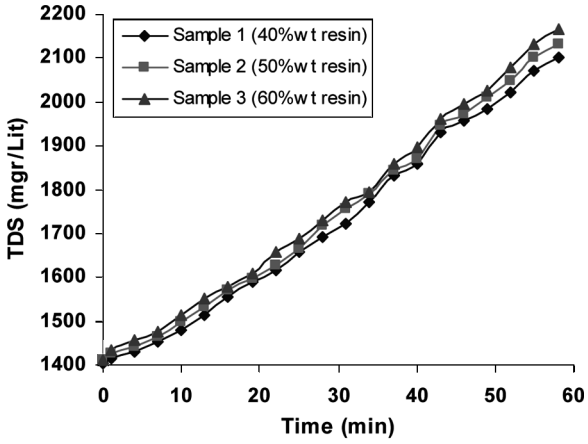


(b)

FIG. 10. Variation of conductivity (a) and TDS (b) with time in permeate section for prepared membranes with various bled ratio of resin to polymer binder; for mono-valent ionic solution (Na^+ ion).



(a)



(b)

FIG. 11. The variation of conductivity (a) and TDS (b) with time in permeate section for the home-made membranes with various ratios of resin loading; for bi-valent ionic solution (Ba^{2+} ion).

were enhanced with the increment of the resin ratio for both types of mono and bivalent ions. This is due to the improvement in ion exchange capacity and water content by increase in resin loading. This provides more and larger channels in the membrane matrix for the ions passage.

Also, the obtained results show that the prepared membranes have higher ionic flux and permeability for Na^+ ions than Ba^{2+} ions. This may be attributed to smaller radius of Na^+ ions (14) and also the formation of a weaker bond of Na^+ ions with membrane's functional groups that can facilitate the ions transportation as was mentioned before in the previous section. However, prepared membranes have lower permselectivity for bivalent ions compared to the monovalent type.

Electrical Resistance

The areal electrical resistance of the membrane was decreased with the increment of resin loading (Fig. 12)

TABLE 6
Ionic permeability and flux of ions for the prepared membranes with various ratios of resin loading

	Ionic permeability (m/s)		Flux of ions ($mol/m^2 \cdot s$)	
Membrane	Na^+ ions	Ba^{2+} ions	Na^+ ions	Ba^{2+} ions
Sample 1	10.72×10^{-7}	9.890×10^{-7}	9.438×10^{-5}	9.021×10^{-5}
Sample 2	11.18×10^{-7}	10.70×10^{-7}	9.705×10^{-5}	9.689×10^{-5}
Sample 3	11.44×10^{-7}	11.33×10^{-7}	10.048×10^{-5}	9.847×10^{-5}

due to the formation of further conducting sites providing higher membrane conductivity. Moreover, at low resin loading which results in lower IEC and water content, ion exchange groups are isolated from each other in the membrane matrix. Consequently, the ions cannot migrate throughout the membrane and so the membrane resistance will be increased.

With the increase of resin loading from 40% to 60%, more large and suitable ion-conducting pathways will be formed throughout the membrane which causes the resistance to decrease strongly (32). Furthermore, with the increase in the resin ratio content, enhancement of surface charge density, surface hydrophilicity, and conducting regions on the membrane surface will make superior electrostatic interaction between ions and membrane surface and strengthen the intensity of the uniform electrical field around the membrane and decrease the membrane areal resistance.

Specific Surface Area Measurements

BET test was used for the evaluation of specific surface areas of the prepared membranes. Figure 13 shows the effect of the resin ratio loading in the casting solution on the specific surface areas of the prepared membranes. The increment of resin content leads to the enhancement of a specific surface area for the prepared membranes. This can be attributed to increasing of resin particles' density on the membrane surface due to higher resin loading which makes a rough surface and increases the specific surface area as shown in the SEM images.

Current Efficiency and Energy Consumption

Results indicate that current efficiency (Fig. 14) is slightly increased and energy consumption (Fig. 15) is marginally decreased with the increment of resin ratio loading in the membranes. This is attributed to the increase in ionic flux and ionic permeability (Eqs. 17, 18) with increasing resin content. Also, results show that prepared membranes have better current efficiency and lower energy consumption for monovalent ions in comparison with the bivalent type because of its higher ionic flux and permeability for monovalent ions.

