

Electrodialytic Transport Properties of Heterogeneous Cation-Exchange Membranes Prepared by Gelation and Solvent Evaporation Methods

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ABSTRACT: The heterogeneous cation-exchange membranes were prepared by employing two different methods: immersing the cation-exchange resin-loaded membranes in gelation bath; evaporating the solvent upon casting a uniform solution of cation-exchange resin on a glass plate. The effect of resin loading on the electrochemical properties of the membranes was evaluated. The permselectivity of these heterogeneous membranes and transport number of calcium ions relative to sodium ions was evaluated with respect to the extent of resin loading and the methods of preparation. It is found that the membrane potential, transport number, permselectivity, and relative transport number are promi-

nently high in the solvent evaporation method compared with the gelation method. The transport number of calcium ions relative to sodium ions in the solvent evaporation method increased monotonously with increasing resin loading. However, the increase of resin loading did not influence much on the relative transport numbers in the gelation method. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 198–207, 2006

Key words: electrodialysis; membrane; transport number; permselectivity; ion-exchange capacity

INTRODUCTION

Ion-exchange membranes are one of the most advanced separation membranes that have been used in various industrial processes: electrodialytic concentration of sea water to produce salt;^{1,2} desalination of saline water by electrodialysis;^{3,4} separator for electrodialysis such as chlor-alkali production; diffusion dialysis to recover acids and alkalis from waste acids and alkalis;^{5,6} separation of acidic gas such as carbon dioxide by carrier transport;^{7,8} and sensing materials such as humidity,^{9–11} carbon monoxide,¹² etc. All these processes are energy efficient and environmentally friendly. This has led to the development of ion-exchange membranes of high chemical, mechanical, and thermal stability, which is of great importance to meet the growing demands of the aforementioned processes.

Currently, most of the commercial ion-exchange membranes are composed of styrene-divinylbenzene copolymer, showing sufficient stability in many processes. However, in harsh environments, the chemical

stability of these membranes is unsatisfactory, and thus, there is a great demand for the developments of new membranes. For applications like membrane fuel cells, where the usage of sulfonated polystyrene-divinylbenzene copolymer membranes fails because of unsatisfactory oxidation stability, the perfluorinated highly stable ionomer Nafion is the only commercially available polymer.^{13,14} However, the high cost of this membrane has prevented its broader commercial applications so far. As substitute for Nafion, sulfonated arylene-main-chain polymers like the poly(ethersulfone)s (PSU) or poly(etherketone)s (PEEK) are the materials of choice because of their excellent workability, chemical, and mechanical strength next to Nafion.^{15–19} In particular, a polysulfone membrane having an excellent chemical resistance has been studied for its application as an ion-exchange membrane by improving the permeability for ultrafiltration and reverse osmosis, or imparting ion permselectivity by introducing ion-exchange groups into the membrane.^{20–22}

Many researchers^{23–25} deal with the preparation of both homogeneous and heterogeneous ion-exchange membranes, being a unique in their nature, which supercedes each other in one way or the other. Homogeneous membranes having good electrochemical properties lack in their mechanical strength, whereas heterogeneous membranes having very good mechanical strength are comparatively poor in their electrochemical performances.

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Keeping this in mind, we have prepared heterogeneous ion-exchange membranes with and without reinforcing fabric by two different methods, using poly(ethersulfone) as binder in which cation-exchange resin particles are dispersed. The physical and electrochemical properties of the membranes were evaluated, and the variation of transport properties with respect to the resin loading in electrodialysis was elucidated and compared between the two methods.

EXPERIMENTAL

Materials

Poly(ethersulfone) (Udel, Gurda Chemicals Ltd., Mumbai, India), cation-exchange resin powder of size $39\ \mu\text{m}$, and nonwoven fabric (polyester) were kindly supplied by CSMCRI, Bhavnagar, India. *N,N'*-Dimethylformamide, dichloromethane, sodium chloride, calcium chloride, Tween-20 surfactant, hydrochloric acid, and sodium hydroxide were obtained from s. d. fine Chem. Ltd., Mumbai, India. All the chemicals were of reagent grade and used without further purification. Deionized water was used in all the experiments.

Preparation of cation-exchange membranes using two different methods

Gelation method

Cation-exchange membranes with different percentage of resin loading were prepared as follows: 15 mass % of poly(ethersulfone)s was dissolved in 85 mass % of *N,N'*-dimethylformamide (DMF). After getting uniform solution, known weights of resin powder were added to obtain resin loading of 30, 40, 50, and 60 mass % and stirred further. The uniform solution thus obtained was spread on a nonwoven polyester support fabric placed on a glass plate. It was then immediately immersed in a gelation bath, containing 1% of DMF, 0.1% of surfactant, and 98.9% of deionized water. The membranes thus obtained were kept overnight in distilled water to remove residual DMF. Before being subjected to electrochemical studies, the membranes were conditioned with 0.1N hydrochloric acid and 0.1N sodium hydroxide solution alternatively several times and then equilibrated with salt solution to be used in the measurements.

Solvent evaporation method

In this method, the membranes were prepared without reinforcing nonwoven fabric, using 15 mass % of poly(ethersulfone), which was dissolved in 85 mass % of dichloromethane. After getting uniform solution, known quantities of resin powder were added so as to obtain resin loading of 30, 40, 50, and 60 mass % and

stirred further. The uniformly distributed solutions were cast onto glass plates and allowed for solvent evaporation. The membranes were then peeled off and kept for conditioning as mentioned in the previous method.

