Dynamically formed hydrous zirconium (iv) oxide-polyelectrolyte membranes. ix. Poly(acrylic acid-co-hydroxyethyl acrylate) and poly(acrylic acid-co-hydroxyethyl methacrylate) membranes

AJ van Reenen*, S Gerber and RD Sanderson
Institute for Polymer Science, University of Stellenbosh, Stellenbosch 7600, South Africa.

Abstract

A series of two different copolymers were synthesised. These copolymers were poly(acrylic acid-co-hydroxyethyl acrylate) (C_1 to C_3) and poly(acrylic acid-co-hydroxyethyl methacrylate) (C_4 to C_6). Hydrous zirconium (IV) oxide - C_1 to C_6 membranes were dynamically formed. The effect of varying feed concentration and pH on these membranes, in terms of the copolymer compositions, is reported.

Introduction

The use of polyelectrolytes other than poly(acrylic acid) as dynamic membrane polyelectrolytes, as well as the effect of polymer composition on membrane properties have been discussed in previous papers (Van Reenen et al., 1988 and 1989; Van Reenen and Sanderson, 1989 a-f). In this paper the use of two new polyelectrolytes as dynamic membranes, poly(acrylic acid-co-hydroxyethyl acrylate) and poly(acrylic acid-co-hydroxyethyl methacrylate) is discussed.

Background

The historical background of dynamic membranes has been discussed previously (Van Reenen et al., 1988). The copolymers discussed in this paper have not been used previously to form dynamic membranes. Similar types of copolymers have been used in the development of a low pressure membrane on flat sheet microporous supports, and the subsequent development of a hollow fibre membrane (NTIS, 1985).

Experimental

Monomer purification

Acrylic acid (AA), hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA) were all purified by distillation under reduced pressure. The distilled monomers could be stored for short periods of time at 4°C.

Polymerisation

Copolymers were prepared from the following monomer feed ratios: AA:HEA 25:75; 50:50; 75:25; AA:HEMA 25:75; 50:50; 25:75. The reaction was carried out as follows:

AA:HEMA 25:75

Acrylic acid (2,26g $3,14\times10^{-2}$ moles), hydroxyethyl methacrylate (12,19g $9,38\times10^{-2}$ moles) and distilled 1,4-dioxane (120 mℓ) were poured into the two-neck round-bottomed flask. The stirred reaction mixture was heated to 348°K by immersing the flask in a preheated oil bath. A nitrogen gas flush was introduced through the side-arm. After 5 min the nitrogen gas flush was terminated and benzoyl peroxide ($6,60\times10^{-2}$g $2,73\times10^{-4}$ moles) dissolved in 20 mℓ 1,4-dioxane was added to the reaction mixture through the side-arm. The side-arm was then sealed and the reaction was allowed to continue at 348°K for 2,5 h. The reaction was stopped by the addition of hydroquinone to the mixture.

The polymer was precipitated by pouring the reaction mixture into 300 mℓ of a non-solvent, diethyl ether, contained in a 500 mℓ beaker. The supernatant liquid was decanted and the precipitated polymer was washed twice with 30 mℓ diethyl ether and then dried to constant mass at 303°K under reduced pressure. The dried polymer was weighed and stored in a sealed container.

Yield

8,72g or 60,35% polymer.

The monomer concentration in the reaction medium was kept below 10% to prevent crosslinking occurring during the course of polymerisation. This polymerisation technique was based on a method described by the National Starch and Chemical Corporation (1965) and was modified according to a technique described by Van Reenen and Sanderson (1989b). The reaction conditions of the other reactions are given in Table 1.

Characterisation

NMR

Carbon-13 NMR was used as a technique to determine the copolymer compostion. Polymer codes and composition analysis are summarised in Table 2. Solution viscometry was used to determine the intrinsic viscosity of each copolymer. This data were compared with the intrinsic viscosity of a poly(acrylic acid) polymer with known molecular mass.

Membrane formation

The membrane formation equipment and technique was previously discussed (Van Reenen et al., 1988) and will not be repeated here.