Membrane Oxidative Stability

The membranes were immersed in an oxidant aqueous solution for oxidative stability measurements. Results (Fig. 16) indicate that the oxidative stability of the prepared membranes is decreased with the increment of the resin ratio. This may be attributed to the higher oxidant solution diffusion in the membrane matrix by the increase of hydrophilic functional groups due to a higher resin content. These functional groups are hydrated by water molecules and therefore, they enhance the possibility of oxidant solution diffusion. Also, the formation of cavities and voids of prepared membranes in bulk will be enhanced with the increment of resin loading which facilitates the

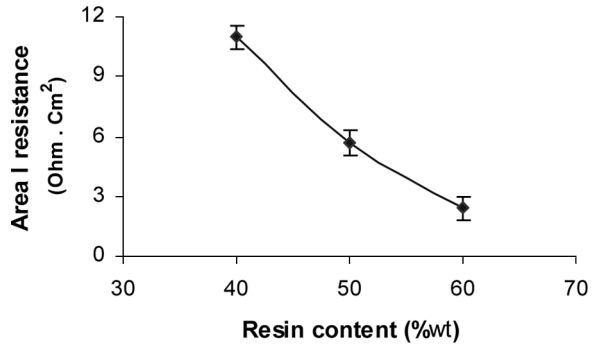


FIG. 12. Areal electrical resistance of the prepared membranes with various ratios of resin loading (resin to polymer binder).

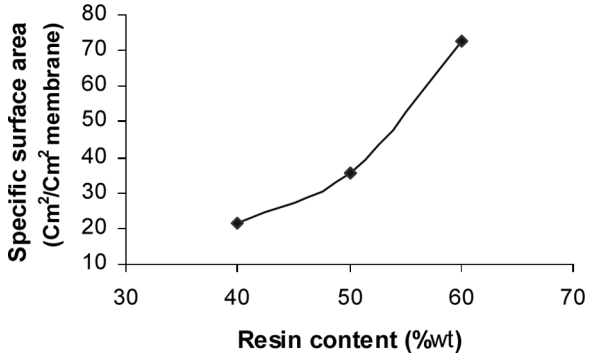


FIG. 13. Specific surface area of the prepared membranes with various ratios of resin loading.

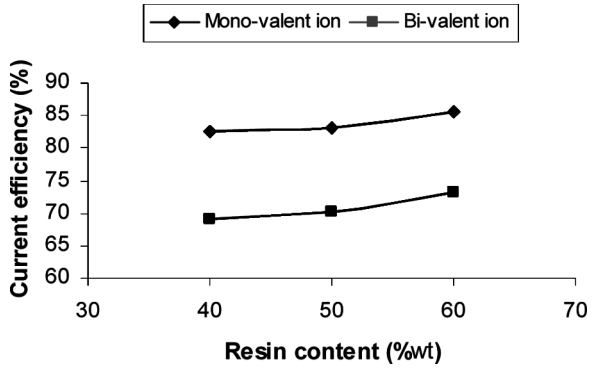


FIG. 14. Current efficiency of prepared heterogeneous cation exchange membranes with various ratios of resin loading for mono and bivalent cations.

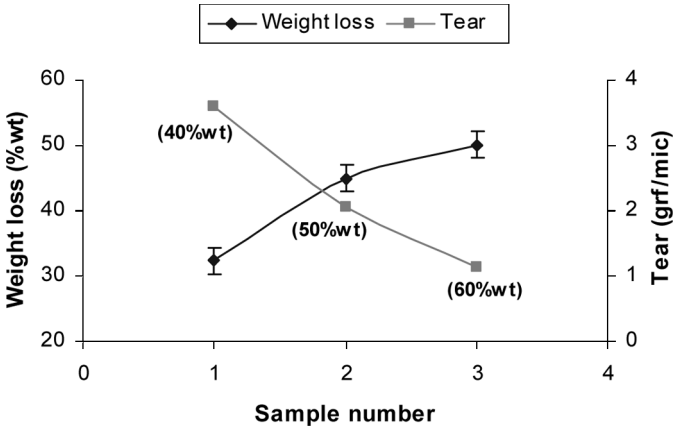


FIG. 16. The effect of resin ratio loading (%wt) on the oxidative stability and mechanical property of prepared membranes.

diffusion of oxidant solution. Moreover, lower oxidative stability for resin particles compared to polymer binder which as was achieved in the experiments.

Mechanical Properties

As were shown in SEM images, the loss of molecules solvent due to evaporation in the preparation stage causes cavities and voids to be formed between the resin particles and polymer binder region. These micro voids are sufficient to accommodate the solvent molecules to solvation of ionic groups in the resin particles. Hence, the solvation does not change membrane dimensions manifestly (8,19). The swelling in the prepared membranes was less than 5% in thickness. Moreover this was negligible in length and width.

