

Initial Flux Decline and Initial Rejection Increase for Swollen Ionic Membranes

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Synopsis

During the initial stage of operation, membrane performance in hyperfiltration experiments will be time dependent. For swollen ionic membranes, fluxes show an initial decrease while rejections initially increase in magnitude. These phenomena, also referred to as compaction, can be described by a model proposed here in which the wet membrane thickness decreases in time as a combined response to stepwise changed process parameters pressure and concentration. The response has been described by a linear first-order differential equation and worked out by use of known concepts of flux and rejection for swollen ionic membranes. Experimental data appear to be in good agreement with model predictions.

INTRODUCTION

Compaction is a concept in membrane research generally used to indicate phenomena like initial flux decline. Nonlinear relations between rejection or flux on the one hand and the operating pressure on the other are also ascribed to "compaction." Because of the practical importance of these phenomena, several authors studied flux changes in time. Bert¹ found for cellulose acetate membranes that the permeability is directly associated with the state of hydration for a given membrane, the hydration being determined by the pressure applied. Yasuda and Schindler^{2,3} gave a mathematical description for the relation between the state of hydration and the flux for highly hydrated membranes. The influence of membrane thickness d on the permeability through cellulose acetate membranes was studied by Baayers and Rosen⁴; they found a linear relationship between the waterflux through the membrane and the inverse value of d .

The influence of the applied pressure on the flux has also been investigated. For ionic membranes, Johnson⁵ and Lopatin and Newey⁶ found that flux and rejection increased nonlinearly with increasing pressure. The latter authors also studied several ionic membranes for the effect of different concentrations of NaCl solution on membrane swelling values and for the effect of pressure on membrane deswelling. The compression under pressure followed closely the theory of Katchalski, Lifson, and Eisenberg.⁷ The swelling values in NaCl solutions were clearly dependent on the salt concentration: differences of up to 50% in water content of the membranes were found at normal pressures for solutions between zero and 0.1N NaCl.

The objective of our investigation was to study the initial flux decline and initial rejection increase for swollen ionic membranes. Although all references cited above deal more or less with the compaction phenomenon, no model that could explain the simultaneous occurrence of an initial flux decline and an initial rejection increase in hyperfiltration experiments has been given up until now. In this paper such a model is proposed.

MODEL

The exact amount of membrane water in a membrane under operation can be determined at any moment with great difficulty only, since the hydration H is a function of pressure p and salt concentration c . We will describe the flux and rejection in terms of the wet membrane thickness d_w as a variable. It is known from process dynamics that the responses on simultaneous step changes in p and c can be summed. This is of importance here, since the decline of the swollen membrane thickness d_w in time cannot be ascribed to the influence of either pressure p or concentration c alone. We therefore propose a model in which the wet membrane thickness decreases in time as a combined response to the stepwise changed process parameters pressure and concentration.

In an ideal relaxation process, the rate of decrease of d_w is dependent on the deviation of d_w from the equilibrium value d_{eq} . This relaxation process can be described by a linear first-order differential equation, with the solution

$$d_w - d_{eq} = (d_w^0 - d_{eq}) \exp(-t/\tau). \quad (1)$$

Experimentally, eq. (1) cannot be verified directly. Since flux and rejection are functions of the volume fraction of hydration water in the membrane and wet membrane thickness d_w , flux and rejection can be studied as functions of time.

To describe the initial changes in flux and rejection, we write the differential with respect to t as follows:

$$\frac{dX}{dt} = \frac{\partial X}{\partial d_w} \cdot \frac{\partial d_w}{\partial t} \quad (2)$$

with $X = -J_w$ or $X = R$. If $\partial X/\partial d_w$ is a constant (which assumption will be discussed below), we can represent the initial flux decline and initial rejection increase by

$$\ln \left\{ -\frac{dJ_w}{dt} \right\}_t = K_1 - \frac{t}{\tau} \quad (3a)$$

$$\ln \left\{ \frac{dR}{dt} \right\}_t = K_2 - \frac{t}{\tau}. \quad (3b)$$

These equations have been tested experimentally, and results will be discussed in the results section. But first we will explore from known concepts of flux and rejection for swollen ionic membranes which conditions should be fulfilled for eqs. (3a) and (3b) to be valid.

