THE ULTRAFILTRATION OF SALT-POLYELECTROLYTE SOLUTIONS

Thesis by

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This thesis is dedicated to my wife, Susan, for her patience and understanding during my graduate study.

ABSTRACT

The ultrafiltration of sodium chloride - sodium polyacrylate solutions was studied using a membrane completely impermeable to the polyelectrolyte but permeable to water and simple salts. The membrane was a synthetic, hydrated polymer membrane with an ionic cross-linked structure. The activity of sodium chloride in the filtration cell was measured using a sodium-sensitive glass electrode/silver-silver chloride electrode pair. The continuous flow filtration cell used contained a stirring blade that was used to eliminate concentration polarization at the membrane surface. The effect of stirring speed was observed. The membrane salt-rejection and permeability characteristics were determined using distilled water and NaCℓ solutions. Independent salt activity measurements in NaCℓ-NaPA solutions were also made.

The sodium chloride activity data were compared with the simple additivity rule or dissociation theory for the activity of simple salts in polyelectrolyte solutions and with theory based upon the cylindrical electrostatic model. Agreement with the electrostatic model was good; expressions based upon the simple dissociation theory underestimated the activity.

Concentration polarization effects during filtration were eliminated only in the case of the lower polyelectrolyte concentrations studied and at relatively low filtration rates using high stirring speeds. Under these conditions, the filtrate flow rate and salt concentration were accurately predicted by flux equations typical of the thermodynamics of irreversible processes. At the solution-membrane interface, where the polyelectrolyte separation takes place, equilibration of the salt leads to an effective concentration equal to the equilibrium salt concentration; thus, the filtrate salt concentration is significantly greater than the salt concentration in the salt-polyelectrolyte solution being filtered. Results of experiments involving concentration polarization were compared with a simple boundary-layer model with only fair success.

The motivation for the research was the possibility of developing a desalination process upon the Donnan membrane equilibrium. The process is described and its performance is evaluated for various operating conditions. Economic considerations indicate only limited use for the process.

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I. INTRODUCTION

Many communities with a potentially abundant groundwater supply must develop other costly water supplies because the groundwater is too saline. The U. S. Public Health Service recommended limit for total dissolved solids is 500 mg/l; many groundwaters have a TDS concentration of 1000 to 2500 mg/l and are therefore unsuitable for water supply unless some form of desalination is used. Present water treatment processes are designed to remove color, turbidity, bacteria and other potentially harmful organisms, iron and manganese, and hardness; but they are not designed to remove dissolved salts,and thus they do not significantly affect the TDS of brackish waters. Thus, a new technology is necessary in the water treatment field for the effective removal of dissolved salts and minerals from large volumes of water at economic costs.

Much interest has been generated in this problem by the Saline Water Act of 1952 authorizing the saline water conversion program of the Department of the Interior and by the formation of the Advanced Waste Treatment Program of the USPHS (now under the Federal Water Pollution Control Administration of the Department of the Interior). These programs have funded much research aimed at developing new methods of treatment.

One of the processes that has developed out of these programs is "reverse osmosis" or "membrane hyperfiltration." This process is based upon the use of membranes permeable to water but relatively impermeable to dissolved salts and many other dissolved substances.

It appears to be more suited to the desalination of slightly brackish waters than to demineralization of sea water or highly brackish water. Reverse osmosis will become an efficient and economical process only if membranes can be developed which 1) do not require pressures greatly in excess of the brackish water osmotic pressure to obtain high salt removal, 2) have higher water permeability than present membranes, and 3) have a long lifetime. For an extensive treatment of the state of the art of reverse osmosis, the reader is referred to the recent book edited by Merten[1].

In this present research, the fundamentals of a new process somewhat related to reverse osmosis have been studied. The process consists of two steps. In the first step, salt water is pumped into two compartments separated by a dialysis membrane permeable to water and simple salts but impermeable to macromolecules. To one solution is added a polyelectrolyte, which cannot diffuse through the membrane. The addition causes salt to diffuse from the polyelectrolyte solution to the other until equilibrium is restored. Some salt is thus removed from the solution containing the polyelectrolyte during dialysis. If the polyelectrolyte can now be removed, and preferably recovered, partial desalination will have been obtained.

In the second step, the polyelectrolyte is separated and recovered by ultrafiltration and returned to the dialysis step. The ultrafiltration membrane used in this step need retain only the polyelectrolyte, not simple salts. The effect of the dialysis, then, is to reduce the filtration requirements from removal of simple salts to removal of polyelectrolytes. For this reason it is expected that higher filtration rates can be obtained with this process than with desalination by reverse osmosis directly.

In order to determine the feasibility of such a process, it is necessary to describe quantitatively its performance as a function of (a) the various operating parameters, such as polyelectrolyte concentration, the applied filtration pressure, and the recirculation ratio; and (b) system characteristics, such as the nature of the two membranes. Useful calculations of the dialysis equilibria may be made for a limited range of polyelectrolyte concentrations based upon thermodynamic studies reported in the literature. The ultrafiltration of salt-polyelectrolyte solutions has received only scant attention in the literature and only for dilute systems. Experimental studies have been concerned with the filtrate composition at low polyelectrolyte concentrations and have not included pressure-flow relations.

Thus, in the present research, thermodynamic studies were made for polyelectrolyte solutions more concentrated than those reported in the literature. Moreover, experimental studies of the ultrafiltration of salt-polyelectrolyte solutions were conducted for the concentrations of practical interest here.

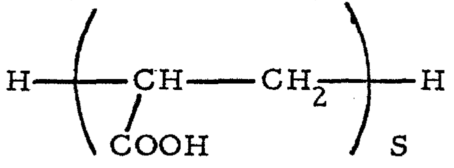
The next chapter contains a description of previous theoretical and experimental results pertaining to the present problem. Also, the flow equations of irreversible thermodynamics are developed to include the case of ultrafiltration of polyelectrolyte solutions. The last section includes a statement of the objectives of the experiments described in the following chapter. In Chapter IV, the experimental results are presented. The thermodynamic results are compared to various theories of polyelectrolyte solutions, and the filtration results are compared with the relations developed in Chapter II. The results are used in Chapter V to describe the performance of the proposed process and to draw conclusions concerning its practical use. Chapter VI contains a summary and the conclusions drawn from this research.

II. BACKGROUND AND THEORETICAL CONSIDERATIONS

Quantitative description of the proposed process is based on thermodynamic concepts. In this chapter, the pertinent experimental and theoretical results of various investigators are presented and the need for additional research on the thermodynamics and the ultrafiltration of salt-polyelectrolyte solutions is indicated.

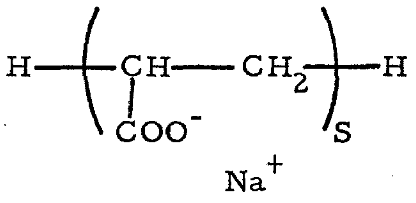
A. The Thermodynamics of Polyelectrolyte Solutions.

1. Definitions. A polyelectrolyte is a polymer which has repeating ionic side groups. There are many types of polyelectrolytes ranging from natural proteins to inorganic polyphosphates to synthetic polyelectrolytes such as sodium polyacrylate. The structural formula of sodium polyacrylate (which was used in this study) is shown below along with the acid form, polyacrylic acid. The sodium salt may be obtained by neutralizing the acid form with sodium hydroxide; the degree of neutralization, if incomplete, is represented by α. ($\alpha = \frac{m_{NaOH}}{m_m}$.)



$$H-\left(\underset{COOH}{CH}-CH_2\right)_S-H$$

Polyacrylic acid (PAA)



$$H-\left(\underset{\underset{Na^+}{COO^-}}{CH}-CH_2\right)_S-H$$

Sodium polyacrylate (NaPA)

In solution, polyelectrolytes partially dissociate, forming a solution of polyions of many units of charge and simple ions of opposite charge called counterions. The sodium ion is the counterion in a solution of sodium chloride and sodium polyacrylate (NaPA).

The chloride ion is called the coion; its charge is of the same sign as that of the polyion.

Polyelectrolyte concentrations will be expressed in either of two ways; as the molality of polymer particles, m_p, or as the molality of monomer units, m_m. The concentration m_m is called the monomolar concentration. The two are related by $m_p = m_m/S$, where S is the average degree of polymerization. For example, a solution containing 72 grams of polyacrylic acid per kilogram of solvent has a monomolar concentration, m_m, of unity. If $S = 1000$, then $m_p = 10^{-3}$ moles of polymer molecules per kilogram solvent.

2. The Donnan Membrane Equilibrium. Consider a system consisting of two solutions separated by a semipermeable membrane which is permeable to water and small ions but impermeable to macromolecules, such as polyelectrolytes. If both solutions contain a simple salt, such as NaCℓ, and one solution contains, in addition, a polyelectrolyte which is a salt of one of the simple ions, such as NaPA, then an interesting distribution of the salt occurs at equilibrium. This equilibrium was first studied by F. G. Donnan in 1911,[2] and is called the Donnan membrane equilibrium.

Equilibrium is obtained when all of the permeable components have distributed themselves such that their chemical potentials are equal on both sides of the membrane. As a result, a salt concentration difference and an osmotic pressure difference are established across the membrane.

The conditions for equilibrium may be written

$$\begin{aligned} RT\,\ell n\, a_s^I + \int_1^{1+\Delta\pi_D} \bar{v}_s\, dp &= RT\,\ell n\, a_s^{II} \\ RT\,\ell n\, a_w^I + \int_1^{1+\Delta\pi_D} \bar{v}_w\, dp &= RT\,\ell n\, a_w^{II} \end{aligned} \tag{1}$$

where $\bar{v}_i$ is the molar volume of component i, a_i is the activity of component i, $\Delta\pi_D$ is the Donnan osmotic pressure difference, and the subscripts s and w denote the salt and water components. The superscript I denotes the solution containing the polyelectrolyte; II denotes the salt solution.

It is assumed that $\bar{v}_w$ is independent of pressure; then the usual expression for osmotic pressure is obtained from the second equation:

$$\Delta\pi_D = \frac{RT}{\bar{v}_w}\,\ell n\,\frac{a_w^{II}}{a_w^I} \quad . \tag{2}$$

For values of $\Delta\pi_D$ less than 15 atmospheres, the integral in the first equation may be neglected with less than 1 per cent error, resulting in the requirement that

$$a_s^I = a_s^{II} \tag{3}$$

at equilibrium. Thus, if the salt activity is known as a function of composition in polyelectrolyte-salt solutions, dialysis equilibrium concentrations may be easily calculated.

As an example, consider the dialysis of a solution containing polyelectrolyte and uni-univalent salt at concentrations m_p and m_s, respectively, with an external salt solution of concentration m_o, which is maintained constant. If each polymer molecule dissociates to give one polyion of negative charge ν, and ν singly-charged counterions, then the total concentrations of positive and negative simple ions are given by

$$\begin{aligned} m_- &= m_s \\ m_+ &= m_s + \nu m_p \ . \end{aligned} \tag{4}$$

Assuming ideal behavior, we may write

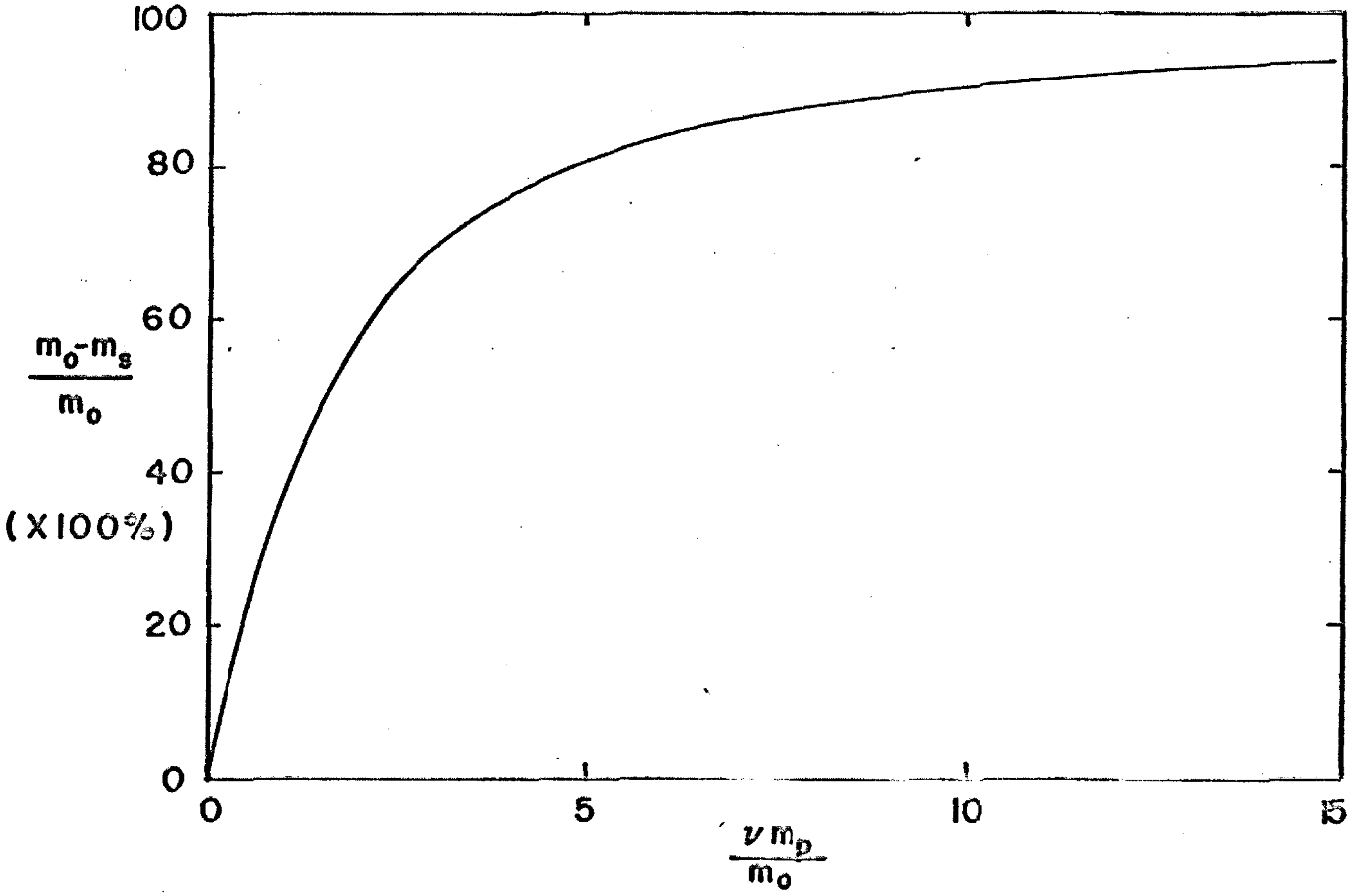
$$\begin{aligned} a_s^{I} &= m_+ m_- = m_s(m_s + \nu m_p) \\ a_s^{II} &= m_o^2 \ . \end{aligned} \tag{5}$$

Equating these activities, m_s may be calculated. In terms of the fraction of salt removed from a salt solution originally at concentration m_o to which polyelectrolyte has been added, the following equation is obtained:

$$\frac{m_o - m_s}{m_o} = 1 + \frac{1}{2}\,\frac{\nu m_p}{m_o} - \sqrt{\left(\frac{\nu m_p}{2m_o}\right)^2 + 1} \ . \tag{6}$$

A graph of this equation is shown in Figure II-1. It shows that if $\nu m_p/m_o = 5$, 80 per cent of the salt is removed by dialysis. It will be seen later that this equation, based upon ideal behavior, describes the salt distribution at equilibrium adequately enough for many purposes. In order to use it, however, ν must be known.

3. Osmotic Pressure and Counterion Activity in Polyelectrolyte Solutions Containing No Salt. When a polyelectrolyte is dissolved in water, the weakly bound counterions tend to dissociate from the polyion and to distribute themselves uniformly throughout the solution. Because of the high charge density of the polyion, however, electrostatic forces prevent complete dissociation and cause the counterions



II-1. Curve of equation (6): the per cent salt reduction obtained in dialysis as a function of the relative polyelectrolyte concentration.

to concentrate near the polyion in an electrical double layer. Hence, the osmotic pressure and the counterion activity are less than expected on the basis of complete dissociation.

The osmotic pressure of a polyelectrolyte solution may be expressed as

$$\pi = RT(1 + \alpha S) m_p \phi_p ,$$

where $1 + \alpha S$ is the total number of ions per polyelectrolyte molecule (1 polyion and αS counterions), and ϕ_p is the molal osmotic coefficient. For typical polyelectrolytes $\alpha S >> 1$; thus, the osmotic pressure is caused primarily by the counterions. Neglecting the one and making the substitution $m_m = Sm_p$, the above expression may be written:

$$\pi = \alpha \phi_p m_m RT \ . \qquad (7)$$

Since αm_m represents the stoichiometric concentration of the counterions, ϕ_p may be considered the effective degree of dissociation of the counterion.

Alexandrowicz[3] and Kern[4] have determined the osmotic coefficient of several vinyl polyelectrolytes and have obtained essentially consistent results. They have found that ϕ_p is most sensitive to the degree of neutralization, α, decreasing as α is increased. It increases slightly with increasing concentration and is independent of the degree of polymerization.

Similar observations have been made concerning the counterion activity coefficient in saltless polyelectrolyte solutions. The counterion activity coefficient is defined by

$$\gamma_+ = \frac{a_+}{m_+} = \frac{a_+}{\alpha m_m} ,$$

and may also be interpreted as an effective degree of dissociation of the counterions. Kern[4], Nagasawa and Kagawa[5], and others[6-10] have found that γ_+ increases slightly with concentration for the sodium salts of many linear polyelectrolytes. Okuba, Nishizaki, and Ise[11] found the sodium activity coefficient to be essentially independent of concentration in solutions of sodium polyacrylate of concentrations between 0.008 and 0.2 moles/liter.

On the other hand, Kagawa and Katsuura[6] found that γ_{Ag^+} decreases significantly with concentration for solutions of silver carboxymethyl cellulose. Lyons and Kotin[8] have shown that a negative slope of γ_+ versus m_m is a result of specific non-electrostatic forces acting on the counterions. Thus, for systems in which no site binding or chemical bonding occurs, γ_+ is expected to increase slightly with concentration.

In their studies of the sodium salts of various polyelectrolytes, Nagasawa and Kagawa found that γ_+ is inversely proportional to the linear charge density of the polymer chain, but is independent of the degree of polymerization, S, and of the structure of the polymer (except as it affects the linear charge density). Molecular weights corresponding to values of S between 400 and 1500 were studied. Strauss and Ander[41] also observed no difference in Donnan equilibrium measurements using sodium polyphosphates of 332,000 and 22,400 molecular weight, corresponding to S = 3300 and 220, respectively.

As will be seen later, these observations are in good agreement with a purely electrostatic model, namely, that the counterion activity coefficient in salt-free polyelectrolyte solutions 1) increases slightly with increasing concentration in systems in which no chemical bonding is expected, 2) is significantly smaller than single ion activity coefficients in simple salt solutions at the same equivalent concentration, 3) is inversely proportional to the linear charge density of the polyelectrolyte, and 4) is independent of the degree of polymerization for sufficiently high values (probably greater than 50 or 100).

4. Salt Activity in Polyelectrolyte-Salt Solutions. In solutions of a polyelectrolyte and a simple electrolyte having one ion in common, the activity of the salt and the activity of the counterion are observed to follow very simple relationships[3, 5, 8, 12]. Nagasawa, et al., observed that the rule of additivity of counterion activity, first proposed as a result of hydrogen-ion activity measurements in polystyrene-vinyltoluene copolymer-hydrochloric acid mixtures[13], was followed for a large range of polymer and salt concentrations[5, 12]. The additivity rule may be expressed for polyanions, with cations as counterions, as

$$a_+(\alpha, m_m, m_s) = a_+^p(\alpha, m_m) + a_+^s(m_s) , \qquad (8)$$

where the single-ion activities appearing on the right are the activity of the counterion in a salt-free polyelectrolyte solution of concentration m_m and degree of neutralization α, and the cation activity in a pure salt solution at concentration m_s.