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*To whom all correspondence should be addressed.
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TABLE 1
REACTION CONDITIONS FOR THE COPOLYMERISATIONS

| Polymer | AA | | HEMA | | HEA | | Dioxane | Benzoyl peroxide | | Temperature (K) | Yield (%) |
	g	mole (x10⁻²)	g	mole (x10⁻²)	g	mole (x10⁻²)	ml	g (x10⁻²)	mole (x10⁻⁴)		
C_2	4,52	6,28	8,12	6,25			120,0	6,01	2,48	348	68,61
C_3	8,97	12,50	5,41	4,16			120,0	6,60	2,74	348	73,40
C_4	2,68	3,72			12,43	10,70	120,0	9,41	3,89	348	31,70
C_5	5,98	8,31			9,67	8,34	120,0	9,23	3,81	348	40,83
C_6	9,02	12,50			4,83	4,16	120,0	8,03	3,32	348	51,84

Membrane evaluation

After membrane formation the membranes were evaluated in terms of their performance, the influence of pH on salt rejection and permeate flux and the effect of feed concentration on salt rejection and permeate flux. For this study two sets of three membranes in series were made for each copolymer. An average value was then taken as being representative of a specific membrane's rejection or flux.

Membrane performance

Flux and rejection measurements were taken 48 h after membrane formation. Test conditions were carefully maintained at 6 m/s crossflow velocity, 6 MPa pressure, 2 000 mg/ℓ $NaNO_3$ feed concentration, pH 7,0, and feed temperature 35°C.

The influence of pH

The pH of the feed solution (0,0235 mole.dm⁻³ $NaNO_3$) was adjusted to pH 5,0 by the addition of 55% HNO_3. Thirty minutes were allowed for the membrane to stabilise, before flux and rejection measurements were taken. The pH was increased to 6,0 by the addition of a 10% solution of NaOH. Again thirty minutes were allowed for stabilisation before flux and rejection measurements were taken. The process was repeated for pH values of 7,0, 8,0 and 9,0. Throughout this test the feed concentration was kept constant at 0,0235 mole.dm⁻³ $NaNO_3$, the temperature at 35°C, the pressure at 6 MPa and the crossflow velocity at 6 m/s.

The influence of feed concentration

The feed concentration was set to 0,235 mole.dm⁻³ $NaNO_3$. After allowing 30 min for the membranes to stabilise, flux and rejection measurements were taken. The process was repeated for feed concentrations of 0,176, 0,141, 0,118, 0,0941, 0,0706, 0,0471, and 0,0235 mole.dm⁻³ $NaNO_3$. The decrease in concentration was effected by dilution with RO permeate water. Throughout the experiment the pH was maintained at 7,0, the pressure at 6 MPa, the crossflow velocity at 6 m/s and the temperature at 35°C.

Results and discussion

Copolymer composition

The composition and codes of the synthesised copolymers are given in Table 2.

TABLE 2
COPOLYMER COMPOSITION

Polymer code	Acrylic acid (%)	Hydroxyethyl acrylate (%)	Hydroxyethyl methacrylate (%)
C_1	21		79
C_2	48		52
C_3	71		29
C_4	24	76	
C_5	50	50	
C_6	73	27	

Molecular mass

The intrinsic viscosities of copolymers are given in Table 3.

TABLE 3
INTRINSIC VISCOSITIES OF COPOLYMERS

Polymer code	% Acrylic acid (%)	Intrinsic viscosity [μ]
C_1	21	0,518
C_2	48	-
C_3	71	0,757
C_4	24	0,062
C_5	50	0,106
C_6	73	0,104
PAA	100	0,678

PAA = poly(acrylic acid) molecular mass = 190 000

Membrane performance

The peak rejection and flux figures for composite membranes $Zr-C_1$ to $Zr-C_6$ are given in Table 4 (feed concentration 0,0235 mole.dm⁻³ $NaNO_3$).

The two functional groups responsible for the rejection and flux exhibited by these copolymer membranes, the carboxylic acid

| TABLE 4 |
| PERFORMANCE OF THE DYNAMICALLY FORMED ZR-C$_1$ TO ZR-C$_6$ MEMBRANES |

Membrane	Rejection (%)	Flux (ℓmd)*
Zr-C$_1$	59,6	2 600
Zr-C$_2$	79,5	1 950
Zr-C$_3$	87,0	2 250
Zr-C$_4$	72,0	3 570
Zr-C$_5$	82,0	2 590
Zr-C$_6$	84,2	2 900

*ℓmd:ℓ/m².d

group of acrylic acid and the 2-hydroxy ethyl acrylate group of hydroxyethyl methacrylate, were present in various proportions in the respective copolymers. These two functional groups were responsible for two different mechanisms of rejection. Rejection due to the carboxylic acid groups was based on an electrokinetic mechanism. Ionised carboxylic acid groups rejected hydrated salt ions due to Donnan exclusion. Rejection by the hydroxy groups occurred by a solution diffusion mechanism based on the ratio of diffusion of hydrated salt ions through water and through the membrane (Van Reenen and Sanderson (1989a). The total rejection of a membrane was a combination of both mechanisms and the contribution of each mechanism towards total rejection depended on the copolymer's composition.

