Dynamic hydrous zirconium (IV) oxide-polyelectrolyte membranes. X. Crosslinked poly(acrylic acid-co-hydroxyethyl acrylate) and poly(acrylic acid-co-hydroxyethyl methacrylate) membranes

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Abstract

A series of 6 hydrous zirconium (IV) oxide dynamic membranes were formed with copolymers of poly(acrylic acid-co-hydroxyethyl acrylate) (C_1 to C_3) and poly(acrylic acid-co-hydroxyethyl methacrylate) (C_4 to C_6). These membranes were crosslinked by a catalysed self-crosslinking reaction utilising an ionic mechanism. The effect of varying feed concentration and pH on the performance of these crosslinked membranes is reported. The influence of copolymer composition on membrane performance is also discussed.

Introduction

Dynamic membranes have several advantages over "conventional" cast reverse osmosis membranes when used for water treatment. The most important of these advantages are their much higher fluxes, wide range of operating temperatures and ease of *in situ* renewal of damaged membrane surfaces.

Dynamic membranes also have disadvantages. Since rejection is partially dependent on an electrostatic mechanism, it is negatively influenced by the build-up of salt ions at the membrane surface (concentration polarisation). These poly(acrylic acid-co-hydroxyethyl acrylate) and poly(acrylic acid-co-hydroxyethyl methacrylate) membranes are also adversely affected by an increase in the salt concentration of the feed solution and are sensitive to changes in the pH of the feed solution (Van Reenen *et al.,* 1990).

Crosslinking will reduce the charge density on the membrane surface and change the chemistry of the membranes. It was therefore envisaged that crosslinking could reduce the dependence of a dynamic membrane's performance on ionic effects.

Background

The historical background to dynamic membranes has been discussed previously (Van Reenen *et al.,* 1988).

The use of copolymers of acrylic acid (AA) and hydroxyethyl methacrylate (HEMA) or hydroxyethyl acrylate (HEA) as dynamic membranes has never been investigated, but the use of crosslinked HEMA membranes for reverse osmosis desalination has been investigated (Jadwin *et al.,* 1970). Chemical crosslinking was used and it was concluded that salt rejection increased with increase in crosslink density, whereas water flux declined accordingly. Salt rejection was found to result from changes in the water - salt diffusion ratios and was linked to the water content of the membrane which declined with increase in crosslinked density. Ionically crosslinked poly-AA membranes formed on a polysulphone support have also been investigated as membranes for desalination by reverse osmosis (Huang *et al.,* 1983). These membranes were shown to be adequate for the desalination of low-concentration salt solutions.

It has been shown that the presence of divalent cations has a deleterious effect on the salt rejection by a composite dynamic membrane (poly-AA deposited on a hydrous zirconium base membrane) (Johnson, 1972). Chelation of the divalent cations by ionised carboxylic acid groups causes a decrease in the membrane's charge density. A decrease in salt rejection in such a case was therefore attributed to a reduction in membrane charge density.

Previously it was believed that salt rejection by dynamic membranes is solely based on electrostatic repulsion. It has been shown that salt rejection is also influenced by salt diffusion ratios (Van Reenen, 1988) in the membrane and in the feed solution as noted previously for the crosslinked neutral HEMA membranes (Wisniewski *et al.,* 1976).

Crosslinking

Various methods are available for the crosslinking of the AA-co-HEA and AA-co-HEMA copolymers used in this study. Chemical crosslinking can be effected by the addition of crosslinking agents such as trimethylol propane trimethacrylate (TPT) (Jadwin *et al.,* 1970) or ethylene glycol dimethacrylate (EGD) (Wisniewski *et al.,* 1976).

Heating these copolymers can also lead to crosslinking, as was proved by differential scanning calorimetry (DSC). The DSC graph of copolymer C_6 (Fig. 1) shows an exotherm between 90°C and 165°C. This exotherm is associated with the energy which is released when crosslinking occurs. Crosslinking can also be effected by a self-crosslinking reaction which can be induced in a polymer solution by the addition of catalysts such as HCl, $Zn(NO_3)_2$ and $AlCl_3$ (Goldberg and Jasinski, 1965).

Ageing at elevated temperatures also produces a crosslinked polymer network. This method, with $Zn(NO_3)_2$ used as crosslinking catalyst, was used here. This method was decided on because of the conditions required by the dynamic membrane formation process. Crosslinking was effected in a post membrane-formation step.

The crosslinking of these copolymer membranes involved two possible reaction mechanisms. The first mechanism involved the carboxylic acid group of AA and the hydroxyl group of HEA or of HEMA. The formation of an ester link between these two reactive groups led to crosslinking. This reaction can be catalysed by an acid such as HCl or even $Zn(NO_3)_2$ and can occur at room temperature or higher.

