

Transport of Sodium Chloride, Urea, and Creatinine Through Membranes Derived From Methylmethacrylate-co-Methacrylic Acid and Its Ionomers

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SYNOPSIS

Permeabilities of cast films of methylmethacrylate-co-methacrylic acid (MMA-MAA) and its 5% neutralized Na¹⁺, CS¹⁺, Zn²⁺, Ba²⁺, and Al³⁺ ionomers for urea, sodium chloride, and creatinine were determined using a double (donor and acceptor) compartment cell. Film permeability was increased as the ionic potential decreased and it was more marked with urea as compared with sodium chloride and creatinine. Tensile properties of the above samples were also tested and variations in Young's Moduli were based on the effect of type of aggregates produced by the cations in the matrix of the copolymer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In general, an ionic polymer is a polymer, either inorganic or organic, which contains both covalent and ionic bonds in its chain or network structure.¹ In the majority of cases, the covalent bonds themselves already exist in the chain, sheet, or network form, which are characteristics of polymers; the ionic bonds are additional to this structure and help to modify the properties (i.e., glass transition temperature,² modulus, viscosity, yield strength, transport properties, and ultimate tensile strength).³ These properties can be changed by altering the parent copolymer, the nature and concentration of the reactive groups, the cations, and the degree of neutralization.⁴

The terms "ion exchange" and "ionomer" are both used to qualify membrane polymers that bear fixed acidic or basic groups or either salts. Although the terms are sometimes used interchangeably, there is a difference in degree; ion exchange is used to refer to those polymers with high capacities, whose strong tendency to hydrate and swell is held in check by high density of covalent crosslinks.

Ionomers, on the other hand, usually contain between 2–15 mol % of monomers with ionic groups present inside the chains. Due to their lower capacities, they often do not require crosslinking to inhibit swelling.⁵ Another difference between traditional ion exchange membranes on the newer ionomeric type is generally the superior film-forming characteristics of the latter.

A series of recent publications have explored the transport properties of ionic polymer membranes.^{6–8}

The perfluorinated, carboxylated, and sulfonated ionomer membranes, which form ionic clusters of a few nm in size, are commonly used as membranes. The ionic clusters strongly affect physical properties of the membranes, for example, the swelling behavior of the membranes (amount of water taken up by the membrane and the amount taken up by a single functional group). The ionic clusters affect crystallinity, the inter lamellar spacing and spherulite size.

For a given equivalent weight, in comparison with the membranes having sulfonic acids, the membranes having carboxylic acids have smaller ionic clusters due to the weaker electrostatic energy released upon the cluster collapse, leading to greater crystallinity and spherulitic structure. The sulfonic acid and sulfonated membranes do not have spherulitic structure. The greater crystallinity of the carboxylic acid membranes, together with a lower af-

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finity of carboxylic acid groups to water, results in a lower amount of water taken up and a smaller single functional group, which in turn results in smaller cluster size in wet, in comparison to the sulfonic-acid membranes.⁹

T. Nakanishi et al. measured the permeabilities of NaBr, and four tetra alkylammonium bromides for negatively charged, positively charged, and neutral poly(methyl methacrylate) stereocomplex membranes in aqueous systems. They reported that for anionic membranes the dependence of salt permeability varies according to the cation size.¹⁰

R. Y. M. Huang used copolymer systems containing a poly(carboxylic acid) as one component, which has been ionically crosslinked in the form of membranes using multivalent metal salts.¹¹ They reported that for the ionically crosslinked membranes, the permeability coefficients decreased exponentially with increasing permeant mol wt. R. Y. M. Huang et al. also studied polysulfone-ionically crosslinked poly(acrylic acid) composite membranes as reverse osmosis membranes and found them suitable for desalination of low concentration salt solutions.¹²

P. G. Glugla measured the permeabilities of aniline, *p*-chloroaniline, *p*-nitroaniline, and urea in perfluorosulfonated ionomer membranes.¹³

We have previously studied transport properties of poly(methylmethacrylate-*co*-methacrylic) acid Poly(MMA-*co*-MAA) ion containing membranes. Several membranes were prepared from the copolymer and its Li⁺ and Zn²⁺ ionomers and they were tested for NaCl, creatinine, and urea permeability.⁸ In this study, we have tried Cs⁺, Na⁺, Ba²⁺, and Al³⁺ ionomer membranes for the same permeants and tried to correlate membrane permeability to charge and size of the cations in the polymer matrix. The tensile properties of the above samples were also investigated and variations in the Young's Moduli with the ionomer type were reported.