It would appear that within these series of copolymers the decrease in acrylic acid content has a deleterious effect on membrane rejection. It seems fair, therefore, to assume that for a polyelectrolyte of this chemical composition, rejection due to Donnan exclusion should be the dominant mechanism of rejection. Correspondingly, one could say that the acrylic acid-hydroxylethyl methacrylate copolymer membranes (Zr-C$_1$ to Zr-C$_3$) have lower fluxes than the corresponding hydroxyethyl acrylate copolymer membranes (Zr-C$_4$ to Zr-C$_6$). Comparison of the two copolymer ranges shows that the C$_4$ to C$_6$ copolymers were more hydrophilic

than the C$_1$ to C$_3$ copolymers. This is due to the absence of the α-methyl group. This increased hydrophilicity led to increased rejection at low acid content since water could be transported with greater ease through the membrane. This phenomenon is also reflected in the behaviour of the homopolymers of the two acrylate monomers: poly(hydroxyethyl acrylate) is water-solube, while poly(hydroxylethyl methacrylate) is not.

The effect of feed concentration

As has been shown by Van Reenen and Sanderson (1989f), the effect of the feed concentration on rejection is affected by the presence (or absence) of charged groups on the polymer. Using the Donnan equilibrium as basis, Sachs and Lonsdale (1971) derived the following relationship:

$$\log(1-R_{obs}) = \log c_f - \log X$$

with:

R_{obs}	= Observed rejection
c_f	= Feed concentration
X	= Charge density

Theoretically, a totally charged ion-exchange body will give a slope of unity when $\log(1-R_{obs})$ is plotted against $\log c_f$ for a uni-univalent salt. If the charge on the body is reduced, the slope should decrease, and become virtually zero for an uncharged body. Therefore, as we change the amount of neutral comonomer in the two acrylic acid copolymer series this change should be reflected in the changing slope of the $\log(1-R_{obs})$ vs $\log c_f$ plots. The results are shown in Fig. 1 and Table 5.

| TABLE 5 |
| THE SLOPES OF LOG(1-R$_{obs}$) vs LOG c$_f$ PLOTS FOR HYDROUS ZIRCONIUM (IV) OXIDE-C$_1$ TO C$_6$ MEMBRANES |

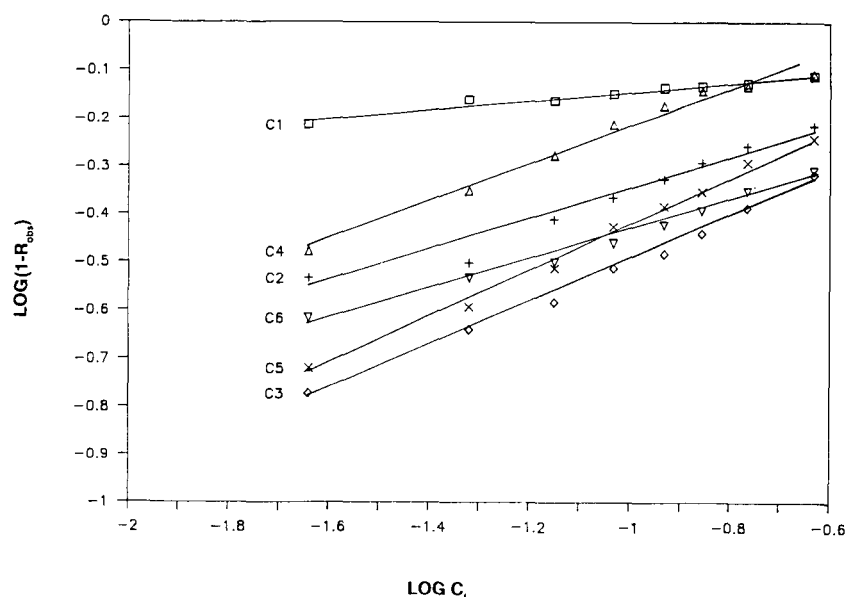| Membrane	Slope
Zr-C$_1$	0,101
Zr-C$_2$	0,337
Zr-C$_3$	0,447
Zr-C$_4$	0,368
Zr-C$_5$	0,476
Zr-C$_6$	0,354

