Dynamically formed hydrous zirconium (IV) oxide-polyelectrolyte membranes. III: Poly(acrylic acid) and substituted poly(acrylic acid) homo, co and terpolymer membranes

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Abstract

A series of acrylic acid and substituted acrylic acid homo, co and terpolymers was synthesised. These polymers were used as polyelectrolytes in dynamically formed hydrous zirconium (iv) oxide-polyelectrolyte membranes. Substitution of the acrylic acid α-hydrogen was done to increase the number of carboxylic acid groups per monomer unit and to change the acid strength of acrylic acid carboxylic acid group. None of these changes improved the salt rejection of these membranes over that of commerically used poly(acrylic acid). Improvement in rejection was found when a hydrophobic comonomer, vinyl acetate, was used in conjunction with acrylic acid in a copolymer dynamic membrane.

Introduction

The rapidly expanding world population is placing the natural resources of the world, and more particularly water, under an increasing strain. In many parts, water has been abused by both industry and individuals.

Problems arising from water shortages are world-wide; in many places they are aggrevated by naturally arid conditions and, more seriously, drought. The obvious solution to the problem of water shortage is to recover and reuse waste waters to produce usable water.

The South African Department of Water Affairs (DWA) (1986) reports that in 1980 the water demand in the Republic was 1,63 x 10^{10} m^3. The three major water users were agriculture (irrigation) (52,2%), industry (6,3%) and municipal and domestic users (9,3%). The DWA estimates that in the year 2010 the total water demand would be 2,59 x 10^{10} m^3. The water usage by industry is expected to more than double by that time (105% increase), while the municipal and domestic water usage will nearly double (95% increase). The agricultural use is expected to increase by 23%. If only 50% of the industrial effluent could be recycled the water saving would be 1,48 x 10^9 m^3, or 5,6% of the total demand. For this, some desalination technique would have to be used. In the search in the past for methods of cleaning or purifying liquids, usually water, a number of processes have been developed.

In recent years the scope of investigations have been widened to include the recovery of usable water from effluents, and a number of processes have been developed. These are distillation, ion exchange, freezing, and membrane processes such as electrodialysis, microfiltration, ultrafiltration and reverse osmosis. Groves *et al.* (1983) state that standard advanced waste-water treatment technology is normally considered to be biological treatment, followed by combinations of flocculation, sedimentation or flotation, filtration, ozonation, activated carbon adsorption and for salt removal, ion exchange, reverse osmosis or electrodialysis. Membrane separation technology, a one-step process, can replace these treatment sequences.

The membrane processes include the use of neutral or nearly neutral membranes or of charged or ion-exchange membranes.

Conventional membrane technology has limitations arising from certain physical properties such as pH, temperature, pressure compatibility and chemical properties of the membranes concerned. Dynamic membranes have the following advantages for treating industrial effluents (Groves *et al.*, 1983):

- High temperature stability
- Long service life of the support tube (conventionally porous stainless steel)
- They are replaceable *in situ* by solution chemistry
- They can be tailored to a particular application
- High membrane fluxes.

Concept

Dynamic membranes are formed by circulating a feed stream containing the membrane-forming materials past a porous support. The membrane is deposited and formed by pH variations. These membranes consist of a hydrous metal oxide base layer, usually hydrous zirconium (IV) oxide, and a polyelectrolyte rejecting layer deposited on the base membrane. The polyelectrolyte is usually poly(acrylic acid). The polyelectrolyte is deposited at pH 2,0, where the pendant carboxylic acid groups are not ionised. The polyelectrolyte interacts with the zirconium by a mechanism of chelation, and the remaining free carboxylic groups are then ionised by raising the pH to 7,0 (Fig. 1). Thus a membrane is formed that has a net negative fixed charge at pH 7,0.