Measurements of basic physical properties of cation-exchange membranes

Water content and membrane thickness

The membranes were immersed in distilled water for 24 h, then their surface moisture were wiped, and the wet membranes were weighed. The weight of the wet membrane was dried at a fixed temperature of 60°C until constant weight was achieved. The water content (W_c) was calculated as:

$$W_c = (W_w - W)/W_w \quad (1)$$

where W_w and W are the weights of a membrane at the equilibrium and dry state, respectively. The membrane thickness was measured at different points using Peacock dial thickness gauge (Model G, Ozaki MFG. Co. Ltd., Japan) with an accuracy of $\pm 2\ \mu\text{m}$. The thickness of the membranes was found to be $40 \pm 2\ \mu\text{m}$.

Ion-exchange capacity (IEC) and fixed ion concentration (A_f)

After dipping in pure water for one day, the membrane samples were immersed for two days in a large volume of 1N HCl solution to convert the membranes into H^+ forms. The membranes were washed with distilled water to remove excess HCl and then equilibrated with distilled water for further 4 h, with frequently changing the distilled water to remove the last traces of acid and then air dried. The air-dried membranes were then equilibrated with 50 mL of 0.5N NaCl solution for 24 h and their ion-exchange capacities were determined from the increase in acidity using acid-base titration. Membranes were then washed and dried in an oven at 60°C for 24 h and their weights were measured. The ion-exchange capacity of the membranes was calculated as:

$$IEC = ab/W \quad (2)$$

where W is the dry weight of the membrane (g), a is the volume of NaOH (cm^3), and b is the concentration of NaOH solution ($\text{mequiv}/\text{cm}^3$). The fixed-ion concentration (A_f) can be calculated as:

$$A_f = IEC/W_c \quad (3)$$

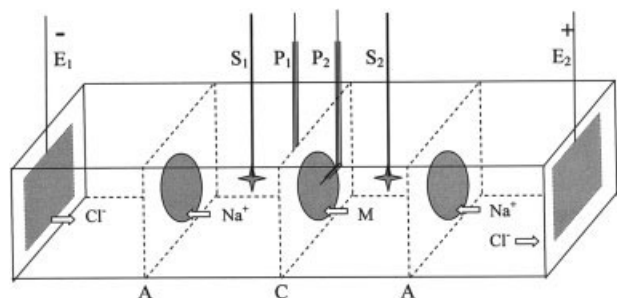


Figure 1 Apparatus for measurement of transport number of calcium ions relative to sodium ions and current efficiency of cation exchange membranes. A: anion exchange membrane; C: cation exchange membrane to be measured; M: Na^+ or Ca^{+2} ; E_1 and E_2 : AgCl electrodes for current supply; P_1 and P_2 : electrodes for measurement of voltage drop across the membrane; S_1 and S_2 : stirrers; effective membrane area: 10 cm^2 ; capacity of each compartment: 100 cm^3 .

Measurements of electrochemical properties of cation-exchange membranes

Electrical resistance

The electrical resistance of the membranes was measured at 1 kHz AC, with an Aplab-4912, Autocompute LCR-SORTESTER, at 25°C using a two-compartment cell with platinum black electrodes.²⁶ The electrical resistance was measured independently in 0.5N NaCl and 0.5N CaCl_2 solutions after the membranes had been equilibrated with respective salt solutions. The resistance of the membrane r (in $\Omega \text{ cm}^2$) was calculated by:

$$r = (r_1 - r_2) \quad (4)$$

where r_1 is the resistance of the solution with membrane and r_2 is the resistance of the solution without membrane.

Membrane potential and transport number

The membrane sample was interposed between two halves of an indigenously designed concentration cell made up of acrylate material as illustrated in Figure 1. The cell was fitted with double junction standard calomel electrodes. The solutions used were 0.1N and 0.01N NaCl; 0.1N and 0.01N CaCl_2 aqueous solutions. To minimize the effect of diffusion at the membrane-solution interphases, the solutions in both the compartments were agitated vigorously with stirrers ($1500 \pm 100 \text{ rpm}$). The membrane potentials were measured at 25°C using an Ion-meter (Jenway-3340) with saturated calomel electrodes, which were reproducible upto 0.10 mV. The transport numbers of the cation exchange membranes were calculated using the following equation:

$$t_+ = (\Delta\Phi + d)/2d \quad (5)$$

where $\Delta\Phi$ is the membrane potential and $d = 0.05,915 \log(C_1\gamma_1/C_2\gamma_2)$. Here C_1 and C_2 are the concentrations of aqueous NaCl or CaCl_2 solution and γ_1 and γ_2 are the corresponding mean molar activity coefficients.

Measurement of transport numbers of calcium ions relative to chloride ions

Apparatus

The same four-compartment cell shown in Figure 1 was used to evaluate the transport properties of the cation-exchange membranes with two types of Ag-AgCl electrodes for current supply and measurement of the voltage drop across the membrane. The effective membrane area of the cell was 10 cm^2 (radius of the membrane = 1.79 cm) and the capacity of each compartment was 100 cm^3 . The area of the Ag-AgCl electrodes for current supply was $4.0 \times 10.0 \text{ cm}$; the electrodes were bent in a wave-like shape in the cell. Wire probe electrodes of Ag-AgCl were placed close to the membrane surfaces (about 2 mm from the membrane surfaces). The sodium chloride solution was used as an anolyte and a catholyte, which were separated by anion-exchange membranes (Neosepta AMX, Tokuyama Corp., Japan). The transport number of chloride ions in the membrane is > 0.98 during the electrodialysis of 0.5N sodium chloride solution at a current density of 20 mA/cm^2 ; electrical resistance is $2.0\text{--}3.5 \Omega \text{ cm}^2$. The two middle compartments were filled with 1 : 1 mixed salt solution of sodium chloride (0.125N) and calcium chloride (0.125N). Electricity was measured by an Autorange digital multimeter (Radio Shack, UK). The voltage drop across the membrane was measured as a function of time with Ag-AgCl probe electrodes on an X-t recorder (EPR-TOA, DKK Electronics, Japan).