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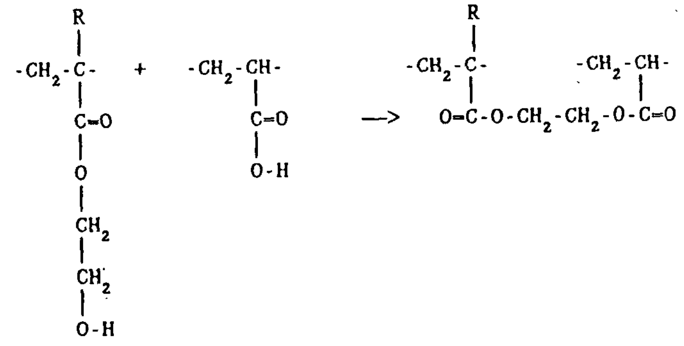
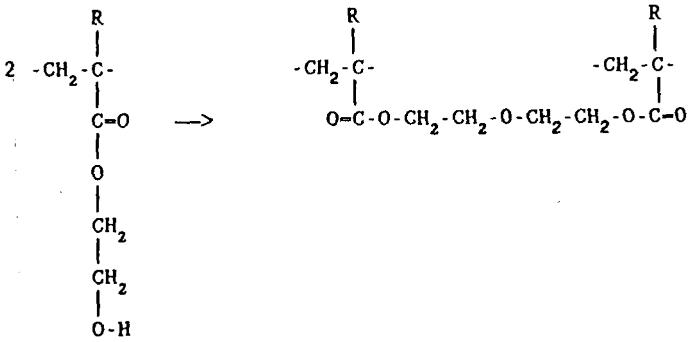


R = H; CH_3

The second mechanism is that of formation of an ether bond between two hydroxyl groups of HEA or of HEMA.



R = H; CH_3

Since the energy requirements for the formation of an ether bond between two hydroxyl groups would be higher than those for the formation of an ester bond, this reaction is more likely to occur at high temperatures while catalysed ester formation could occur more readily at room temperature, as noted previously. It was therefore assumed that ester formation would be the dominant crosslinking mechanism.

Experimental

The monomer purification and polymerisation, and characterisation of the copolymers were discussed previously (Van Reenen *et al.*, 1990). The compositions of the copolymers used for the formation of these membranes are given in Table 1. The membranes were formed on Millipore filters that are made of cellulose acetate nitrate, with a pore size rated 0,45 microns. The membrane formation equipment and technique were also discussed previously (Van Reenen *et al.*, 1988) and will not be repeated here.

Membrane crosslinking

The pH was set at 7,0, the $NaNO_3$ concentration at 0,0235 $mol.dm^{-3}$ and the feed tank was filled to 30 ℓ. Crosslinking was effected by the addition of $Zn(NO_3)_2$.

For this, 120 g (0,460 moles) $Zn(NO_3)_2$ was dissolved in water and added to the feed. The temperature was set at 333 K, the back-pressure was kept at 6 MPa, and the flow rate at 6 $m.s^{-1}$. The system was allowed to run for 24 h before the feed tank was drained and the system flushed with reverse osmosis permeate. After flushing was completed the feed tank was refilled to 30 ℓ, the temperature set at 308 K and the pH set at 7,0.

Membrane evaluation

The crosslinked membranes were evaluated in terms of the influence of pH on salt rejection and permeate flux and the effects of feed concentration on salt rejection and permeate flux.

The influence of pH. The pH of the feed solution (0,0235 mol $.dm^{-3}$ $NaNO_3$) was adjusted to 5,0 by the addition of 55% HNO_3. Thirty minutes were allowed for the membrane to stabilise, before the flux and rejection were determined. The pH was increased to 6,0 by the addition of a 10% solution of NaOH. Again 30 min were allowed for stabilisation before the flux and rejection were determined. The process was repeated for pH values of 7,0; 8,0 and 9,0. Throughout this test the feed concentration

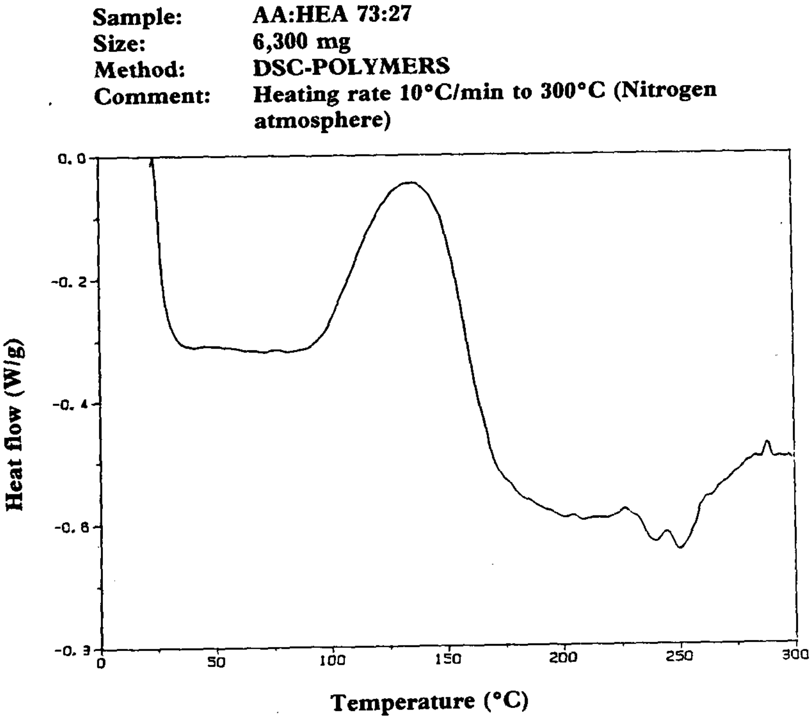


Figure 1
DSC-scan of copolymer C_6

TABLE 1
COPOLYMER COMPOSITION

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

was kept constant at 0,0235 mol .dm^{-3} $NaNO_3$, the temperature at 308 K, the pressure at 6 MPa and the crossflow velocity at 6 m.s^{-1}.