Initial Flux Decline

Yasuda and Schindler^{2,3} used the following equation to describe the influence of the volume fraction of hydration water in the membrane on the water flux for highly swollen membranes:

$$J_w = K_0(\Delta p - \Delta\pi) \cdot \exp \left[-B \left(\frac{1-H}{H} \right) \right] \tag{4}$$

In the case of flat homogeneous (nonporous) membranes, the following relation between H and the membrane thickness is valid:

$$H = \frac{d_w - d_d}{d_w} \tag{5}$$

Combination of eqs (1), (2), (4), and (5) gives

$$\frac{dJ_w}{dt} = -K \cdot A \cdot \exp(-t/\tau) \tag{6}$$

with

$$K = [K_0(\Delta p - \Delta\pi) \cdot B \cdot d_d \cdot \{(d_w^0 - d_{eq})/\tau\}]$$

$$A = \{(d_w - d_d)^2 \cdot \exp\{B \cdot d_d/(d_w - d_d)\}\}^{-1}$$

The term $(d_w - d_d)$ varies from $(d_w^0 - d_d)$ to $(d_{eq} - d_d)$ and can be expressed by

$$(d_w - d_d) = \omega \cdot d_d \tag{7}$$

with

$$\frac{d_{eq}}{d_d} \leq \omega + 1 \leq \frac{d_w^0}{d_d}$$

With this expression, eq. (6) can be rewritten as

$$\ln \left(-\frac{dJ_w}{dt} \right) = K_1 - \frac{t}{\tau} - \ln[\omega^2 \cdot \exp(B/\omega)] \tag{8}$$

with

$$K_1 = \ln \{K_0(\Delta p - \Delta\pi) B (d_w^0 - d_{eq})/d_d \tau\}$$

Since ω depends on t , the term $(K_1 - \ln [\omega^2 \cdot \exp(B/\omega)])$ can decrease as d_w approaches the equilibrium wet membrane thickness d_{eq} .

Comparing eq (8) with eq. (3a), we expect that eq. (3a) will be followed for initial flux decline if the term $\ln [\omega^2 \cdot \exp(B/\omega)]$ does not depend too much on t in comparison with the term t/τ .

In the description given above, the possible influence of changes in $\Delta\pi$ on the flux, eq. (4), through an initial increase in the rejection has been neglected.