Evaluation of relative transport properties of cation-exchange membranes

The transport number of calcium ions relative to sodium ions and the current efficiency were measured. The transport number of calcium ions relative to sodium ions was defined as follows:

$$P_{Na}^{Ca} = \frac{t_{Ca}/t_{Na}}{C_{Ca}/C_{Na}} \quad (6)$$

where t_{Ca} and t_{Na} are the transport numbers of calcium and sodium ions in the membrane, C_{Ca} and C_{Na} are the average concentrations of calcium and sodium ions in the solution before and after electrodialysis. P_{Na}^{Ca} is the number of equivalents of calcium ions permeated through the membrane when one equivalent of so-

dium ions permeates through it (because 1:1 mixed salt solution as equivalent was used).

Procedure

The cation-exchange membrane was placed in the middle of the cell and the two middle compartments were filled with 100 cm³ of the 1 : 1 mixed salt solution (sodium chloride and calcium chloride). The concentration of the mixed salt solution was 0.125N. Both anolyte and catholyte were filled with 100 cm³ of 0.125N sodium chloride solution. Electrodialysis was carried out at a current density of 10 mA/cm² for one hour under vigorous agitation (1500 ± 100 rpm) with stirrers to minimize the ion deposition at the boundary layers of the membrane-solution interfaces. After electrodialysis, the solutions of the middle compartments were analyzed using Flame photometer (Jenway-PEP 7). Thus, the relative transport number was calculated from the change in the concentration of respective cations in each compartment. The current efficiency was calculated from the change in concentrations of cations in each compartment, and from the amount of current passing through the membrane, which was measured with an Autorange digital multimeter.

RESULTS AND DISCUSSION

Dimensional stability and equilibrium swelling

Cation-exchange membranes of the present study are heterogeneous in nature with dispersed ion-exchange resin particles in the base poly(ethersulfone) matrix. Ion-exchange resin particles used here are crosslinked polystyrene (PS) having ion-exchangeable functional groups. It is noticed that with increase of resin loading, the membranes become more and more brittle, and at the same time, it is also noticed that the finer the resin particles are, the more flexible is the membrane.¹⁴ Hence, with resin particles having mesh sizes of -300 and + 400 BSS (39 μm), it is possible to obtain the flexible membranes upto 60 mass % of resin loading. With a further increase in resin loading, phase inversion takes place and crosslinked PS particles tend to form a continuous phase and binder PSU as a discrete phase. PS being more brittle in nature compared with PSU fails to act as impact modifier and crack propagation becomes facile, resulting in a brittle membrane. In the present study, we have developed membranes by varying the resin loadings of 30, 40, 50, and 60 mass % using both the gelation and solvent evaporation methods.

Keeping in view of the practical applications of electrodialysis membranes, their dimensional stability in different ionic forms is the most desirable criteria for any commercial ion-exchange membranes. In case

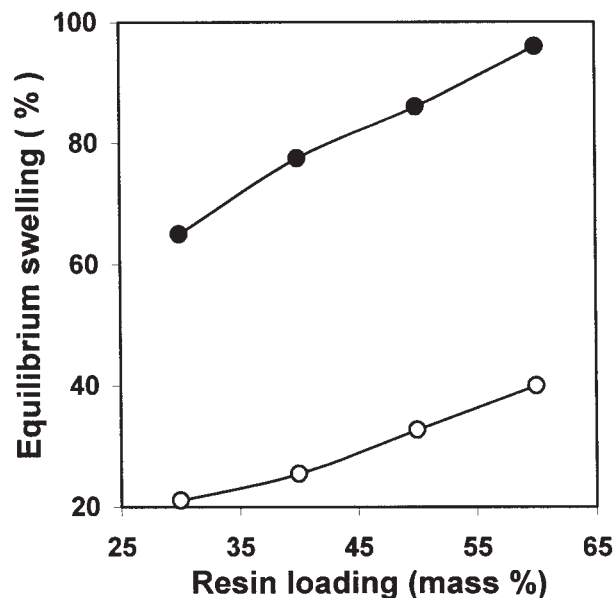


Figure 2 Variation of equilibrium swelling versus different mass % of resin-loaded membranes prepared by (●) gelation method and (○) solvent evaporation method.

of the heterogeneous cation-exchange membranes synthesized in the present work, it is observed that there is no noticeable change in the area of the membrane from one ionic form to another, i.e., $H^+ \rightarrow Na^+$, $H^+ \rightarrow Ca^{2+}$, and $Na^+ \rightarrow Ca^{2+}$. In addition, there is no appreciable change in the dimension of the membrane in different ion concentrations of NaCl solution (say 1000, 3000, 5000, and 10,000 ppm). Such a dimensional stability may be due to the presence of micro voids in the membranes that are generally introduced between the resin and poly(ethersulfone) binder regions during their preparations. These micro voids can accommodate the solvent molecules and thereby solvate the ionic species in the resin, and as a result of which dimensional changes do not occur.