Figure 1
Log(1-R$_{obs}$) vs log C$_f$ for C$_1$ to C$_6$ copolymer membranes

With the exception of the Zr-C$_6$ membrane, the slopes of the plots for the various membranes follow the expected trend. As the acrylic acid content is decreased, the slope decreases, indicating a decrease in the influence of feed salt concentration on salt rejection. Also noticeable (again with the exception of Zr-C$_6$) is that the slopes for the acrylic acid-hydroxyethyl methacrylate copolymer membranes are all lower than the corresponding acrylic acid-hydroxethyl acrylate membranes. Once again, this can be ascribed to the more neutral nature of the hydroxyethyl methacrylate as opposed to the hydroxyethyl acrylate groups.

The influence of pH

In general it would be expected that a lowering of the pH from 7,0 to 5,0 would lead to a decrease in the number of ionised carboxylic acid groups (fixed charges) present in the polyelectrolyte, because protonation of these groups will occur. The result of this decreased charge density would be twofold. First, rejection due to the ion-exchange properties (Donnan exclusion) of the membrane will decrease. Second, a decrease in charge density will lead to a decrease in the hydrodynamic volume of the polyelectrolyte since swelling is caused by electrostatic repulsion of the fixed ionised carboxylic acid groups. The amount of water bound by the ionised carboxylic acid groups will also decrease. This will lead to a decrease in the frictional forces inhibiting water transport through the membrane causing an increase in membrane flux. Frictional forces in the membrane inhibiting water transport through the membrane will also be decreased due to the reduced charge density and volume. Increasing the pH from 5,0 to 9,0 will lead to a reversal of the trends discussed above. The influence of pH on rejection and flux as discussed above is illustrated in Figs. 2 to 13.

Copolymer influence

A comparative study was done to determine to what extent the pH dependence of the various copolymers was influenced by their composition. The changes in rejection and flux between pH 5,0 and pH 7,0 and pH 5,0 and pH 9,0 were used for comparison according to a method used by Van Reenen and Sanderson (1989c) in similar studies.

As had been done previously (Van Reenen and Sanderson, 1989c), two values R'' and J'' were defined, where R'' and J'' represent the membrane's susceptibility to pH change for rejection and flux respectively. If R_i and J_i represent the rejection and flux at pH=i, and R_j and J_j represents the rejection and flux at pH=j, j>i, then let:
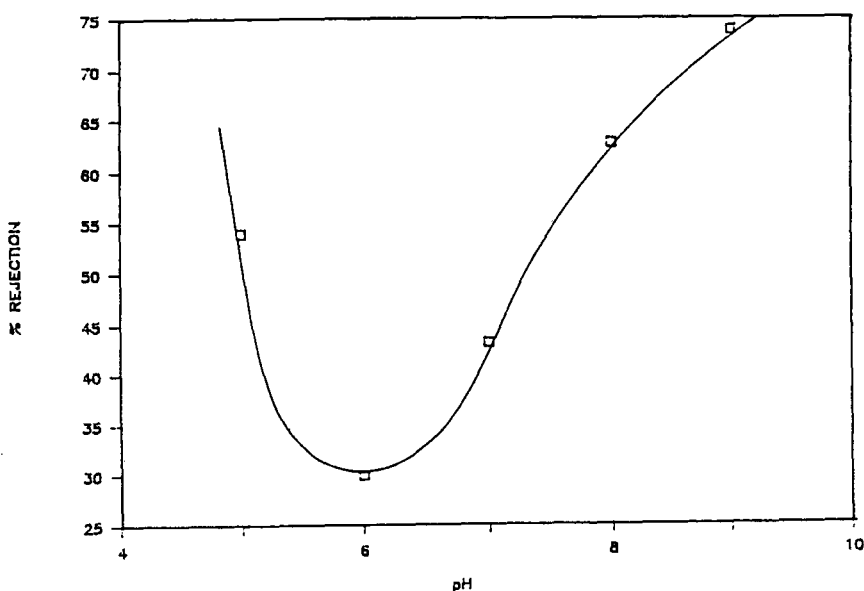