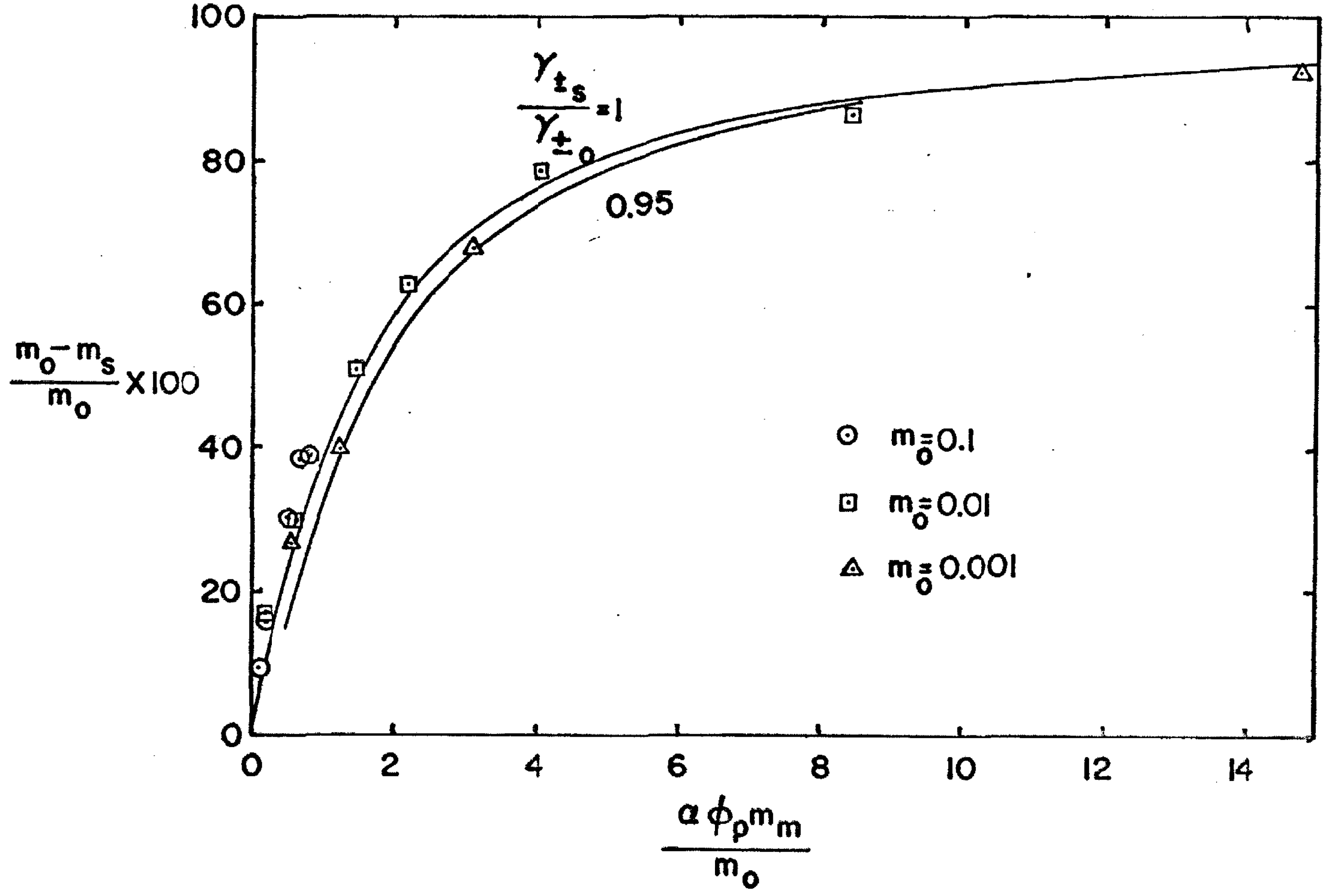
Thus, Alexandrowicz[3] has found that the empirical equation

$$a_s = (\alpha\phi_p m_m + m_s) m_s \gamma_{\pm_o}^2 \qquad (9)$$

approximately describes the salt activity in the presence of a polyelectrolyte. ϕ_p is the osmotic coefficient of the pure polyelectrolyte and represents the effective degree of dissociation. Interactions between simple ions are accounted for by the quantity $\gamma_{\pm_o}$, the mean molar activity coefficient of a simple salt solution at an ionic strength of $m_s + \frac{1}{2}\alpha\phi_p m_m$. Although this expression underestimates the activity of the salt at low salt concentrations (by about 15 per cent), it may be used to calculate the quantity $\frac{m_o - m_s}{m_o}$ (representing the fraction of salt removed in dialysis) with fair success. One obtains

$$\frac{m_o - m_s}{m_o} = 1 + \frac{\alpha\phi_p m_m}{2m_o} - \sqrt{\left(\frac{\alpha\phi_p m_m}{2m_o}\right)^2 + \left(\frac{\gamma_{\pm_s}}{\gamma_{\pm_o}}\right)^2} \qquad (10)$$

where $\gamma_{\pm_s}$ is the activity coefficient of the salt solution. This equation is similar to equation (6); the quantity $\alpha\phi_p m_m$ has replaced the quantity νm_p, and activity coefficients are included. Their effect is small, however, since only in extreme cases is their ratio significantly different from one. Equation (10) is shown in Figure II-2 for $\gamma_{\pm_o}/\gamma_{\pm_s} = 1.0$ and 0.95. Also included are points calculated from the data of Alexandrowicz[3] for the NaPA - NaBr system. Polyelectrolyte concentration m_m ranged from 0.004 to 0.45. For all these data, $0.95 < \gamma_{\pm_o}/\gamma_{\pm_s} < 1.0$; therefore, the points should lie within the two curves if equation (9) is valid. The agreement is satisfactory for many practical purposes, including the present, but it is to be



II-2. Comparison of Alexandrowicz's data with equation (10) for $\gamma_{\pm_o}/\gamma_{\pm_s}$ equal to 1.0 and 0.95.

observed that this equation does underestimate the effect of the polymer at higher polymer concentrations. More elaborate models have been proposed to describe polyelectrolyte solutions, and they are discussed in the next section.

The osmotic pressure of salt-polyelectrolyte solutions is also described by an additivity rule similar to equation (8):

$$\pi(\alpha, m_m, m_s) = \pi^p(\alpha, m_m) + \pi^s(m_s)$$

or

$$\pi = (\alpha\phi_p m_m + 2m_s\phi_s)RT \quad . \tag{11}$$

ϕ_s is the osmotic coefficient of a pure salt solution. Equation (11) predicts the experimental data with an error of less than 5 per cent over the range of concentration studied[3, 14]. The theoretical models discussed next predict essentially the same results as this expression.

5. <u>Theoretical Models of Polyelectrolyte Solutions</u>. Because charged polyions repel each other and thus tend to assume positions of maximum distance from each other, most theories use the cell model of solutions. Thus, a unit volume of solution containing $N_A m_p$ polyions is divided into $N_A m_p$ cells of volume $1/N_A m_p$. N_A is Avogadro's number. Each cell contains one polyion that establishes in the cell a central electrostatic potential ψ that is assumed to govern the distribution of the simple ions and to determine the solution's colligative properties.

From symmetry the gradient of the potential is zero at the cell boundary, R. The strong electrostatic forces of the polyion are not acting on the mobile ions in the boundary region; therefore, the solution in this region is considered ideal in that activities are proportional to concentration. Setting $\psi(R) = 0$, the electrochemical potential of the mobile species i at the boundary (and thus throughout the solution since equilibrium is assumed) is given by

$$\mu_i = \mu_i^o + RT\ln m_i(R)$$

where ideal behavior at composition $m_i(R)$ is assumed. Introducing bulk concentrations and activity coefficients gives

$$\mu_i = \mu_i^o + RT\ln \gamma_i^R \bar{m}_i \quad ;$$

hence,

$$\gamma_i^R = m_i(R)/\bar{m}_i$$

where γ_i^R is the bulk activity coefficient of i based upon ideal behavior at composition $\sum_i m_i(R)$, and $\bar{m}_i$ is the bulk concentration of i. That the solution at the cell boundary does not behave ideally is accounted for in an approximate manner by applying the Debye-Hückel activity coefficient (for a solution of the same ionic strength as the boundary solution) to the final results[3, 9, 10, 15]. Langmuir was the first to point out that the colligative properties of colloidal systems are given by the ion concentrations at the cell boundaries[16, 17]. Thus, it is the aim of specific models of polyelectrolytes to predict the composition of the boundary solution given the bulk concentrations.

<u>(a) Salt-Free Polyelectrolyte Solutions.</u>- Except for some stiff biocolloids, polyions are flexible chains which are continuously changing shape and thus cannot be characterized by a single set of geometrical parameters. Early attempts to deal explicitly with charged macromolecules endowed with a random spatial distribution

of the segments encountered insurmountable mathematical difficulties so that drastic approximations had to be made in order to obtain manageable expressions[18]. Thus, the approach adopted has been to make calculations based on some average polymer configuration, implicitly assuming that all of the energetically important configurations are similar and have the same interaction energy between polyion and mobile ions[15]. Simple geometries are used for the polyion (sphere, cylinder, ellipsoid) and the charged groups are treated as an effective surface charge. The ionic distribution is then calculated using the Poisson-Boltzmann equation.

While this approach allows a rigorous mathematical treatment, the choice of the right model becomes of critical importance. For example, the sphere attracted much attention when it was realized that polymeric coils are essentially spherical in shape. In using the spherical model, one must somehow smear out the fixed charges over the sphere, resulting in the loss of the extremely densely charged regions along the polymer chain and their replacement by an "equivalent" sphere with relatively low charge density. More rigorous studies[19, 20] have shown that the underestimation of the potential through use of the sphere model is substantially offset by the use of the linear approximation in the Poisson-Boltzmann equation, and that agreement with experiment was due to cancellation of these errors.

For these reasons, the cylindrical model[21-23] is preferred for the more realistic representation of the local charge density along the polymeric chain. While one would not expect the stiff cylindrical model to account for any shape-dependent properties of a flexible polyion, the colligative properties are observed to depend, by and large, on the linear charge density of the chain. This observation indicates the predominant role of the electrostatic field which surrounds the chain skeleton with cylindrical symmetry. Thus, the cylindrical model is expected, within limitations, to provide correct predictions for electrochemical properties of polyelectrolyte solutions[9].

Lifson and Katchalsky[21] have solved the Poisson-Boltzmann equation rigorously for the cylindrical case without linearizing the exponential. They calculated ϕ_p and found that it is strongly dependent on the linear charge density of the cylinder and increases slightly with increasing polymer concentration, which enters into the calculation through R, the cell radius. The approximate expression

$$\phi_p = \frac{1 - \beta^2}{\lambda} \qquad (12)$$

was found, in which $\beta(R, \lambda)$ is a constant of integration and λ is a dimensionless linear charge density. For $\lambda > 1$ (corresponding to $\alpha > 0.2$ in NaPA solutions), β is essentially independent of λ; thus, ϕ_p (or γ_{+}^{p}) is inversely proportional to the linear charge density. Though the shape of the calculated curves was identical with the slope of the data, calculated values were approximately double the measured values. In order to fit the data, an "effective charge density" (which was approximately twice that calculated on the basis of a completely stretched polymer chain) was used. The use of a larger λ could be justified if the chain is not completely stretched. Also, since the dielectric constant is in the denominator of λ and the value corresponding to bulk water was used, using a lower value (on the basis of the high electric field near the polymer)would also increase λ, thus lowering the calculated value of ϕ_p. Thus, it is not unreasonable to use an "effective" linear charge density in order to fit the data. The value used for the radius of the model cylinder was estimated from the molar volume of the polyelectrolyte.

(b) Solutions Containing Salt. - The solution of Lifson and Katchalsky for the electrical potential, ψ, has also been used to explain the mean activity coefficient of salt in a salt-polyelectrolyte solution by Marcus[15]. He assumed that an infinitesimal amount of salt added will not affect ψ appreciably. Therefore, he was able to calculate the salt activity from $m_+(R) \cdot m_-(R)$. Again, agreement with experimental data could be obtained by adjusting λ.

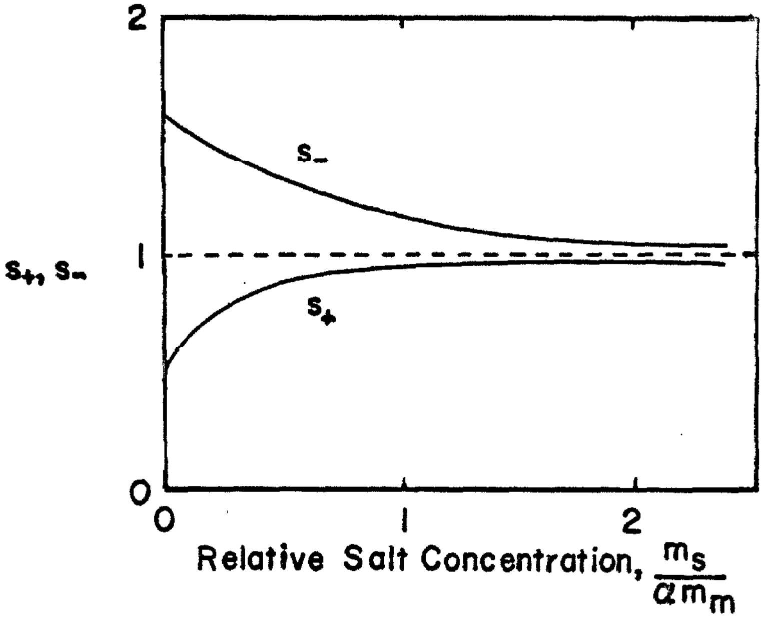
For the limiting case of an excess of salt, numerical solutions of the linearized Poisson-Boltzmann equation were obtained by Kotin and Nagasawa[24] for the cylindrical case. These calculations pointed out the serious errors involved in linearizing the equation.

In order to investigate the empirical additivity rule, Alexandrowicz[22] sought a solution valid for all ratios of polymer and salt concentrations. The numerical solution was based upon the following model: the annular region between the surface of the polyion at a and the surface of the cell boundary at R is divided into two shell-like subregions at $r = b_o$. The value of b_o is determined by the condition that between a and b_o, the potential ψ is so high that the exponential term involving coions may be neglected in the Poisson-Boltzmann equation and the equation assumes the form for a salt-free polyelectrolyte solution. In the outer subregion -- b_o to R -- the approximation $|\frac{e\psi}{kT}| \ll 1$ is made in order to permit solution of the linearized Poisson-Boltzmann equation in this region. Physically, these assumptions say that within b_o, the Donnan exclusion of the salt is very high, while outside of b_o the effect of the polyion is slight, because of screening by the counterions. Katchalsky, Alexandrowicz, and Kedem[17] have extended this treatment. If b_o is chosen so that $|\frac{e\psi}{kT}|$ becomes equal to unity there, and the fraction of the polymer counterions outside of b_o is calculated, the result is approximately ϕ_p, independent of concentrations. Thus, ϕ_p (really $\alpha\phi_p$) represents an effective degree of ionization or ion "mobilization" where a counterion is considered associated or bound (not site bound) if $|\frac{e\psi}{kT}| \geq 1$. This treatment is analogous to Bjerrum's ion-pair theory.

The same value of λ was used that satisfied equation (12) for the salt-free case. To facilitate comparison between the empirical relations and the results of this theoretical treatment, two parameters S_+ and S_- were introduced[22]. They are defined by

$$a_s = (\alpha\phi_p m_m + S_+ m_s)(S_- m_s)\gamma^2_{\pm_o} \quad . \tag{13}$$

Thus, the additivity rule is expected to hold when $S_+ = S_- = 1$. Figure II - 3 shows a typical plot of S_+ and S_- calculated from this theory for various ratios of salt to polyelectrolyte, $m_s/(\alpha m_m)$. From this figure it is seen that the difference between the empirical and theoretical results is not large and becomes smaller as $m_s/(\alpha m_m)$ becomes larger. The error involved when calculating the sum $a_+ + a_-$



II-3. Dependence of the parameters S_+ and S_- on the relative salt concentration in polyelectrolyte solutions.

(when calculating the salt activity) becomes small. Alexandrowicz[3] has found that when the difference between the "theoretical" and "empirical" results is larger than the experimental error, the theoretical equation (13) provides better agreement with osmotic data than the empirical equation. However, it overestimates the salt activity at low salt concentrations, and for these cases, the empirical equation provides a better fit of the data. At higher salt concentrations the difference between the "theoretical" and "empirical" equations becomes small as S_+ and S_- approach unity.

In conclusion of this part, salt-polyelectrolyte solutions have been studied in some detail for polyelectrolyte concentrations up to approximately 0.5 m and over a wide range of salt concentrations. Surprisingly simple relationships called "additivity rules," equations (9) and (11), have been found to describe such solutions in terms of parameters measured in saltless polyelectrolyte solutions and pure salt solutions. Useful calculations of the Donnan equilibrium salt distribution may be made from these. Electrostatic models based upon solutions of the Poisson-Boltzmann equation can be used to fit the data of saltless polyelectrolyte solutions and they predict the "additivity rules" for the case of an excess of salt.

B. Ultrafiltration of Salt-Polyelectrolyte Solutions.

1. Previous Studies. When a salt-polyelectrolyte solution is filtered with a membrane impermeable to the polyelectrolyte but permeable to the dissolved salt, the filtrate salt concentration is, in general, different from that in the polyelectrolyte solution. If the membrane does not filter salt and if filtration is carried out slowly

enough that the boundary layer effects at the membrane surface are negligible, then the salt activity of the filtrate should be equal to that of the polyelectrolyte solution. Thus, under these conditions, the filtrate represents the dialysis "equilibrium solution" corresponding to the salt polyelectrolyte solution being filtered.

This fact has been used by various investigators to study macromolecular electrolyte solutions[25-27]. The only study of salt-polyelectrolyte solutions seems to be that of Dobry-Duclaux and Ulinska[27] in which NaBr-NaPA solutions were filtered. They conducted batch experiments in which pressure was applied and filtrate collected as the polymer was concentrated until flow stopped corresponding to an osmotic pressure difference equal to the applied pressure. The pressure was then increased and another filtrate sample collected. It was found that the filtrate salt concentrations in successive samples were equal and were greater than the original salt concentration of the salt-polyelectrolyte solution. This concentration was interpreted as the salt concentration of the intermicellar liquid of the polyelectrolyte solution. The salt-to-polymer ratio was high, however, such that the effect of the polymer was to increase the salt activity only 5 per cent.

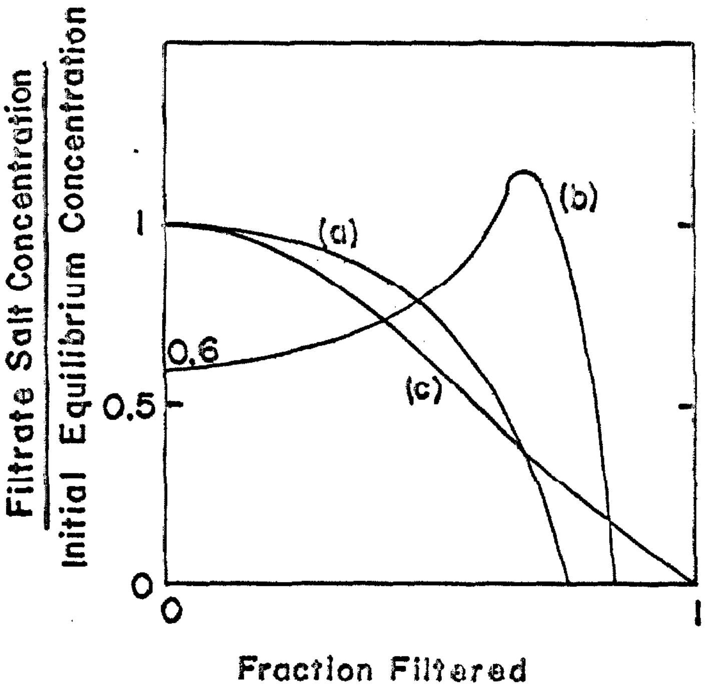
Bolt[25] and Lagerwerff[26] studied the ultrafiltration of salt-clay systems and interpreted the results of batch filtration experiments in view of two theories of Bolt[28] corresponding to "slow" and "fast" ultrafiltration. He defined filtration as "slow" if continuous equilibration occurs between the suspension and successive drops of filtrate. Thus, the composition of each drop of filtrate is such that the salt activity equals that in the solution being filtered; then the filtrate represents the "equilibrium solution." In a batch experiment, the initial filtrate concentration will be higher than the salt concentration in the suspension; as filtration proceeds, the filtrate concentration must eventually decrease as can be seen by considering a salt balance.

The effect of using a membrane that partially filters salt was accounted for simply by assuming the filtrate concentration is a constant fraction, p, of the equilibrium concentration. In a batch experiment, the salt retention causes the salt concentration in the suspension to become higher than it would be if no salt retention took place. Hence, as filtration proceeds, the filtrate salt concentration increases to a maximum and then decreases.

In "fast" filtration, the salt concentration of the filtrate is determined by the condition that the salt activity remains constant in the suspension as the suspension is concentrated. This case was apparently considered by Bolt[25] because of its being susceptible to easy mathematical treatment and does not correspond to any realistic physical process.

Curves of the filtrate concentration as a function of the extent of filtration (the fractional volume filtered) are shown in Figure II-4 for the various cases considered by Bolt. The curves are drawn for the same initial concentrations of clay and salt, thus requiring their areas to be equal.

The data of Bolt[25] and Lagerwerff[26] were compared with the curves for slow filtration. Curves similar to curve (b) were ob-



II-4. Theoretical curves for the filtrate salt concentration in batch experiments for the various cases considered by Bolt[28]: (a) slow filtration; (b) slow filtration with salt retention (p = 0.6); and (c) "fast" filtration.

tained in most cases, even though the membranes used (membrane filters) do not filter salt by themselves in pure salt solutions. Fair agreement with the data could be obtained by adjusting the value of p; values used ranged from 0.5 to 0.9. It was found that smaller values were needed as membranes of increasing pore size were used, indicating that the "salt filtration" was probably due to pores clogged with clay particles. Clay mats, observed on the membranes following filtration, may also have effected some salt filtration. In these experiments, p is simply an empirical constant used to describe the data for the particular clay-membrane system studied and its value was not related to properties of the membranes by independent experiment, such as by filtering salt solutions through the membrane after a clay filtration experiment.

While the theory of Bolt is not quantitatively applicable to the filtration of salt-polyelectrolyte solutions, it does provide some insight as to what may be expected. The most noteworthy omission of the above considerations is that of any pressure-flow relations. A more general theory would enable one to predict the filtrate concentration and flow rate as a function of the polyelectrolyte solution properties, the membrane properties, and the conditions of filtration such as applied pressure and degree of agitation.