EXPERIMENTAL

Material

Poly(MMA-*co*-MA), with a ratio of carboxyl to ester groups of 1 : 2 and mol wt of 135,000, was obtained from Rohm Pharma. All other chemicals, such as organic solvents, organic and inorganic compounds, as well as metal salts, were Merck products.

Preparation and Characterization of Ionomers

The acid content of the MMA-MAA copolymer was partially neutralized to the required degree with

suitable cations by stirring the copolymer-ion solution overnight at room temperature. Degrees of neutralization were checked by back titration with 0.1 N NaOH and the solutions of ionomers were precipitated in deionized water and vacuum dried till constant weight.

The ionomers were characterized by viscometric measurements using an Ubbelohde viscometer in Dioxane and acetone at 20°C.¹⁴

Film Casting and Characterization of Membrane 1

2.5 mL of 5 wt % solution of the copolymer in ethyl-alcohol was casted on a glass plate (9 cm × 9 cm) and after a gelation period of 10 min, it was immersed in deionized water and the film was removed. The thickness of the membranes thus prepared were approximately 50 μm–100 μm.

Membranes 2, 3, 4, 5, 6

The copolymers were 5% neutralized with suitable cations, that is, NaOH, CsCl, Zn(AC₂H₅O₂)₂, Ba(OH)₂, and Al(OH)₃, respectively, and membranes were prepared in the same way as membrane 1.

Mechanical tests on the membranes were performed by using an Instron tensile testing machine. The samples were pressed with a Platon press at a temperature 50°C above the glass transition temperatures.

Permeability Measurements

Permeation was conducted at 23°C using the double (donor and acceptor) compartment cell previously described.⁸ The effective membrane area was 9.07 cm². At time zero, the donor compartment of the cell was filled with 90 mL of aqueous solution that dissolved the substrate (NaCl, Urea, or Creatinine) and in the acceptor compartment, water. Both compartments were magnetically stirred at a constant rate. Samples were taken at hourly intervals and were analyzed for urea and creatinine by Perkin-Elmer UV spectrophotometry, (UV-160), at absorptions λ = 435 nm and λ = 555 nm and NaCl by electric conductivity (EM 776). Permeation rates were calculated.

RESULTS AND DISCUSSION

The results of viscometric measurements of membranes were shown in Figure 1. It is clearly observed from the figure that at low polymer concentrations, the polymer chain expanded in polar solvents, due

to solvation and the repulsive nature of the ionic charges, increases the reduced viscosity, and as a result the polyelectrolyte effect is observable.¹⁵ This behavior was considered to be the characteristic property of an ionomer.

The permeability coefficients for all the membranes were calculated using the following equation.¹⁶

$$J_s = P_2 \frac{\Delta C}{\lambda} \quad (1)$$

Where J_s , ΔC , and λ are solute flux (mol/cm^2), concentration difference (mol/cm^3) across the membrane and membrane thickness, respectively. The coefficient P_2 was calculated from the expression

$$P_2 = \frac{2.303\lambda V''}{\left(1 + \frac{V''}{V'}\right) A t} \log_{10} \frac{c_o}{c_o - \left(1 + \frac{V''}{V'}\right) C_t''} \quad (2)$$

where V' , V'' , A , C_o , and C_t'' are the volumes of the donor and acceptor compartments, effective membrane area, initial concentration of the concentrate and the concentration of the diluent at sampling time t , respectively. Rearranging eq. (2) and assuming:

$$\left(1 + \frac{V''}{V'}\right) A t = x \text{ and}$$

$$\left(2.303 V'' \log \frac{C_o}{C_o - \left(1 + \frac{V''}{V'}\right) C_t''}\right) = y$$

P_2 was calculated as the slope of the X vs. Y line and the results are reported in Figures 2, 3, and 4 and in Table I for NaCl, urea, and creatinine, respectively. Permeability coefficients changed, depending on the nature of the cation and the permeant.