Initial Rejection Increase

According to Shor et al.,⁸ the rejection of an ionic membrane can be written as

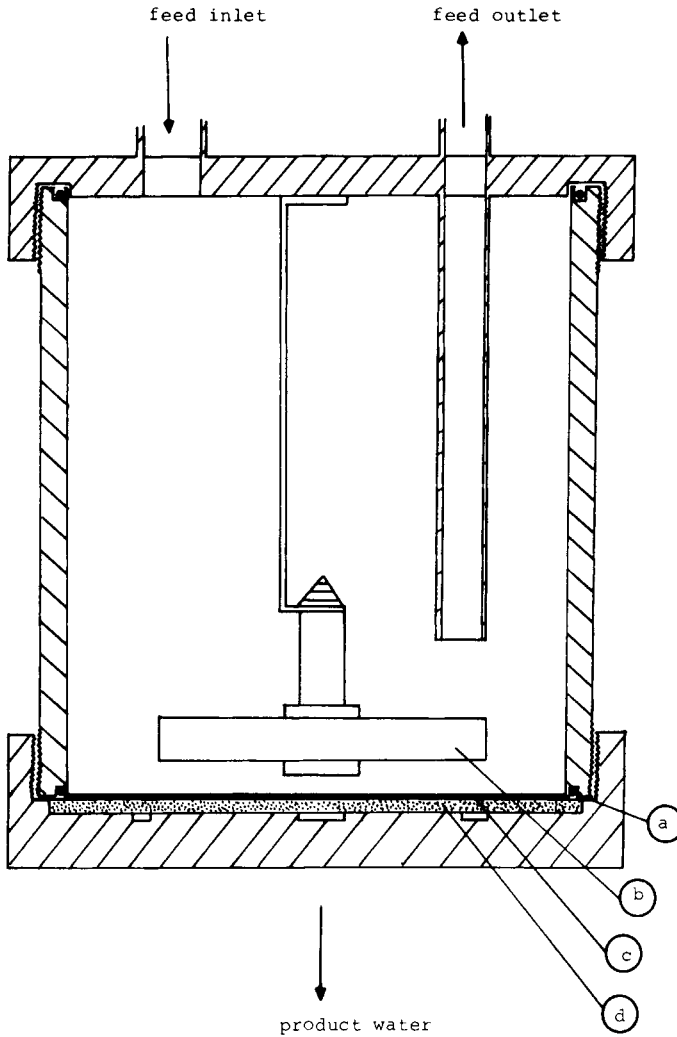


Fig. 1. High-pressure reverse osmosis cell: (a) O-ring; (b) magnetic stirrer; (c) membrane; (d) sintered metal disc.

$$D_{\alpha}^* \left[\frac{C^*}{c_s} + z D_{\alpha}^* \right]^z \Gamma^{z+1} = z^z \quad (9)$$

where $R = (1 - \beta D_{\alpha}^*)$ and generally $\beta = 1$. After substitution of $\{C_d^* \cdot (1 - H/H)\}$ for C^* and eq. (5) for H , eq. (9) can be differentiated with respect to d_w . Assuming $d\Gamma/dd_w = 0$, eq. (2) can be worked out to give

$$\ln \left(\frac{dR}{dt} \right)_t = \left[\ln \left\{ \frac{C_d^* (d_w^0 - d_{eq})}{c_s \cdot \tau \cdot d_d} \right\} \right] - \frac{t}{\tau} + \ln \left\{ \frac{z(1-R)}{\omega^2(1-R)(z+z^2) + \left(\frac{C_d^* \cdot \omega}{c_s} \right)} \right\}. \quad (10)$$

Since $\omega^2(1-R)(z+z^2)$ is much smaller than $(\omega \cdot C_d^*/c_s)$, eq. (10) becomes

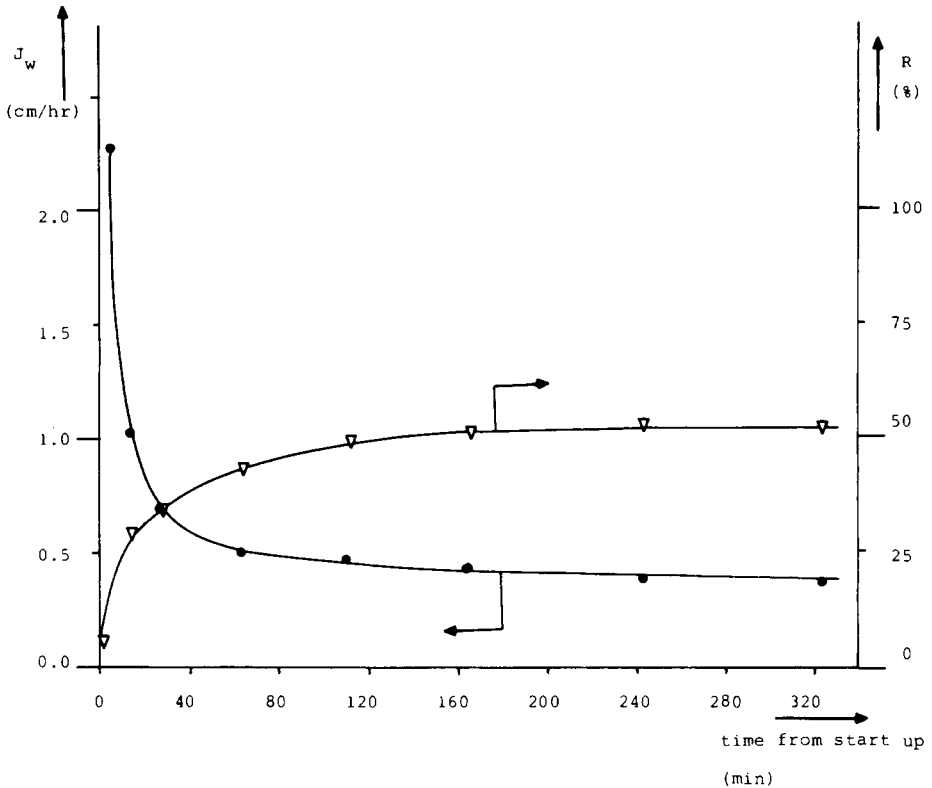


Fig. 2. Initial flux decline and initial rejection increase for an ionic S-I-S-48.3 membrane at 40 atm with a 2100 ppm NaCl feed solution.

