Trans-membrane pressure in nanofiltration

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Abstract

Most studies to date of Donnan exclusion in membrane separation of mixed solutions of permeating and completely retained salts with shared mobile counter-ions have focused on its effects on negative salt rejection. A theoretical examination is presented here of the effects of Donnan exclusion on flux in general and the threshold trans-membrane pressure for nonzero flux in particular. These effects are expressed through the osmotic pressure of the different solutions in equilibrium with the membrane, which is directly affected by the value of the activity coefficient of the polyelectrolyte counter-ion, \( \phi_p \). The osmotic pressure of polyelectrolyte solutions is determined by measuring the threshold trans-membrane pressure for non-zero flux, and from this the activity coefficient is evaluated. The activity of the permeating salt in a mixed solution can then be predicted and used to estimate the partition coefficient, \( \beta \), of the permeating salt between the mixed and pure salt solution separated by a semipermeable membrane. This value is found to be in reasonable agreement with partition coefficients determined directly in dialysis experiments. Finally, the depression of the threshold trans-membrane pressure for nonzero flux upon adding salt to a polyelectrolyte system is reasonably estimated from values of the permeating salt partition coefficient, \( \beta \), previously determined in dialysis experiments.

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1. Introduction

Negative salt rejection in nanofiltration of mixtures has been observed and analyzed in a number of systems [1–6]. However, the relation between volume flow, applied pressure and salt rejection has not been explicitly treated in these studies. In the following, the pressure–flux relationship for nanofiltration of solutions based on irreversible thermodynamics is briefly reviewed for one-solute and two-solute systems with no common ions. The influence of negative salt rejection in mixed solutions on the flow/pressure relation is then analyzed.

Concentration polarization may significantly influence salt rejection and the effective trans-membrane pressure. While it is not considered in the transport equations for membranes presented here, the feed concentration has to be corrected for polarization in any practical application. In this study most measurements are carried out at very low fluxes where concentration polarization effects are expected to be less pronounced, given that the tangential velocities in the flat test cells used were 0.62 m/s with Reynolds number ~2500. The relatively low concentration polarization is illustrated for sodium polyacrylate used as a polyelectrolyte in this study. The mass transfer coefficient for sodium polyacrylate with MW of 2100 was previously estimated to be around \( 3.5 \times 10^{-5} \) m/s [6]. At a flux of 10 L/m² h this gives a concentration polarization of 1.08 and it will be correspondingly less at the lower pressures.

2. Theory

2.1. Transport equations for RO and NF

In highly selective RO membranes, water flux and salt flux can be described separately. Water flux, which is practically equal to volume flux, is proportional to the difference of its chemical potential between the two sides of the membrane in a wide range of pressures and compositions:

\[
J_v = \frac{L_p}{V_w} \Delta \mu_w = L_p (\Delta P - \Delta \Pi) \tag{1}
\]

where \( \Delta P \) and \( \Delta \Pi \) refer to the differences between the external feed and permeate solutions adjacent to the membrane.
The small solute flux is proportional to its concentration gradient:

\[ J_s = P_s \Delta C \quad (2) \]

In less selective RO and in NF, both fluxes are important. Water and solute flows have to be treated simultaneously and the interaction between them has to be taken into consideration, following the formal framework of non-equilibrium thermodynamics.

For the large flows and forces characterizing the RO/NF process, differential transport equations are used [7]:

\[ J_s = -\bar{P}_s \frac{dc}{dx} + J_v (1 - \sigma), \quad \bar{P}_s = P_s \Delta x \quad (3) \]

\[ J_v = -L_p \left( \frac{dp}{dx} - \sigma \frac{d\pi}{dx} \right), \quad L_p = L_p \Delta x \quad (4) \]

where \( x \) is the coordinate perpendicular to the membrane surface within the membrane, \( \bar{P}_s \) the local solute permeability, \( L_p \) the local hydraulic permeability, \( \sigma \) the reflection coefficient and \( \Delta x \) is the membrane thickness. The concentration \( c \) is the corresponding concentration, defined as the concentration in a hypothetical thin layer of aqueous solution that would be at equilibrium with the membrane at point \( x \) [7]. It defines the composition dependent part of the thermodynamic potential. Following this corresponding concentration, \( \pi \) is the corresponding osmotic pressure. (Note that here and in the following, capital letters denote parameters in the feed and product solutions, small letters the corresponding parameters in the membrane.)