Figure 2
Effect of pH on rejection 21% acrylic acid

Figure 3
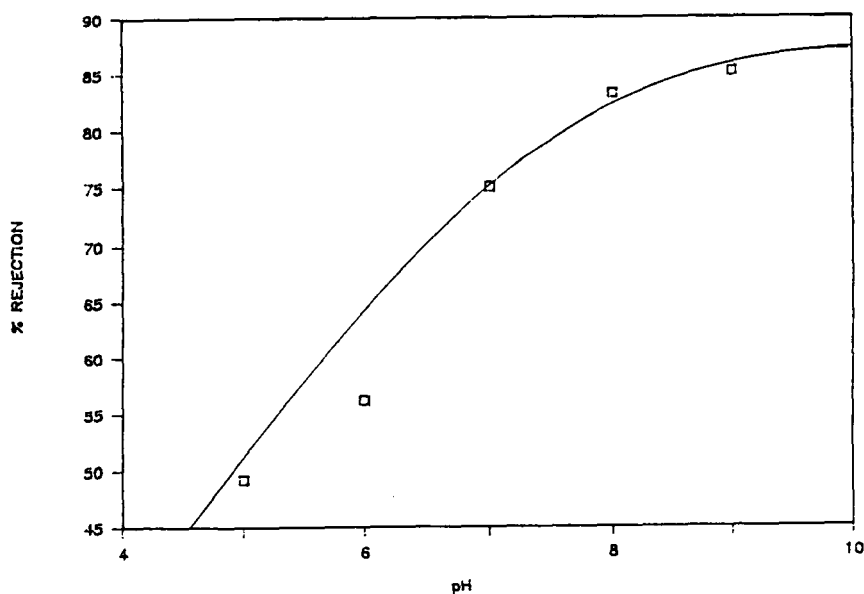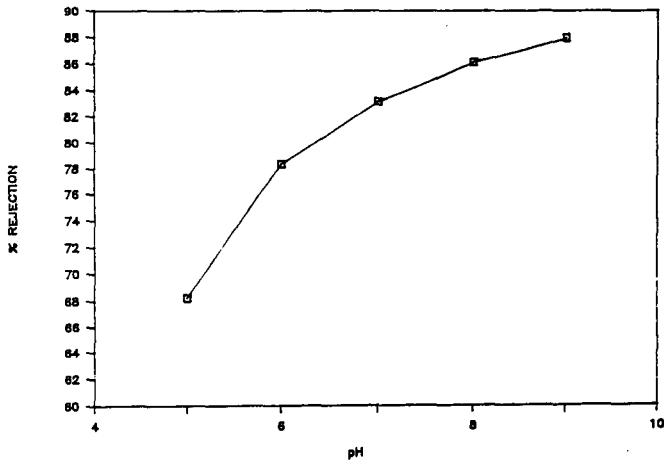*Effect of pH on rejection 48% acrylic acid*

Figure 4
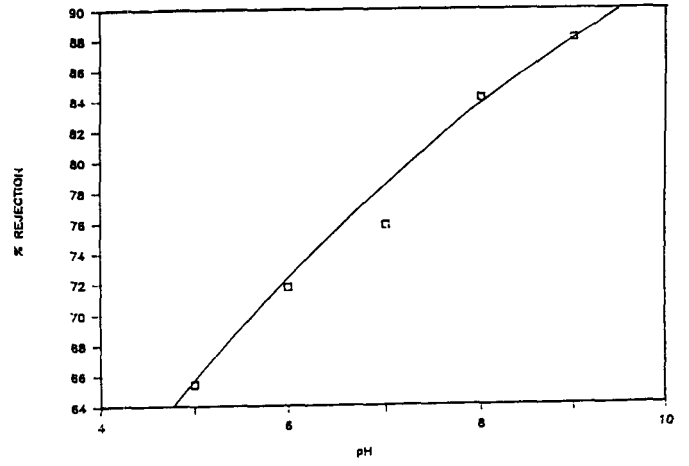*Effect of pH on rejection 71% acrylic acid*

Figure 7
Effect of pH on rejection 73% acrylic acid
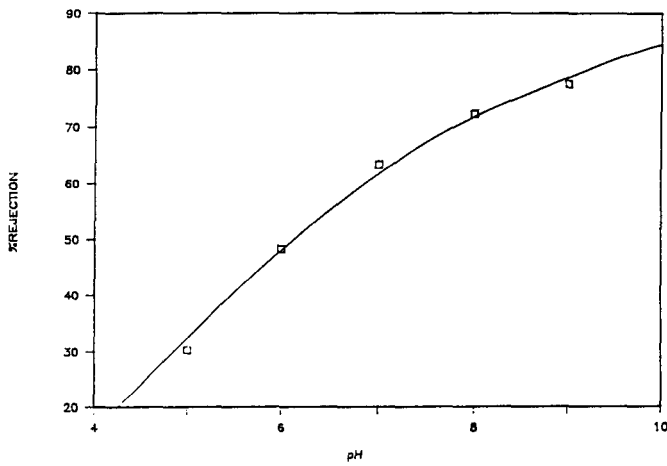