$$\ln \left(\frac{dR}{dt} \right) = \ln \left[\frac{(d_w^0 - d_{eq}) \cdot z \cdot (1 - R)}{\omega \cdot \tau \cdot d_d} \right] - \frac{t}{\tau} \tag{11}$$

We see that eqs. (11) and (3b) become identical if $\ln(1 - R)/\omega$ does not depend on t . With the help of eqs. (1), (7), and (11), eq. (12) can be shown to be valid for $z = 1$ (and in general for all n - n electrolytes):

$$\frac{\partial \ln \left[\frac{1 - R}{\omega} \right]}{\partial t} = - \left\{ \frac{1}{\omega} \cdot \frac{d\omega}{dt} + \frac{1}{1 - R} \cdot \frac{dR}{dt} \right\} = 0 \tag{12}$$

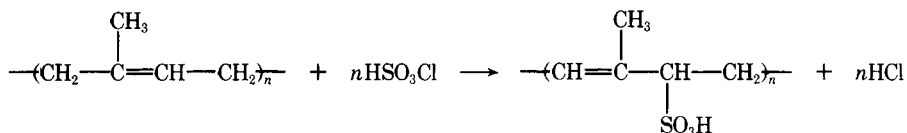
EXPERIMENTAL

Membranes

The negatively charged polymeric material used for preparing the membranes was made from a commercially available polystyrene-polyisoprene-polystyrene (S-I-S) block copolymer (Cariflex TR 1108). The preparative methods have been described elsewhere^{6,9} and are summarized below.

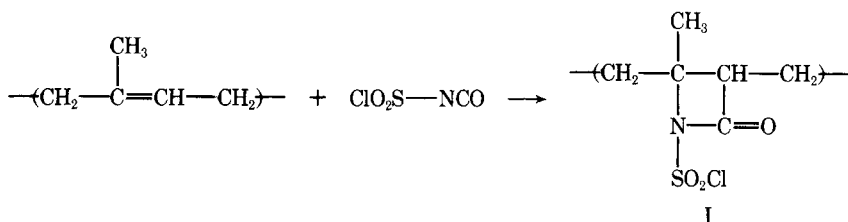
S-I-S-48.3. To a 8% S-I-S solution in dioxane, HSO_3Cl was added at

room temperature. The polyisoprene middle block reacts with the acid as follows⁶:

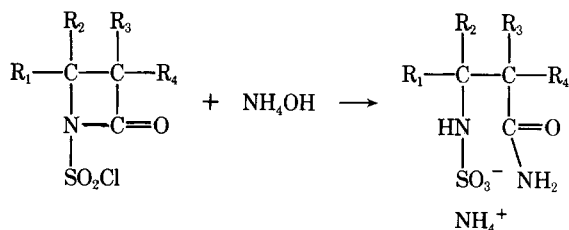


If all the isoprene would be modified in this manner, we would obtain a water soluble polyelectrolyte. For membrane preparation purposes we modified part of the isoprene in the middle block (48.3%). The polymer solution was cast on a glass plate with a doctor's knife, the solvent evaporated overnight, and finally the film was immersed in a KOH solution to form the salt.

S-I-S-S-20-HOM. To a 12.8% S-I-S solution in toluene, a certain amount of N-chlorosulfonyl isocyanate (NCSI) was added. The NCSI reacts with isoprene according to



The ratio (moles NCSI added/moles isoprene) was 20%. From a solution of polymer I in toluene a film was cast on a glass plate. After evaporation of the toluene, the film was hydrolysed in 1.65*M* ammonia for 45 min. Polymer I reacts with ammonia as follows⁹:



All membranes were rinsed with water before they were used. During the test, the membranes were supported by Schleicher and Schuell filter paper.