Background

Rejection has previously been described in terms of the so-called fixed-charge model, which was developed from the Donnan equilibrium, which assumes global electroneutrality. It can be deduced (Sachs and Lonsdale, 1971) that:

$$\log (1\text{-}R) = \log c_f - \log X$$

R : Rejection ($1\text{-}c_p/c_f$)
c_f: Feed salt concentration
c_p: Permeate salt concentration
X : Charge density

Theoretically, therefore, the higher the value of X, for a constant feed concentration, the greater the rejection, R, will be. The initial dynamic membrane research at the Institute for Polymer Science

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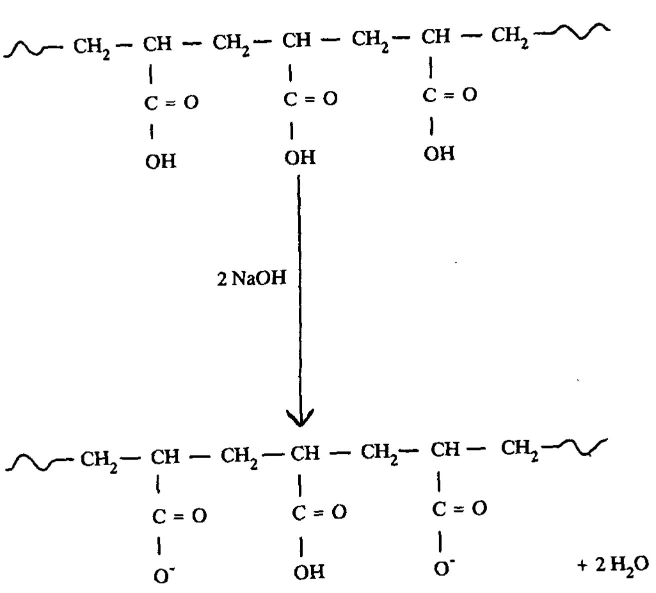
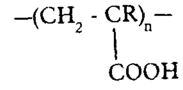


Figure 1
Schematic representation of the ionisation of poly(acrylic acid)

was planned on this premise. It was decided that by (a) changing the acid strength of the carboxylic acid group, and (b), increasing the amount of carboxylic acid groups per monomer unit the charge density of these membranes could be altered. A series of substituted acrylic acids were synthesised, and these monomers homo, co and terpolymerised. These resulting polymers would then be used to make dynamic membranes.

Substitutions



$$-(CH_2 - \underset{\displaystyle COOH}{\underset{|}{CR}})_n-$$

repeat unit in polymer

Substitution (R =)	Monomer	Type of change
-H	Acrylic acid	-
$-CH_3$	Methacrylic acid	(a)
-CI	2-Chloro acrylic acid	(a)
$-CH_2COOH$	Itaconic acid	(b)

Experimental

Membrane formation and evaluation equipment

The equipment is shown schematically in Fig. 2.

The equipment consisted of a 40 ℓ capacity polyethylene feed tank, equipped with a cooling coil for feed-temperature control. The feed was pumped from the feed tank by a Hydracel D10 triplex diaphragm pump to the test section. The piping in the equipment was of 316 stainless steel. The feed line was split at a high-pressure bypass valve to allow control of the feed flow rate through the test section. The test section consisted of three flat cells (stainless steel) in series. The cell design featured a tortuous flow path, designed to promote turbulent flow. The tortuous flow was caused by an acrylic insert in the cell. The membrane supports used in these flat cells were Millipore ultrafilters (HA, rated 0,45 μm). Backing material consisted of filter paper disks.