The influence of feed concentration. The feed concentration was set at 0,235 mol .dm^{-3} $NaNO_3$. After 30 min had been allowed for the membranes to stabilise, the flux and rejection were measured. The process was repeated for feed concentrations of 0,176; 0,141; 0,118; 0,0941; 0,0706; 0,0471 and 0,0235 mol .dm^{-3} $NaNO_3$. The feed concentration was decreased 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^{-1} and the temperature at 308 K.

Results and discussion

The influence of crosslinking on membrane properties

As was discussed previously crosslinking occurred either by ester or ether formation, and ester formation was assumed to be dominant. The result of crosslinking would be to reduce the amount of carboxylic acid groups available for ionisation. This reduction in the number of fixed charges would reduce the membrane charge density and therefore influence rejection due to Donnan exclusion (Van Reenen *et al.,* 1990; Gerber, 1990). It would also incluence swelling of the polymer network and the frictional forces exerted on water being transported through the membrane. The hydrophilic character of the membrane would also be altered, since some hydrophilic acid and alcohol groups would be removed by the crosslinking and be "replaced" by less hydrophilic ester groups.

pH dependance

Rejection

Since crosslinking "removed" a certain number of ionisable carboxylic acid groups and changed the chemical nature of the membrane, it was expected that rejection would be influenced and that rejection due to Donnan exclusion would be reduced. Crosslinking could therefore also give an indication of the relative importance of Donnan exclusion (based on electrostatic repulsion) and the diffusion ratios of salt ions in the membrane and feed solution in rejection by these dynamic membranes (Van Reenen *et al.,* 1990). The increase in rejection with increasing pH showed by the plot of rejection vs. pH of the HEA-2 membrane (Fig. 2) is also exhibited by the other membranes (Gerber, 1990). This seemed to indicate that the reduced membrane charge density (Donnan exclusion) had the biggest influence on rejection by these crosslinked membranes. It is also important to note that HEA-1 showed rejection values of over 50% at pH 7 (Gerber, 1990). This illustrated that the diffusion ratios of salt ions also play an important role in rejection by these dynamic membranes.

Flux

The flux of a composite dynamic membrane declines when the pH is raised because of an increase in the number of ionised carboxylic acid groups in the membrane. These ionised carboxylic acid groups will increase the extent of swelling and the amount of bound water in the polyelectrolyte, resulting in increased friction being exerted on the permeating water. It was shown previously that the incorporation of a neutral monomer into the polyelectrolyte reduced this effect. Since crosslinking reduced the number of ionisable carboxylic acid groups, it could reduce this effect even further. Crosslinking will also reduce the hydrophilicity of the polyelectrolyte as discussed previously, and create a denser polymer network. This would cause an increase in the frictional forces exerted on the permeating water and a decrease in flux could occur for the whole pH range. This line of reasoning is supported by the graph in Fig. 3, which shows a reduced flux which is influenced to a lesser extent by the change in pH.

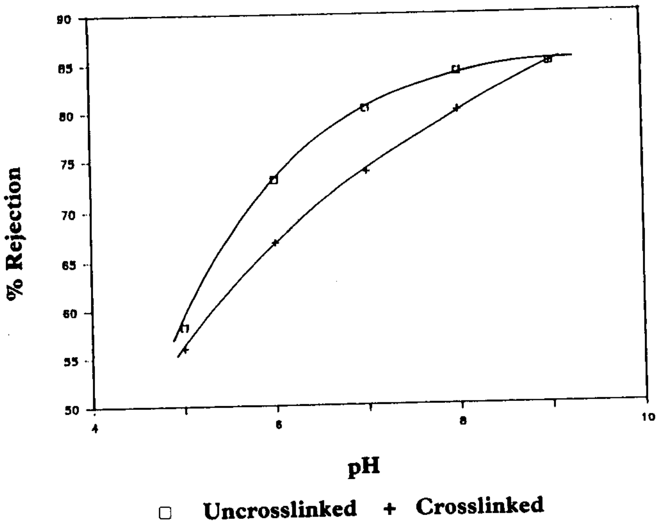


Figure 2
The effect of pH on rejection of HEA-2

Copolymer influence

A comparative study similar to previous work (Van Reenen *et al.*, 1990; Van Reenen and Sanderson, 1989 a) on the influence of copolymer composition on the pH dependance of rejection and flux was done. The results, shown in Table 2, are similar to those for the uncrosslinked membranes (Van Reenen *et al.*, 1990). As had been done previously, two values R'' and J'' were defined (Van Reenen *et al.,* 1990; Van Reenen and Sanderson, 1989 a) where R'' and J'' represent the membranes' 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 represent the rejection and flux at pH = j, j < i, then let:

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

Thus R'' and J'' were calculated for the membranes between the pH values of 5 and 7, and the pH values of 5 and 9. Results are given in Table 2.