Apparatus

An Amicon high-pressure cell type 420 (Fig. 1) was used for the hyperfiltration tests. The cell was connected with a salt solution reservoir and the whole system was put under pressure by means of nitrogen gas. The salt solution directly above the membrane was mixed with a magnetic stirrer (450 cycles per min). The rejection was determined by measuring the salt concentration conductometrically:

$$R = \frac{c_{\text{feed}} - c_{\text{permeate}}}{c_{\text{feed}}} \cdot 100\% \quad (13)$$

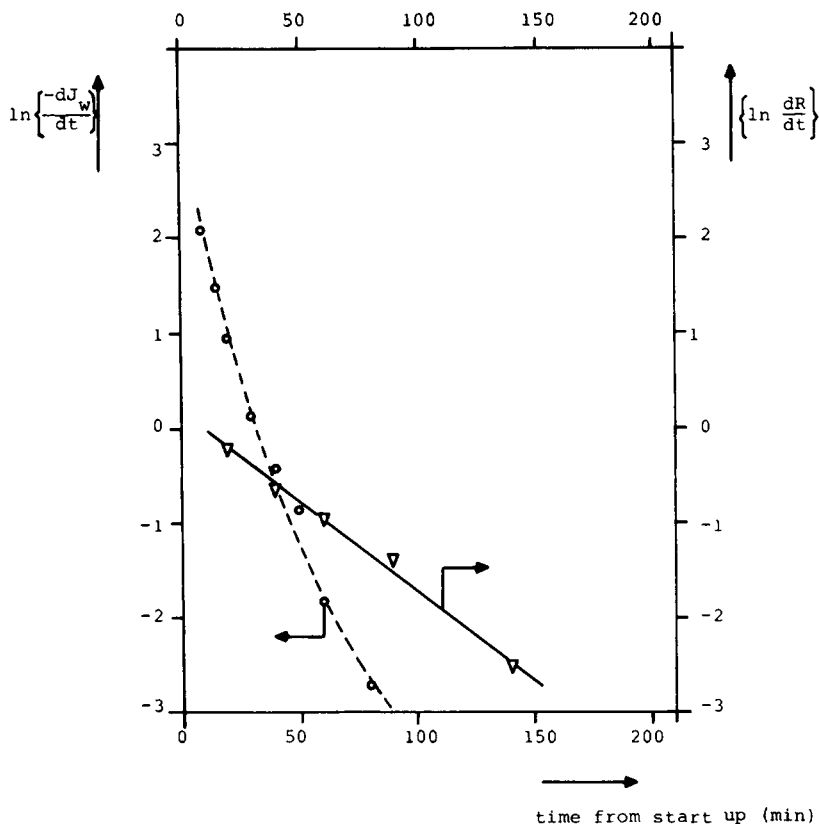


Fig. 3. Plot of the natural logarithm of dR/dt and $-dJ_w/dt$ vs. time for an ionic S-I-S-48.3 membrane at 40 atm, with a 2100 ppm NaCl feed solution.

RESULTS AND DISCUSSION

Equations (3a) and (3b) were tested with two different types of ionic membranes. The sulfonated S-I-S-48.3 membrane was tested with a 2100 ppm NaCl solution at 40 atm. The initial flux decline and rejection increase are shown in Figure 2. In Figure 3, $\ln(dR/dt)$ and $\ln(-dJ_w/dt)$ are given as a function of time.

The S-I-S-S-20-HOM membranes were tested with different salts and pressures. In Figures 4a and 4b, the results are given for tests carried out with a 4500 ppm NaCl solution at 40 atm. For this membrane, we could not measure a significant initial flux decline. In Figure 5a, the rejections are shown for tests at 30 and 40 atm, respectively, with a 7700 ppm Na_2SO_4 solution. The final rejection values at these two pressures are almost equal, indicating that d_{eq} (30 atm) is just a little larger than d_{eq} (40 atm).