Membrane formation

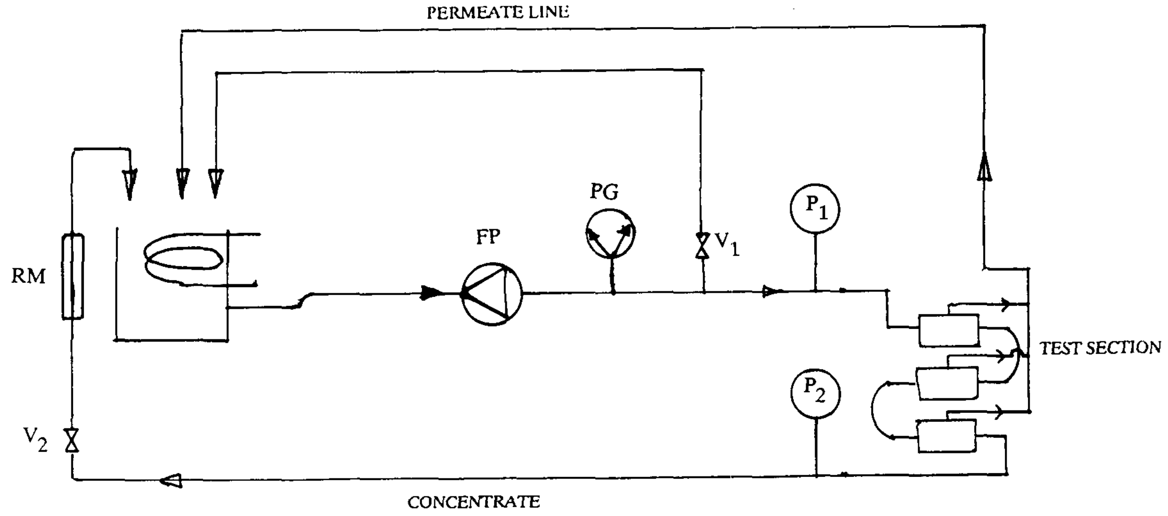
Zirconium membrane

The formation procedure followed was developed after the technique of Tanny and Johnson (1978) with modifications suggested by Buckley (1984), and some modifications developed by Dowler (1985) and Van Reenen (1985). Briefly, the zirconium membrane was formed as follows: the feed solution was circulated past the membrane supports at a pressure of less than 1 MPa, a flow velocity of less than 2 m/s, at pH 4 and the feed salt concentration at about 0,0235 M ($NaNO_3$). A solution of zirconium nitrate was freshly prepared in a glass beaker, the mass of zirconium nitrate being the amount required to make the final concentration of zirconium in the feed solution 1 x 10^{-4}M. The zirconium solution was then added to the feed tank. This caused a drop in the pH of the feed solution. The pH was then adjusted to 3,60 by addition of a 10% solution of NaOH. As the zirconium membrane was deposited on the membrane support, the flow rate increased, the latter effect being noticeable in the change of the rotameter reading. When this occurred the flow rate was adjusted to 6 m/s and the back pressure to 2 MPa. The back pressure was then adjusted in increments of 1 MPa every 5 min with the flow rate being kept constant. With the back pressure at 6 MPa the rejection of each of the cells was monitored until the rejection reached a level of 45 -55%. At this stage a final reading was taken of both the flux and the rejection. The pH of the system was then adjusted to 2 by adding 55% nitric acid. The feed tank was then drained and flushed through with RO permeate, while the pH was maintained at 2. After the system had been flushed for 5 min the feed tank was allowed to fill to volume determined by the mass of polymer to be added. The pH was carefully adjusted to 2,00 and sodium nitrate added to a concentration of about 0,0235 M.

Polyelectrolyte membrane

With the feed circulating at 6 m/s and at a pressure of 6 MPa past the zirconium membrane and with the pH membranes adjusted to 2,00 the polyelectrolyte (in solution) was added. The concentration of the polyelectrolyte in the feed was 50 mg/ℓ. After addition of the polymer, the pH of the feed solution was increased in increments of 0,5 pH units every 30 min until pH 5,00 was reached, and then by 1 pH unit every 30 min until pH 7,00 was reached. Finally, the feed concentration was adjusted to 0,0235 M (sodium nitrate). The flux and rejection were monitored throughout the formation period.

The formed membrane was allowed to run for one hour at the feed concentration of 0,0235 M before a flux and rejection reading was taken. Further readings were then taken 24 h and 48 h after formation. At least two hours prior to either of these readings the pH was carefully adjusted to 7,0 and the feed concentration to 0,0235 M. The back pressure was maintained at 6 MPa and the flow rate at 6 m/s throughout.



RM : ROTAMETER
V_1 : BY-PASS VALVE
V_2 : BACK-PRESSURE VALVE
P_1 : INLET PRESSURE GAUGE
P_2 : OUTLET PRESSURE GAUGE
FP : DOUBLE CONTACT PRESSURE GAUGE

Figure 2
Schematic representation of the membrane formation and evaluation equipment

Polymerisations

The following polymers were synthesised:

(i) Poly(acrylic acid), according to the method of Habert *et al.* (1979), code PAA.
(ii) Poly(itaconic acid), according to the method of Marvel and Shepherd (1959), code PIA.
(iii) Poly(2-chloro acrylic acid), according to the method of Minsk an Kenyon (1950), code PCIAA.
(iv) Poly(methacrylic acid), according to the method of Silberberg *et al.* (1957), code PMAA.
(v) The (i)-(ii) copolymer, code PAA/IA.
(vi) The (i)-(iii) copolymer, code PAA/CIAA.
(vii) The (i)-(iv) copolymer, code PAA/MAA.
(viii) The (iv)-(iii) copolymer, code PMAA/CIAA.
(ix) The (i)-(iii)-(iv) terpolymer, code TERP.
(x) Poly(acrylic acid-co-vinyl acetate), code PAA/VAC.