Assuming constant coefficients, integration of the differential equations over large concentration and pressure gradients can then be carried out. At the membrane surfaces, equilibrium of solute and water is maintained between the adjacent solutions and the membrane phase. With concentrations of feed and product solutions, the mutual coupling between the solute flux and volume flux namely,

\[ J_s = J_v \]

The gradient of the thermodynamic potential of the water, \( \mu_w \), is a function of the applied pressure and osmotic pressure:

\[ \frac{d\mu_w}{dx} = \bar{V}_w \left( \frac{dp}{dx} - \frac{d\pi}{dx} \right) \quad (5) \]

Neglecting the pressure dependent part of the thermodynamic potential of the solute, the gradient of the osmotic pressure is directly related to it by

\[ \frac{d\mu_s}{dx} = \frac{1}{c} \frac{d\pi}{dx} \quad (6) \]

Assuming an ideal solution, the gradient of osmotic pressure is written in terms of the concentration gradient as

\[ \frac{d\pi}{dc} = \nu RT \frac{dc}{dx} \quad (7) \]

where \( \nu \) is the number of ions per molecule of salt.

Introducing Eq. (6) and (7) into Eq. (4a), an alternative form of the flux equation is obtained:

\[ J_v = -L_p \left( \frac{1}{\bar{V}_w} \frac{d\mu_w}{dx} + (1 - \sigma) \frac{d\mu_s}{dx} \right) \]

\[ = -L_p \left( \frac{dp}{dx} - \frac{d\pi}{dx} \right) - L_p (1 - \sigma) \nu RT \frac{d\pi}{dx} \quad (4b) \]

According to Eq. (3) the solute flow is driven by the gradient of its concentration dependent thermodynamic potential and by the convective coupling to volume flow.

Similarly, the volume flow – which practically equals the water flow – is driven by the thermodynamic potential gradient of the water, and dragged along by the diffusing solute (Eq. (4b)).

As pointed out above, one of the basic assumptions of membrane transport is that equilibrium is maintained at the solution–membrane interfaces. Thus \( \mu_w \) is continuous and

\[ \Delta \mu_w = \bar{V}_w (\Delta P - \Delta \Pi) \quad (8) \]

where \( \Delta P \) and \( \Delta \Pi \) refer to the differences of applied and osmotic pressures between the external feed and permeate solutions adjacent to the membrane.

Integrating Eq. (4b) assuming constant \( L_p \), the volume flow across the membrane is then:

\[ J_v = L_p (\Delta P - \Delta \Pi) + L_p (1 - \sigma) \nu RT (\pi' - \pi'') \quad (9a) \]

Note that the first term on the right hand side of Eq. (9a) refers to external solutions whereas the second term refers to the corresponding osmotic pressures in the membrane at the solution–membrane interface. The relation between trans-membrane pressure and flux is determined by the boundary conditions that define the values of these corresponding osmotic pressures, \( \pi' \) and \( \pi'' \).

Writing Eq. (9a) in terms of corresponding concentrations we have:

\[ J_v = L_p (\Delta P - \Delta \Pi) + L_p (1 - \sigma) \nu RT (c' - c'') \quad (9b) \]

2.2. Trans-membrane pressure in nanofiltration of a single salt

In a solution of a single salt the corresponding osmotic pressures near the surfaces are equal to those of the solutions:

\[ \pi' - \pi'' = \Delta \Pi \quad (10) \]

Introducing Eq. (10) into Eq. (9a) the volume flow is obtained:

\[ J_v = L_p (\Delta P - \sigma \Delta \Pi) \quad (11) \]
Eq. (11) can be rewritten in terms of the applied pressure and by introducing the salt rejection:
\[
\Delta \Pi' = \Pi' R \quad \text{and} \quad \Delta P = \sigma R \Pi' + \frac{J_v}{L_p}
\]  

Examining Eq. (12) we see that the minimal pressure required for positive flow at a given feed concentration is lower than in highly selective RO for two reasons: the osmotic gradient is smaller \((R < 1)\) and the convective interaction between salt and water flows contributes to the volume flow \((\sigma < 1)\).