Since Na_2SO_4 is not a n-n electrolyte, $\partial \ln[(1-R)/\omega]/\partial t$ in eq. (12) becomes negative, while K_2 in eq. (3b) decreases in time according to

$$K_2 = \ln \left[\frac{z(d_w^0 - d_{eq})}{\tau d_d} \right] + \ln \left(\frac{1-R}{\omega} \right). \quad (14)$$

Since now K_2 is time dependent, the linear relation between $\ln(dR/dt)$ and t does not hold any longer. In Figure 5b, we can see that for both experiments

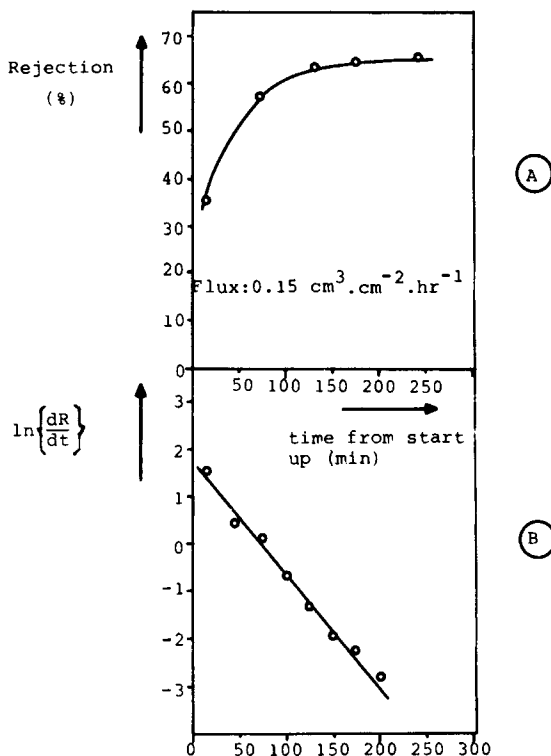


Fig. 4. Initial rejection increase for a S-I-S-S-20-HOM membrane at 40 atm, with a 4500 ppm NaCl feed solution.

the experimental points deviate more and more from the drawn lines with increasing time. Calculation of a relaxation time from Figure 5b is not possible for this reason.

Figure 3 demonstrates that the slopes for the lines describing the initial flux decline and rejection increase differ from each other. According to eqs. (3a) and (3b), however, both slopes should be equal to $1/\tau$. The deviation between experimental data and model predictions may be due to the presence of the term $\ln[\omega^2 \cdot \exp(B/\omega)]$ in eq. (8). The experimental flux data in Figure 3 indicate that the term $\ln[\omega^2 \cdot \exp(B/\omega)]$ is not constant in time. Consequently, a relaxation time cannot be calculated from our experimental flux data.

A similar phenomenon can be observed in the work of Yasuda and Lamaze.^{10,11} These authors investigated the dependence of the permeability of solutes through uncharged membranes, $P_{2,13}$, when hydration H varied. They found the following relation between $\ln P_{2,13}$ and $1/H$:

$$\ln(P_{2,13}/D_{2,1}) = \ln[\alpha \cdot H \cdot \phi(q_2)] - B(q_2/V_{f,1}) \left[\frac{1}{H} - 1 \right]. \quad (15)$$

Yasuda and Lamaze explained their experimental data by a linear relation between $\ln P_{2,13}$ and $1/H$, without exploring the significance of the term $\ln H$.

In Figure 6, the model is checked with data for hydrous Zr(IV) oxide membranes.⁵ Both $\ln(dR/dt)$ and $\ln(-dJ_w/dt)$ are linear in t with a negative