Polymer characterisation

Polymer molecular mass was determined by the Univeral Calibration method (Grubusic *et al.*, 1967), which employs the experimental techniques of gel permeation chromatography and viscometry. The reactivities of all the monomers used in the polymerisations were, with the exception of the copolymer PAA/VAC, similar, so the composition of the final products was assumed to be similar to the reaction mixture make-up.

Results and discussion

The results are given in Table 1 and in Figs. 3 to 6.

As can be seen from Table 1, all the polyelectrolytes evaluated formed dynamic membranes.

Figs. 3 to 6 show the rejection and flux behaviour of these membranes during membrane formation. As the pH was increased, the polyelectrolytes ionised, and the rejection increased, while the flux decreased. Virtually all the polyelectrolytes showed this typical response, with the exception of the poly(2-chloro acrylic acid) membrane. In the pH range 3,5 to 5,5 the rejection and flux remained constant. This was due to the formation of lactone and ester linkages between the polymer chains (Marvel *et al.,* 1940). This caused the removal of ionisable carboxylic groups through crosslinking reactions. At pH values approaching neutral and above neutral, these chemical (ester) crosslinks are saponified, leading to the formation of a poly(2-hydroxy acrylic acid) polymer.

All the polyelectrolyte membranes show an improvement in rejection at pH values above neutral. In the case of PAA, PAA/VAC and PMAA membranes, i.e. where a single carboxylic group was present, the rejection maximum was obtained at pH 8. In the case of PIA and PIA copolymers, and in the case of chlorine-containing polymers the rejection increased as the pH was raised from 8 to 9. In the case of the chlorine-containing polymer membranes this increase was due to the continuing saponification of ester links formed during membrane formation. In the case of homo and copolymers from the dicarboxylic acid monomers the increase in rejection was solely due to the fact that shielding of non-ionised carboxylic groups by ionised carboxylic acid groups was more severe in these cases than would have been the case with the monocarboxylic acid polymers. This shielding had the effect that when the pH was raised above 8 the previously unionised carboxylic acid groups would ionise. The number of unionised groups at neutral pH would be determined by the charge density.

It was expected that an increase in the acid strength of the carboxylic group as in the case of poly(2-chloro acrylic acid), or in the number of avialable ionisable groups per monomer unit, such as in the case of poly(itaconic acid) would lead to better membrane properties. As can be seen from Table 1, this was not so. The carboxylic acid homo, co and terpolymer membranes all gave rejections lower than poly(acrylic acid) did, although much higher fluxes were ahcieved. The only polyelectrolyte that gave a membrane that was better than that achieved with poly(acrylic acid) was the poly(acrylic acid-co-vinyl acetate) polymer. In this instance we have a copolymer of an ionisable monomer (acrylic acid) and a neutral, non-ionisable monomer (vinyl acetate). The presence of the neutral vinyl acetate appears to have a beneficial effect on the rejection and flux properties of the hydrous zirconium (IV) oxide-polyelectrolyte membrane formed with this polymer. It has recently been suggested (Keuhl and Sanderson, 1988) that there is a maximum value for the rejection attainable due to the charge on the membrane, and that this maximum is less than the membranes' intrinsic rejection capability. It is clear from the above results that the rejections by these membranes are not solely determined by

TABLE 1
POLYELECTROLYTE CHARACTERISTICS AND MEMBRANE PERFORMANCE DATA

Polymer code	Composition	Mol. mass	pH 7[1]		pH 8		pH 9	
	(Monomer ratio)		R	J	R	J	R	J
PAA	-	75 000	90,4	2 080	93,2	1 810	90,2	1 900
PIA	-	43 200	54,7	10 150	57,8	10 150	61,0	9 600
PCIAA	-	99 000	60,6	8 880	64,1	8 520	65,6	8 335
PMAA	-	138 000	71,8	9 780	77,1	8 340	75,2	8 520
PAA/MAA	50/50	30 000	Not evaluated as membrane					
PAA/IA	65/35	41 000	78,0	5 980	81,9	5 250	85,9	4 350
PAA/CIAA	60/40	95 200	79,2	8 520	79,8	7 970	84,5	7 250
PMAA/CIAA	50/50	50 000	58,1	12 500	60,1	11 960	63,6	11 050
TERP	40/35/25	63 500	61,7	11 420	66,8	10 700	69,2	10 330
PAA/VAC	-	113 600	93,2	3 900	95,4	3 350	93,5	3 530