Moreover, the mechanical strength of the membranes was decreased with the increment of resin loading (Fig. 16). With the increase of resin content, phase inversion occurs and the polymer binder tends to form the discrete phase. Furthermore, insoluble and infusible ion exchange particles are incapable of forming a film. Therefore, with the increment of resin loading crack propagation becomes facile and a brittle and weaker membrane will be obtained (12,17). Also, at high ionic content the more absorbed water molecules play a role in reducing the ion-ion interaction by hydration of functional groups. This is the reason for reducing the mechanical strength of the membranes.

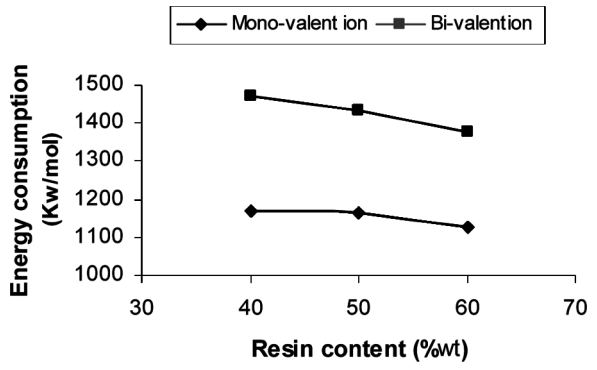


FIG. 15. Energy consumption of prepared membranes with various ratios of resin loading for mono and bivalent cations.

Superior Membrane

Among the prepared membranes, heterogeneous cation exchange membrane with 60%wt resin loading (sample 3), with superior ionic flux, permeability, conductivity, and suitable selectivity and oxidative stability, highest current efficiency and lowest energy consumption showed a more appropriate performance compared to other prepared membranes in this research. However, the mechanical strength was low compared to the others. The mechanical properties of the prepared membranes can be improved by an external non-woven fitting fabric.

The obtained results are comparable with the other reported heterogeneous cation exchange membranes in the literature. The prepared membrane showed appropriate electrochemical properties such as high ionic conductivity and permeability with suitable selectivity. The membranes may be applied in industrial scale ED process for water recovery and wastewater treatment possessing advantages over reported heterogeneous (1,2,4,13–15,18,22,28,31–33) and commercial membranes. It is necessary to mention that membrane ionic conductivity is an important factor due to its relation with energy consumption in the process.

CONCLUSION

The increment of resin content resulted in a more uniform phase distribution of resin particles in the prepared membranes. Moreover, the formation and propagation of voids, cavities, and cracks were facilitated with the increment of resin ratio loading. It was found that the higher resin ratio in casting solution led to the increase in

water content, surface hydrophilicity, ion exchange capacity, and fixed ion concentration for the prepared membranes. The results indicated that membrane potential, transport number, and permselectivity of the membranes were increased in monovalent and decreased in bivalent ionic solution with the increment of resin ratio loading. The ionic permeability and flux of ions through the membranes were enhanced with the increment of resin ratio for both types of mono and bivalent ions. Results showed that prepared membranes have higher ionic flux and permeability for sodium ions compared to barium ions. Also membrane electrical resistance was decreased with increment of resin loading from 40 to 60%wt in the membranes. In addition, increase of resin loading in the casting solution led to the enhancement of a specific surface area for the membranes. Current efficiency was increased and energy consumption decreased with the increment of resin loading. The home-made membranes possessed a better current efficiency and lower energy consumption for mono-valent ions in comparison with the bivalent type. Additionally, oxidative stability and the mechanical strength of the prepared membranes were decreased with the increment of resin ratio loading. The swelling of the prepared membranes was negligible. The obtained results are comparable with other reported IEMs in the literature and may be applied in electro-membrane processes, particularly ED, for water recovery and wastewater treatment.

ACKNOWLEDGEMENTS

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NOMENCLATURE

W_{wet}; W_{dry}	Weight of wet membrane; dry membrane (gr)
a	Milli-equivalent of ion exchange groups in membrane (meq)
$E_{Measure}$	Membrane potential (mV)
t_i^m; t_0	Transport number of counter ions in membrane phase; in solution
R	Universal gases constant ($J\,mol^{-1}\,K^{-1}$)
T	Temperature (K)
n, Z_i	Electrovalence of ion
a_1, a_2	Solutions electrolyte activities
P_s	Membrane ionic permselectivity
P	Diffusion coefficient of counter ions (m/s)
d	Membrane thickness (m)
N	Ionic flux ($mol/m^2 \cdot s$)
C, C_1, C_2	Cations concentration in the cell compartments (M)
A	Membrane surface area (m^2)
V_0	Volume of each compartment in the used test cell
Q	Conductivity (micro-S)
t	Time (min)
r	Specific electrical resistance (ohm · cm)
R	Electrical resistance (ohm)
Δn	number of transported moles through membrane
V	Potential (voltage, V)
F	Faraday constant
I	current intensity (A)
M_w	Molecular weight

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