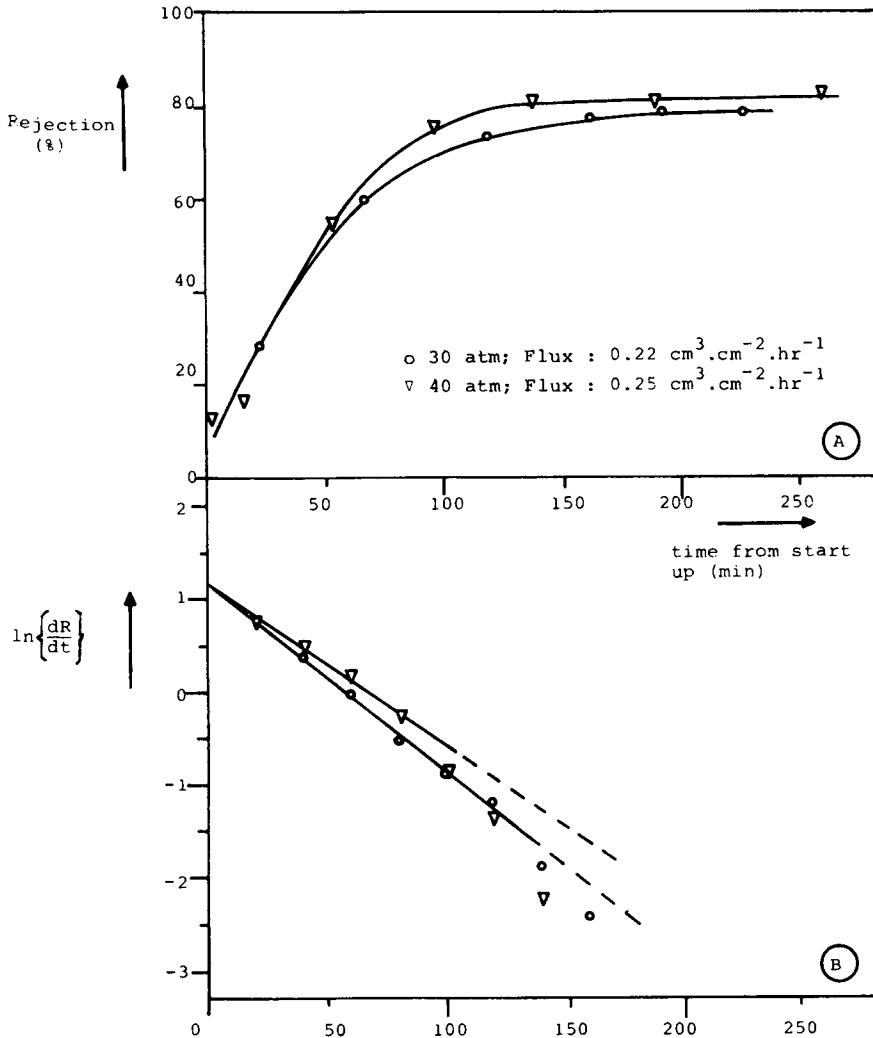


Fig. 5. Initial rejection increase for a S-I-S-S-20-HOM membrane at 30 atm (○) and 40 atm (▽), with a 7700 ppm Na_2SO_4 feed solution.

slope which is practically equal for both lines, showing that eqs. (3a) and (3b) are followed. In the foregoing discussion, the time dependence of H was studied for swollen ionic membranes. This initial deswelling of the membrane is due to removal of the loosely bound hydration water.

Yasuda and Schindler² approached the flux also in a different way than given in eq. (4), by using a relation in which the flux is described by a diffusion dependent constant K_d and a viscous flow dependent constant K_f :

$$J_w = (K_d + K_f) (\Delta p - \Delta \pi). \tag{16}$$

According to Peterlin, Yasuda, and Olf¹² the viscous flow-dependent term K_f is linear in $H/(1 - H) = \omega$. This means that K_f as well as d_w decrease exponentially in time, as a response to the stepwise changed process parameters.

Since the initial decline of d_w at constant applied pressure can be compared with the decrease of d_{eq} when the applied pressure increases, the analy-