There are two main factors that affect the permeability of the ionomer membranes. One of them is the structural features of the ionomer membranes, which are mainly determined by the types of the cations.

If the MMA-MAA copolymer matrix is considered, it consists of segments of homogeneous phase, that is, the hydrocarbon chain segment, and inhomogeneous micro phase of great cohesive strength due to ionic forces. The inhomogeneous region in the copolymer consists of ionized carboxyl groups and the cation aggregation.¹⁷ There are also various types of ionic domains where ionic forces, unlike the covalent bonds found in chemical crosslinking, are diffuse and nondirectional.

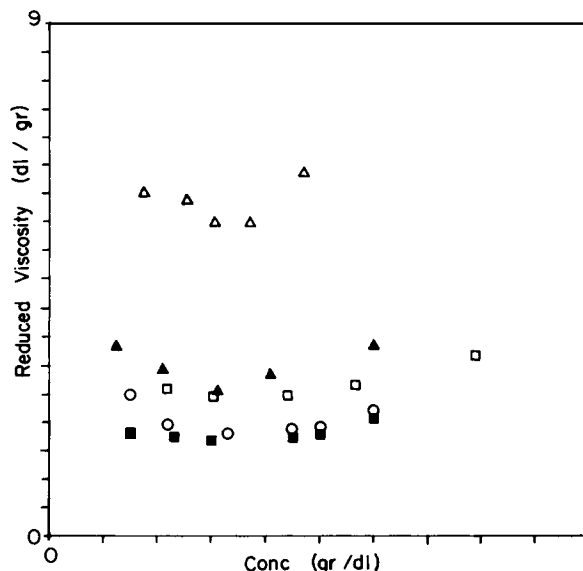


Figure 1 Reduced viscosity vs. concentration curves. Ionomers: Δ (Al^{+3}); \blacktriangle (Ba^{+2}); \square (Na^{+1}); \blacksquare (Cs^{+1}); \circ (Zn^{+2}).

In such a case, the valency at the ions is a convenient way to measure the intensity of the forces involved, due to the fact that the degree of ionization on the polymer chain has a fundamental effect, because it represents the intensity of the coulombic forces in the ionic domains. This phenomenon gives an indication of the spacing between sides of high interchain attractions.

The permeability of these membranes is explained by the capillary model, allowing for slightly tortuous sides.¹⁸ The pores in these membranes are caused by interstices between the homogeneous regions, so that the sizes of the interstices are important, which implies that as the size of the cation aggregation increases, a large average cavity volume in the polymer will be produced. It is reasonable to assume that each ion species will behave differently because of the ratio of charge intensity to ionic radius effect, which is called ionic potential.

The higher the ionic potential of the metallic ion, the larger the repulsive forces between the cations and the more difficult it becomes to form ionic clusters. This will lead to the ionic species being dispersed in the polymer matrix as the crosslinking agent, causing a decrease both in the pure size and in the size of the interstices resulting tortuous pores and less permeable membrane. This fact is reflected in Tables I and II; the permeability is highest in the case of the Cs^+ ionomer, which has the lowest ionic potential with the largest interstices size, thus causing larger pore size. The Al^{3+} ionomer has lower

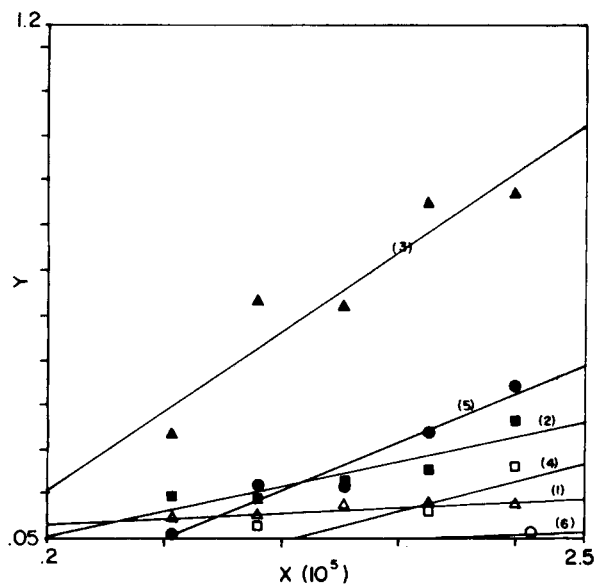


Figure 2 NaCl permeability curves. (1) Copolymer; (2) Na⁺ Ionomer; (3) Cs⁺ Ionomer; (4) Zn²⁺ Ionomer; (5) Ba²⁺ Ionomer; (6) Al³⁺ Ionomer.