Figure 5
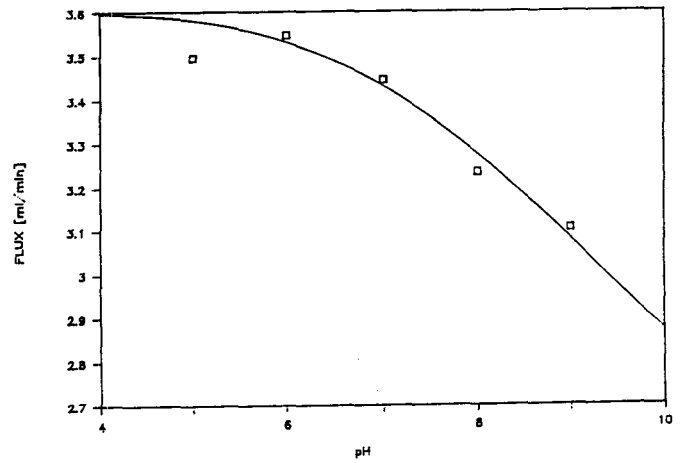*Effect of pH on rejection 24% acrylic acid*

Figure 8
Effect of pH on flux 21% acrylic acid
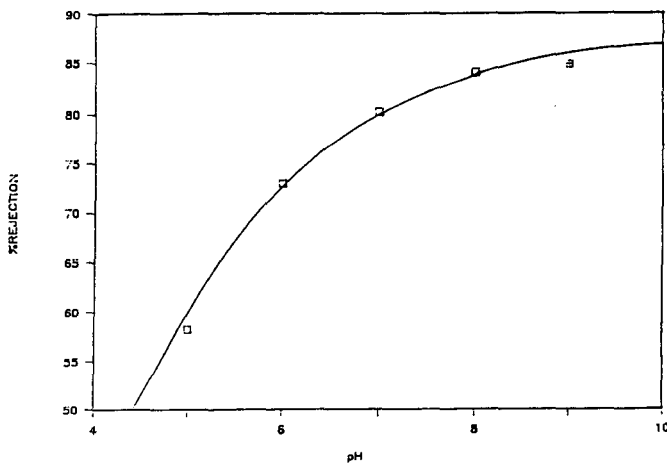

Figure 6
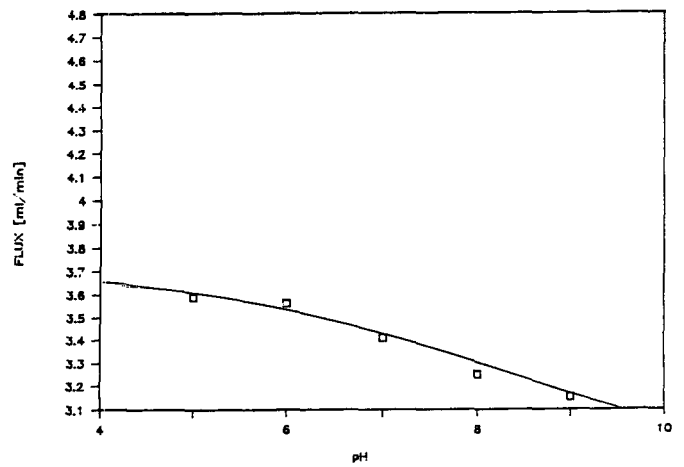*Effect of pH on rejection 50% acrylic acid*