Similar to the uncrosslinked membranes, the crosslinked membranes became less sensitive to an increase in pH as the AA content increased. This indicated that crosslinking did not "remove" all the carboxylic acid groups, and that upon ionisation (when the pH was raised) the uncrosslinked carboxylic acid groups showed a marked influence on rejection which was more pronounced for the low-acid content membranes, highlighting the important contribution of Donnan exclusion here. In comparison with the uncrosslinked membranes, rejection by these crosslinked membranes was influenced to a lesser extent by the change in pH.

Also as with the uncrosslinked membranes the influence of pH on flux increased with the increase in acid content of the polyelectrolytes. This was due to a higher charge density associated with the higher carboxylic acid content of the polyelectrolyte, which led to a higher bound-water content in the membrane when the pH was raised. A comparison of the crosslinked and uncrosslinked membranes showed that the flux of the crosslinked membranes was influenced to a lesser extent by a change in the pH of the feed in both copolymer ranges. This could be attributed to the change in membrane chemistry and reduced charge density.

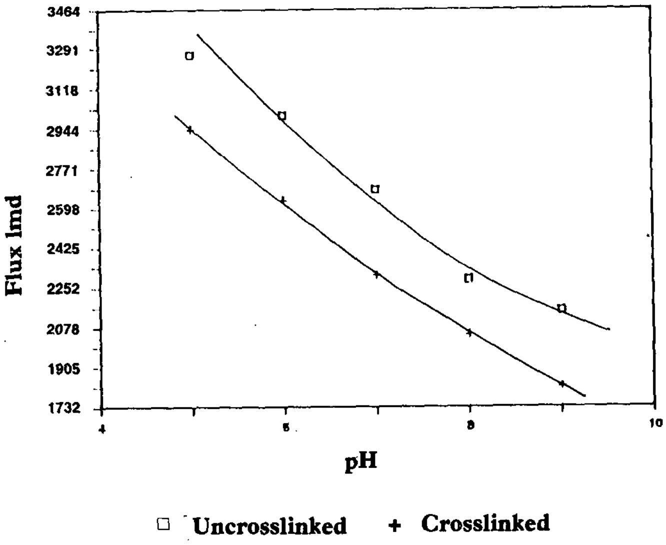


Figure 3
The effect of pH on the flux of HEA-2

TABLE 2
pH DEPENDENCE OF REJECTION AND FLUX AS A FUNCTION OF COPOLYMER COMPOSITION

(UNCROSSLINKED MEMBRANES)

Membrane code	Acrylic acid mol %	R'' (pH 5-7)	J'' (pH 5-7)	R'' (pH 5-9)	J'' (pH 5-9)
HEMA 1	21		-0,009	0,149	-0,032
HEMA 2	48	0,172	-0,026	0,105	-0,034
HEMA 3	71	0,089	-0,169	0,056	-0,198
HEA 1	24	0,261	-0,057	0,152	-0,092
HEA 2	50	0,137	-0,110	0,078	-0,132
HEA 3	73	0,069	-0,186	0,064	-0,200

(CROSSLINKED MEMBRANES)

Membrane code	Acrylic acid mol %	R'' (pH 5-7)	J'' (pH 5-7)	R'' (pH 5-9)	J'' (pH 5-9)
HEMA 1	21	0,063	-0,025	0,121	-0,055
HEMA 2	48	0,146	-0,053	0,096	-0,076
HEMA 3	71	0,083	-0,179	0,060	-0,172
HEA 1	24	0,203	-0,044	0,137	-0,088
HEA 2	50	0,120	-0,134	0,085	-0,154
HEA 3	73	0,057	-0,168	0,047	-0,173

Feed-salt concentration

TABLE 3
THE EFFECT OF FEED CONCENTRATION ON REJECTION

Membrane	Acrylic acid	Slopes of log(1-R) vs. log(M) plots	
code	mole %	Uncrosslinked	Crosslinked
HEMA 1	21	0,101	0,115
HEMA 2	48	0,403	0,395
HEMA 3	71	0,447	0,383
HEA 1	24	0,368	0,271
HEA 2	50	0,476	0,343
HEA 3	73	0,354	0,355

Rejection

Theory predicts that a plot of log (1-R) vs. log (M) should give a slope of unity for a totally charged body (Van Reenen *et al.,* 1990; Sachs and Lonsdale, 1971). If the charge is reduced the slope should decrease. The presence/absence of charged groups in the polymer influence the effect of feed concentration on membrane rejection (Van Reenen and Sanderson, 1989b). Crosslinking would reduce the number of ionisable carboxylic acid groups in the membrane (as discussed previously) and would cause a decrease in membrane charge density. It was therefore expected that the various crosslinked membranes would be less influenced by an increase in feed-salt concentration. This would be shown as reduced values of the slopes of the log(1-R) vs. log(M) plots for the crosslinked membranes (Fig. 4). This line of reasoning was supported by the data in Table 3. The crosslinked membranes showed a general decrease in the value of the slope (except for HEMA 1) indicating reduced dependence of rejection on the feed salt concentration.