The percent of equilibrium swelling was calculated for all the membranes using equation 1 and data are plotted as a function of mass % of resin loading. Poly(ethersulfone) used as a binder has the hydrophobic character, and hence, the equilibrium swelling mainly depends upon the hydrophilic resin particles. From Figure 2, it is observed that as the resin loading increases, the equilibrium swelling of the membrane also increases. For the membranes prepared by the gelation method, the equilibrium swelling is nearly three times higher than those prepared by the solvent evaporation method; yet, membranes show good dimensional stability. Such a high equilibrium may be due to larger pore size distribution in the membranes. Generally, equilibrium swelling can be considered as the extent of solvation of the resin particles. In the gelation method, membrane swells more during gelation, thereby increasing the free volume space in the

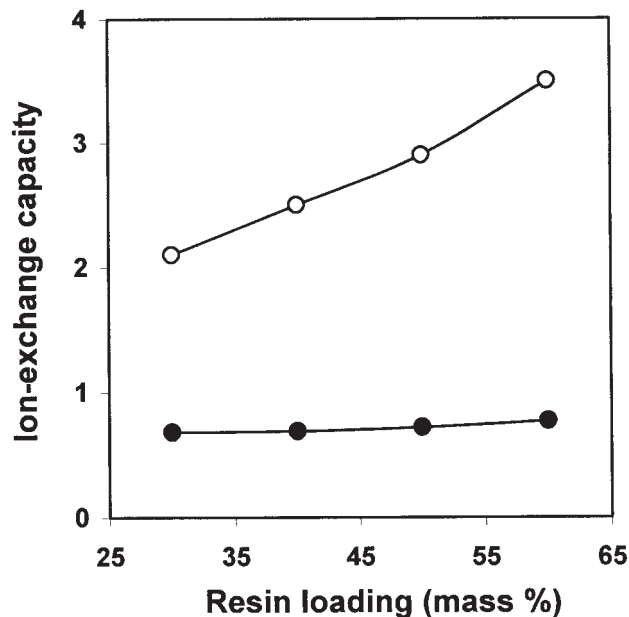


Figure 3 Variation of ion-exchange capacity versus different mass % of resin-loaded membranes. Symbols are similar to those in Figure 2.

membrane, and thus, maximum surface area of the resin particles gets exposed to the solvent molecules, thereby affecting maximum solvation. Equilibrium swelling of the membranes prepared by the solvent evaporation method is low probably because of the smaller pore size distribution of the membranes. As the pore size decreases, the free volume space in the membrane decreases, and so small surface area of the resin particles gets exposed to the solvent molecules, thereby affecting the less solvation of the resin particles and thus, decreases the equilibrium swelling.

Ion-exchange capacity

Apart from the dimensional stability and equilibrium swelling, ion-exchange capacity of the membranes is another important property of the electro dialysis membranes. The membranes should have a reasonable ion-exchange capacity with very low electrical resistance. The ion-exchange capacity of the membranes was calculated using equation 2 and these data are plotted as a function of resin loading in Figure 3. Ion-exchange capacity of the membranes depends on their fixed-ion concentration. As the fixed-ion concentration increases with increasing resin loading, ion-exchange capacity also increases. The membranes prepared by the gelation method exhibit low ion-exchange capacity and there is no appreciable change with increasing resin loading. This might be due to the leaching out of some of the resin particles during gelation step and because of the presence of coions in the free space of the membranes. However, the mem-

branes prepared by the solvent evaporation method have comparatively higher ion-exchange capacity, and this has increased further linearly with increasing resin loading. This might be due to increased fixed ionic charges, as the resin loading increases as well as due to the absence of coions in the free space of the membranes because of smaller pore size.

Membrane resistance

The electrical resistance of the membranes was measured in 0.5N sodium chloride and 0.5N calcium chloride solutions, and the resulting data were plotted as a function of resin loading shown in Figures 4 and 5, respectively. It is observed that membrane resistance decreases with increasing resin loading irrespective of nature of solutions and methods of preparation as due to increase in number of charges per unit area. However, the decreasing tendency is less significant for the membranes prepared by the gelation method. This is because of leaching out of resin particles during the gelation and subsequently accommodating more number of coions in the membranes. In the case of solvent evaporation method, the magnitude of resistance is almost double for calcium chloride solution as compared with the resistance measured in NaCl solution, owing to higher charge density of the calcium ion. This trend decreases in both the solutions remarkably, as the resin loading increases further, owing to the increased charge density of ion-exchange groups on the membranes.

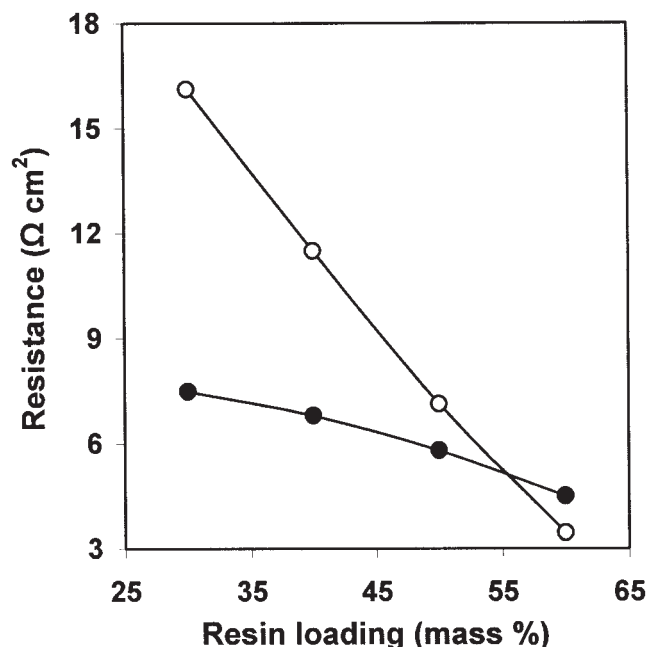


Figure 4 Variation of resistance versus different mass % of resin-loaded membranes measured in NaCl solution. Symbols are similar to those in Figure 2.