R: Rejection of $NaNO_3$(%).
J: Permeate flux (ℓ/m^2.d).
Superscript 1: 24 h after membrane formation. Subsequent readings (pH) taken at 30 min intervals after this reading.

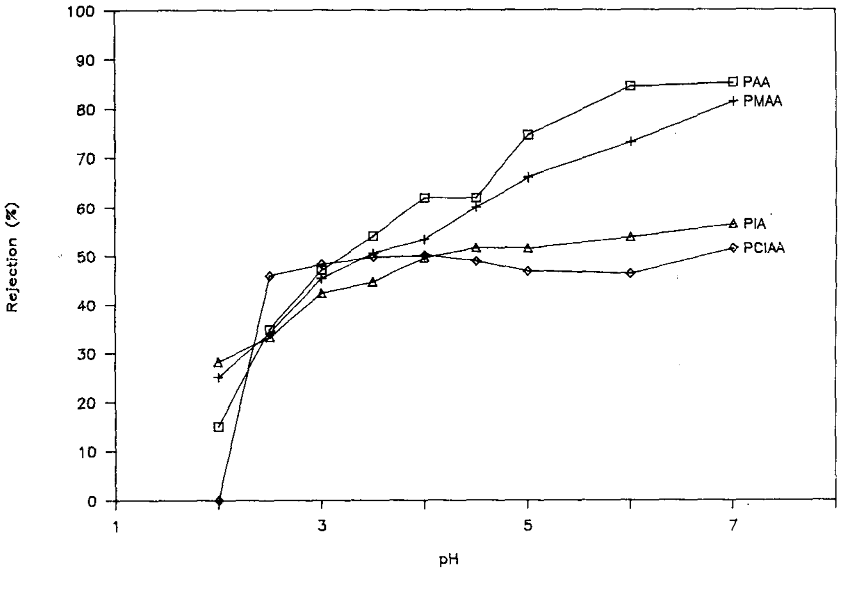


Figure 3
The change in salt rejection during membrane formation: Homopolymer membranes. Pressure 6 MPa, crossflow velocity 6 m/s, temperature 35°C, feed concentration 0,0235 M $NaNO_3$.

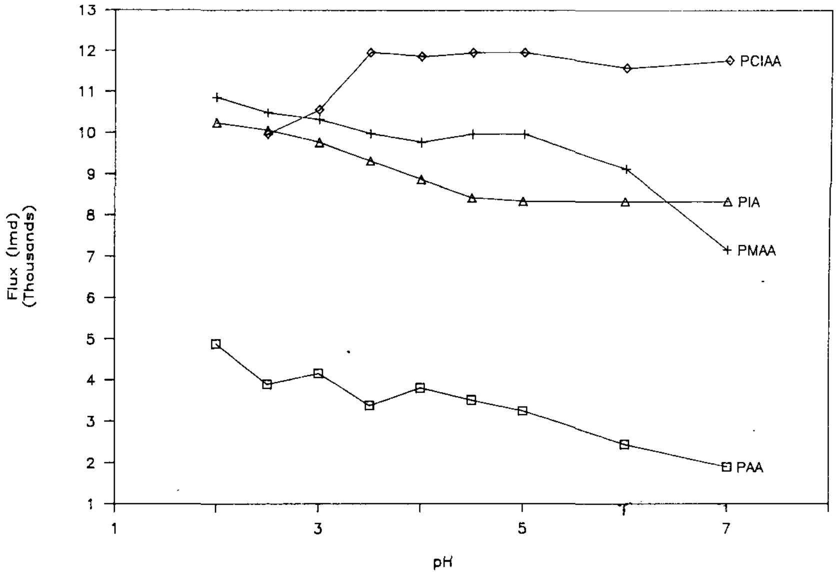


Figure 4
The change in flux during membrane formation: Homopolymer membranes. Pressure 6 MPa, crossflow velocity 6 m/s, temperature 35 °C, feed concentration 0,0235 M $NaNO_3$.