2. General Expressions for the Filtration of Simple Salt Solutions. The most general expressions for the description of transport across a membrane are those based upon the thermodynamics of irreversible processes. It is assumed that the flux of the i^{th} component depends linearly on the forces experienced by each of the

components present in a phase[29]:

$$F_i = L_{ii}X_i + \sum_j L_{ij}X_j \tag{14}$$

where the L's are the phenomenological coefficients whose magnitude determines the relationship between the fluxes F and the forces X.

In describing the membrane filtration of a simple salt solution, two flow equations are necessary. If the flow components are taken as the flow of salt and of water, the corresponding forces are the difference in the chemical potentials, $\Delta\mu$, of the salt and water, respectively, across the membrane. Equation (14) becomes

$$J_w = L_{ww}\Delta\mu_w + L_{ws}\Delta\mu_s \tag{15}$$

$$J_s = L_{sw}\Delta\mu_w + L_{ss}\Delta\mu_s \tag{16}$$

and the Onsager reciprocity relation requires $L_{ws} = L_{sw}$.[29] These linear rate laws are expected to be good in systems close to equilibrium with small space and time gradients of the thermodynamic variables. Their range of validity must be determined by experiment.

In the case of small concentration differences (slight salt filtration), the following relations may be used for the differences in chemical potential:

$$\Delta\mu_w = RT\Delta\ell na_w + \bar{v}_w\Delta P = \bar{v}_w(\Delta P - \Delta\pi)$$

$$\Delta\mu_s = RT\Delta\ell na_s + \bar{v}_s\Delta P = \frac{n_w\bar{v}_w}{n_s}\Delta\pi + \bar{v}_s\Delta P$$

where $\bar{v}$'s are partial molar volumes, ΔP is the applied pressure difference, $\Delta\pi$ is the osmotic pressure difference ($= \frac{RT}{\bar{v}_w}\Delta\ell na_w$), and n's are mole fractions. The expression for $\Delta\mu_s$ is a direct result of the Gibbs-Duhem equation. Substituting these expressions into (15) gives

$$J_w = A(\Delta P - \sigma\Delta\pi) , \tag{17}$$

where

$$A = L_{ww}\bar{v}_w + L_{ws}\bar{v}_s ,$$

$$\sigma = (L_{ww}\bar{v}_w - L_{ws}\bar{v}_w \frac{n_w}{n_s})\frac{1}{A} .$$

A is the membrane permeability, and σ is the Staverman reflection or selectivity coefficient[30]. For an ideal semi-permeable membrane $\sigma = 1$; $\sigma = 0$ for a non-selective or completely permeable membrane. This equation with $\sigma = 1$ agrees with experiments with cellulose acetate membranes for pressures up to 80 atm. and osmotic pressures of 1 and 37 atm.[31]. Higher pressures apparently compact the membrane resulting in reduced values of A.

For the filtration experiments described here, it is convenient to use the following expression for the salt (instead of expressions based upon equation (16)):

$$m_f = m_f(J_w, a_m) . \tag{18}$$

Here, the filtrate concentration, m_f, is written as a function of the water flux and the salt activity at the upstream membrane face, a_m. Thus, the properties of the membrane, A, σ, $m_f(J_w, a_m)$, are experimentally determined quantities. Once known, they may be used with thermodynamic data of salt-polyelectrolyte solutions to describe the filtration of such solutions.

3. General Expressions for the Filtration of Salt-Polyelectrolyte Solutions. Consider filtration through a membrane which is

impermeable to the polyelectrolyte, but permeable to water and salt, though it may effect some salt filtration. It is assumed that the membrane properties are not affected by the polyelectrolyte; thus, it is assumed that the polyelectrolyte is completely rejected at the membrane surface and does not penetrate the membrane to cause reduced permeabilities. That the polymer does not pass through the membrane means that its concentration will tend to build up at the membrane surface as more is convected to the surface. This increase of concentration at the membrane surface continues until the diffusion of polymer back into the solution equals the convection toward the membrane. Thus, a steady state is reached in which the net polymer flux is zero and its concentration at the membrane surface is larger than the bulk value. This phenomenon is called "concentration polarization" and the region of increased concentration adjacent to the membrane is called the "concentration boundary layer."

Since the membrane responds only to conditions at its upstream surface, consideration of this effect is important. For the moment, it will be assumed, as in the preceding section, that the concentrations adjacent to the membrane are known and the filtrate flux and salt concentration will be related to these concentrations. This assumption is good, for instance, if mixing is sufficiently great that concentration polarization effects are negligible; in this case, the concentrations at the membrane surface equal those of the bulk solution. In cases involving concentration polarization, the equations for transport through the membrane and through the boundary layer must be solved simultaneously.

In filtering a polyelectrolyte solution with a membrane that is completely impermeable to the polymer, a discontinuity in polymer concentration exists at the membrane surface. The chemical potentials of the water and salt must be continuous across this interface, however, since these components are permeable. Thus, an equilibration must take place at the membrane surface at which the polyelectrolyte-salt solution is separated identical to the Donnan membrane equilibria discussed above. Equating the chemical potential of the water just within the membrane with that just within the polyelectrolyte solution results in the following expression for $\Delta\mu_w$:

$$\Delta\mu_w = \bar{v}_w(\Delta P - \Delta\pi_T) = \bar{v}_w(\Delta P - \Delta\pi_D - \Delta\pi_f) , \qquad (19)$$

where the total osmotic pressure drop, $\Delta\pi_T$, has been divided into the Donnan osmotic pressure difference, $\Delta\pi_D$, corresponding to the separation and equilibration at the membrane surface, and the osmotic pressure difference through the membrane corresponding to the difference between the filtrate concentration, m_f, and the equilibrium salt concentration, m_e, which corresponds to a salt activity of a_m in the salt-water system. Because of the osmotic pressure drop of $\Delta\pi_D$ at the membrane surface, assuming the chemical potential is continuous, the effective pressure just within the membrane is $(P-\Delta\pi_D)$. A force corresponding to the pressure drop $\Delta\pi_D$ is transmitted to the membrane structure by the forces which exclude the polyelectrolyte molecules.

The chemical potential drop for the salt becomes:

$$\Delta\mu_s = RT\Delta\ln a_s + \bar{v}_s(\Delta P - \Delta\pi_D) = \frac{n_w\bar{v}_w}{n_s}\Delta\pi_f + \bar{v}_s(\Delta P - \Delta\pi_D) .$$

It is important to note that application of the Gibbs-Duhem equation is based upon the two-component system (salt and water) with salt activity varying between a_m and that corresponding to the filtrate concentration m_f; for this difference the osmotic pressure difference is $\Delta\pi_f$. Substituting the expressions for $\Delta\mu_s$ and $\Delta\mu_w$ into (16) gives

$$J_w = A(\Delta P - \Delta\pi_D - \sigma\Delta\pi_f) \tag{20}$$

where A and σ are the same quantities as in (17) above. This equation represents the filtrate flux for the ultrafiltration of the three-component system, polyelectrolyte—salt—water, through a membrane which completely filters the polyelectrolyte and, depending on the value of σ, partially filters the salt. Two limiting cases may be considered. If no salt filtration occurs, $\sigma = 0$, and

$$J_w = A(\Delta P - \Delta\pi_D) ,$$

which is correct, since $\Delta\pi_D = \Delta\pi_T$ in this case. If the salt is completely filtered, $\sigma = 1$ and

$$\begin{aligned} J_w &= A(\Delta P - \Delta\pi_D - \Delta\pi_f) \\ &= A(\Delta P - \Delta\pi_T) , \end{aligned}$$

which is also correct. Thus, equations (18) and (20) predict the filtrate concentration and flux rate for the salt-polyelectrolyte filtration based upon membrane properties determined with salt-filtration experiments. It has been assumed that

1) The polymer is completely filtered by the membrane.
2) The polymer does not affect the properties of the membrane, in particular, by clogging the pores. This assumption obviously makes a simpler system to study than

the more porous membrane systems of Bolt, but only in this way may the membrane effects be distinguished from the solution characteristics, such as concentration polarization.

3) These equations are written in terms of the concentrations and activities of the polyelectrolyte solution at the membrane surface. For systems with an adequate degree of mixing or agitation, concentration polarization is negligible and the concentrations at the membrane surface are essentially the same as the bulk concentrations.

C. Experimental Objectives.

In order to calculate the performance of the desalination process briefly described in the Introduction, it is necessary to 1) be able to describe the Donnan equilibrium of salt-polyelectrolyte solutions, and 2) know how the filtrate flow rate and salt concentration depend upon the solution composition, the membrane characteristics, and the applied pressure in the ultrafiltration of salt-polyelectrolyte solutions. As seen above, the Donnan equilibrium can be described reasonably well by the simple dissociation or additivity theory, and various investigators have confirmed this theory for polyelectrolyte concentrations up to 0.45 m. The results of these studies are adequate for the description of the first step of the process.

Expressions were developed above to describe the ultrafiltration of salt-polyelectrolyte solutions in terms of the osmotic pressure and salt activity in the solution and the membrane properties. In order to verify them, ultrafiltration experiments were conducted using sodium chloride - sodium polyacrylate solutions. This polyelectrolyte was chosen because NaPA solutions have been studied in some detail and because it is, structurally, probably the simplest and most flexible polyelectrolyte. The latter consideration is important regarding the viscosity of polymer solutions; the more rigid the polymer, the higher the viscosity of the solution.

Calculations indicated that for partial desalination of solutions of practical interest (800 to 1500 mg/l TDS = 0.014 to 0.025 m as $NaC\ell$), the polyelectrolyte concentration in the filtration step would have to be from 0.5 to 1.5 m. Since activity data were necessary to compare the ultrafiltration results with the above expressions, and since these concentrations are above any previously studied, additional activity data were needed.

The specific experimental objectives were:

1) to measure the salt activity in $NaC\ell$-NaPA solutions;
2) to measure the permeability and salt rejection characteristics of a suitable ultrafiltration membrane with water and with $NaC\ell$ solutions;
3) to conduct ultrafiltration experiments with $NaC\ell$-NaPA solutions measuring the filtrate flow rate and salt concentration as a function of the applied pressure, the solution composition, and the degree of stirring.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

The ultrafiltration of sodium polyacrylate - sodium chloride solutions was studied using a continuous-flow filtration cell containing a stirring paddle for mixing and electrodes for measuring the sodium chloride activity during filtration. The filtrate flow rate and composition were measured for various pressures and solution compositions. The effect of stirring speed was also determined. The following data were also taken: sodium chloride activity, viscosity and density of $NaC\ell$ - NaPA solutions, osmotic pressure of sodium polyacrylate solutions, and water permeability and salt rejection of the membrane at various salt concentrations.

In this chapter, the procedures and apparatus used in the experiments are described. The results are presented and discussed in the following chapter.

A. Preparation of Stock Sodium Polyacrylate Solution.

A stock solution of sodium polyacrylate was prepared by neutralizing polyacrylic acid with sodium hydroxide. Polyacrylic acid was obtained[*] as an aqueous solution of 25 per cent solids. Technical data supplied with the polymer solution stated that the average molecular weight was between 80,000 and 110,000; the maximum concentration of inorganics was 0.2 per cent. The solution was purified with respect to inorganic salts by dialysing 250 ml portions for 24 hours in a continuously-flushed dialysis cell having an exponential decay time of four hours; thus, the maximum concentration of inor-

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[*] B. F. Goodrich Chemical Company, Cleveland, Ohio.

ganics was reduced to approximately 0.0005 per cent = 10^{-4} m/l as NaCℓ. The resulting solution was diluted 2:1 to obtain a stock polyacrylic acid solution.

The concentration of this stock solution was determined by two methods. First, total solids were determined by evaporation at 105°C and weighing. The monomolar concentration was calculated using a molecular weight of 72 for the monomer unit. Second, the polyacrylic acid was titrated to the endpoint at pH 10 with NaOH. The two methods resulted in values of 1.61 and 1.62 moles/liter, respectively, in monomolar units. This agreement indicated that the polymer was completely in the acid form and that total nonvolatile impurities were less than 1 per cent of the polymer concentration.

A stock solution of sodium polyacrylate was prepared from this solution by neutralizing, to the degree of 80 per cent, with sodium hydroxide. The resulting concentration was 1.46 moles/liter and $\alpha = 0.8$. The pH of the solution was 7.1.

B. Measurement of Solution Properties.

1. Sodium Chloride Activity Measurements. The sodium chloride activity was measured using a sodium-sensitive glass electrode/silver-silver chloride electrode pair. A Beckman* sodium ion electrode (# 39278) and a Beckman silver electrode (# 39261) were used. The silver electrode was electrolytically coated with silver chloride according to the directions supplied with the electrode. It was stored in 1 per cent NaCℓ when not in use. The sodium electrode

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* Beckman Instruments, Inc., Fullerton, California.

was stored in 0.1 M $NaC\ell$ for several days before using and when not in use.

Glass sodium-ion electrodes are similar to pH electrodes; the major difference is the composition of the glass in the membrane tip. In the sodium electrode, the composition is such that the sensitivity to sodium is enhanced. However, just as alkali metal ions may interfere with pH determinations at low hydrogen ion activity (high pH), interferences by other ions must be considered when using a sodium ion electrode[32]. The electrodes used in these experiments were found to be approximately 100 times more sensitive to the hydrogen ion than to the sodium ion. This result is in agreement with the supplied technical data which also stated that the silver ion sensitivity is approximately 300 times that of the sodium ion. The electrodes are also slightly sensitive to the other alkali metal ions. But since sodium, silver, and hydrogen ions were the only ones present, with the possible exception of impurities, these were the only ones of interest.

These results mean that for straightforward measurements of the sodium-ion activity without interferences, the hydrogen ion and silver ion concentrations (or activities) must be sufficiently small compared to the sodium ion activity. For an error of less than $\frac{1}{2}$ per cent, the pH and the pAg must be 4.3 and 5.0 units, respectively, greater than the pNa of the solution ($pNa = -\log(a_{Na^+})$, etc.). These conditions were met in all the experiments reported here.

The potential difference developed between the two electrodes was measured with a Heath[*] recording (vibrating reed) electrometer (EUW-301). The electrodes were calibrated in sodium chloride solutions by adding 1.00 M NaCℓ by buret to 50 ml of deionized water and recording the potential. In this way, a series of different salt concentrations could be easily measured. Constant stirring was provided with a magnetic stirrer and the temperature was maintained at 25 ± 0.05°C. A special water-jacketed beaker connected to a circulating water bath was used for this purpose. In order to obtain steady readings not influenced by bodily movement near the apparatus, such as reaching for the buret, it was necessary to enclose the beaker and electrodes in a Faraday cage. A cylindrical cage was made from window screen and was grounded to the potentiometer ground. The buret, electrodes, and thermometer fitted through holes in the top of the cage.

The activity of the sodium chloride was calculated using the activity coefficient data of Robinson and Stokes[33]. Nernstian behavior was observed. Figure III-1 shows a typical calibration curve obtained in the manner just described. Straight lines were always found with slopes ranging from 116 to 119 mv/decade of activity. The Nernst equation predicts a slope of 118 mv at 25°C. Since the electrode - potentiometer system was calibrated frequently, this discrepancy was of no concern.

To measure the salt activity in NaCℓ-NaPA solutions, 50 ml of the pure NaPA solution at the desired polyelectrolyte concentration

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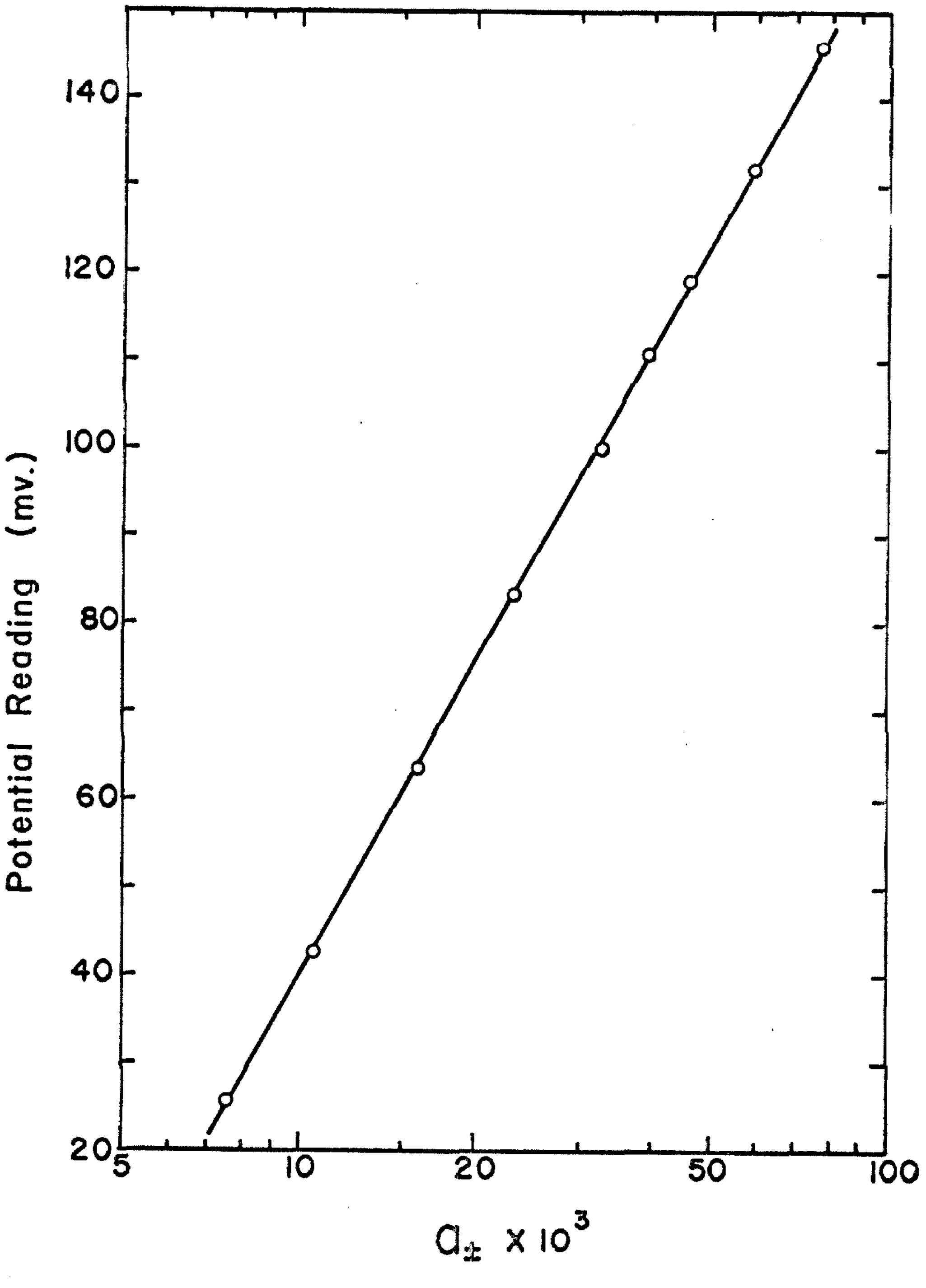
[*] Heath Company, Benton Harbor, Michigan.



III-1. Typical calibration curve for the sodium glass electrode/silver-silver chloride electrode pair in NaCℓ solutions.

was titrated with 1.00 M $NaC\ell$. The potential was measured as a function of the amount of $NaC\ell$ added. The solution was stirred continuously and its temperature held constant at 25°C. For most of the measurements, the potentiometer reading approached a constant value within 2 or 3 minutes after addition of the salt solution. The response was slower for the more concentrated polyelectrolyte solutions, sometimes taking 4 or 5 minutes to reach a constant value. This effect may have been caused by the increased viscosity of the solutions. As a precaution, the potential was recorded for 10 to 20 minutes for each point.

With progressive titration, the polyelectrolyte concentration was reduced slightly by dilution. This reduction was minimized by using 1 M $NaC\ell$ and was taken into account in the calculations as described in the following chapter.

2. Osmotic Pressure. The osmotic pressure of NaPA solutions was measured so that the value of ϕ_p could be determined (equation (7)). A Mechrolab* Vapor Pressure Osmometer (Model 301 A) was used. This instrument measures the vapor pressure of the solvent in a solution by measuring the temperature difference between a drop of solvent and a drop of solution in an atmosphere saturated with solvent. Using special syringes the drops are placed on two small thermistors which form two sides of a Wheatstone bridge.

The instrument was calibrated with $NaC\ell$ solutions with concentrations between 0.01 and 0.20 M using the osmotic pressure data presented in Robinson and Stokes[33]. Figure III-2 shows the calibra-

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* Mechrolab Division of Hewlett Packard, Avondale, Pennsylvania.

tion curve used.

3. Viscosity. Two types of viscometers were used to measure the viscosity of the polyelectrolyte solutions in order to observe any shear rate dependence. A Brookfield* Viscometer (Model LVF) provided shear rates from 1.4 to 14 $\sec^{-1}$. In this instrument, a right circular cylinder is rotated at four different speeds inside a stationary cylindrical chamber. The torque required to rotate the cylinder is measured. The shear rate was calculated from the surface velocity of the rotating cylinder and the annular spacing.