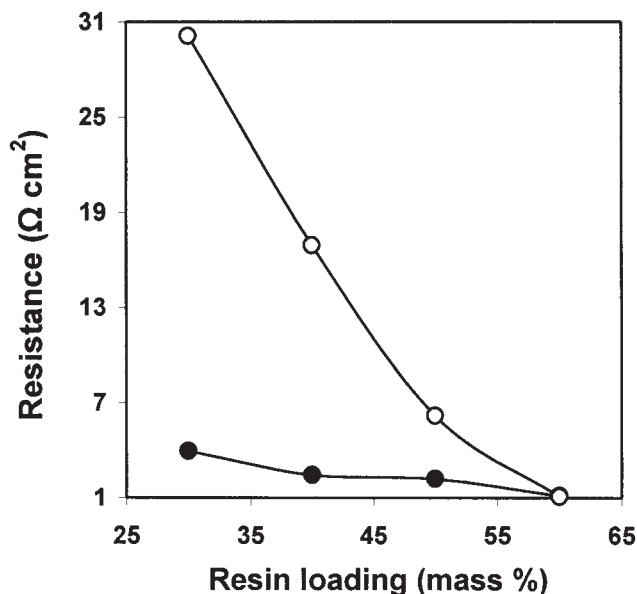


Figure 5 Variation of resistance versus different mass % of resin-loaded membranes measured in CaCl₂ solution. Symbols are similar to those in Figure 2.

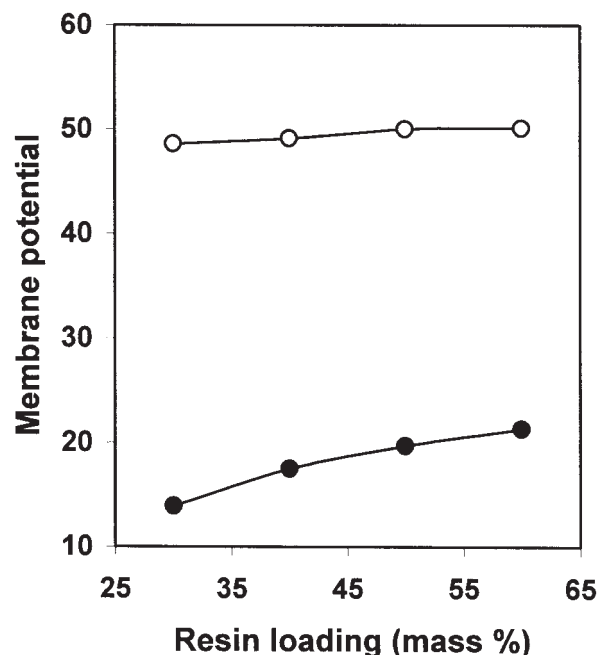


Figure 6 Variation of membrane potential versus different mass % of resin-loaded membranes measured in NaCl solution. Symbols are similar to those in Figure 2.

Membrane potential

When a membrane separates solutions of unequal concentrations of an electrolyte, an electrical potential difference develops across the membrane. This is due to difference in mobility of counter ions and coions in the solutions. The magnitude of this potential depends upon the characteristic charge of the membrane as well as the nature and concentration of electrolyte solution used.^{18,19} The membrane potential data obtained using cation-exchange membranes in sodium chloride and calcium chloride solutions of unequal concentrations ($C_1/C_2 = 10$) are presented in Figures 6 and 7, respectively. The higher value of membrane potential when compared with liquid junction potential for the electrolyte solutions indicates the charged nature of cation-exchange membranes. In the case of the gelation method, the membrane potential is increased with increasing resin loading, and this trend is more significant for calcium chloride solution as compared with sodium chloride. However, in the case of solvent evaporation method, membrane potential did not change much in either solution with increasing resin loading. But, the magnitude of membrane potential in sodium chloride solution is almost double that of calcium chloride solution. This is due to differences in pore size and charges of the counter ions in the membranes.

rent through the membranes carried out by anions and cations are different than the transport numbers of these ions in free solution. For a cation selective membrane, very high fraction of the electrical current can be transported by the cations. In such cases, the transport num-

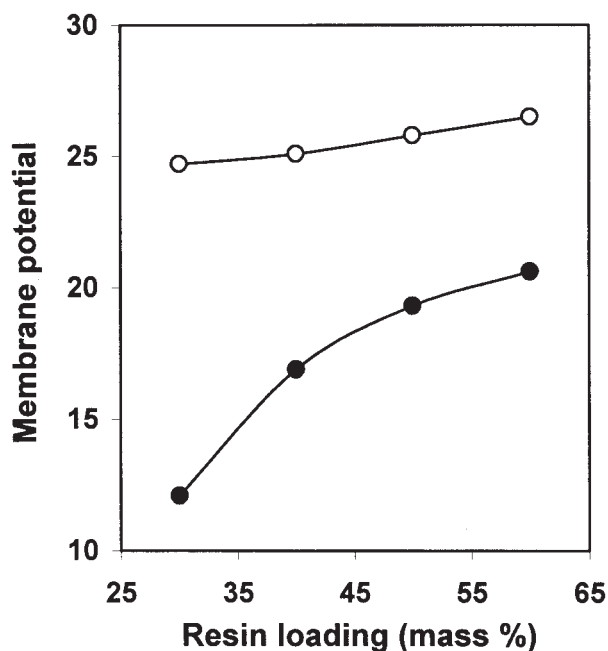


Figure 7 Variation of membrane potential versus different mass % of resin-loaded membranes measured in CaCl₂ solution. Symbols are similar to those in Figure 2.