For very high volume flow, the salt rejection approaches \(\sigma\). For
\[
J_v \rightarrow \infty, \quad R \rightarrow \sigma, \quad \Delta P = \sigma^2 \Pi' + \frac{J_v}{L_p}
\]

In practice, this maximal rejection may not be reached because of mass transfer and osmotic pressure limitations.

2.3. Nanofiltration of salt in the presence of completely rejected neutral solute

The thermodynamic properties of a solution containing salt and an additional component depend on the interaction between the solutes in any specific system.

In the absence of specific interactions, the activity of the salt may be unchanged and the osmotic pressure of the mixture will be equal to the sum of each component’s separate contribution to the osmotic pressure:
\[
\Pi' = \Pi'_s + \Pi'_c
\]

For example, this was found to be the case for a solution containing salt and polyethylene glycol (PEG) as the uncharged solute [8].

If the membrane is impermeable to the neutral component, the corresponding salt concentration in the membrane at the feed boundary is equal to the salt concentration in the external feed solution \((c'_s = C_s)\). Thus, the corresponding osmotic pressures are given in terms of the external solutions by the following:
\[
\pi' = \Pi'_s \quad \text{and} \quad \pi'' = \Pi''
\]

Introducing the osmotic pressure (1) and these values of the corresponding osmotic pressures into the general Eq. (9a):
\[
J_v = L_p(\Delta P - \Pi_i - \Pi'_s + \Pi''') + L_p(1 - \sigma)(\Pi'_s - \Pi'')
\]

and the trans-membrane pressure is
\[
\Delta P = \Pi_i + \sigma \Delta \Pi_s + \frac{J_v}{L_p}
\]  

Expressing this trans-membrane pressure in terms of salt rejection we have
\[
\Delta P = \Pi_i + \sigma \Pi'_s R + \frac{J_v}{L_p}
\]

where the reflection coefficient is as measured for nanofiltration of the single salt. As seen in Eq. (17), the contributions of the salt and the completely rejected neutral solute to the required pressure at a given volume flow are additive. Note that at zero flow, \(\Delta P = \Delta \Pi_i\).

Including the effect of polarization, Eq. (17b) can be modified as follows:
\[
\Delta P = \Pi_{i,b} \exp \left( \frac{J_v}{k_{d,i}} \right) + \sigma \Pi'_{s,b} \exp \left( \frac{J_v}{k_{d,s}} \right) + \frac{J_v}{L_p} \]  

2.4. Mixture of one completely rejected polyelectrolyte and one uni-univalent salt, with common ion

For a system containing a small salt in solution with polyelectrolytes which cannot pass the membrane and possess common mobile counter-ions, salt rejection phenomena have been analyzed previously [6], while osmotic pressure in such systems was measured in dialysis experiments over forty years ago [8].

The strong electrostatic interaction between a large ion carrying multiple charges and its counter-ions causes significant deviations from ideality. In studies of sodium polyacrylate (NaPAA), osmotic pressure was determined by the equilibration of water between salt-free solutions of NaPAA and solutions of PEG of known osmotic pressure across a membrane that was impermeable to both polymers [8]. The results showed that for polyelectrolyte solutions of this type, the non-ideal interaction could be represented in terms of fractions of bound and free counter-ions, in which the latter behave ideally. Thus the osmotic pressure of salt-free solution of a polyelectrolyte with molar concentration \(C_i\) was given by
\[
\Pi_i = RT(C_i + \phi_p C_M). \quad \text{where} \quad C_M = vC_i
\]

And \(v\) is the number of charges carried by the pol-y-ion. For high molecular weight polyelectrolytes \(v \gg 1\) and the contribution of \(C_i\) to osmotic pressure can be neglected, but this would not be true for a large mobile ion carrying a few charges, such as, e.g., citrate. It was also found that the osmotic factor, \((\phi_p)\), was not a function of concentration and could be interpreted as the fraction of free counter-ions.