To obtain higher shear rates, two sizes of Cannon-Fenske glass viscometers were used. The standard procedure described in ASTM D 445-65 was followed. The shear rates were calculated from the expression

$$\dot{\gamma} = \left(\frac{ag\Delta H}{2BL}\right)\frac{1}{T} \quad \sec^{-1} ,$$

where a and L are the radius and length of the capillary, ΔH is the driving head, T is the efflux time, and B is the calibration constant in $(\mathrm{cm}/\sec)^2$ defined by $\nu = BT$, where ν is the kinematic viscosity in $\mathrm{cm}^2/\sec$. Shear rates up to approximately 180 $\sec^{-1}$ were obtained using viscometers # 100 and # 200. No shear rate dependence was observed for the range of shear rates studied.

All viscosity measurements were made at 25°C. National Bureau of Standards calibrating solutions were used to calibrate the viscometers.

4. Density Measurements. The density of sodium - poly-

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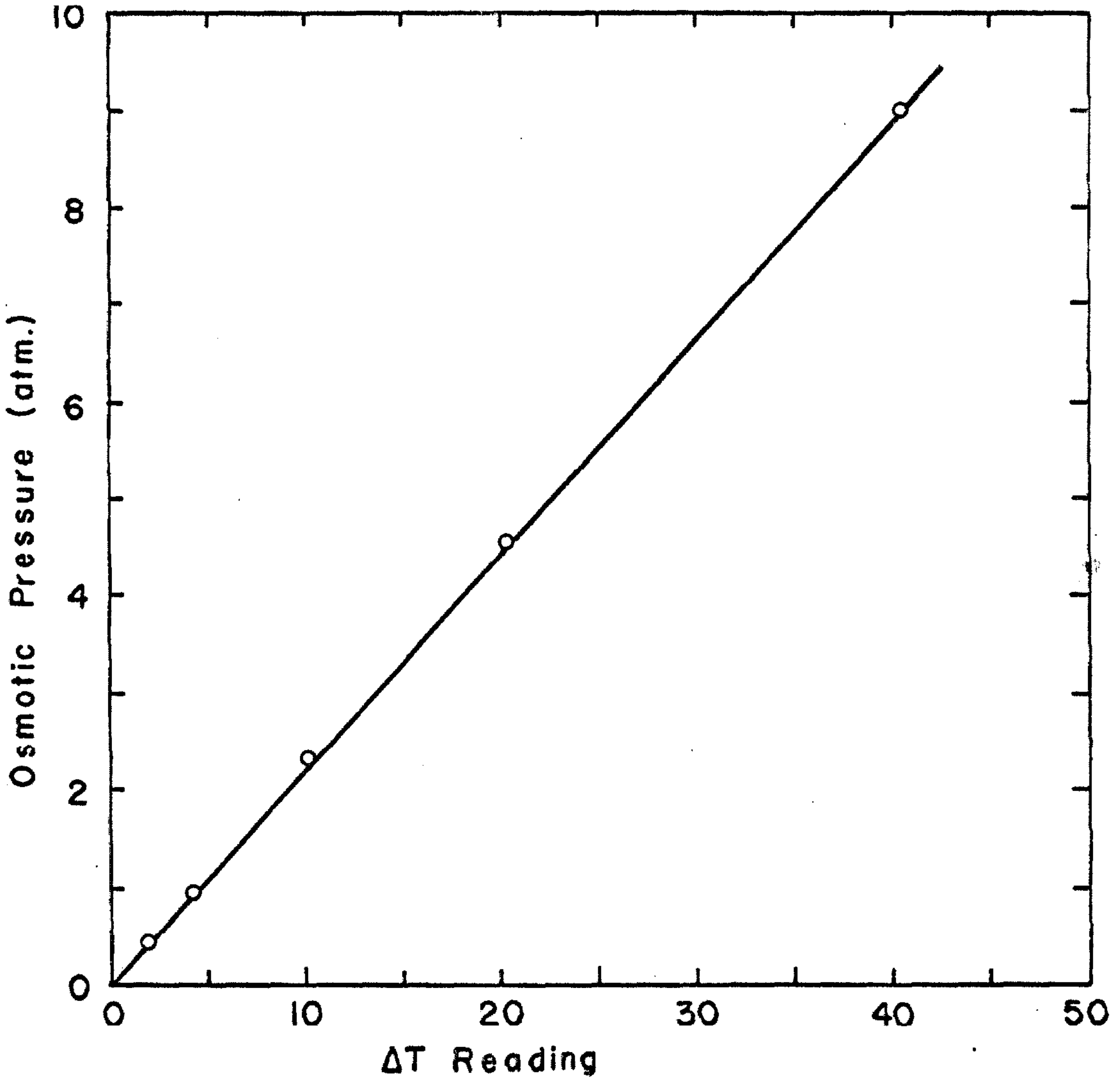
* Brookfield Engineering Laboratories, Stoughton, Mass.



III-2. Calibration of the vapor pressure osmometer.

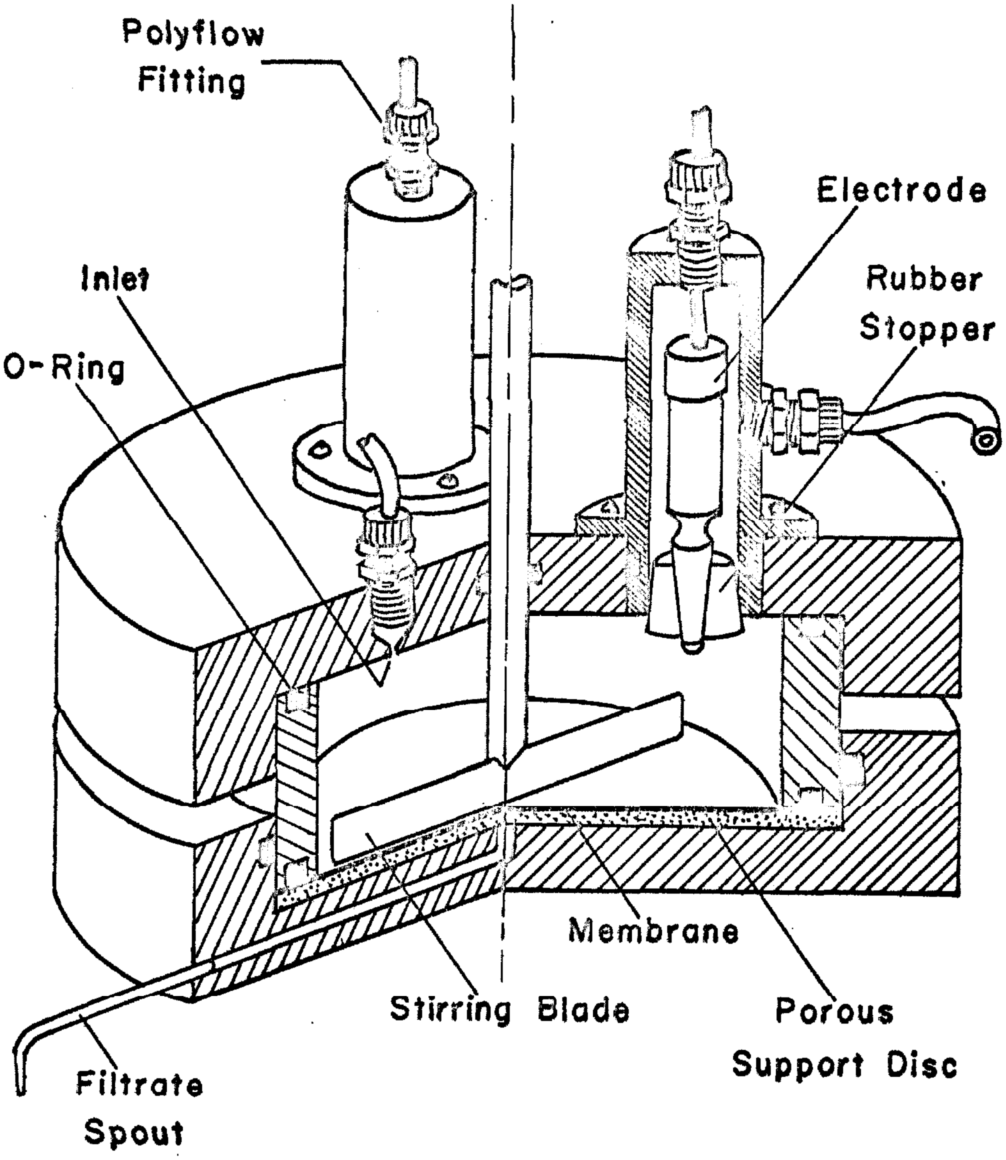
acrylate solutions was measured directly with a Christian Becker specific gravity balance (an early model similar to type SG-1). Samples were equilibrated in a 25°C bath before measurements were taken.

C. Filtration Experiments.

1. Description of the Filtration Cell. A continuous-flow filtration cell was developed and used to study the ultrafiltration of sodium chloride - sodium polyacrylate solutions. Continuous-flow experiments were conducted instead of batch experiments so that steady-state measurements could be made. The establishment of a steady state provides confidence that irreversible changes are not occurring in the membrane or at the membrane surface (such as plugging of the membrane). Furthermore, data obtained from steady-state (or near-steady-state) measurements are generally more convenient for the purpose of analysis.

A sectioned drawing of the filtration cell is shown (approximately full size) in Figure III-3. Acrylic plastic was used throughout. Not shown are the bolts used to close the cell, two ports used to fill or empty the cell while it was assembled, nor the retainer bushings on the stirrer shaft. Because the internal pressure tended to push the stirring shaft out, a brass washer was mounted to the inside of the lid to serve as a bearing for the inner retainer bushing. The bushings, stirring shaft, and paddle were stainless steel. The volume of the cell was approximately 100 ml.

Beckman electrodes # 39046 and 39048 were mounted in



III-3. Schematic drawing of filtration cell.

special electrode capsules which were pressurized with nitrogen to a pressure equal to that in the cell. In this way, rubber stoppers could be used to hold the electrodes and maximum versatility was achieved. Either electrode could be replaced without disassembling the cell.

As with the beaker experiments, a Faraday cage was necessary to obtain steady measurements with the filtration cell electrodes. The filtration cell was enclosed with window screen grounded to the potentiometer ground. The electrode output was found to be independent of applied pressure (pressures up to 70 psi were used) and stirring speed. At high stirring speeds (450 to 500 rpm) the output often fluctuated very rapidly with an amplitude of 2 to 10 mv for periods of time from one to ten minutes, after which it would return to a steady reading. On some days this noise was never encountered, while on others it prevented any useful data taking. The cause of these disturbances was not determined.

A 3-inch Diaflo* membrane Type UM-3 was used with a 3-inch porous support disk. The exposed membrane area was 36.7 cm^2. Diaflo membranes are described as synthetic hydrous polymers resulting from the interaction of polycations and polyanions[34]. They have an ionic cross-linked structure. Type UM-3 (the most selective) was chosen because it has a net negative fixed charge, and it was felt that the fixed negative charge would repel the polyacrylate ion and thus minimize clogging problems. The membrane has a

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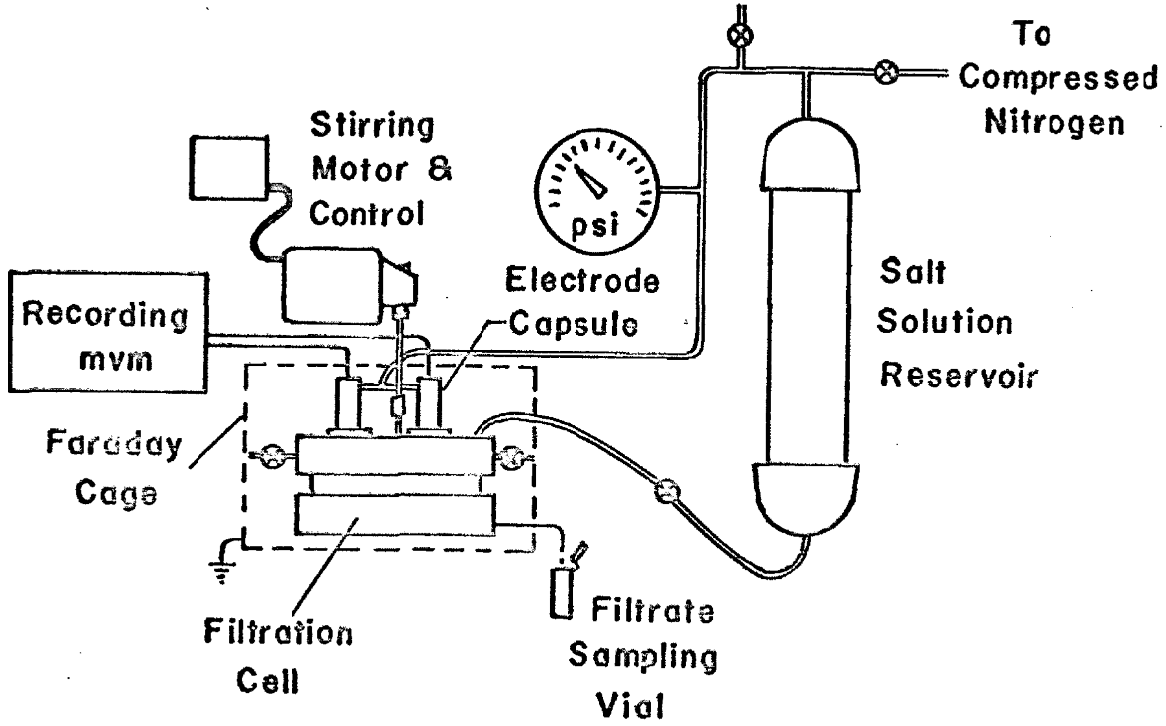
* Amicon Corporation, Cambridge, Massachusetts.

solute cutoff of 300; solutes of greater molecular weights are completely filtered. Partial rejection of NaCℓ was observed with this membrane.

2. Associated Apparatus and Experimental Procedure. The stirring blade was driven by a variable-speed DC motor (Gerald K. Heller Company, Las Vegas, Nevada, Model GT 21). Its rotational speed was measured with a Strobotac (General Radio Company, Model 631 BL). Since the filtration cell was used differently for conducting experiments with salt-polyelectrolyte solutions and with pure salt solutions, the procedures are described separately below.

(a) Filtration of Salt-Polyelectrolyte Solutions. - The experimental set-up for the filtration of salt-polyelectrolyte solutions is shown in Figure III-4. A salt-solution reservoir, made from an 18-inch length of 3-inch PVC pipe capped at both ends, was connected as shown to the salt solution inlet in the lid of the filtration cell. Polyethylene tubing (1/4 inch) was used throughout. The inlet consisted of a tube fitting leading to a small hole (# 60 drill) in the lid (Figure III-3). The cell was filled with a salt-polyelectrolyte solution of desired concentration. When pressure was applied to the reservoir with compressed nitrogen (that also pressurized the electrode capsules), salt solution flowed into the cell at the same rate as filtrate permeated the membrane. The inlet hole was small enough to prevent the back-mixing of polyelectrolyte into the salt feed line but was large enough so that the pressure drop across it was negligible at the flow rates measured. A correction of 0.4 to 0.6 psi was applied to the gauge pressure reading because of the difference in elevation between



III-4. Arrangement of apparatus for the salt-polyelectrolyte ultrafiltration experiments.

the liquid surface in the reservoir and the tip of the filtrate spout.

A steady-state condition was reached when the concentration of the filtrate equaled the concentration of the feed solution in the reservoir. Thus, as filtration proceeded at constant pressure and stirring rate, the salt concentration in the cell approached that value that resulted in equal filtrate and feed concentrations.

Filtrate samples (approximately 5 ml) were collected in tared polyethylene vials for measured time intervals. The flow rate was determined by weighing and the salt concentration was determined by titrating the chloride ion with mercuric nitrate[35]. The concentration of NaPA was measured before and after each experiment by a solids determination.

Once it was established that steady-state conditions could be obtained during which no significant changes occurred in the membrane, specifically by plugging, "near-steady-state" experiments were conducted in order to obtain more experimental data to compare with equations (18) and (20) over a wider range of conditions. In these experiments, several data points were determined in one experiment simply by not waiting for the system to come to a steady state. When it was close to steady-state conditions (within 5 to 10 per cent as measured by the difference between the filtrate and feed salt concentrations), the filtrate concentration changed sufficiently slowly with time that meaningful measurements could be made. Five to twenty-five minutes were required to collect a filtrate sample; during this time it was important that changes in the system were small. Generally 4 to 5 samples were taken in succession beginning after about

10 mls of filtrate had been wasted following a change in pressure or stirring rate. The last two or three samples gave essentially the same results.

By applying the pressure in the (unmixed) reservoir, problems caused by gas solution and subsequent dissolution on the low pressure side of the membrane were eliminated. In earlier experiments,run in a stirred batch filtration cell, such problems were encountered.

(b) Salt Filtration Experiments. - The salt filtration characteristics of the membrane were measured by connecting the salt solution feed line to one of the valved filling ports. The other port was partially opened so that when pressure was applied, a waste flow of approximately 10 to 20 times the filtrate flow was obtained. The filtrate flow rate and salt concentration were measured. The salt concentration of the waste flow was also measured, and was always within 3 per cent of the feed concentration. The ratio of filtrate salt concentration to filtrand salt concentration was calculated on the basis of the measured waste filtrand concentration.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

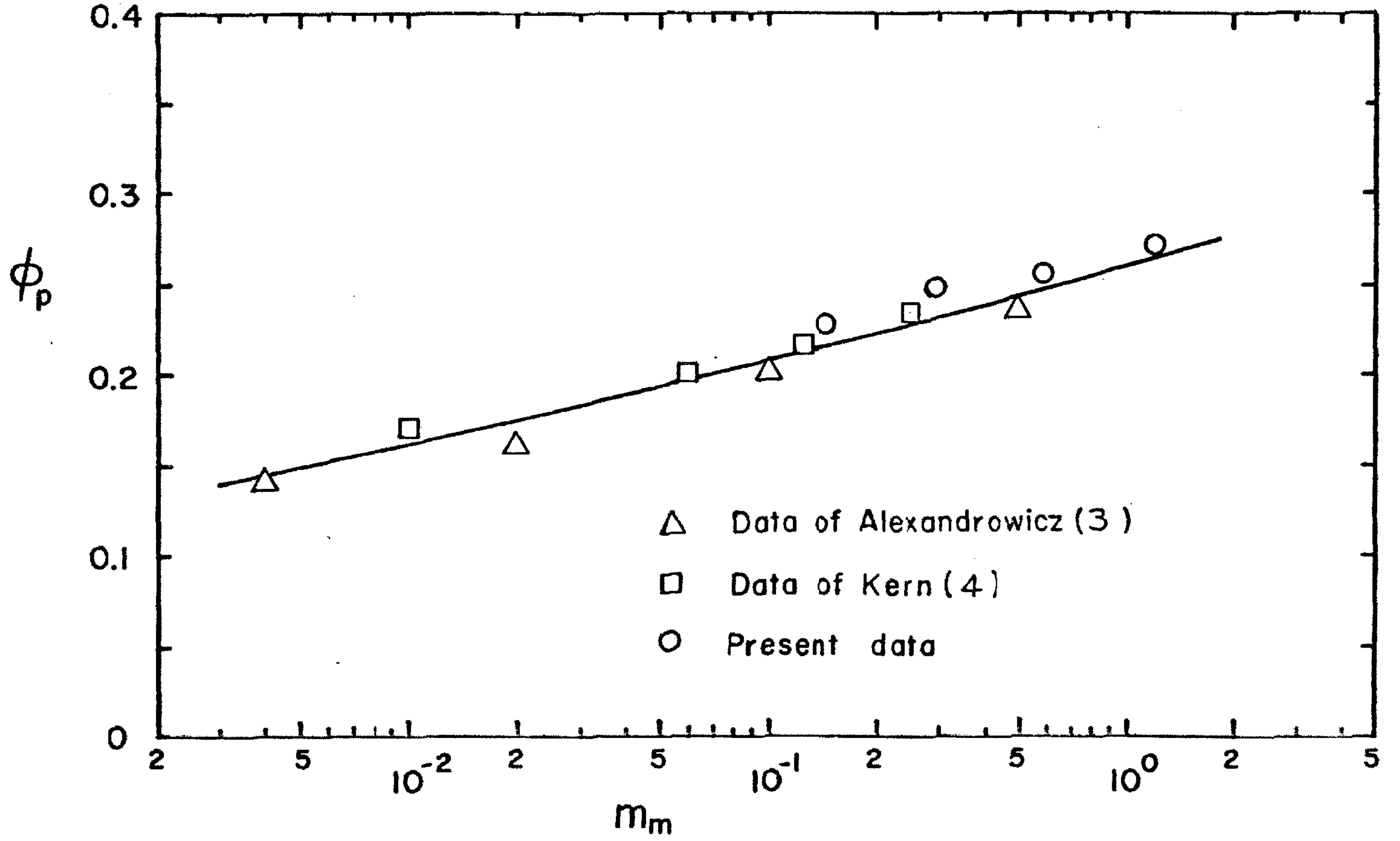
A. Solution Properties.

1. Density and Osmotic Pressure of Sodium-Polyacrylate Solution. The density of sodium-polyacrylate solutions was measured so that concentrations could be expressed in molal units rather than molar units. The density data are given in Table IV-1, along with the monomolar concentrations calculated in the usual manner. For the low relative salt concentrations studied here, the effect of the salt was found to be negligible upon the density, and thus the same conversion factors were used for salt-polyelectrolyte solutions as were used for saltless NaPA solutions. Since the conversion correction was small anyway, the error involved in this correction is inconsequential for the present purposes.