Figure 9
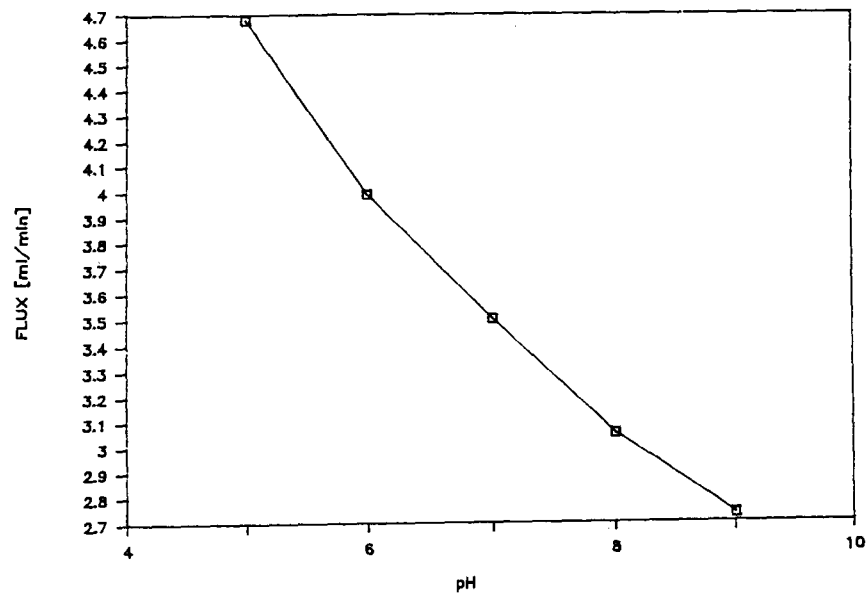*Effect of pH on flux 48% acrylic acid*

Figure 10
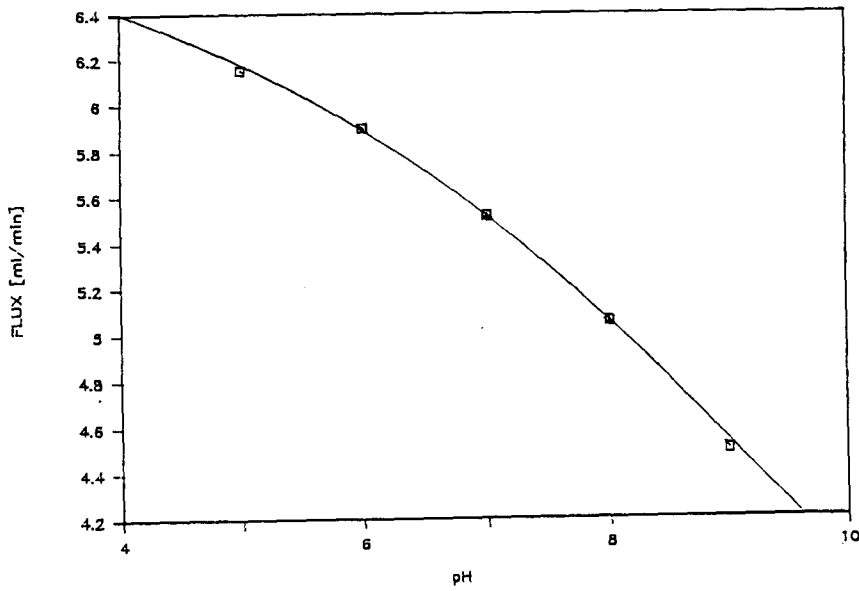*Effect of pH on flux 71% acrylic acid*