Further studies [8] were conducted measuring the osmotic pressure and activity of salt in a mixed solution containing NaPAA at concentration, \(C_i\) and NaCl at a concentration, \(C_s\) separated by a dialysis membrane from a second solution containing NaCl at concentration \(c\) and polyethylene glycol of known osmotic pressure. In such a system the distribution of salt across the dialysis membrane is given by the Donnan equilibrium expression shown in Eq. (19), assuming ideal solution behavior for the salt and the free counter-ions contributed by the polyelectrolyte [8]:
\[
(C_M \phi_p + C_s)C_s = c^2
\]

Hence the distribution coefficient for salt between the two sides of the membrane is given by
\[
\frac{c}{C_s} = \beta = \left( 1 + \frac{C_M \phi_p}{C_s} \right)^{1/2}
\]

It is important to note that unlike the salt and water, the polyelectrolyte is not in equilibrium across the dialysis membrane which is impermeable to it.
It was found [8] that the osmotic pressure of the mixed solution is additive so that for the solution on the feed side of the dialysis membrane the osmotic pressure was given by

$$\Pi_f = \Pi_i + \Pi_s$$

(21)

where \(\Pi_i\) is the osmotic pressure of a salt solution at concentration \(C_s\) and \(\Pi_s\) is as defined in Eq. (18). The fraction of counter-ions contributed by the polyelectrolyte which behave as free ions, \(\phi_p\), was found to be unchanged by the addition of salt.

The results from this older dialysis study help to understand what happens during nanofiltration of a polyelectrolyte–salt mixture. Salt and water in the feed solution equilibrate with the membrane surface adjacent to the feed solution. For the salt species this is analogous to the equilibrium reached in a dialysis experiment (see Fig. 1): the thermodynamic potential of salt in the membrane adjacent to the feed surface (Fig. 1a) is equal to its potential in the mixed feed solution just as it would be in a salt solution after equilibration in a dialysate compartment separated by a dialysis membrane from a mixed salt–polyelectrolyte solution of the same composition as the feed in the nanofiltration experiment (Fig. 1b).\(^1\)

Hence, the corresponding concentration in the NF membrane adjacent the feed solution is given by the same Donnan distribution factor defined for the case of dialysis in Eq. (20), where \(C_s\) will now be the concentration of salt in the NF feed solution (\(C'_s\)). The distribution coefficient \(\beta\) can be predicted from the concentration of polyelectrolyte counter-ions \(C_M\), if \(\phi_p\) is known, or \(\beta\) can be measured directly by dialysis [6].

Returning to the equations for membrane transport, the equilibration between feed solution and the membrane adjacent to the feed surface gives the following boundary condition on the membrane at the feed surface:

$$c' = \beta C'_s$$

(22)

and near the product surface:

$$c'' = C''_s$$

(23)

as above in the single salt case.

With these boundary conditions, integration of the local salt flux Eq. (3) gives the salt rejection, \(R\) [1,6]:

$$R = 1 - \frac{(1 - \sigma)\beta}{1 - \sigma F}, \quad F = \exp \left[ -\frac{J_v(1 - \sigma)}{P_s} \right]$$

(24)

At vanishing volume flow, \(F\) approximates 1 and the rejection tends to the Donnan equilibrium:

$$R = 1 - \beta \quad (J_v = 0)$$

(25)

In order to obtain the volume flow in nanofiltration of the mixed solutions, the corresponding concentrations for these solutions (\(c'\) and \(c''\)) and the osmotic pressure of the feed solution have to be introduced into the general equation for volume flow, (9b), \(J_v\) in a mixed solution is given by

$$J_v = L_p[\Delta P - (\Pi'_i + \Pi'_s - \Pi''_s)] + L_p(1 - \sigma)\nu RT(\beta C'_s - C''_s)$$

(26)

In terms of osmotic pressure:

$$J_v = L_p[\Delta P - (\Pi'_i + \Pi'_s - \Pi''_s)] + L_p(1 - \sigma)(\beta \Pi'_s - \Pi''_s)$$

(27)

The total pressure difference between feed and product as a function of flux is then given by

$$\Delta P = \Pi'_i + \Pi'_s(1 - \beta) + \sigma(\beta \Pi'_s - \Pi''_s) + \frac{J_v}{L_p}$$

(28)

---

\(^1\) The dialysis experiments reported here were carried out between mixed solutions of polyelectrolyte and salt on one side and salt solution on the other side without adding PEG. As shown in Ref. [8] this does not influence the salt distribution between the two sides. Therefore, the distribution coefficient obtained in our experiments is appropriate for the analysis of the NF situation.
At vanishing volume flow, following Eq. (25), \( \beta \Pi'_s = \Pi''_s \). Thus the minimal pressure required to produce volume flow, \( \Delta P_0 \), is lower in the presence of salt and the reduction of this minimum pressure upon addition of salt is

\[
\Pi_i - \Delta P_0 = \Pi'_s(\beta - 1)
\]  
(29)