Also given in Table IV-1 are the osmotic pressure data obtained and the values of the osmotic coefficient calculated from equation (7). These data are compared to those of Kern[4] and Alexandrowicz[3] for $\alpha = 0.8$ in Figure IV-1. Kern measured the osmotic pressure of NaPA solutions using a membrane osmometer, while Alexandrowicz used a "concentration osmometer" in which a NaPA solution was equilibrated against a polyethyleneglycol (PEG) solution separated by a semipermeable membrane. Knowing how the water activity behaved in the PEG solution and measuring the concentrations of NaPA and PEG at equilibrium enabled measurement of the water activity in the polyelectrolyte solution. Thus, the three sets of data represent three different experimental techniques. It is observed that the present data form a smooth extension of the previous

TABLE IV-1. Density and Osmotic Pressure of NaPA Solutions. $\alpha = 0.8$.

NaPA Concentration, C_m (M)	Density ρ (gm/mℓ)	NaPA Concentration, m_m (m)	Osmotic Pressure π (atm.)	Osmotic Coefficient ϕ_p
0.058	1.002	0.058	-	-
0.145	1.0055	0.146	0.65	0.228
0.290	1.013	0.294	1.42	0.246
0.580	1.029	0.594	2.96	0.256
0.87	1.042	0.902	-	-
1.16	1.061	1.21	6.40	0.271



IV-1. Comparison of the osmotic coefficient data with those of Alexandrowicz[3] and Kern[4] for NaPA solutions (α = 0.8).

data, perhaps agreeing more closely with that of Kern. That the NaPA sample behaved like those used in previous studies indicates that the salt activity should also agree quantitatively with the previous studies.

2. Sodium-Chloride Activity in NaCℓ - NaPA Solutions.

(a) Analysis of Data. - As mentioned in the preceding chapter (III. B. 1.), addition of the salt solution to the pure NaPA solution during the activity measurements caused slight dilution of the NaPA. Thus, each series of measurements corresponded to a wide range of salt concentrations and a narrow range of polyelectrolyte concentrations. The data were adjusted by plotting them as activity versus polymer concentration for the various salt concentrations studied. Each point was moved parallel to the curves obtained to the abscissa corresponding to the initial polyelectrolyte concentration. These corrections were all less than 3 per cent. The adjusted data are presented in the first two columns of Table IV-2.

(b) Comparison with the Dissociation Theory and with the Electrostatic Model. - For the purposes of comparison, the mean molal activity coefficient of the sodium chloride was calculated from the expression:

$$\gamma_{\pm} = \frac{a_{\pm}}{\sqrt{m_{Na^+} m_{C\ell^-}}} = \frac{a_{\pm}}{\sqrt{(m_s + \alpha m_m) m_s}} .$$

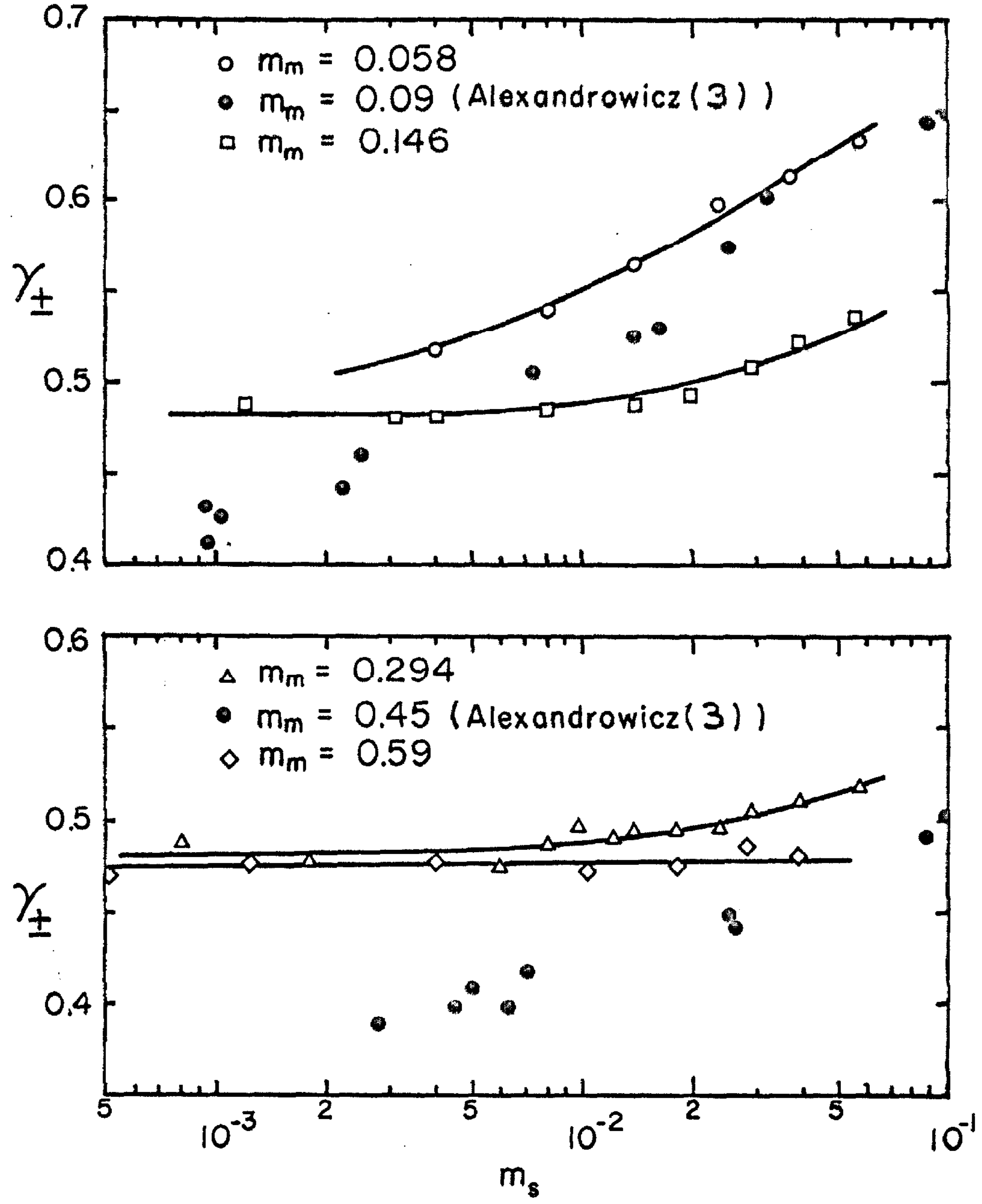
These results (Table IV-2) are compared with those of Alexandrowicz[3] in Figure IV-2. In each graph, the data should bracket those of Alexandrowicz. This seems to be true only at higher salt concentrations. At low salt concentrations, the activity data are greater

TABLE IV-2. Activity Data and Results for NaCℓ - NaPA Solutions. $\alpha = 0.8$.

NaCℓ Concentration, m_s (m)	NaCℓ Activity $a_\pm$	Activity Coefficient $\gamma_\pm$ (m^{-1})	$\frac{\alpha\phi_p m_m}{m_o}$	$\frac{m_o - m_s}{m_o}$
NaPA concentration = m_m = 0.0582				
0.0040	0.0074	0.518	1.18	0.503
0.0080	0.0113	0.540	0.75	0.363
0.0139	0.0164	0.564	0.51	0.252
0.0237	0.0244	0.598	0.33	0.166
0.0368	0.0340	0.612	0.24	0.088
0.0572	0.0488	0.633	0.16	0.038
m_m = 0.146				
0.00121	0.00583	0.488	4.12	0.808
0.00322	0.00945	0.480	2.49	0.692
0.00403	0.0106	0.480	2.21	0.658
0.00806	0.0153	0.483	1.50	0.535
0.0140	0.0209	0.488	1.08	0.418
0.0200	0.0257	0.492	0.87	0.335
0.0296	0.0335	0.508	0.66	0.255
0.0391	0.0408	0.522	0.53	0.204
0.0574	0.0538	0.537	0.39	0.130
m_m = 0.294				
0.00081	0.00675	0.488	7.66	0.890
0.00182	0.0181	0.472	5.14	0.834
0.00608	0.0181	0.472	2.73	0.706
0.00811	0.0217	0.488	2.25	0.676
0.0101	0.0247	0.495	1.96	0.647
0.0122	0.0269	0.490	1.79	0.614
0.0141	0.0292	0.493	1.64	0.590
0.0180	0.0333	0.493	1.42	0.543
0.0239	0.0389	0.494	1.21	0.487
0.0298	0.0447	0.503	1.04	0.450
0.0393	0.0530	0.510	0.87	0.395
0.0578	0.0675	0.518	0.67	0.315

TABLE IV-2 (Continued).

m_s	$a_\pm$	$\gamma_\pm$	$\frac{\alpha\phi_p m_m}{m_o}$	$\frac{m_o - m_s}{m_o}$
		$m_m = 0.594$		
0.00051	0.0073	0.47	15.5	0.936
0.00123	0.0115	0.475	9.6	0.904
0.00409	0.0211	0.476	5.07	0.832
0.00614	0.0257	0.473	4.12	0.795
0.01024	0.0333	0.472	3.12	0.741
0.0182	0.0451	0.475	2.26	0.666
0.0281	0.0578	0.485	1.73	0.605
0.0397	0.0690	0.481	1.43	0.539
		$m_m = 0.90$		
0.00207	0.0178	0.459	9.59	0.898
0.00415	0.0253	0.460	6.61	0.859
0.00622	0.0311	0.461	5.31	0.830
0.00830	0.0363	0.466	4.50	0.808
0.0124	0.0446	0.466	3.61	0.769
0.0205	0.0574	0.465	2.75	0.710
0.0305	0.0697	0.460	2.23	0.650
0.0402	0.0807	0.460	1.91	0.606
		$m_m = 1.21$		
0.00021	0.0065	0.45	38.3	0.970
0.00042	0.0093	0.46	26.4	0.959
0.00209	0.0203	0.451	11.6	0.910
0.00418	0.0295	0.462	7.82	0.880
0.00627	0.0360	0.460	6.32	0.854
0.00836	0.0418	0.462	5.39	0.834
0.01254	0.0510	0.460	4.35	0.799
0.0207	0.0655	0.457	3.33	0.746



IV-2. Comparison of sodium chloride activity data with those of Alexandrowicz[3].

than those of Alexandrowicz. The reason for this disagreement is not known. The data obtained were reproducible and the experimental variations do not seem to be as great as those of Alexandrowicz. As will be seen later, the results of the ultrafiltration experiments lend support to the present data.

In order to compare the experimental data to theoretical predictions, the mean molal activity coefficients were calculated based upon equations (9) and (13) to obtain

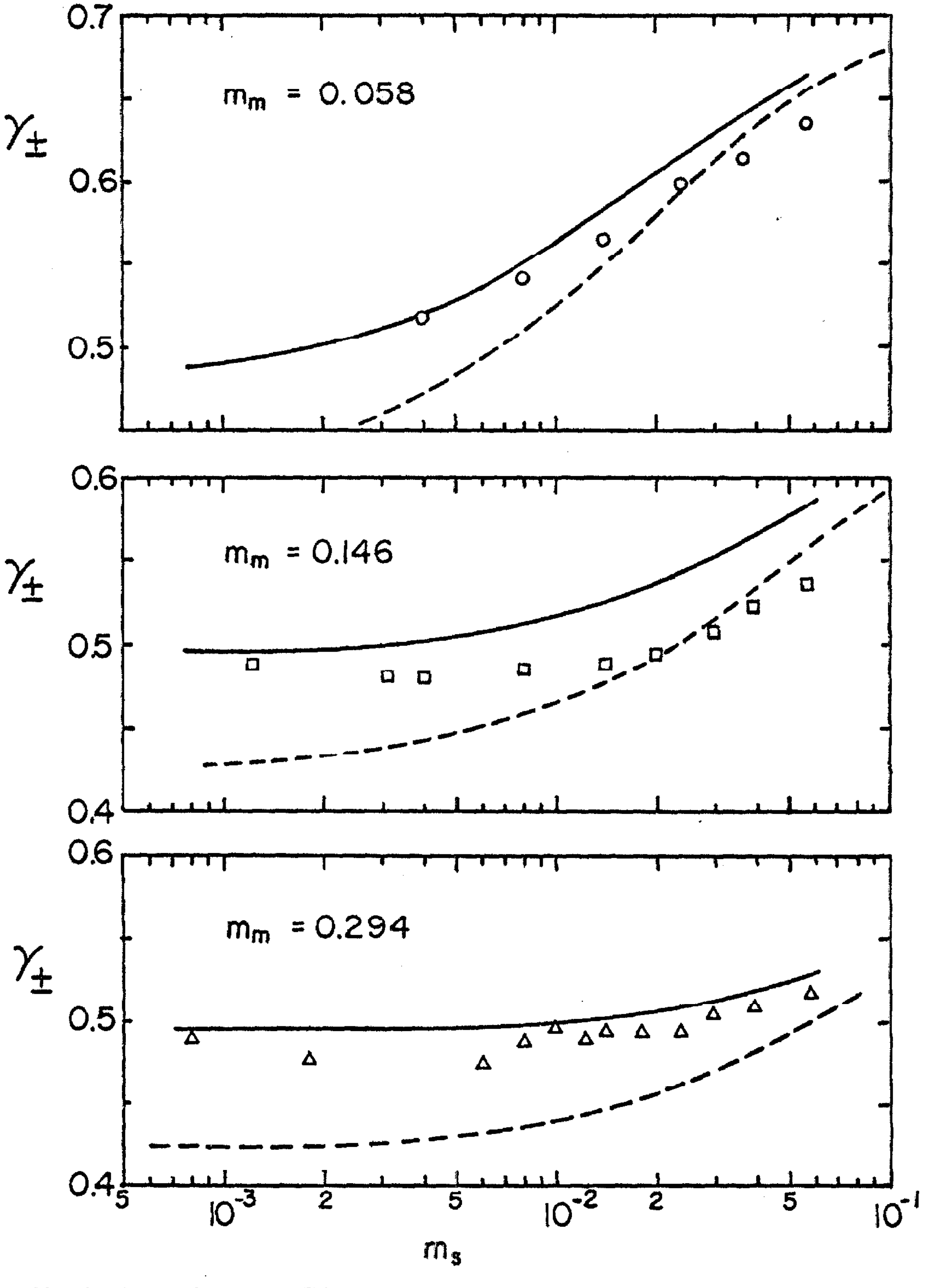
$$\gamma_{\pm} = \left(\frac{a_s}{m_+ m_-}\right)^{\frac{1}{2}} = \sqrt{\frac{\alpha\phi_p m_m + m_s}{\alpha m_m + m_s}}\ \gamma_{\pm_o} \qquad (21)$$

and

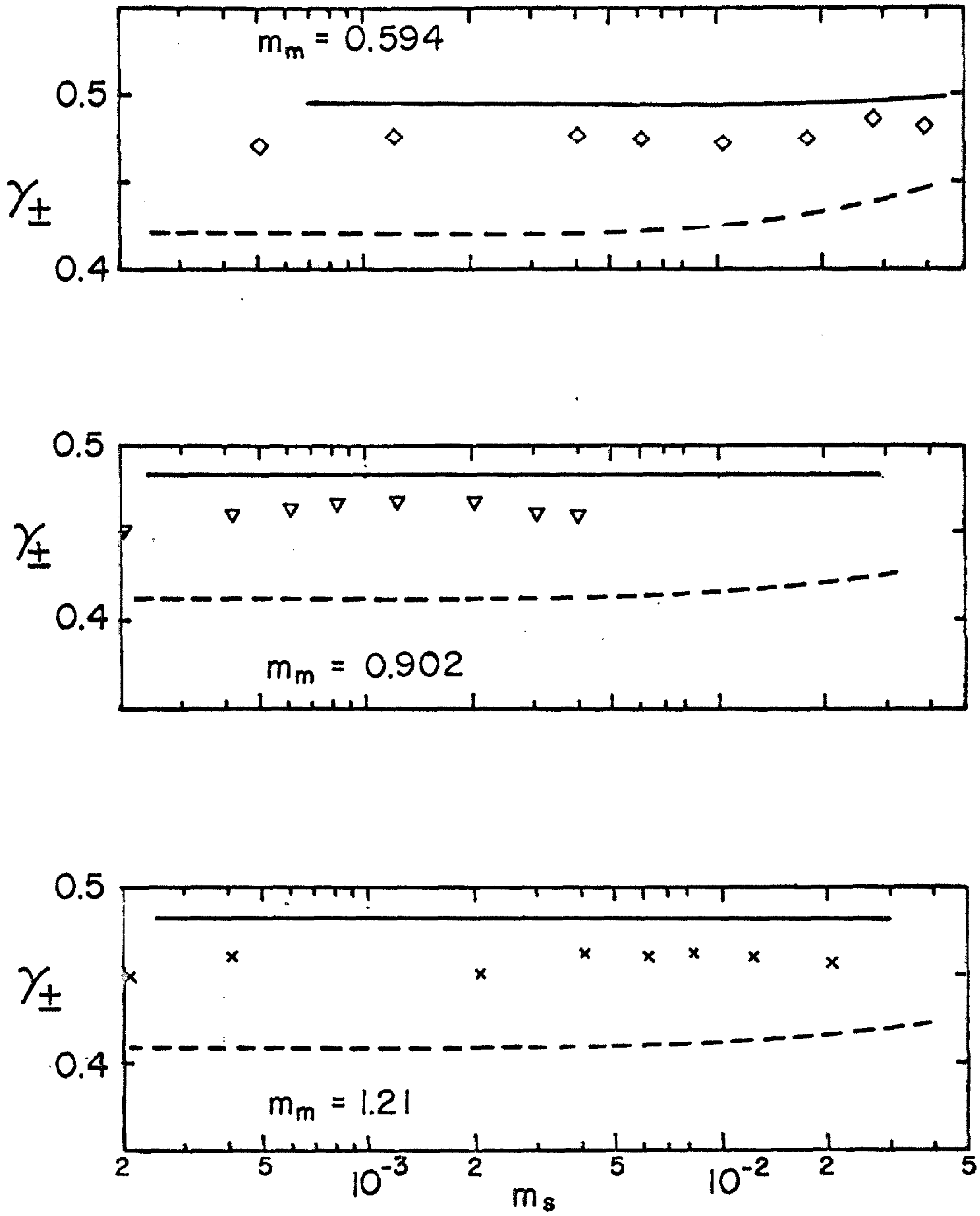
$$\gamma_{\pm} = \sqrt{\frac{S_-(\alpha\phi_p m_m + S_+ m_s)}{\alpha m_m + m_s}}\ \gamma_{\pm_o}\ , \qquad (22)$$

respectively. These expressions are compared to the data in Figures IV-3 and IV-4. Values of S_+ and S_- were interpolated from the calculations of Alexandrowicz[22]. Both predict the qualitative behavior of the salt-polyelectrolyte solutions. The theoretical equation (22) appears to agree quantitatively better than equation (21). Considering the complexity of salt-polyelectrolyte solutions and the simplifying assumptions necessary in order to be able to make calculations based on the electrostatic model, the agreement of the theoretical equation with the data is excellent. It must be noted, however, that this theory is still of an empirical nature in that a value of the linear charge density of the model cylinder was obtained by fitting the theory to the data for the salt-free case[22].

(c) Per Cent Salt Removal in Donnan Dialysis. For the pres-



IV-3. Variation of the NaCℓ activity coefficient with salt concentration in NaPA solutions of various concentrations and comparison of the data with the simple dissociation theory (eqn. 21) (---) and with the electrostatic model of Alexandrowicz (eqn. 22) (——).