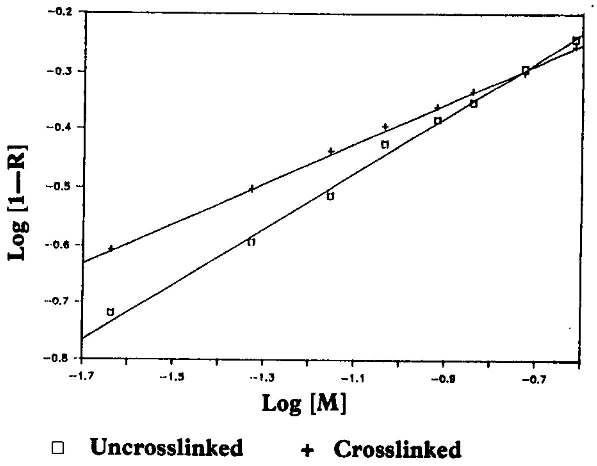


Figure 4
Effect of feed Concentration on rejection of HEA-2

Flux

The decrease in membrane flux associated with the increase in feed-salt concentration was explained in terms of frictional forces between water and cations and water and the membrane (Van Reenen, 1988). Since water and cation fluxes are coupled (Meares, 1976), the charge density of a membrane would influence the flux. The effect of crosslinking would be to reduce the membrane charge density, decrease hydrophilicity and create a denser more "perfect" structure, therefore it was expected that the effect of varying feed-salt concentration on flux would be influenced. This is shown in Fig. 5.