The relative reduction is given by

\[
\frac{\Pi_i - \Delta P_0}{\Pi_i} = \frac{\Pi'_s(\beta - 1)}{\Pi_i}
\]  
(30)

If the reflection coefficient is zero, pressure as well as salt rejection are defined by the Donnan equilibrium also at non-zero volume flow, as shown by Eqs. (28) and (24). For \( \beta = 1 \), Eq. (28) reduces to Eq. (17a) for neutral rejected solutes.

3. Experimental

3.1. Determination of distribution coefficient by dialysis

The dialysis experiments were conducted with 11 mm wide regenerated cellulose dialysis sacks (SpectraPor 7, Spectrum Scientific). A 10 ml samples of sodium polyacrylate (NaPAA) (Sigma–Aldrich, 2000 MW polyacrylic acid titrated with sodium hydroxide to neutral pH) were placed in a series of separate dialysis sacks each containing a different concentration of sodium chloride and with final concentrations of sodium polyacrylate of 0.414 M. The NaCl concentrations were varied to be at values estimated to be above and below the concentration that would equilibrate with the large well-stirred reservoir in which the dialysis bags were placed. In series A, the reservoir contained 0.207 M NaCl and in series B the reservoir contained 0.452 M. At times of 0, 15, and 30 min after insertion of the dialysis bags into the large reservoirs, the bags contents were sampled and the chloride content was determined by argentometric titration.

A preliminary osmosis experiment was conducted with dialysis sacks containing sodium polyacrylate solution suspended in a reservoir of water or pure sodium chloride solution so that the osmotic pressure difference between the sodium polyacrylate solution in the dialysis sack and solution in the reservoir is as large as any value expected from the series of dialysis experiments conducted in this work. The osmotic flow to or from the dialysis sacks was estimated based on the change in the TOC inside the dialysis sacks. It was found that this flow would have a negligible effect on the results of the dialysis experiment.

An experimental flow loop was used to determine the pressure at which the flux through the membrane would be zero for a variety of solutions, including sodium polyacrylate and mixtures of sodium chloride with sodium polyacrylate. This flow loop is depicted schematically in Fig. 2. The feed solution is maintained in a pressurized feed tank by a nitrogen gas cylinder equipped with a regulator to control the pressure in the feed loop. The solution is recycled with a gear pump (Ismatec, model 122P) through a flat membrane module at a flow rate of 1.5 L/min. The Plexiglas test cell had a flow channel of 2 mm height and 2 cm width (flow rate of 0.625 m/s and \( Re \sim 2500 \)) and was loaded with a nanofiltration membrane (NF-200 from Dow-Deutschland, Rheinmunster) with an effective membrane area of 16 cm². The temperature was kept constant by a heat exchanger within a cooled water bath and the temperature was determined by thermocouple. The permeate flow rate was determined by collecting samples at 10 min intervals in tared test tubes and weighing the samples. The system was operated for 10–20 min after each pressure change before samples were taken. In those cases where sample size was adequate, the amount of chloride in the permeate was determined by argentometric titrations.

4. Results

4.1. Osmotic pressure of sodium polyacrylate (NaPAA) solution

In the polymer we used, not all acrylic monomers carry carboxylic groups. Table 1 gives the concentration of the polymer

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temp (°C)</th>
<th>Concentration of NaPAA (g/l)</th>
<th>[P] (monomol/l)</th>
<th>[Na⁺] (M)</th>
<th>( \alpha ) (%)</th>
<th>Osmotic pressure bar</th>
<th>Osmolarity of solution (M)</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>48.0</td>
<td>0.515</td>
<td>0.411</td>
<td>79.9</td>
<td>4.89</td>
<td>0.198</td>
<td>0.43</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>47.3</td>
<td>0.509</td>
<td>0.396</td>
<td>77.9</td>
<td>4.68</td>
<td>0.189</td>
<td>0.43</td>
</tr>
</tbody>
</table>
in monomol/l, [P], the concentration of sodium counter-ion, \( C_M \), and hence the fraction \( \alpha \) of ionizable groups.