Figure 11
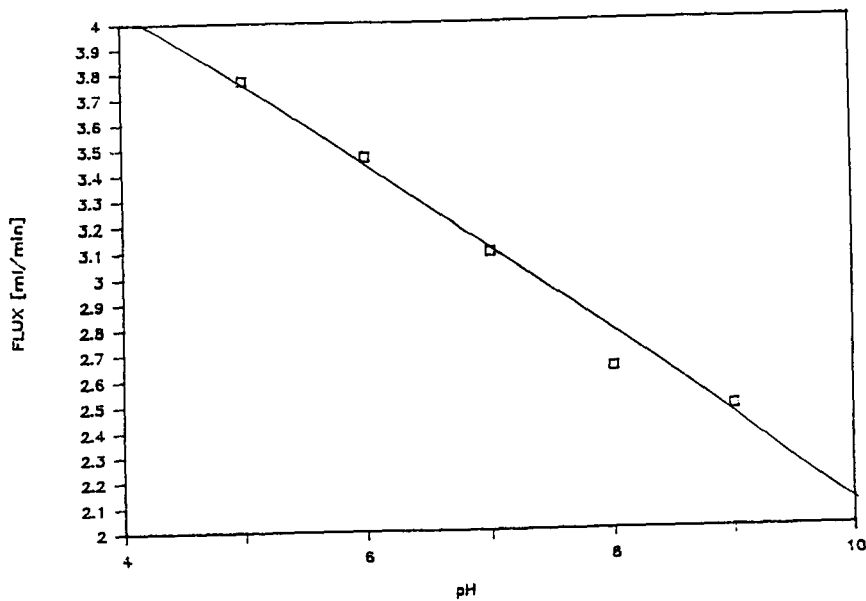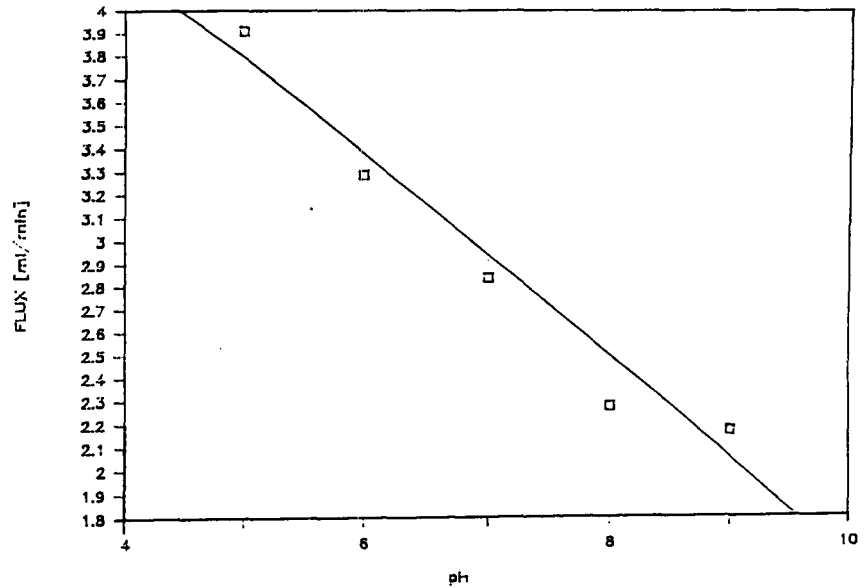*Effect of pH on flux 24% acrylic acid*

Figure 12
Effect of pH on flux 50% acrylic acid

Figure 13
Effect of pH on flux 73% acrylic acid

$R = R_i/R_j$ and $J = J_i/J_j$
$R' = 1 - R;$ $\quad R'' = R'/(j-i)$
$J' = 1 - J;$ $\quad J'' = J'/(j-i)$

Thus R'' and J'' were calculated for the membranes between the pH values of 5,0 and 7,0 and the pH values of 5,0 and 9,0. These values were introduced since a change in rejection at low pH values (e.g. 10 % at 50 % salt rejection) will be more significant than the same change at higher rejection values e.g. 80 %. This will be expressed as such through these values. Results are given in Table 6.

TABLE 6
pH DEPENDENCE OF REJECTION AND FLUX AS A FUNCTION OF COPOLYMER COMPOSITION

Polymer code	Acrylic acid (%)	R'' (pH 5-7)	J'' (pH 5-7)	R'' (pH 5-9)	J'' (pH 5-9)
C_1	21		-0,009	0,149	-0,032
C_2	48	0,172	-0,026	0,105	-0,034
C_3	71	0,089	-0,169	0,056	-0,198
C_4	24	0,261	-0,057	0,152	-0,092
C_5	50	0,137	-0,110	0,078	-0,132
C_6	73	0,069	-0,186	0,064	-0,200
PAA	100	0,065	-0,147	0,051	-0,314

From Table 6 it can be seen that these membranes became less sensitive to an increase in pH as the acrylic acid content increased, and that poly(acrylic acid) was the least sensitive. This indicated that the increase in rejection due to the presence of fixed charges (Donnan exclusion) was much more pronounced for low acid content polyelectrolytes than for those with higher acid content. This supported the theory that Donnan exclusion is the most important mechanism of rejection for these membranes.

The influence of pH on flux increased with the increase in acid content of the polyelectrolytes. This was due to the increased amount of swelling and bound water brought about by higher charge density.

Conclusions

Hydrous zirconium (IV) oxide polyelectrolyte membranes can be dynamically formed when the polyelectrolytes are a range of poly(acrylic acid-co-hydroxyethyl acrylate) and poly(acrylic acid-co-hydroxyethyl methacrylate) copolymers, with the acrylic acid content varying between 20% and 80% in both copolymer ranges.

Although the presence of the comonomers with acrylic acid in these copolymers does not lead to increased salt rejection, the presence of the comonomers makes the membranes less sensitive to variations in the feed salt concentration. It might be possible to increase membrane performance by using different molecular mass materials.

Acknowledgement

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