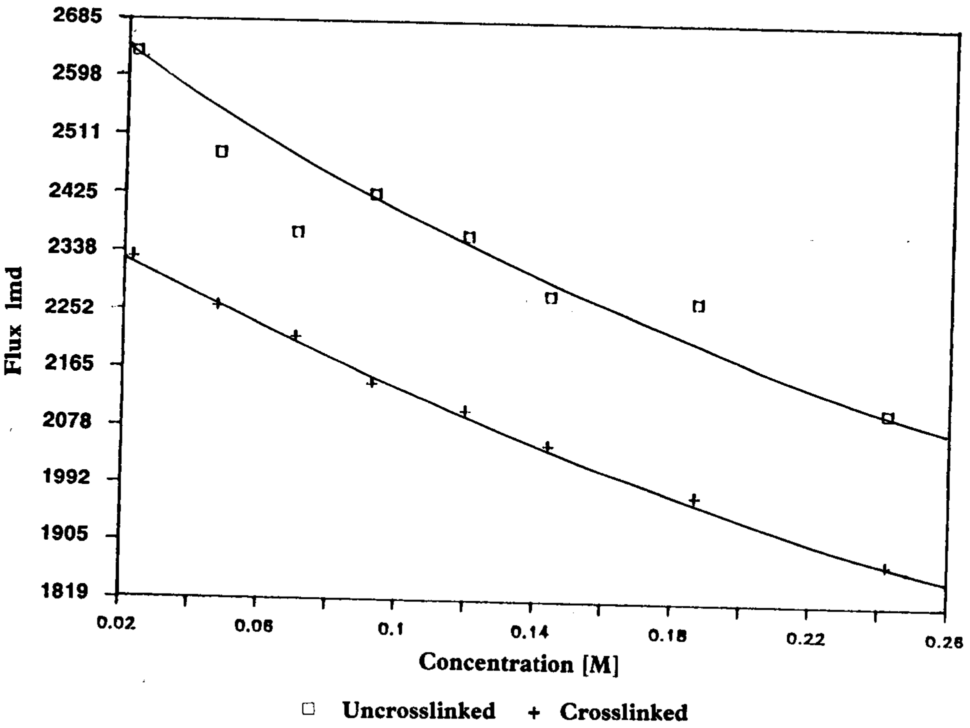


Figure 5
Effect of feed Concentration on flux of HEA-2

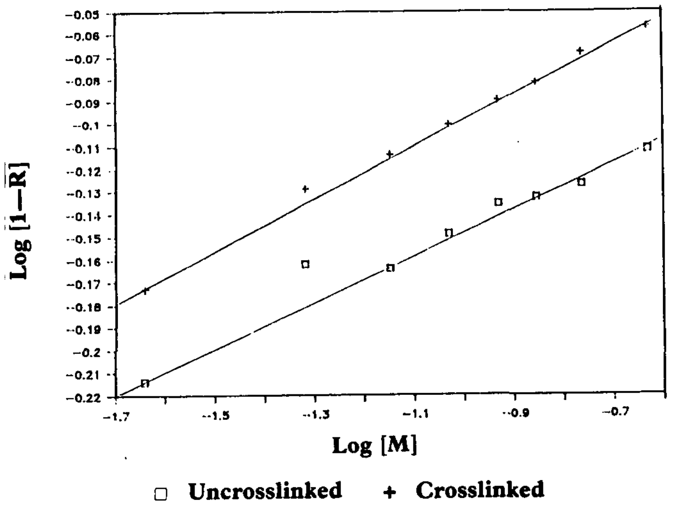


Figure 5.1
Effect of feed Concentration on rejection 21% 2-propenoic acid

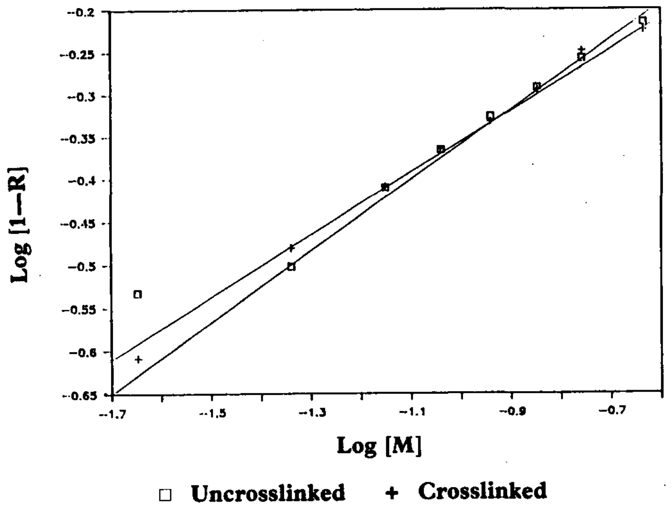


Figure 5.2
Effect of feed Concentration on rejection 48% 2-propenoic acid

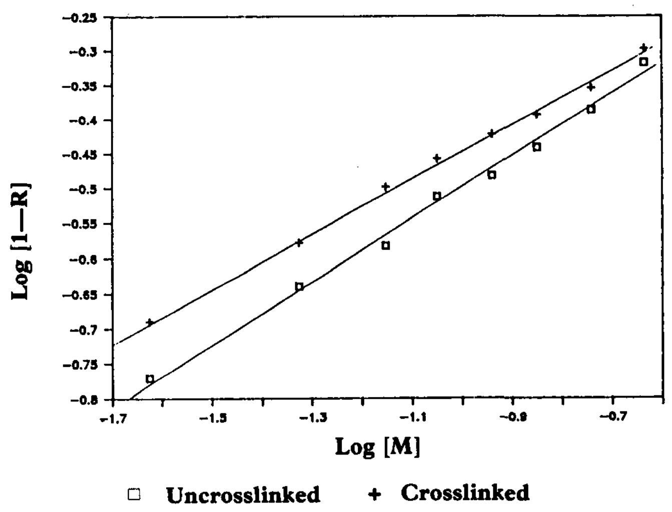


Figure 5.3
Effect of feed Concentration on rejection 71% 2-propenoic acid

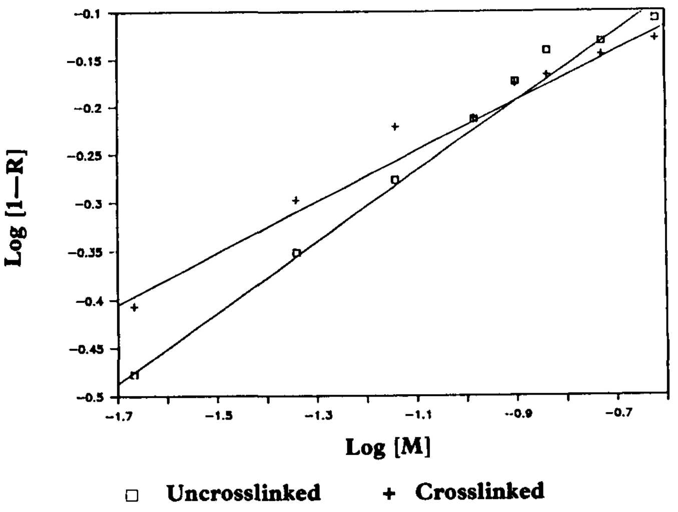


Figure 5.4
Effect of feed Concentration on rejection 24% 2-propenoic acid

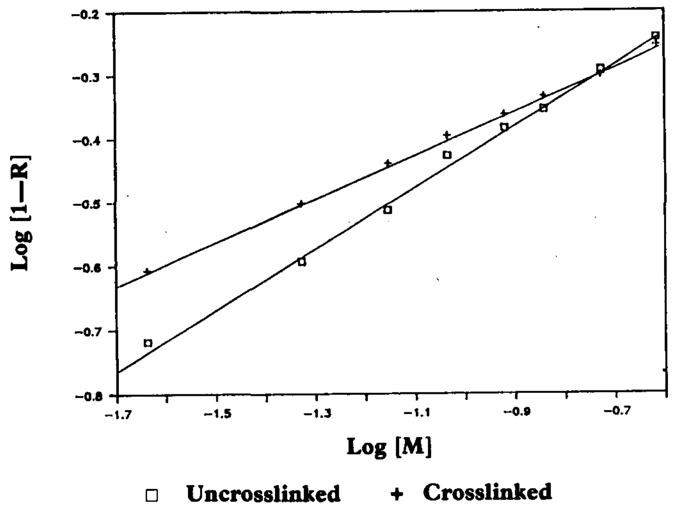


Figure 5.5
Effect of feed Concentration on rejection 50% 2-propenoic acid

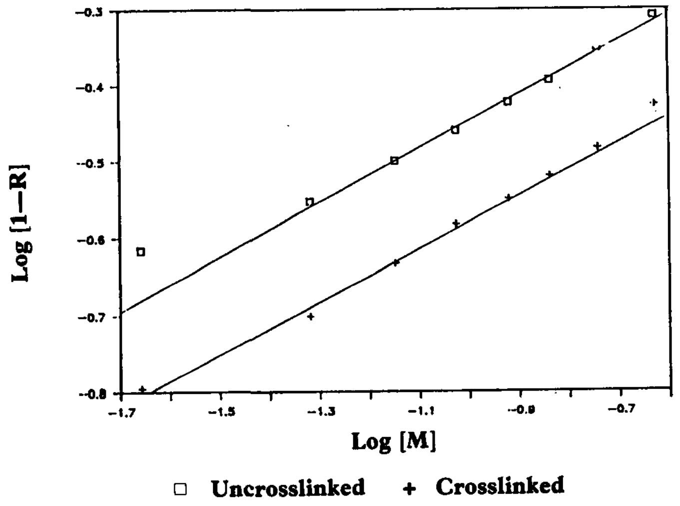


Figure 5.6
Effect of feed Concentration on rejection 73% 2-propenoic acid

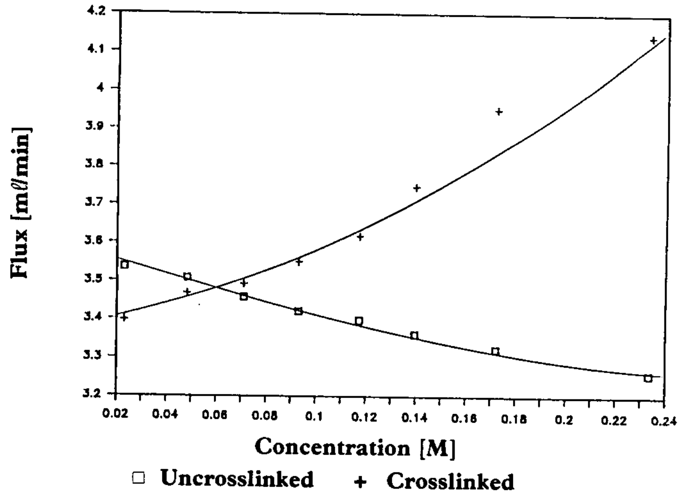


Figure 5.7
Effect of feed Concentration on flux 21% 2-propenoic acid

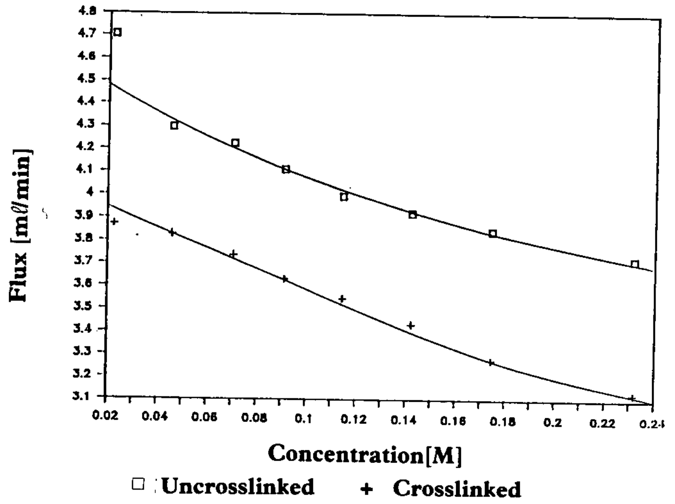


Figure 5.8