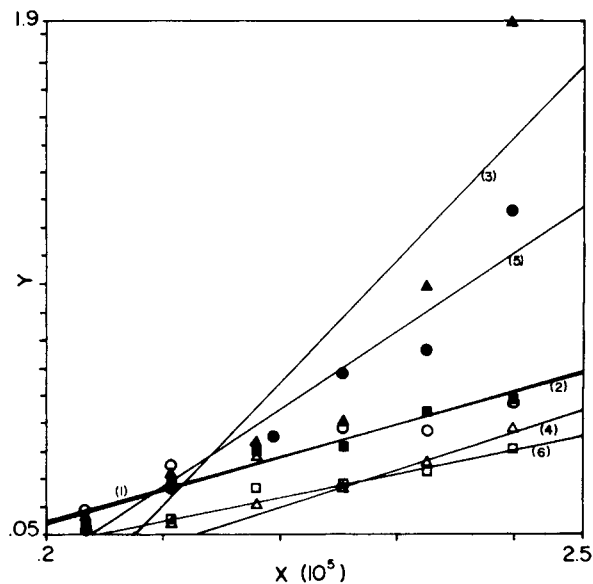


Figure 4 Creatinine permeability curves. (1) Copolymer; (2) Na⁺ Ionomer; (3) Cs⁺ Ionomer; (4) Zn²⁺ Ionomer; (5) Ba²⁺ Ionomer; (6) Al³⁺ Ionomer.

permeability, due to its highest ionic potential, thus producing a highest percentage of crosslinking through the chains, which lead to tortuous pores.

As a second factor, membrane permeability is affected also by the type of permeant, as listed in Table I. All the membranes are considerably more per-

meable to urea than sodium chloride, although they have almost the same molecular size. This can be explained on the basis of swelling behavior of membranes. It is suggested that urea promoted film swelling by disrupting hydrogen bonds in the polymer structure,¹⁹ while sodium chloride reduced the swelling by competitively blocking water sorption to hydrophilic (cationic) sites in the polymer. Interaction of charged groups on the membrane pore walls with ionic solutes to cause attraction and/or repulsion has been proposed as a solute mechanism for lower permeability of ionic solutes in polymer membranes.^{20,21}

Hydration of the cations may also be an important factor for the transport properties of the mem-

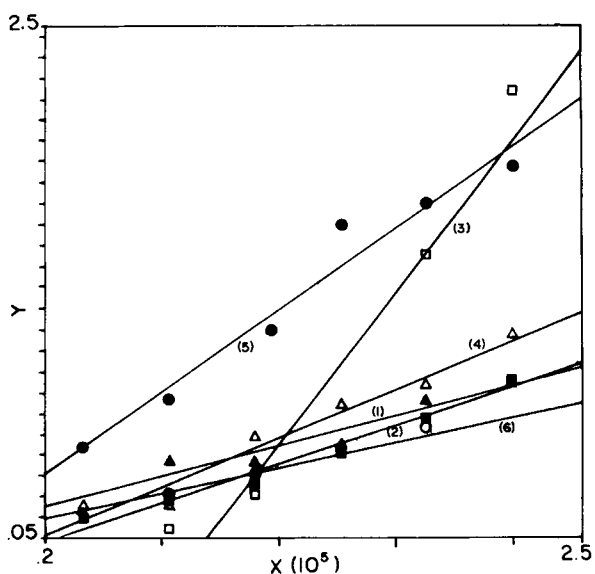


Figure 3 Urea permeability curves. (1) Copolymer; (2) Na⁺ Ionomer; (3) Cs⁺ Ionomer; (4) Zn²⁺ Ionomer; (5) Ba²⁺ Ionomer; (6) Al³⁺ Ionomer.