Transport number

Since transport number is the fraction of total current carried by the counter ions, the transport of electric cur-

ber of cations in the membrane phase is higher than in free solution (without membrane), and thereby the transport number of anions in the membrane phase is lower than in free solution. For an ideal cation selective membrane, the transport number of cation ($t_+ = 1$) is unity and for anion, it is zero ($t_- = 0$). To get the ideal selective membrane, the transport number of the membranes should be equal or near to one. In the present study, the transport numbers of membranes prepared by the solvent evaporation method are found to be in the range of 0.94–0.95, which are close to the transport number of an ideal membrane. However, the transport numbers for the membranes prepared by the gelation method were found to be in the range of 0.63–0.69, which are lower than that of an ideal membrane, and these values are slightly higher than that of an electrolyte solution used.

The transport number of nonelectrolytes through the membrane is determined by the size of the pore they pass through. However, the diffusion path of electrolytes depends on geometric factor as well as an electric factor because of the repulsion of fixed charge ions of the same sign. To determine the transport of ions, one may consider the membranes to be made up of pores with fixed charges on their walls. The fixed charges cannot move, and hence, they are unable to take part in diffusion or in the transport of electrical current through the membrane. If the diameter of the pore is small and the concentration of fixed charges is high, then coions are repelled by the fixed ions. As a result, only the counter ions take part in the transport phenomenon through the membranes, but the repulsion decreases as the polarity of the membrane increases. In such circumstances, coions may also take part in the transport phenomenon in the membrane phase. This occurs when the concentration of an external electrolyte in the solution increases, thereby amount of electrolyte entering the pores of the membrane increases. As a result, the permselectivity of the pores and the transport number of counter ions decreases. At sufficiently high concentrations, some of the electrolytes may penetrate through even the tightest pores, which will decrease their optimal ion selectivity due to the expansion of pore size.

The membranes prepared by the different methods in the present investigation showed different porosity. The pore size of the membranes prepared by the gelation method is higher than those prepared by the solvent evaporation method. Because of the bigger pore size in the membranes prepared by the gelation method, the transport of both coions and counter ions occurs through the membrane. This results in decrease in membrane potential and transport number of the membrane. On the other hand, membranes prepared by the solvent evaporation method may have smaller pore size, which allows only counter ions to pass through while the coions get repelled. Here, the major fraction of the total current is carried only by the

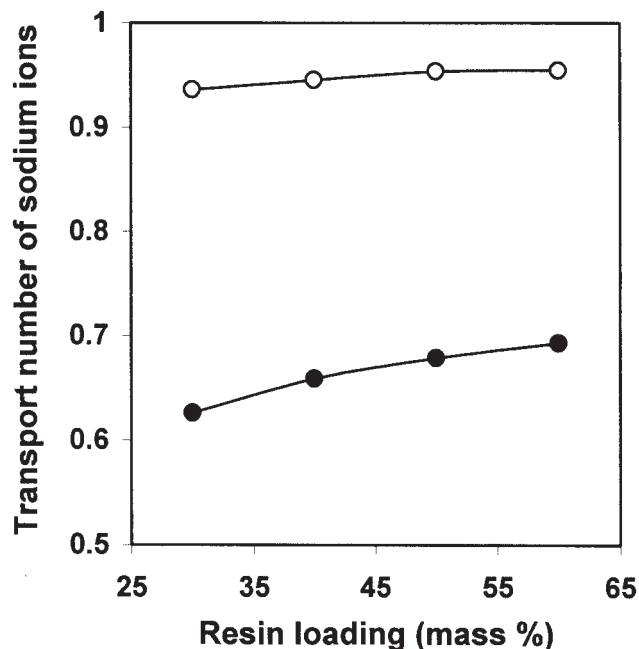


Figure 8 Variation of transport number of sodium ions versus different mass % of resin-loaded membranes. Symbols are similar to those in Figure 2.

counter ions, and hence, the membrane potential as well as the transport characteristics of the membrane increase. If the membrane is porous with no charge, then the transport number of both counter ions and coions taking place through the membrane is equal to the transport number of ions in the solution. But, the present membranes have shown that the transport number of counter ions is higher than that of electrolyte solution, which indicates that membranes prepared here have charged nature.

The membranes prepared with different mass % of resin loading show the expected trends in the transport number, i.e., as the resin loading increases, transport number also increases. This is due to increase of fixed charge density in the membrane. With a further increase in loading, the negative character of the membrane also increases such that the coions repelled from the membrane, and hence, the counter ions enter easily into the membrane. This type of easy transport of counter ions through the membrane increases the membrane potential as well as the transport number.