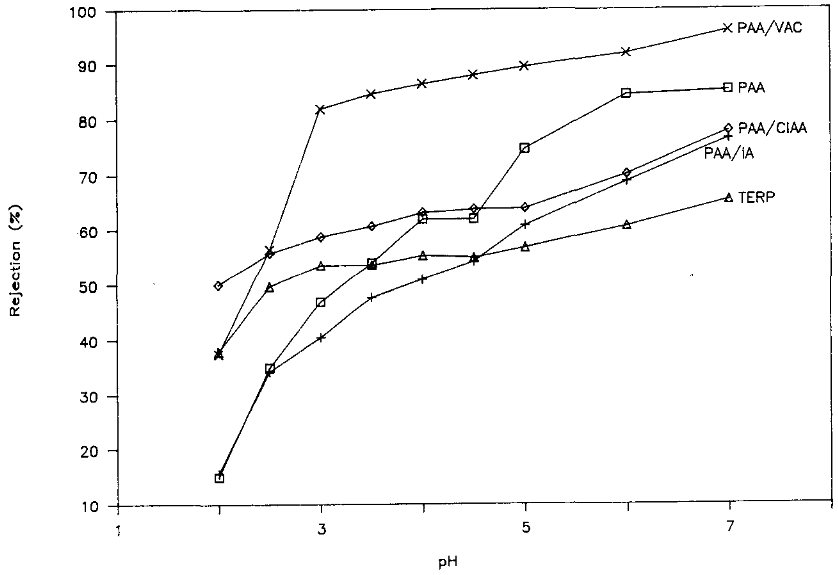


Figure 5
The change in salt rejection during membrane formation: Co and terpolymer membranes. Pressure 6 MPa, crossflow velocity 6 m/s, temperature 35 °C, feed concentration 0,0235 M $NaNO_3$.

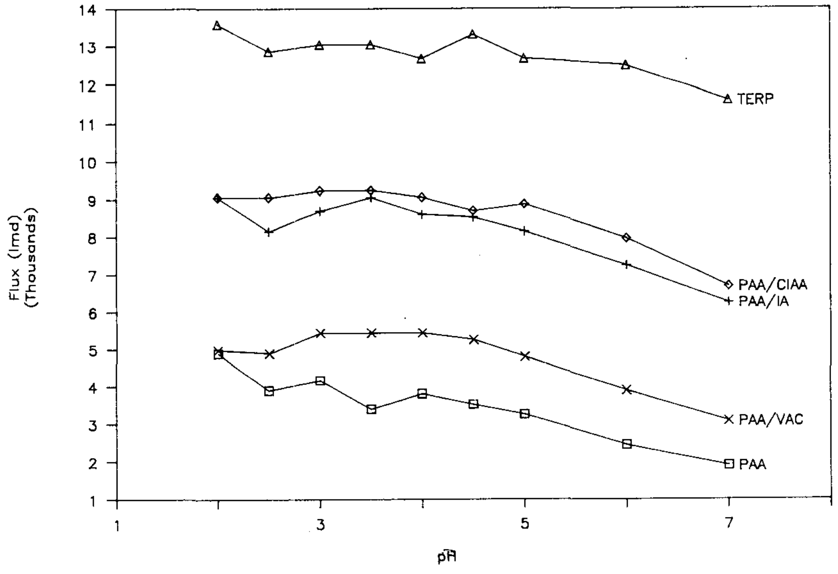


Figure 6
The change in flux during membrane formation: Co and terpolymer membranes. Pressure 6 MPa, crossflow velocity 6 m/s, temperature 35 °C, feed concentration 0,0235 M $NaNO_3$.

the Donnan exclusion mechanism, but there is also salt rejection due to the hydrophobic (uncharged) sections of the polyelectrolyte membrane. These results led directly to the further development of the research into dynamic membranes (Van Reenen, 1988; Van Reenen and Sanderson, 1989).

Conclusion

All the polyelectrolytes used formed dynamic membranes. It could be assumed that other, similar substitutions to acrylic acid would also lead to polyelectrolytes that would form dynamic membranes. The results obtained show that the salt rejection of these membranes is not due solely to the Donnan exclusion effect, but also to the presence of the uncharged section of the polyelectrolyte.

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