Effect of feed Concentration on flux 48% 2-propenoic acid

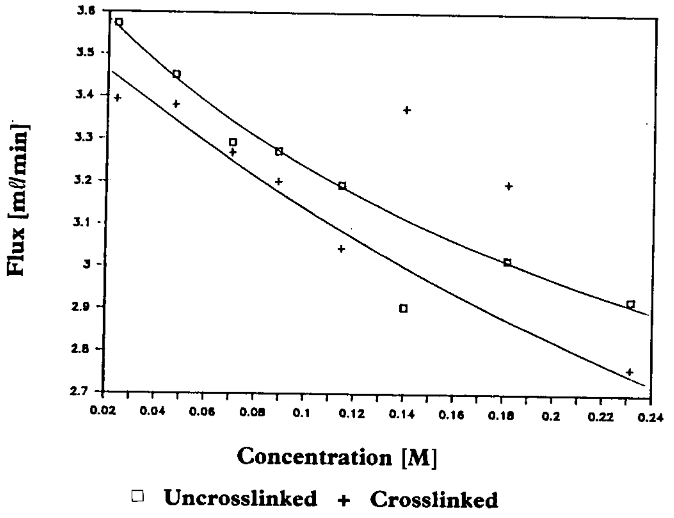


Figure 5.9
Effect of feed Concentration on flux 71% 2-propenoic acid

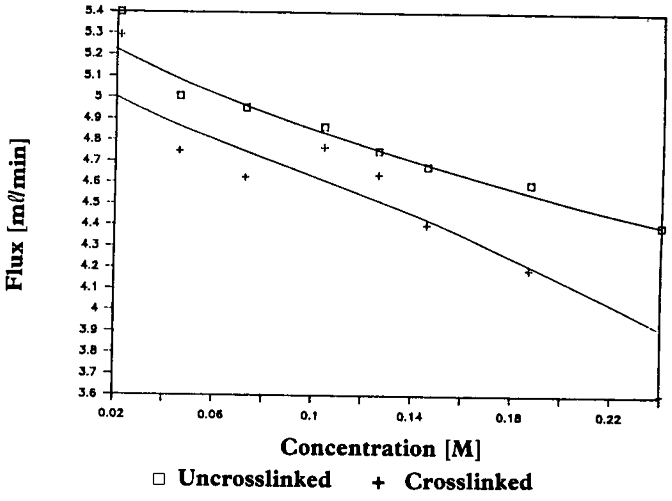


Figure 5.10
Effect of feed Concentration on flux 24% 2-propenoic acid

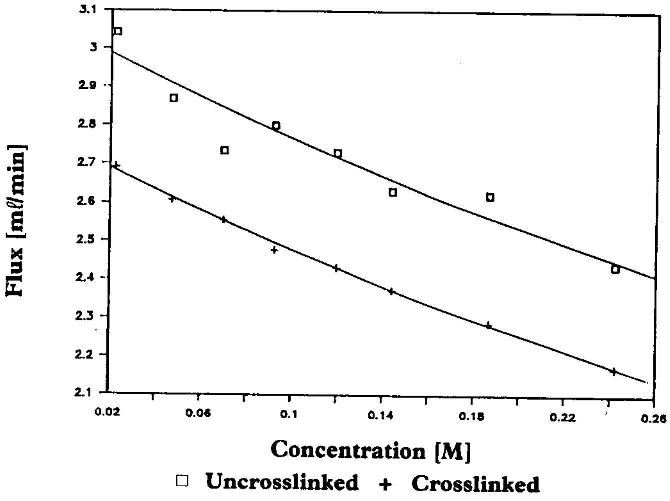


Figure 5.11
Effect of feed Concentration on flux 50% 2-propenoic acid

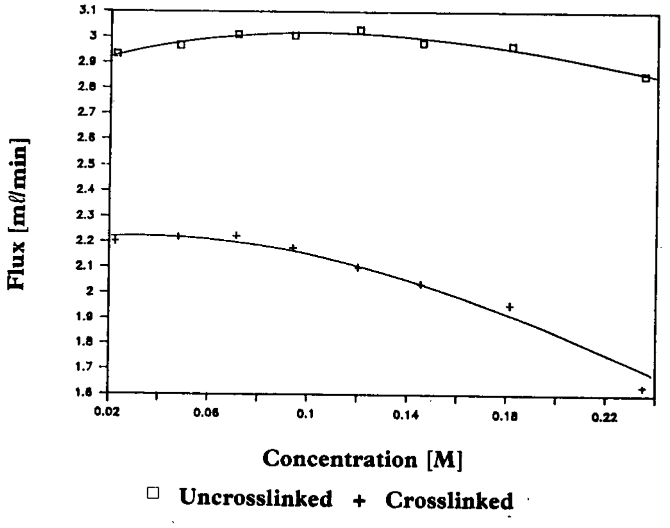


Figure 5.12
Effect of feed Concentration on flux 73% 2-propenoic acid

Conclusions

Dynamic hydrous zirconium oxide (IV) polyelectrolyte membranes formed with a range of polyelectrolytes of poly(acrylic acid-co-hydroxyethyl acrylate) and poly(acrylic acid-co-hydroxyethyl methacrylate) copolymers can be crosslinked via a self-crosslinking reaction at an elevated temperature utilising $Zn(NO_3)_2$ as crosslinking catalyst. Crosslinking reduced the membrane charge density due to the "removal" of ionisable carboxylic acid groups, changed the chemistry of the membrane, and had a marked influence on rejection and flux. It reduced peak rejection values, but had the advantage that it reduced the influence of pH. Peak flux values were also reduced with a similar advantage of a reduced influence of pH on flux.

The trend of reduced sensitivity to increasing pH with increasing AA content in the polyelectrolyte exhibited by these crosslinked membranes highlighted the dual character of the rejection mechanism and the importance of Donnan exclusion for these membranes.

The influence of feed salt concentration on rejection was reduced by crosslinking. This was pointed out by reduced values for the slopes of log(1-R) vs. log(M) plots. The influence of feed-salt concentration on flux was also reduced.

Although crosslinking reduced peak values, the influence of ionic effects on the performance of these copolymer membranes was markedly reduced.

Acknowledgement

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