Figures 8 and 9 display the dependence of transport number of Na^+ and Ca^{2+} ions, respectively, on the resin loading. It is observed that transport number of Ca^{2+} ions is lower than that of Na^+ ions on the resin loading in both the methods. This may be due to the bigger size of the hydrated calcium ions as well as strong electrostatic interactions occurring between calcium ions and water molecules. As the size of the hydrated ion increases, molecular sieving of ions by the membrane also increases because of the difference

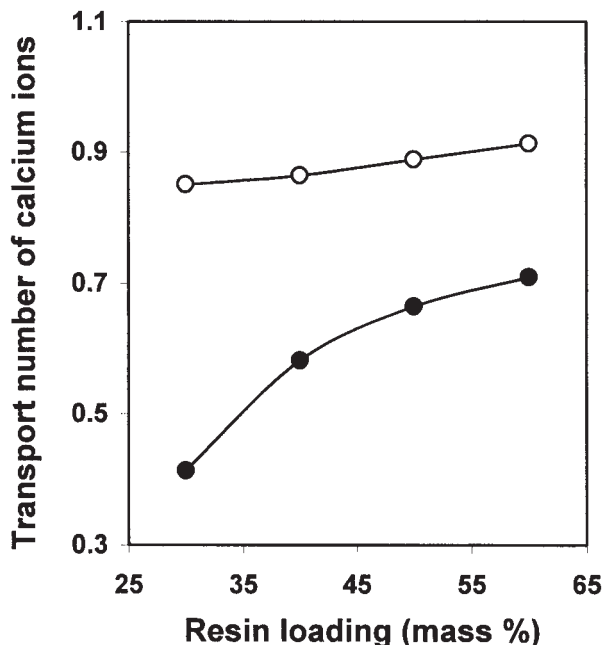


Figure 9 Variation of transport number of calcium ions versus different mass % of resin-loaded membranes. Symbols are similar to those in Figure 2.

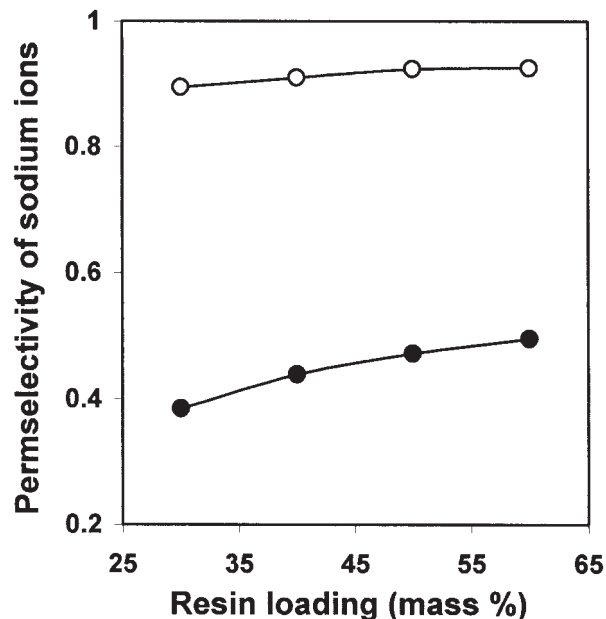


Figure 10 Variation of permselectivity of sodium ions versus different mass % of resin-loaded membranes. Symbols are similar to those in Figure 2.

in the pore size of the membranes. The sieving effect for the membranes prepared by the solvent evaporation method is significantly higher for Ca^{2+} ions than that for Na^+ ions because of the formation of smaller pore size in the membranes as compared with the membranes prepared by the gelation method. As a result, the transport number of calcium ions is comparatively lower than that of sodium ions. On the other hand, a sharp increase is observed for the transport number of Ca^{2+} ions with increasing resin loading as compared with Na^+ ions for the membranes prepared by the gelation method. This is due to increase in fixed negative charge, bigger pore size of the membrane as well as bivalent character of Ca^{2+} ions, which reduce the transport of coions through the membrane, and hence, the transport number is greatly increased by the counter-ions.

Permselectivity

Ion exchange membrane is endowed with permselectivity P_s , which relates to the transport of electric charges by specific counter-ion to the total transport of the electrical charge through the membrane, which can be defined as:²⁷

$$P_s = \frac{(t_i^M - t_i)}{(1 - t_i)} \tag{7}$$

where t_i^M and t_i are the transport of counter-ions in the membrane and in solution, respectively. The perms-

electivity values obtained for different membranes are plotted as a function of resin loading, in Figures 10 and 11. It is observed that the permselectivity of the ions for the membranes prepared by the gelation method is quite lower than the membranes prepared by the solvent evaporation method. Such a low perm-

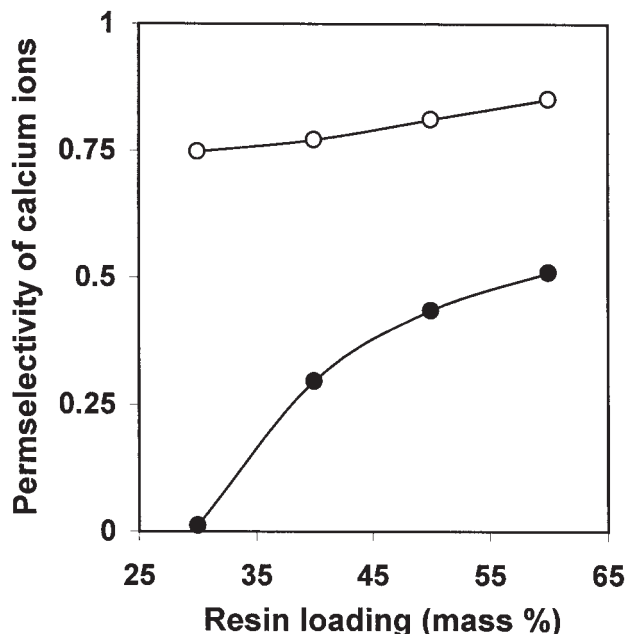


Figure 11 Variation of permselectivity of calcium ions versus different mass % of resin-loaded membranes. Symbols are similar to those in Figure 2.