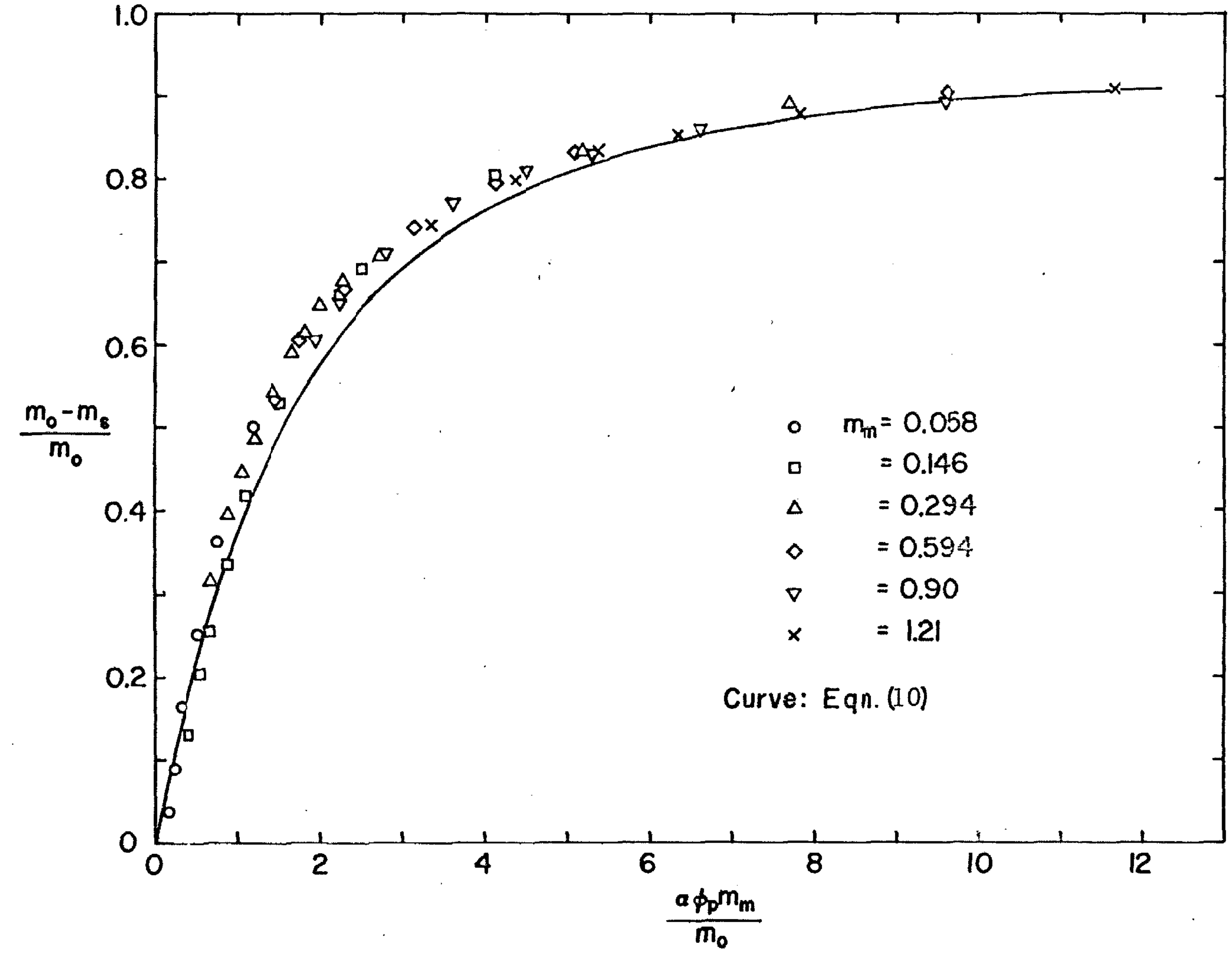
IV-4. Variation of the NaCℓ activity coefficient with salt concentration in NaPA solutions with various concentrations and comparison of the data with the simple dissociation theory (eqn. 21 (---) and with the electrostatic model of Alexandrowicz (eqn. 22) (——).

ent purposes, equation (9) based on the simple dissociation theory adequately describes the salt activity in salt-polyelectrolyte solutions. This equation was used to predict the fraction of salt removed in dialysis given by equation (10). In Figure IV-5, the present data have been calculated in terms of the fraction removed assuming that equilibrium is reached, in which case $m_o = m_e$, the equilibrium salt concentration (see Table IV-2). The results of these calculations are compared with equation (10) with the approximation $\gamma_{\pm_o}/\gamma_{\pm_s} = 1$. The curve obviously underestimates the effect of the polymer, but this is to be expected in view of Figures IV-3 and IV-4, in which the dissociation theory underestimates the salt activity coefficients. Because of its simplicity, however, equation (10) is used in the next chapter rather than expressions based on equation (13).

B. Ultrafiltration of NaCℓ - NaPA Solutions.

1. Characterization of Membrane Properties. The membranes used in this study were found to be very stable and did not exhibit significant changes in their properties after long periods of use. In fact, all of the experiments reported here were conducted using the same membrane. The major factor determining the stability of a membrane seemed to be the care taken in handling it. It was for this reason that the filtration cell was constructed in the way described in the previous chapter. Once installed, it was not necessary to remove the membrane to inspect or change electrodes or to fill or empty the cell.

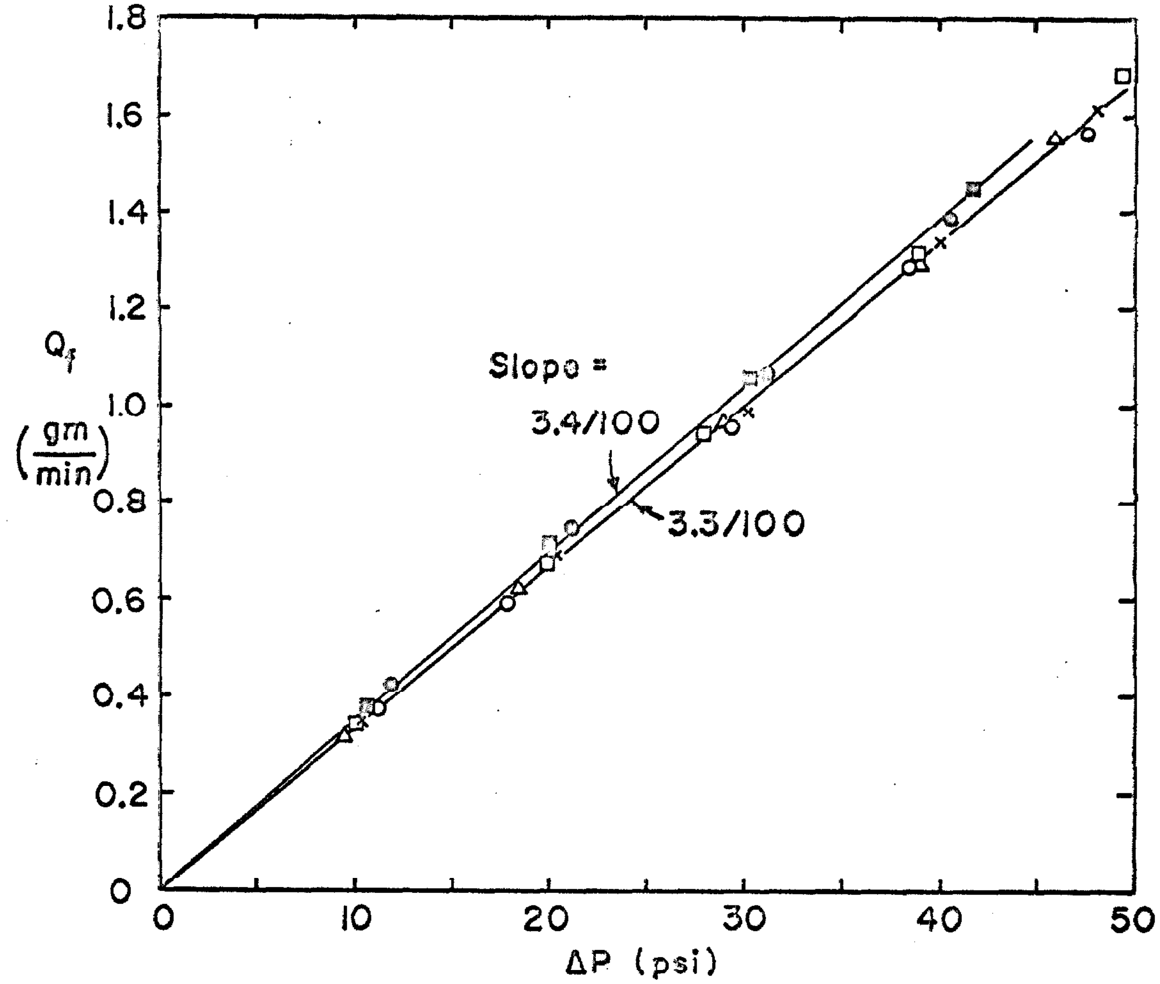
The filtrate flow rate was directly proportional to the applied



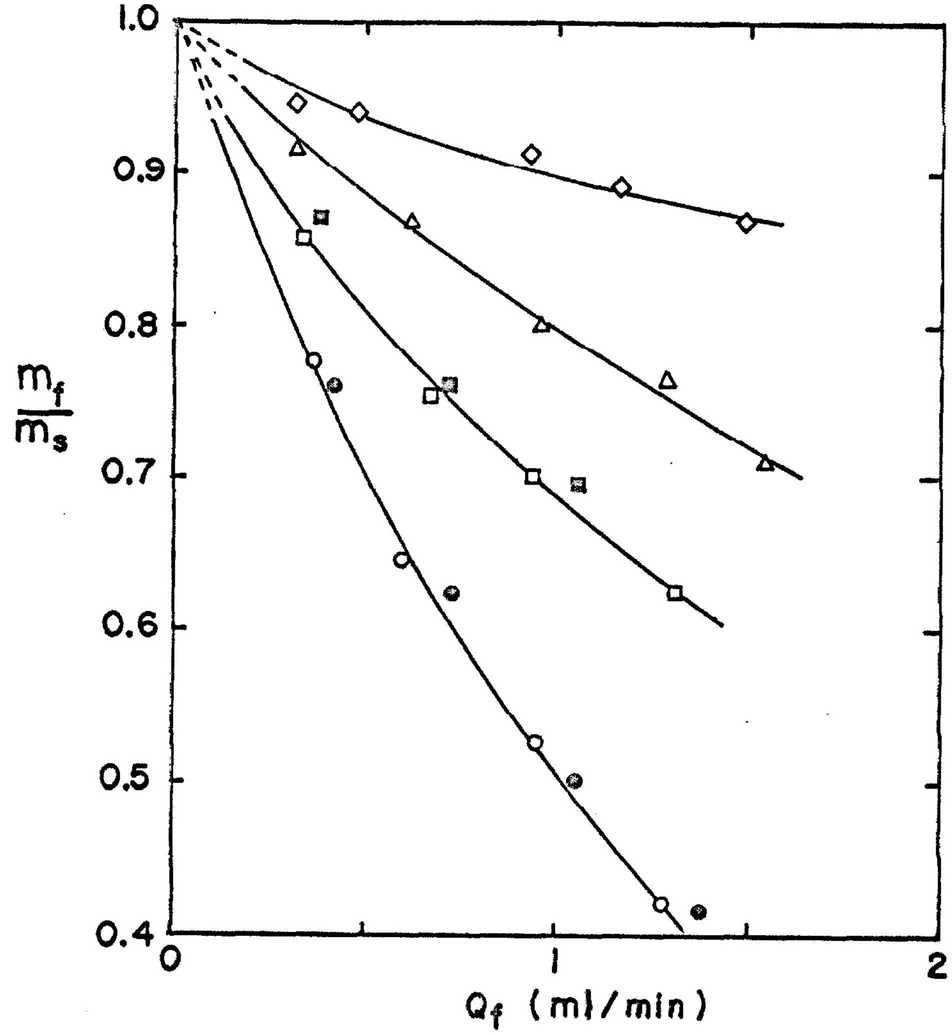
IV-5. Comparison of activity data with equation (10) with $\gamma_{\pm_o}/\gamma_{\pm_s}$ equal unity.

pressure, with a membrane permeability of 3.35 ml/min/100 psi (for a membrane area of 36.7 cm^2). In Figure IV-6 are shown the filtration results characterizing the membrane before and after the salt-polyelectrolyte experiments (the solid symbols represent data taken after the experiments). The permeability increased slightly during the experiments from approximately 3.3 to 3.4 ml/min/100 psi. The various symbols represent different salt concentrations. It is observed that they all fall on the same straight line, thus indicating that the $\sigma\Delta\pi$ term in equation (17) (and hence equation (20)) is negligible. For the higher flow rates, $\Delta\pi$ was generally between 1 and 2 psi. At lower flow rates, it was less. Since filtration is not complete, then $\sigma < 1$. At the higher salt concentrations, σ may be close to zero since there was little salt filtration. Assuming $\sigma = 0.25$, the $\sigma\Delta\pi$ term is always less than 0.5 psi, which is only slightly greater than the experimental error. Thus, it is reasonable to assume that the $\sigma\Delta\pi$ term is negligible and that the flow rate is directly proportional to the applied pressure for all salt concentrations over the pressure range studied.

The salt filtration characteristics of the membrane are strongly dependent upon the salt concentration (or activity), Figure IV-7. This behavior is expected for a membrane in which salt rejection is largely an electrochemical process as in an ion-exchanger type of membrane. The salt rejection decreased slightly over the period of the experiments; this behavior is indicated by the solid symbols in Figure III-7. Thus, over a period of approximately three months, the



IV-6. The filtrate flow rate as a function of applied pressure difference for NaCl solutions of concentration 0.005 m (o), 0.01 m (□), and 0.02 m (△), and for distilled water (X). Empty symbols represent data taken before the experiments; solid symbols represent data taken after the experiments.



IV-7. The relative filtrate concentration as a function of the filtrate flow rate for NaCℓ solutions of concentration 0.005 m (o), 0.01 m (□), 0.02 m (△), and 0.05 m (◇). Empty symbols represent data taken before the experiments; solid symbols represent data taken after the experiments.

permeability increased slightly and the salt rejection decreased. This change could have resulted from the formation of pin-hole leaks through the membrane; however, any leaks which developed were sufficiently small that the rejection of NaPA did not suffer and remained essentially complete. The repeated application and relaxation of pressure during experimentation may have weakened the membrane matrix, resulting in a looser and more permeable structure.

The salt rejection characteristics of the membrane are accurately described by the empirical expression:

$$\frac{m_f}{m_s} = \exp\left(\frac{-0.0082\, Q_f}{m_s^{0.83}}\right) . \tag{21}$$

Q_f is the filtrate flow rate. This equation is equivalent to equation (18). A serious attempt to compare this expression with various membrane models was not made; however, it may be noted that the exponential dependence on Q_f is in agreement with a charged membrane model[1].

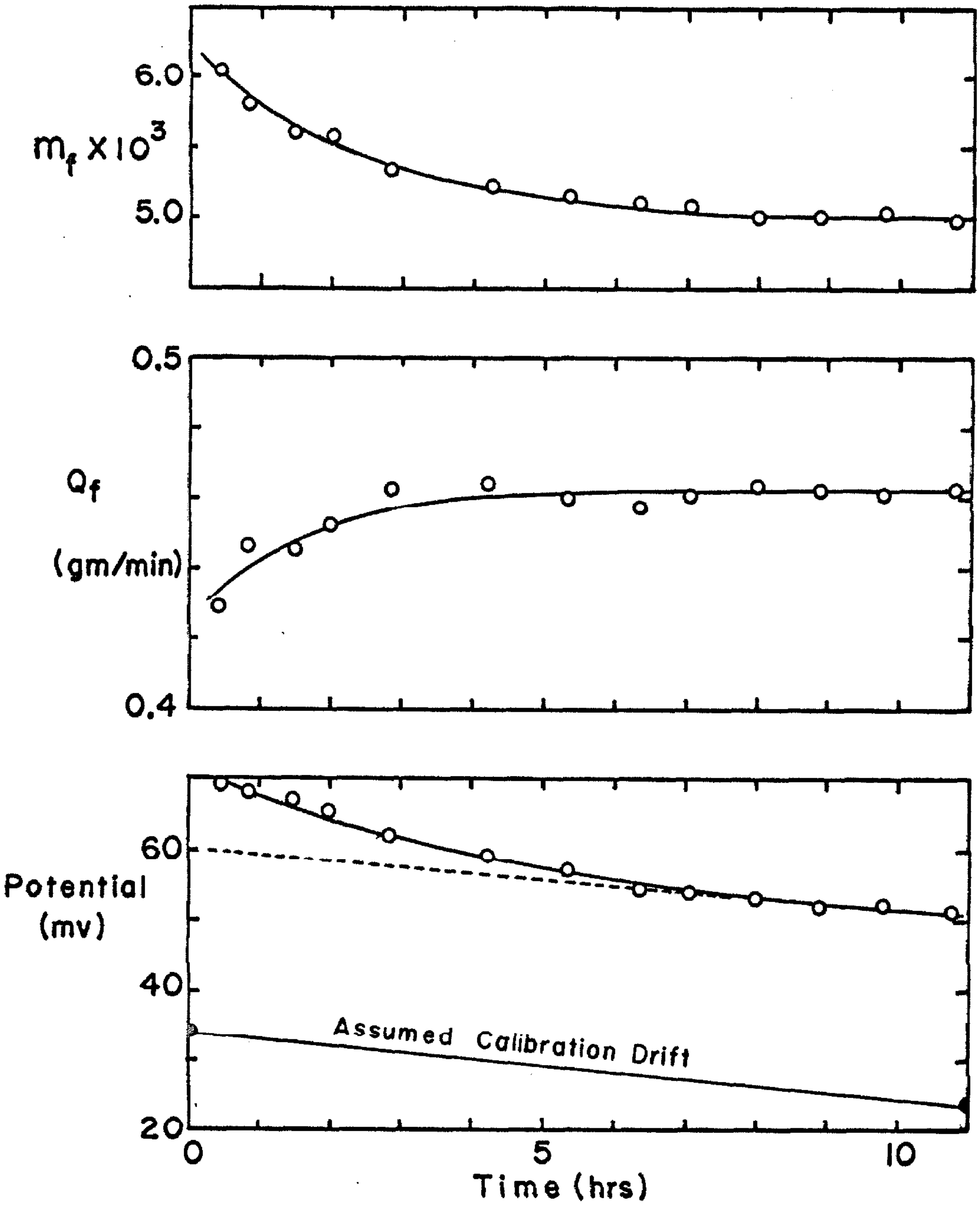
2. Results of Steady-State Experiments. Four steady-state experiments were conducted, all with a salt feed concentration of 0.005 m and a polyelectrolyte concentration of 0.146. The results are presented in Table IV-3. The approach to a steady state is shown in Figure IV-8 for Test No. 1. The time required to reach a steady state could be made reasonable by adjusting the initial salt activity in the polyelectrolyte solution. For example, the initial activity in Test No. 1 was 9.8×10^{-3}, and the steady-state value was 8.0×10^{-3}.

In all of the steady-state experiments, the rejection of NaPA

TABLE IV-3. Results of Steady-State Ultrafiltration Experiments.

Polyelectrolyte concentration = 0.146 m. Filtrate salt concentration (= feed salt concentration) = 0.005 m.

Test No.	Pressure Difference ΔP (psi)	Stirring Speed N (rpm)	Filtrate Flow Rate Q_f (ml/min)	NaCℓ Activity $a_{\pm} \times 10^3$	NaCℓ Concentration $m_s \times 10^3$ (m)	Equilibrium Salt Concentration $m_e \times 10^3$ (m)	Filtrate Concentration Ratio m_f/m_e	Donnan Osmotic Pressure Difference $\Delta\pi_D$ (psi)	Concentration Ratio Predicted (eqn. 23) m_f/m_e
1	23.8	200	0.462	8.0	2.3	8.8	0.57	4.5	0.825
2	24.1	470	0.656	6.38	1.45	6.95	0.72	5.4	0.72
3	28.8	510	0.805	6.82	1.7	7.40	0.68	5.6	0.68
4	32.2	505	0.925	7.12	1.8	7.75	0.645	5.0	0.65



IV-8. The time dependence of the filtrate salt concentration, the filtrate flow rate, and the potential of the electrode pair during steady-state experiment no. 1.

by the membrane was complete. Solids tests gave the same results (within 1 per cent) on samples taken before and after filtration for three of the experiments. In Test No. 2, the first long-term experiment at a high stirring speed, the NaPA solution was cloudy after the experiment and solids results indicated a 4 per cent increase in solids. This cloudiness and solids increase was caused by wear of the plastic lid of the filtration cell by the inner retaining collar. A brass washer was inserted to serve as a bearing surface and the problem was not encountered again. The filtrate was analyzed for NaPA by a solids test, and the results were negative. Since the sensitivity of the solids test was approximately 0.001 moles NaPA/kg, the rejection of NaPA was greater than 99.3 per cent. Based upon the before and after solids tests of the NaPA solution, rejection was better than 99.8 per cent. Since the molecular weight of the polyelectrolyte was much greater than the solute cutoff molecular weight of the membrane, it is assumed that rejection was complete.

Permeability and salt rejection experiments with sodium chloride solutions conducted between experiments indicated little change in the membrane's properties, and therefore plugging was ruled out. Thus, the conditions listed in Section II. B. 3. above were satisfied and the relations (18) and (20) should describe the filtration experiments. The data are compared with these expressions in Section 4 below.

In three of the steady-state experiments, the calibration of the electrode pair changed during the experiment. The electrodes were calibrated (by reading the potential produced by a standard

NaCℓ solution) before and after each experiment. For the purposes of analyzing the steady-state conditions only the final calibration was necessary. However, the calibration change appeared to be linear with time. (Compare the slope of the assumed calibration line to the slope of the last four or five points in Figure IV-8.) This assumption of a linear drift was used in analyzing the data of the near-steady-state experiments for cases in which the calibration before and after experiments was unequal. Generally, the different was less than 5 mv.

3. Results of Near-Steady-State Experiments. Experiments were conducted for polyelectrolyte concentrations of 0.146, 0.29, and 0.59. Only for the low concentration of 0.146 was it possible to stir fast enough to eliminate concentration polarization effects.

As the stirring rate was increased at constant pressure, the filtrate flow rate increased and approached a limiting value. This limiting value represents complete mixing in the solution right up to the membrane surface and, hence, no concentration polarization. The data in Table IV-4 represent these limiting conditions. The effect of stirring speed is seen in Tables IV-5 and IV-6. In IV-5, data for $m_m = 0.146$ are presented, and in this case a limiting value is attained. In Table IV-6, giving data for $m_m = 0.29$ and 0.59, the limiting value was nearly obtained at the lower polyelectrolyte concentration. For $m_m = 0.59$, the flow is nearly linear with stirring speed for the range 250 to 500 rpm, the maximum speed possible, and the limiting value was not approached.

TABLE IV-4. Data from Near-Steady-State Ultrafiltration Experiments Using High Stirring Rates. Polyelectrolyte concentration = 0.146 m.