Table I Permeability Coefficients of the Membranes

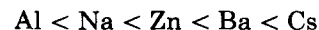
Membrane Ionomers	Permeability Coefficients × 10 ⁻⁶		
	NaCl	Urea	Creatinine
H ⁺	0.5	3.00	2.5
2	0.75	3.75	1.75
3	3.5	22.5	6.00
4	1.5	4.25	3.25
5	2.00	7.50	4.75
6	0.25	1.60	1.75

branes. A useful treatment of ions in solution has been developed by Henry S. Frank and his coworkers.²² They have concluded that for ions in aqueous solution, it is possible to distinguish three different zones in the neighborhood of the solute molecule. In the immediate vicinity of the ion, there is a shell of water molecules that are more or less immobilized by the high field due to the cation. Surrounding this, there is a second region; the third region around the ion comprises all the water sufficiently far from the ion that its effect is not felt. As a result, the smaller the ion, the greater the binding energy between the ion and a water molecule and thus the immobility is lower for such ions.

The arrangement of the water molecules around the ions is dependent on the coordination number of the ions. As shown below, there are more than one coordinate number for an ion and as this number increases, the hydrated radius is increased.

Ion	Coordinate Number	Ionic Radius (Pm)
Al ³⁺	4	53
	5	62
	6	67.5
Ba ²⁺	6	149
	7	152
	8	156
	9	161
	10	166
	11	171
Cs ⁺	12	175
	6	181
	8	188
	9	192
	10	195
	11	199
Na ⁺	12	202
	4	113
	5	114
	6	116
	7	126
	8	132
Zn ²⁺	9	138
	12	153
	4	74
	5	82
	6	88
	8	104

As can be concluded from the above information, it is difficult to give an exact value for the hydrated radius of a cation. Yet, it can be concluded that the larger the ionic radius, and the higher the coordination number, the more permeable will be the membrane. If the data in Table I is reconsidered, the permeability of the membranes increase in the order:



Therefore, the lower permeabilities of all the membranes initially are due to the occurrence of diffusion of localization-activated jumps from one preexisting cavity to another and the activation energy involves the hundred rotations of a few contiguous monomer segments with perhaps some bond stretching to allow the passage of the penetrant. Creatinine has less permeability than urea, due to the difference in molecular size, however, greater permeability compared to sodium chloride is observed because it is a covalently-bonded molecule and no interaction is expected with the membrane.

The results, which are reported in Table II, show that the tensile strength is affected by the nature of the cations, which are located on the carboxylic groups. This behavior can be understood by examining the Bonotto Bonnen model,⁵ where there are submicroscopic regions of the polymer in which lamellar domains are interspersed with "ionic pockets." In these ionic regions, there may be several intermolecular associations involving carboxyl, carbonyl, and carboxylate groups, and the cations. The number of ionic association is determined primarily by the percent of ionization and the original acid content of the copolymer.

It is helpful to consider the pockets as a multi-functional ionic "filler" units reinforcing the dispersed lamella, in this term it is easy to see why the strength properties of the polymer are improved by the ionization and the type of cation. In more general terms, the mechanical behavior and the strength of ionomers appear dominated by the existence of "hard" regions of the ionic groups, which strengthen the cohesion in the hard domains as crosslinks.²⁰

The types of cations used in neutralization also show different influences on the mechanical properties of monomers. The tensile strength of the ionomers decreases in the following order.



This also shows that the ionic potential of the metallic ions is an important factor influencing the

Table II The Results of Tensile Strength Measurements

Membrane Ionomers	Stress at Break (MPa)	Strain at Break ($\times 10^{-3}$)	Young (dyne/cm ²) Modulus ($\times 10^3$)
1	18.58	3.98	5.50
2	24.95	3.98	8.00
3	20.00	3.41	7.50
5	26.53	3.98	11.00
6	33.66	3.98	15.00

properties of an ionomer. The higher the ionic potential, the more dispersed ionic clusters are and, therefore, the greater the strength of the ionomer. Hence, the univalent cations possess lower tensile strength than those of di- or trivalent cations; this is due to the presence of larger proportions of carboxylic-groups crosslinks between two macromolecules.²²

CONCLUSION

The rate of transport of NaCl, Urea, and creatinin in poly(MMA-co-MAA) ionomer membranes is controlled by the ionic potential of the ions in the ionomer. The permeability coefficients increased as the ionic potential decreased. The stress at the break and the Young's Moduli of the membranes were also studied; the variation again confirmed the ionic potential effect in the polymer matrix.

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