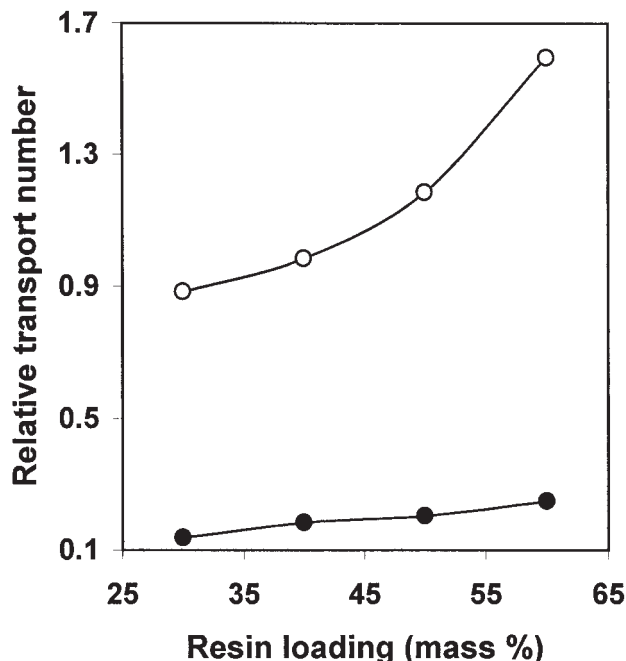


Figure 12 Variation of relative transport number versus different mass % of resin-loaded membranes. Symbols are similar to those in Figure 2.

selectivity of the ions for the membranes prepared by the gelation method may be due to an increase in the pore size of the membrane. As the pore size increases, both the coions and counter-ions can migrate through the membrane easily, and hence, the contribution of the counter-ions to carry the current is reduced drastically. It is also observed that the permselectivity increased sharply for the hydrated Ca^{2+} ions than that of Na^+ ions for the membranes prepared by the gelation method. This may be due to increase of negative charge on the membrane as well as bivalent character of Ca^{2+} ions as the resin loading increased. On the other hand, no such sharp increase is observed either for Ca^{2+} ions or for Na^+ ions for the membranes prepared by the solvent evaporation method. This might be due to the difference in pore size of the membranes prepared by these two methods.

Relative transport number

Figure 12 shows the relative transport number between Ca^{2+} and Na^+ ions in the membranes prepared by the gelation and solvent evaporation methods. As discussed above, the sieving effect of Ca^{2+} ions vary with the methods of preparation as well as by change in the negative character of the membrane. It is observed that as the pore size of the membrane increased, the transport number of counter ion decreases. As a result, the relative transport number of Ca^{2+} ions with respect to Na^+ ions increased monot-

onously with increasing resin loading in case of solvent evaporation method. This is because of increase in electrostatic repulsion between the coions and fixed negative charges of the membranes. On the contrary, the relative transport number of Ca^{2+} ions is low with respect to Na^+ ions for the membranes prepared by the gelation method, suggesting that the membranes have bigger pore size.

CONCLUSIONS

The heterogeneous cation-exchange membranes were prepared by employing different methods. The effect of resin loading and methods of preparation were evaluated and discussed based on the electrochemical properties of the membranes. Swelling behavior indicated that dimensional changes of the membranes do not manifest in both the methods, owing to the formation of micro voids between resin and poly(ethersulfone). The membranes prepared by the gelation method have low ion-exchange capacity and did not change further appreciably as the resin loading increased. This is because of leaching out of some resin particles from the membranes during the gelation process, which is responsible for increase of coions in the free space of the membranes. This further tends to decrease in resistance in both the solutions used, but decrease in resistance is less significant in calcium chloride solution. However, membrane potential increased with increasing resin loading and it is more significant in calcium chloride solution as compared with sodium chloride solution. On the other hand, membranes prepared by the solvent evaporation method have high ion-exchange capacity and increased further with increasing resin loading. This is due to smaller pore size and increase of fixed charges, which further tend to decrease the resistance in both the solutions. However, the observed resistance in calcium chloride solution is less than that of sodium chloride solution because of higher charge of the calcium ions. On the contrary, the membrane potential did not change as the resin loading increased, but the magnitude of membrane potential is almost double in sodium chloride solution as compared with calcium chloride solution. The transport numbers were found to be in the range of 0.94–0.95, which are close to the transport number of ideal membranes, while for the membranes prepared by the gelation method, the transport numbers are in the range of 0.63–0.69, which are not close to the value of ideal membranes. Because of the smaller pore size in the solvent evaporation method, membranes allow only the counter ions to pass through, and hence, membrane potential as well as transport number increases. With increasing resin loading, negative charge increased on the membrane, which leads to the repulsion of coions from the membrane, and hence, both transport number and mem-

brane potential increased. The transport number of Ca^{2+} ions is lower than Na^+ ions with respect to the resin loading in both the methods, because of bigger pore size of the hydrated calcium ion as well as electrostatic interaction occurring between Ca^{2+} and water molecules. This further tends to a significant sieving effect for Ca^{2+} ions because of smaller pore size of the membranes prepared by solvent evaporation method. Increase of pore size enhances the migration of both coions and counter ions through the membranes. As a result, contribution of counter ions to carry the current is reduced drastically. For the membranes prepared by gelation method, the permselectivity increased sharply for the Ca^{2+} ions due to increase in negative charge on the membrane upon increasing the resin loading as well as bivalent nature of calcium ion. Accordingly, transport number of Ca^{2+} ions relative to sodium ions increased monotonously with increasing resin loading in case of solvent evaporation method. However, the transport number of Ca^{2+} ions is low relative to Na^+ ions for the membranes prepared by gelation method. Therefore, in the present study, the solvent evaporation method yielded the most desirable sodium-selective membranes, which can be used for the commercial applications in electro dialysis processes.

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