Pressure Difference ΔP (psi)	Stirring Speed N (rpm)	Filtrate Flow Rate Q_f (ml/min)	NaCℓ Activity $a_\pm \times 10^3$	NaCℓ Concentration $m_s \times 10^3$ (m)	Equilibrium Salt Concentration $m_e \times 10^3$ (m)	Filtrate Salt Concentration $m_f \times 10^3$ (m)	Concentration Ratio m_f/m_e	Donnan Osmotic Pressure Difference $\Delta\pi_D$ (psi)	Predicted Concentration Ratio (eqn. 23)
Feed Salt Concentration = 0.01 m									
13.0	455	0.275	9.4	3.1	10.4	9.14	0.88	3.8	0.91
17.2	485	0.443	10.2	3.6	11.3	9.47	0.835	3.5	0.86
19.3	501	0.513	10.2	3.6	11.3	9.25	0.82	3.5	0.84
21.2	515	0.596	10.2	3.6	11.3	9.33	0.82	3.5	0.82
24.3	513	0.706	12.1	5.0	13.5	11.1	0.82	2.7	0.81
28.6	506	0.877	11.5	4.5	12.9	9.85	0.76	2.8	0.77
Feed Salt Concentration = 0.005 m									
13.4	410	0.277	5.83	1.2	6.31	5.37	0.85	5.7	0.86
16.2	408	0.339	5.57	1.05	6.03	4.87	0.81	5.8	0.82
18.8	415	0.446	6.05	1.3	6.53	4.90	0.75	5.6	0.79
21.4	410	0.518	5.83	1.2	6.31	4.83	0.77	5.7	0.75

TABLE IV-5. Results of Near-Steady-State Experiments Showing the Effect of Stirring Speed. Polyelectrolyte Concentration = 0.146 and Feed Salt Concentration = 0.01 m.

ΔP (psi)	N (rpm)	Q_f (ml/min)	$a_{\pm} \times 10^3$	$m_s \times 10^3$ (m)	$m_e \times 10^3$ (m)	$m_f \times 10^3$ (m)	m_f/m_e	$\Delta\pi_D$ (psi)	$\left(\frac{m_f}{m_e}\right)_{pred}$ (eqn. 23)
19.3	210	0.385	9.8	3.4	10.9	8.8	0.81	3.7	0.88
19.2	302	0.488	10.6	3.9	11.8	9.7	0.825	3.3	0.85
19.2	424	0.517	10.4	3.8	11.5	9.5	0.835	3.4	0.84
19.3	501	0.513	10.2	3.6	11.3	9.25	0.82	3.5	0.84
24.3	299	0.638	10.7	3.9	11.9	9.3	0.78	3.3	0.81
24.2	364	0.675	11.9	4.8	13.2	10.4	0.79	2.8	0.82
24.2	436	0.695	11.3	4.4	12.5	10.05	0.80	3.1	0.80
24.3	513	0.706	12.1	5.0	13.5	11.1	0.82	2.7	0.81
28.6	300	0.765	12.4	5.2	13.9	9.8	0.705	2.5	0.80
28.6	369	0.830	12.1	5.0	13.5	9.75	0.72	2.6	0.78
28.7	446	0.870	11.9	4.8	13.4	10.1	0.75	2.7	0.77
28.6	506	0.877	11.5	4.5	12.9	9.85	0.76	2.8	0.77

TABLE IV-6. Results of Near-Steady-State Experiments Showing the Effect of Stirring Speed. Feed Salt Concentration = 0.01 m.

ΔP (psi)	N (rpm)	Q_f (ml/min)	$a_\pm \times 10^3$	$m_s \times 10^3$ (m)	$m_e \times 10^3$ (m)	$m_f \times 10^3$ (m)	m_f/m_e	$\Delta\pi_D$ (psi)	$(\frac{m_f}{m_e})_{pred}$ (eqn. 23)
$m_m = 0.29$									
25.5	296	0.322	11.3	2.3	12.6	10.5	0.83	12.7	0.905
25.4	402	0.376	11.0	2.1	12.2	10.2	0.84	13.0	0.89
25.5	445	0.377	11.2	2.2	12.5	10.3	0.825	12.8	0.89
25.3	501	0.380	10.8	2.1	12.0	10.1	0.84	13.2	0.88
34.9	295	0.452	10.3	1.9	11.4	8.7	0.755	13.5	0.86
34.8	435	0.563	11.2	2.1	12.3	9.6	0.78	12.8	0.84
34.8	505	0.594	10.4	1.9	11.5	9.15	0.795	13.4	0.82
$m_m = 0.59$									
60.0	245	0.321	12.3	1.4	13.8	9.4	0.68	35.2	0.91
60.2	295	0.340	15.5	2.3	17.6	12.4	0.705	32.7	0.92
60.2	395	0.401	13.1	1.6	14.8	11.0	0.74	34.4	0.90
60.1	490	0.450	12.8	1.5	14.4	10.6	0.74	34.7	0.88

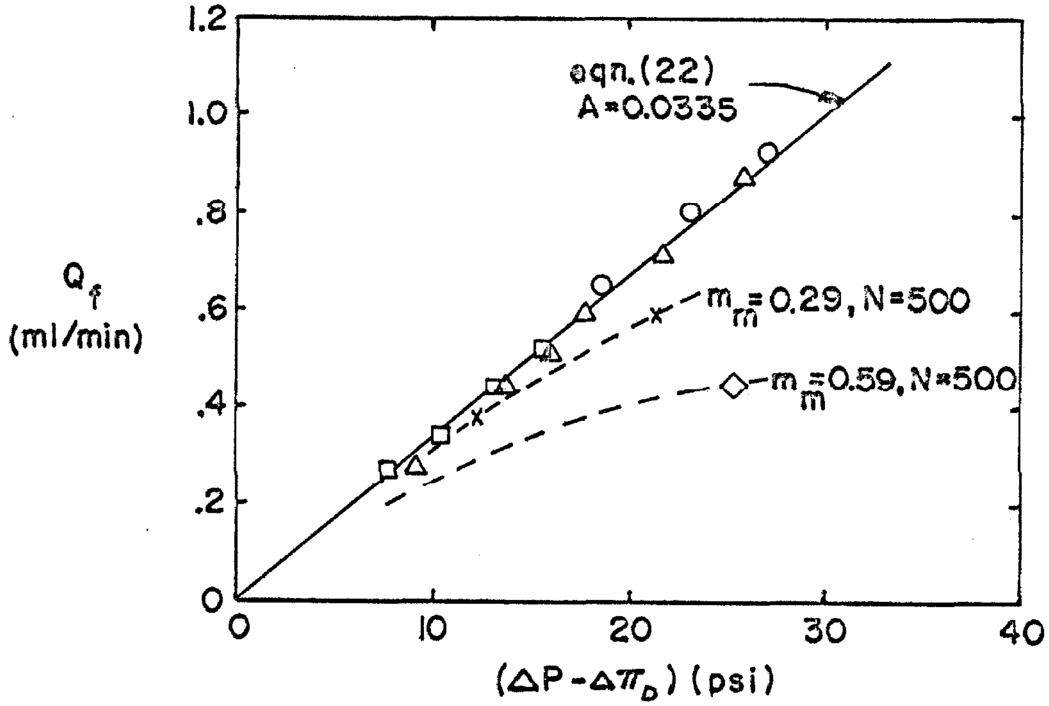
4. Comparison of Ultrafiltration Results with Theory.

(a) Pressure - Flux Relation. - Since the $\sigma\Delta\pi$ term was negligible in filtration of salt solutions, equation (20) reduces to the simple form

$$J = A(\Delta P - \Delta\pi_D) \ . \tag{22}$$

For the evaluation of $\Delta\pi_D$, the Donnan osmotic pressure difference, a curve of $\Delta\pi_D$ versus $a_\pm$, the mean activity of the salt, was prepared for the three polyelectrolyte concentrations studied. For a given salt activity, the equilibrium concentration is found immediately using published data for NaCℓ solutions[33]. The salt concentration in the polyelectrolyte solution may be obtained using the thermodynamic data obtained for NaCℓ - NaPA solutions. The Donnan osmotic pressure is just the difference between the osmotic pressure of the salt-polyelectrolyte solution (which was calculated using equation (11)) and the osmotic pressure of the equilibrium solution (which was obtained from published data). Once these curves were constructed, $\Delta\pi_D$ could easily be read for each point. The resulting values are given in the tables of results.

In Figure IV-9 the data corresponding to negligible concentration polarization for $m_m = 0.146$ are compared with the theoretical expression based upon the measured permeability (A = 0.0335 ml/min/psi). The agreement is excellent. Also shown on the graph are flow data for $m_m = 0.29$ and 0.59 for a stirring speed of approximately 500 rpm, the maximum speed used. These data fall below the curve because of concentration polarization. For $m_m = 0.29$, it is reasonable to assume that the data in Table IV-6 approach flow rates of 0.41



IV-9. Comparison of the filtration data with eqn. (22) (using A = 0.0335 ml/min/psi) for high stirring speeds. Polyelectrolyte concentrations and filtrate salt concentrations were: $m_m = 0.146$ and $m_f = 0.005$ (o, □); $m_m = 0.146$ and $m_f = 0.01$ (△); $m_m = 0.29$ and $m_f = 0.01$ (×); and $m_m = 0.59$ and $m_f = 0.01$ (◇). (o = steady state results.)

and 0.72 as limiting values, which would move the two points up to the curve. Thus, equation (20) is confirmed for the limited range of polyelectrolyte concentrations and pressures used.

(b) Filtrate Salt Concentration. - The salt activity, $a_{\pm}$, of the salt-polyelectrolyte solution being filtered and the filtrate salt concentration, are included in the preceding tables of results. Values of the equilibrium salt concentration, m_e, were calculated based upon the measured activities. The measured activity was also used to estimate the salt concentration of the filtrand, m_s. These concentrations are also presented in the tables.

It is observed that m_f is nearly equal to m_e and significantly larger than m_s (Tables IV-3 and IV-4). According to the considerations of Section II. B. 3., the differences between m_f and m_e are due to the salt rejection by the membrane, assuming that the conditions listed in that section are satisfied. Equation (21) was used to calculate the filtrate salt concentration using the equilibrium concentration, m_e, in place of m_s in that equation. This is the same as expressing equation (21) in terms of the upstream salt activity and then using activities for the calculation, since m_e is just another way of expressing the activity of the salt in polyelectrolyte solutions.

For comparison with the data, the results are expressed in the ratio m_f/m_e calculated from

$$\frac{m_f}{m_e} = e^{\frac{-0.0082\, Q_f}{m_e^{0.83}}} \tag{23}$$

and are compared with the data in Tables IV-3 through IV-6.

It is seen that the predicted values are in excellent agreement with the data for those cases in which concentration polarization effects are eliminated, namely, steady-state tests 2 - 4 and the data in Table IV-4. Thus, for the system studied, the thermodynamic data and the expression characterizing the membrane may be used to predict the salt concentration and flow rate of the filtrate, providing boundary layer considerations are not important. The remainder of the data indicates that the result of concentration polarization is to cause m_f to be smaller than it would be for the same flow rate in the absence of polarization.

5. Concentration Polarization Effects. Concentration polarization effects were greater than anticipated in the stirred filtration cell. Polarization effects were eliminated only for low polyelectrolyte concentrations using high stirring speeds and for low filtrate flow rates, Q_f. For example, for $m_m = 0.146$ and $Q_f = 0.5$ ml/min, polarization was negligible for stirring speeds greater than approximately 400 rpm. At a flow rate of 0. 9, a stirring speed of 450 to 500 rpm was necessary to eliminate polarization (Table IV-5). For $m_m = 0.29$ and $Q_f = 0.37$ ml/min, a stirring speed of 400 to 450 rpm was necessary. Polarization was not eliminated at a speed of 500 rpm for $Q_f = 0.6$ at the same concentration, nor for $Q_f = 0.45$ for $m_m = 0.58$ (Table IV-6). Thus, the stirring speed necessary to eliminate polarization effects increases with both the filtrate flow rate and the polyelectrolyte concentration. The strong dependence upon the concentration is related to the increase in viscosity with NaPA concentration. The viscosity of NaPA solutions was 10. 9, 17. 2, and 31. 2 cm^2/sec

at $m_m = 0.146$, 0.29, and 0.59, respectively. Thus, as the concentration is increased, the effectiveness of the stirring decreases.

Polarization manifested itself by a dependence of the flow rate on the stirring speed for a given applied pressure. Also observed was a decrease in the filtrate salt concentration from the value expected based upon equation (23). While a rigorous treatment of the boundary layer is not feasible for the type of cell geometry used, the decrease in effective pressure (or increase in $\Delta\pi_D$) and the decrease in the filtrate salt concentration can be qualitatively explained using the simple model shown in Figure IV-10. The boundary layer is taken as an unmixed layer of solution of thickness δ adjacent to the membrane and complete mixing outside of this layer is assumed. Writing flow equations for each of the three dissolved species gives

$$-D_+ \frac{\Delta m_+}{\delta} + J_w m_+ + E\mathfrak{F} z_+ m_+ \omega_+ = J_s$$

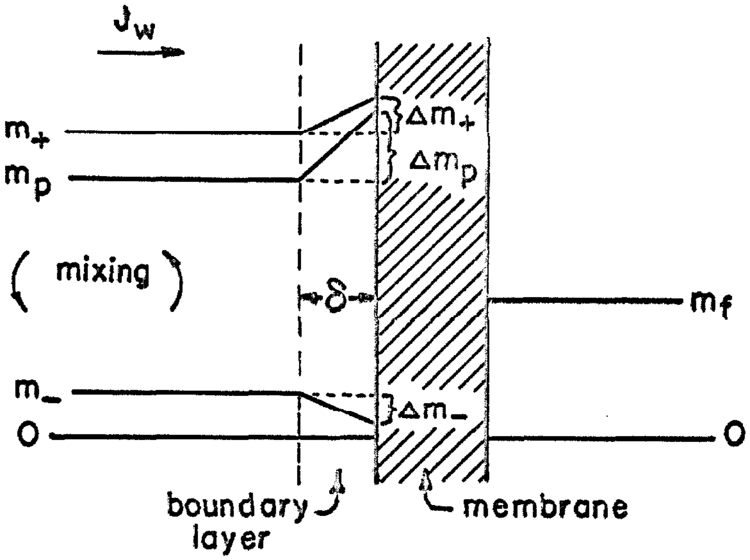
$$-D_- \frac{\Delta m_-}{\delta} + J_w m_- - E\mathfrak{F} z_- m_- \omega_- = J_s$$

$$-D_p \frac{\Delta m_p}{\delta} + J_w m_p - E\mathfrak{F} z_p m_p \omega_p = 0$$

where D_i , ω_i , and z_i are the diffusion coefficient, mobility, and the charge of the i^{th} species, respectively. E is the average electric field strength, J_w is the filtrate velocity, J_s is the salt flux, and $\mathfrak{F}$ is the Faraday constant. Electroneutrality requires that:

$$m_+ = z_p m_p + m_-$$

for $z_+ = z_- = 1$. Using this relation and the Stokes-Einstein relation between mobility and diffusivity ($\omega = D/RT$), E may be eliminated, obtaining:



IV-10. A schematic representation of the concentration profiles in the boundary layer during ultrafiltration, showing the nomenclature used in the text.

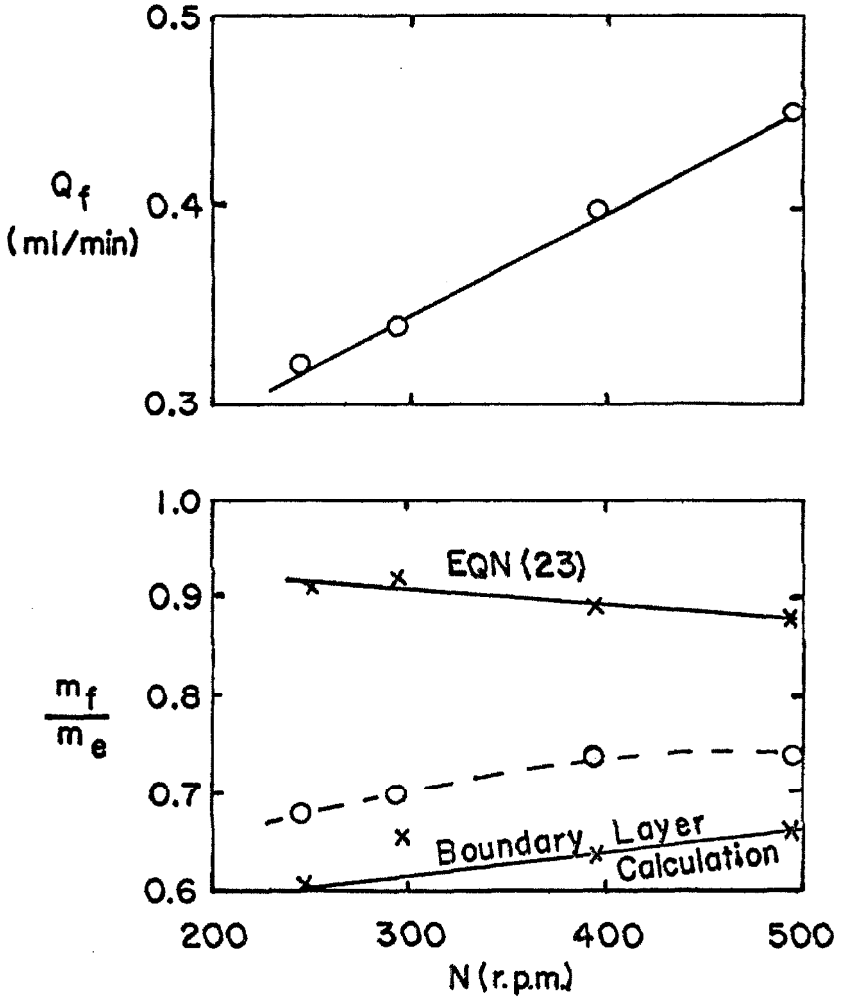
$$\left(1 + \frac{z_p^2 m_p}{m_+}\right)\frac{\Delta m_+}{\delta} - \frac{\Delta m_-}{\delta} = \left(\frac{1}{D_p} + \frac{z_p}{D_+}\right) J_w m_p z_p - \frac{z_p^2 m_p}{D_+ m_+} J_s \ ,$$

$$\frac{m_-}{m_+}\frac{\Delta m_+}{\delta} + \frac{\Delta m_-}{\delta} = \left(\frac{1}{D_+} + \frac{1}{D_-}\right) J_w m_- - \left(\frac{1}{D_+ m_+} + \frac{1}{D_- m_-}\right) m_- J_s \ .$$

Using the experimental values of J_w ($= Q_f$/membrane area) and J_s ($= J_w m_f$), the composition of the solution at the membrane surface was calculated for various values of the boundary layer thickness, δ. Values of ω_p were estimated from the electrolysis data of Huizenga, Grieger, and Wall[36]. The data of Wall, Terayama, and Techakumpuch[37] indicate that the degree of dissociation of sodium ion increases in transport studies with increasing electric field strength to a limiting value of approximately $2\phi_p$. This value is not significantly affected by the presence of salt[38]. Since the field strength increases from zero at the edge of the boundary layer to a maximum value at the membrane surface, an average value of $1.5\,\phi_p$ was taken as the degree of dissociation for these calculations. Thus, the composition of the solution adjacent to the membrane surface was calculated, and then the Donnan osmotic pressure and salt activity there were calculated using the simple dissociation theory (degree of dissociation = ϕ_p).

For all calculations, $\Delta\pi_D$ was greater and the salt activity was smaller at the membrane surface than in the bulk solution. This result qualitatively agrees with the experimental results, and may be interpreted physically as follows. Since the equilibration and separation at the membrane surface result in a filtrate salt concentration greater than the salt concentration in the solution, convection alone cannot transport enough salt to the membrane through the boundary layer. Therefore, an activity (or concentration) gradient must be established in the boundary layer, and a decrease in salt activity at the membrane must take place. The increase in $\Delta\pi_D$ with polarization is caused by the increased polyelectrolyte (and counterion) concentration at the membrane surface.

Quantitative comparisons were made by calculating the Donnan osmotic pressure and the salt activity at the membrane surface for various values of δ. The measured flow rate was used to obtain δ by choosing that value giving the value of $\Delta\pi_D$ that satisfied equation (22). Using this value of δ and the corresponding salt activity at the membrane surface, the filtrate salt concentration was calculated. The calculated values were generally lower than the experimental values (see Figure IV-11 for $m_m = 0.59$). Furthermore, the values of δ obtained (0.001 to 0.008 cm) seem small considering the viscosity of the solutions and the spacing between the membrane and the stirring blade (~0.15 cm).



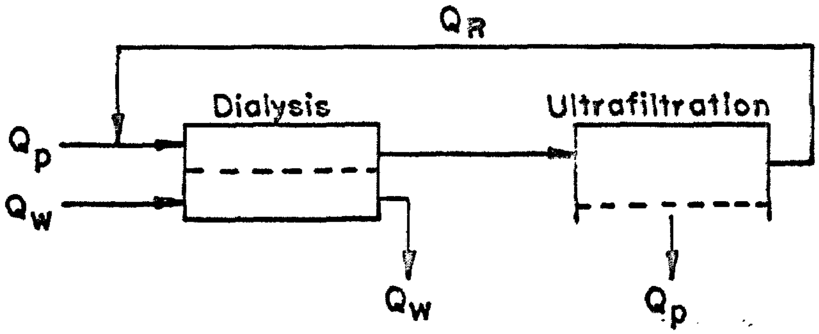
IV-11. Concentration polarization effects for $m_m = 0.59$, and a comparison of the filtrate salt concentration data with boundary-layer calculations. m_e is the equilibrium concentration of the salt-polyelectrolyte solution far from the membrane. Also shown are calculations from eqn. (23) neglecting boundary layer effects.