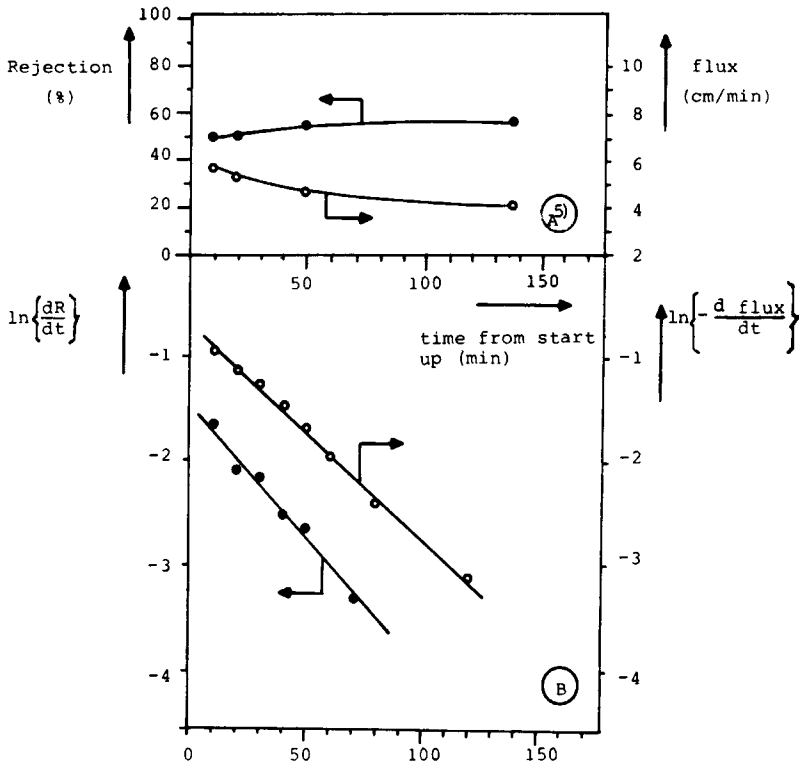


Fig. 6. Initial flux decline and rejection increase for hydrous Zr(IV) oxide membranes at 67 atm; feed solution contains 2900 ppm NaCl and 10^{-4} M hydrous Zr(IV) oxide.⁵

sis given here can also be applied to flux/rejection measurements at different pressures.

CONCLUSIONS

The physical meaning of the model proposed here lies in the initial removal of the loosely bound hydration water due to the influence of pressure as well as salt concentration. This removal of water can be described by an exponential decrease of the wet membrane thickness d_w .

The validity of the model is demonstrated for rejection measurements with 1:1 electrolytes and contains a function to explain the deviation of asymmetrical electrolytes. Generally, it is not possible to calculate relaxation times from the flux data due to uncertainty in the value of ω , assumed constant in time.

Experimental data show that information on membrane performance can be obtained by dynamic measurements.

Greek Symbols

α	constant
β	constant mostly 1
Γ	$\gamma_{\pm}^x / \gamma_{\pm}$
γ_{\pm}^x	mean ionic activity coefficient of salt in the membrane

γ_{\pm}	mean ionic activity coefficient of salt in the salt solution
$\phi(q_2)$	this term describes the sieve mechanism by which small molecules are permitted to diffuse and larger molecules are rejected because the macromolecular network has no hole of appropriate size
$\Delta\pi$	osmotic pressure difference across the membrane (atm)
τ	relaxation time (min)
ω	time-dependent variable

Nomenclature

B, C	constants
c_f	salt concentration in filtrate (mole/l.)
c_m	salt concentration in membrane (mole/l.)
c_s	salt concentration in salt solution (mole/l.)
C^*	membrane capacity (eq/kg membrane water)
C_d^*	ion exchange capacity (meq/g dry polymer)
d_{eq}	equilibrium wet membrane thickness at $t = \infty$ under operating pressure (cm)
d_d	dry membrane thickness at $t = \infty$ under operating pressure (cm)
d_w	wet membrane thickness at time t and under operating pressure (cm)
d_w^0	wet membrane thickness at zero time (cm)
D_{α}^*	equilibrium distribution coefficient of component α (c_m/c_s)
$D_{2,1}$	diffusion coefficient of solute in water (cm^2/sec)
H	volume fraction of water in the membrane
J_w	water flux through the membrane ($\text{cm}^3/\text{cm}^2 \text{ hr}$)
K_i	constants
Δp	applied pressure (atm)
$P_{2,13}$	permeability of solute through water-swollen membrane (cm^2/sec)
q_2	cross-sectional area of the diffusing molecule
R	rejection ($1 - \frac{c_f}{c_s}$)
t	time from startup (min)
$V_{f,1}$	free volume of pure water
X	R or $-J_w$
z	charge of coion

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