V. APPLICATION TO DESALINATION

The motivation for this research was the possibility of developing a desalination process upon the Donnan effect. Such a process was described briefly in the Introduction. In this chapter, the results of the preceding chapters are used to describe the process quantitatively and to evaluate its practicability.

A flow diagram of the process is presented in Figure V-1. The recycle stream (R), containing the polyelectrolyte, is combined with the influent saline stream and the resulting solution is dialyzed with a waste flow, Q_w, of additional saline water. In the dialysis, the polyelectrolyte causes salt to diffuse through the membrane (which is impermeable to the polyelectrolyte) into the waste stream. The high osmotic pressure of the polyelectrolyte solution causes a flow of water through the membrane from the waste stream into the polyelectrolyte solution. This flow is neglected, however, as it is small compared to the flows Q_p and Q_w. Preliminary dialysis experiments (as well as those used to purify the polyelectrolyte solutions) indicated that the salt approaches its equilibrium concentrations quickly compared to the transport of water. The effect of including this water flow would represent only a small correction to the results obtained by neglecting it.

The effect of the dialysis is to remove some salt with the addition of the polyelectrolyte. To obtain the product water of reduced salt concentration, the polyelectrolyte must be removed and preferably recovered for reuse. Although various methods exist for removing it, ultrafiltration is considered here because of its



V-1. Flow diagram of the Donnan desalination process.

relative simplicity and because it lends itself to easy reuse of the polyelectrolyte. Thus, the dialyzate proceeds to the ultrafiltration unit in which the filtrate becomes the product water and the concentrated polyelectrolyte is recycled. Comparing this process with reverse osmosis (or "hyperfiltration"), it is seen that the effect of the dialysis is to reduce the filtration requirements from the rejection of simple salts to the rejection of polyelectrolyte molecules. For this purpose, more permeable membranes may be used than are used in reverse osmosis.

In evaluating the performance of the process, it is of interest to calculate the required filtration pressure and polyelectrolyte concentration necessary to effect a given salt removal. (All references to the polyelectrolyte concentration in this chapter refer to its concentration in the recycle stream.) The following assumptions concerning the operation of the process are made:

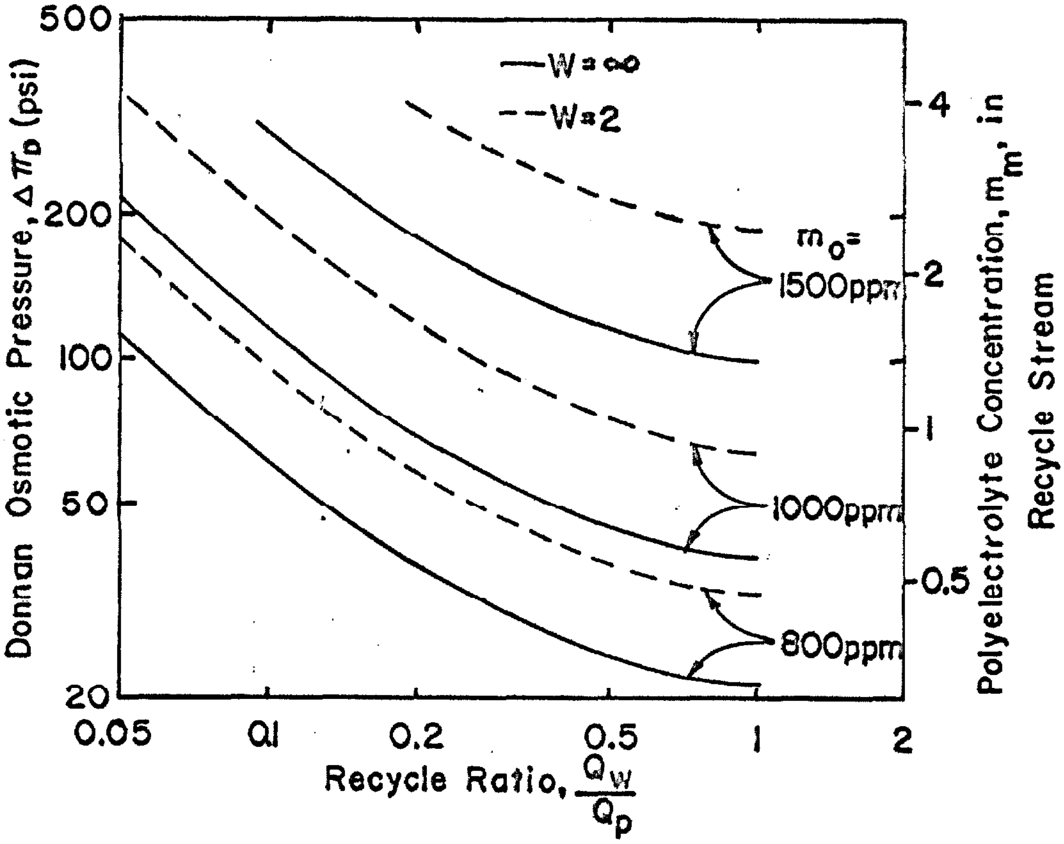
1) Q_w is much larger than Q_p , or $W = Q_w/Q_p = \infty$. Thus, the salt concentration of the waste stream, m_w, is approximately equal to the original salt concentration, m_o.
2) The dialysis proceeds to completion with respect to the salt equilibrium. This means that the two streams leaving the dialysis unit have equal salt activities.
3) The ultrafiltration membrane is impermeable to the polyelectrolyte and completely permeable to the salt. Thus, no salt rejection occurs and the filtrate salt concentration equals the equilibrium salt concentration.

4) No concentration polarization takes place in the ultrafiltration.

These conditions represent the most ideal conditions under which to examine the performance of the process. The effects of relaxing these conditions are discussed below.

The process was studied by choosing the polyelectrolyte and original salt concentrations, and the recycle ratio, Q_R/Q_p. By making the appropriate mass balances and using equation (9) for the salt activity to describe the dialysis equilibrium and to relate the filtrate salt concentration to the composition of the recycle stream, the product salt concentration was calculated as well as the Donnan osmotic pressure in the filtration unit. In view of equation (22), this osmotic pressure represents the minimum pressure required in the ultrafiltration step. The results of these calculations were used to obtain the solid curves in Figure V-2, which show the dependence of the Donnan osmotic pressure on the recycle ratio for the production of 500 mg/l water from waters with initial TDS concentrations of 800, 1000, and 1500 mg/l. The polyelectrolyte concentration in the concentrated recycle stream is given on the right ordinate.

The minimum pressure requirements are high for these relatively low salt reductions. Assuming complete pressure recovery of the flow Q_R, the minimum energy for this process is $Q_p \cdot \Delta\pi_D$. If this value is compared with the thermodynamic minimum energy required for the above separations, $Q_p \cdot [\pi(m_o)-\pi(m_s)]$, it is found that the process requires a minimum energy approximately 7 times the thermodynamic minimum energy (for a recycle ratio of one).



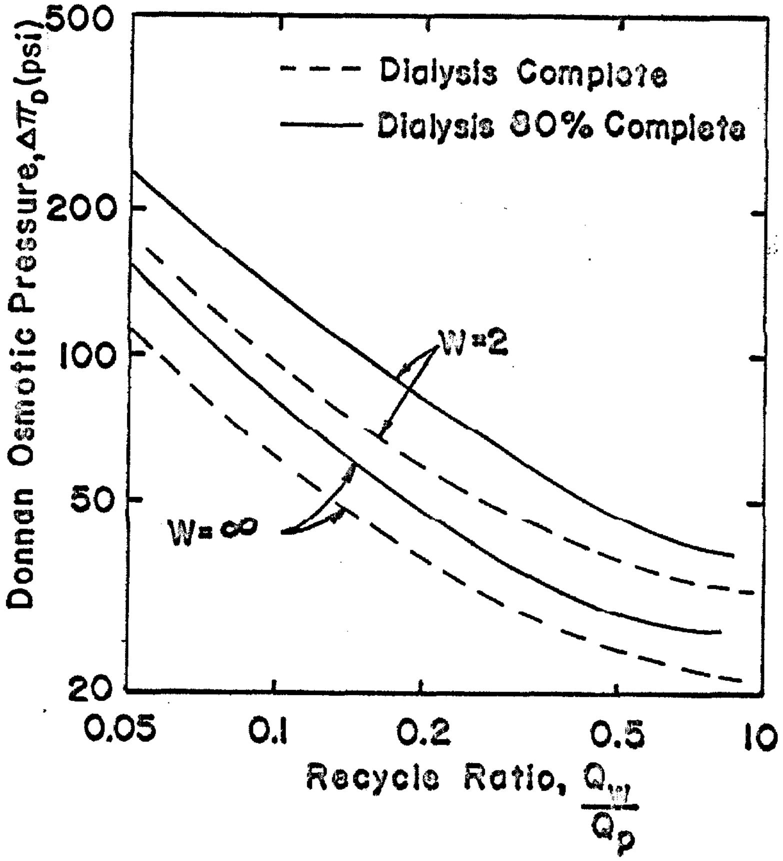
V-2. Polyelectrolyte concentration and minimum pressure required as a function of the recycle ratio for W = ∞ and W = 2 for various initial salt concentrations.

There seems no way to reduce the energy requirements for such a process based upon the Donnan membrane equilibrium; for the process to work, the macromolecular electrolyte chosen must contain a sufficient number of dissociating counterions or be used at sufficient concentration to produce a substantial Donnan effect in the first place, and it is these counterions that cause the large osmotic pressures in the separation process.

The effect of not having an infinite waste flow is illustrated by the dashed curves of Figure V-2, drawn for W equal to 2, corresponding to a product yield of 33 per cent. The effect of increasing the product yield, $Q_p/(Q_p+Q_w)$, is to increase the required polyelectrolyte concentration and pressure significantly. The fractional increase is independent of the recycle ratio, but increases with increasing initial salt concentration.

In Figure V-3 the effect of incomplete dialysis on the Donnan osmotic pressure is shown. $\Delta\pi_D$ was calculated for the production of water of 500 mg/l TDS from an initial concentration of 800 mg/l for the two cases $W = \infty$ and $W = 2$ and with dialysis carried to 80 per cent completion. The osmotic pressure is increased about 25 per cent above that for complete dialysis. For $W = 2$ the Donnan osmotic pressure is approximately double the value calculated under the "ideal" conditions listed above.

In design, the recycle ratio would be chosen to obtain minimum overall costs. As the recycle ratio is increased, the size of the dialysis unit must be increased; therefore, the consideration of dialyzer size indicates a small recycle ratio. On the other hand, if complete



V-3. The effect of incomplete dialysis on the minimum pressure required for an initial salt concentration of 800 mg/l .

pressure recovery is obtained in the recycle stream, pumping costs are proportional to $\Delta P \cdot Q_p$ and larger values are indicated to decrease the necessary pressure requirements. Increasing the recycle ratio also decreases the required polyelectrolyte concentration. If pressure recovery is not complete, then the pumping costs dictate lower recycle ratios.

To obtain some idea of the size of the units required with this process, a calculation was made using a recycle ratio of 0.2. Also, 80 per cent completion in dialysis and a product yield of 33 per cent were assumed for the production of 500 mg/l water from an 800 mg/l source. A dialysis coefficient of 2×10^{-2} cm/sec was used[39]. For the dialysis of simple salts, the salt flux equals the dialysis coefficient times the salt concentration difference across the membrane dialysis cell. As seen in the above ultrafiltration studies, the salt activity (or equilibrium salt concentration) should be used rather than salt concentration in cases such as the present in which the activity of the salt is significantly influenced by the presence of a second solute (the polyelectrolyte). Therefore, the salt flux was calculated from the product of the dialysis coefficient and the difference between the equilibrium salt concentration of the polyelectrolyte solution and the salt concentration in the waste stream. For the separation described above with dialysis carried to 80 per cent completion, 140 square feet of dialysis membrane are required per 1000 gallon/day capacity. A permeability of 175 gallons/square foot/day/100 psi[*] was assumed for the ultrafiltration membrane. (This value

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[*] A filtrate flow rate, Q_f, of 1 ml/min in the ultrafiltration experiments corresponds to a flux of 10 gal/square foot/day.

corresponds to a commercially available membrane of the same type as those used in the experiments that is more permeable and does not filter salt.) If a flux of 50 gal/square foot/day is desired, then 20 square feet of membrane are necessary and a pressure of 115 psi must be used. Thus, for the production of 1000 gal/day with a TDS concentration of 500 mg/l from a 3000 gal/day source originally at 800 mg/l, the following requirements were calculated for a recirculation ratio of 0.2 and dialysis 80 per cent complete: (1) 140 square feet of dialysis membrane, (2) 20 square feet of ultrafiltration membrane, (3) an operating pressure of 115 psi, and (4) a polyelectrolyte concentration of approximately 1.2 moles (of monomer)/liter.

By comparison, typical results to date indicate that flow rates of approximately 2.5 gal/ft^2/day are obtained in the reverse osmosis process using cellulose acetate membranes with an applied pressure of 200 psi[40]. The salt concentration is reduced approximately 95 per cent; if blending is used to produce a product of 500 mg/l TDS, a total membrane area of approximately 160 square feet must be used. Thus, the Donnan desalination process requires only one eighth the filtration membrane area required in reverse osmosis, but the dialysis unit is additional. The development of membranes of higher permeability and lower salt rejection, made especially for treating waters of low salt content, may be expected to decrease the membrane requirements of reverse osmosis and thus to improve its efficiency.

The effects of concentration polarization have not been considered in the above discussion. Since the filtrate flow rates considered are nearly five times those obtained in the experiments, it is apparent that polarization effects will be significant if the same polyelectrolyte were used. Use of a polyelectrolyte of smaller molecular weight would decrease polarization effects because of its higher diffusivity and lower solution viscosity. Polarization will cause the filtrate flux to be less than predicted above; or conversely, it will require increased pressure to obtain the desired flux. Its effect is therefore to decrease process efficiency.

VI. SUMMARY AND CONCLUSIONS

Many communities with a potentially abundant groundwater supply must develop other costly water supplies because the groundwater is too saline. The U. S. Public Health Service recommended limit for total dissolved solids is 500 mg/l; many groundwaters have a TDS concentration of 1000 to 2500 mg/l and are therefore unsuitable for water supply without some form of partial desalination. Desalination is also necessary if water reuse is practiced extensively; a single "use" (water treatment - domestic and industrial use - waste treatment) increases the TDS concentration by approximately 300 mg/l.

Since present treatment processes are not designed to remove dissolved salts and do not affect the TDS concentration significantly, new water treatment processes are necessary for large-scale economical desalination of water. The motivation for this research was the possibility of developing a desalination process on the Donnan membrane equilibrium. The process considered consists of two steps. In the first, water to be treated is mixed with a polyelectrolyte solution and dialyzed against more of the original water using a membrane permeable to water and simple salts but impermeable to the polyelectrolyte. Equilibrium is obtained when the activities of the permeable species (salt and water) are the same on both sides of the dialysis membrane. The addition of the polyelectrolyte causes an increase in the salt activity and thus causes a net transport of salt away from the solution containing the polyelectrolyte. If the polyelectrolyte can be removed from the salt-polyelectrolyte solution, a solution of reduced salt content will be obtained. In the second step, the polyelectrolyte is removed by ultrafiltration and recycled to the beginning of the process; the filtrate becomes the product water.

A. Ultrafiltration of Salt-Polyelectrolyte Solutions.

Quantitative description of the process is based upon thermodynamic principles. Previous experimental and theoretical studies of the activity of simple salts in salt-polyelectrolyte solutions make it possible to calculate the distribution of the salt in the dialysis. The literature is sparse, however, concerning the ultrafiltration of salt-polyelectrolyte solutions. Previous studies have dealt primarily with the salt concentration of the filtrate and have not considered filtrate flow-rate relations. Furthermore, the effect of the membrane on the filtrate salt concentration is accounted for in only an approximate way.

For the purpose of studying the ultrafiltration of salt-polyelectrolyte solutions, a continuous-flow filtration cell was developed which could be used to obtain steady-state conditions and which contained a stirring paddle to reduce concentration polarization at the membrane surface. The sodium chloride - sodium polyacrylate system was studied; the polyelectrolyte had a molecular weight between 80,000 and 110,000. The degree of neutralization was 0.8. The filtration cell also contained a sodium-sensitive glass electrode/silver-silver chloride electrode pair to measure the salt activity during filtration. The membrane used was a synthetic hydrated polymer membrane with an ionic cross-linked structure. The filtrate flow rate and salt concentration were measured as a function of the applied pressure and the stirring speed for various salt and polyelectrolyte concentrations. Polyelectrolyte concentrations of 0.146, 0.29, and 0.59 moles (of monomer)/liter were used. The salt-rejection and permeability characteristics of the membrane were determined using distilled water and NaCℓ solutions. Independent measurements of the NaCℓ activity in NaCℓ-NaPA solutions were also made.

The sodium chloride activity data were compared with the simple additivity rule or dissociation theory for the activity of simple salts in polyelectrolyte solutions and with theory based upon the cylindrical electrostatic model. Agreement with the electrostatic model was good; expressions based upon the simple dissociation theory underestimated the activity by approximately 20 per cent.

Concentration polarization effects during ultrafiltration were eliminated only in the case of the lower polyelectrolyte concentrations studied and at relatively low filtration rates using high stirring speed. For these cases, an expression derived from the linear laws of the thermodynamics of irreversible processes was found to relate the flow rate data to the permeability of the membrane obtained by independent measurement. The general expression

$$J_w = A(\Delta P - \Delta\pi_D - \sigma\cdot\Delta\pi_f) \qquad (20)$$

was derived. For the particular membrane used here, this expression reduced to

$$J_w = A(\Delta P - \Delta\pi_D) \ . \qquad (22)$$

J_w is the flow rate, A is the membrane permeability, and ΔP is the applied pressure difference. $\Delta\pi_D$ is the Donnan osmotic pressure difference of the salt-polyelectrolyte solution, and $\Delta\pi_f$ is the osmotic pressure difference (across the membrane) caused by the rejection of salt by the membrane. σ is the Stavermann reflection coefficient; it is related to the salt rejection of the membrane.

The equilibration that takes place at the membrane surface leads to a filtrate salt concentration which is different from that of the salt-polyelectrolyte solution being filtered. For high polyelectrolyte concentrations, the filtrate concentration is several times the salt concentration in the filtration cell. By using the equilibrium salt concentration (defined as the concentration of a pure salt solution having the same salt activity as the salt-polyelectrolyte solution) with the equation that describes the salt rejection of the membrane, the filtrate concentration was calculated. The results agreed very well with the measured concentrations for cases not involving concentration polarization.

Concentration polarization was manifested by a dependence of the filtrate flow rate and salt concentration on the stirring speed. At high speeds, results were independent of the stirring speed. As the stirring speed was decreased, a point was reached at which, with further reduction, the filtrate flow rate and salt concentration decreased. This behavior was interpreted in view of a simple boundary-layer model consisting of a layer of unmixed solution adjacent to the membrane surface. Calculations based upon this model were in qualitative agreement with the observations; quantitative agreement was only fair. In view of the simplicity of the model, this disagreement was not surprising.

B. Application to Desalination.

The results of the ultrafiltration experiments were used to evaluate the performance of the desalination process, considered above, for various operating conditions. The requirements of high polyelectrolyte concentration and high pressures limit the process to the desalination of waters of low TDS concentrations (less than 1000 mg/l). The process requires approximately one eighth the ultrafiltration membrane area that is required in the reverse osmosis process; in addition, though, it requires a dialysis membrane area approximately equal to the filtration membrane area required in reverse osmosis. Thus, economic savings due to the need for less ultrafiltration membrane (and equipment) are at least partially balanced by the need for the dialysis unit. Concentration polarization was not considered in the calculations, but it is obvious (in light of the ultrafiltration experiments) that the effects of polarization would be significant and would severely limit the use of the process in the water supply field.

NOTATION

Symbols used only in one section are not included in this list.

a	activity
A	membrane permeability (ml/min/psi for 36.7 cm^2 membrane area)
m	molal concentration (moles/kg H_2O)
m_e	equilibrium salt concentration
m_f	filtrate salt concentration
m_m	concentration of polyelectrolyte monomer units (monomolal concentration)
m_o	initial salt concentration
m_p	concentration of polyelectrolyte molecules
m_s	salt concentration
m_+	cation concentration
m_-	anion concentration
N	stirring speed (rpm)
P	pressure (psi)
Q_f	filtrate flow rate (ml/min)
RT	gas constant × absolute temperature
S	degree of polymerization (dimensionless)
S_+, S_-	dimensionless parameters in the electrostatic model of salt-polyelectrolyte solutions
$\bar{v}$	molar volume (ml)
α	degree of neutralization = m_{NaOH}/m_m
π	osmotic pressure (psi)
μ	chemical potential (cal/mole)
ν	number of dissociating counterions

ϕ_p	osmotic coefficient of polyelectrolyte
ϕ_s	osmotic coefficient of salt
γ	activity coefficient, $(\text{moles}/\text{kg } H_2O)^{-1}$

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