The osmotic pressure of NaPAA solution was determined in pressure/flux measurements with an NF-200 membrane (triangle symbols in Figs. 5 and 6). The pressure at zero flux is equal to the osmotic pressure, since this membrane is impermeable to the polymer.

It is seen in Table 1 that the osmolarity obtained, is smaller than the concentration of the sodium ions, as expected for poly-electrolyte solutions. The osmotic factor, \( \phi_p \), is given in the last column of the table.

4.2. The distribution coefficient, \( \beta \)

For characterization of the salt distribution which determines the transport behaviour, we set up dialysis measurements to represent the equilibria at the feed-solution–membrane interface. The mixed solutions in the dialysis sack represent the nanofiltration feed solution, and the dialysate bath solution concentration, \( c_d \), will give the corresponding concentration in the membrane at the feed boundary, \( c' \) (see Fig. 1).

Fig. 3 shows the dependence of dialysis sack salt concentration (\( C_s,f \)) on time. A polynomial fitting of concentration with time allows the differentiation and evaluation of the derivative at time \( t = 0 \). Fig. 4 shows the results for two different dialysate concentrations, \( c' \). By plotting the rate of chloride concentration change in the dialysis sacks at zero time against the chloride concentration in the sack, the intersection with the \( x \)-axis provides the equilibrium chloride concentration in the sack, which is analogous to \( C'_s \). From this we can then calculate the Donnan distribution coefficient:

\[
\beta = \frac{c'}{C'_s} \left( \frac{dC_{s,f}}{dr} \right)_{t=0} = 0
\]

(31)

The coefficients obtained are shown in Table 2.

Using the values of \( \phi_p \) calculated (see Eq. (18)) from the measured osmotic pressure of the polyelectrolyte solutions as shown in Table 1, the expected distribution coefficients can be calculated from Eq. (20) for polyelectrolyte/salt solutions of a given composition. These calculated distribution coefficients are given in the last column of Table 2. As can be seen, the values are in reasonable agreement between the osmotic pressure and the dialysis measurements.
4.3. Zero flux pressures for sodium chloride/sodium polyacrylate mixtures

Nanofiltration of mixed solutions is shown in Figs. 5 and 6 carried out with two samples of NF-200 membranes. Extrapolation of flux versus pressure gives the minimal pressure for positive flux, \( \Delta P_0 \). It can be seen that the addition of sodium chloride to a sodium polyacrylate solution lowers the threshold pressure of zero flux as is expected from the theoretical treatment. Table 3 compares the actual threshold pressure to that calculated from Eq. (29) with \( \beta \) values determined by osmotic pressure (Section 4.1). The osmotic pressure-based \( \beta \) was used, since compositions in the flux experiment were not identical, though close, to those in the dialysis experiment. The threshold pressure observed by addition of salt is given in column 3, and the threshold pressure expected from Eq. (30) is in the last column. The effect is clearly demonstrated, though agreement is not quantitative. The largest source of uncertainty is the extrapolation to zero flux.

5. Conclusion

The operating range of nanofiltration membranes is usually limited to relatively low pressures. Nevertheless, it is possible to achieve partial separations in rather concentrated solutions of charged solutes with high osmotic pressures. This is due to the negative rejection of salt in the presence of polyelectrolyte and the consequent reduction of the minimal pressure required for positive flux. The reduction can be predicted from the osmotic pressure of the rejected solute and salt distribution in Donnan equilibria.

Table 3
Trans-membrane pressure for non-zero flux

<table>
<thead>
<tr>
<th>( C_s' )</th>
<th>( C_M )</th>
<th>( \Delta P_{0,exp} ) (bar)</th>
<th>( \Delta P_{0,calc} ) (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>0.411</td>
<td>1.82</td>
<td>1.56</td>
</tr>
<tr>
<td>0.375</td>
<td>0.396</td>
<td>0.68</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Acknowledgements

We thank Rosa Fainstain and Marina Milman for their extensive help in carrying out the experiments.

Nomenclature

- \( a_+ \) activity of the counter-ion (Fig. 1)
- \( a_- \) activity of the co-ion (Fig. 1)
- \( c \) corresponding concentration, i.e. concentration in a solution that would be at equilibrium with the solute in the membrane at point \( x \) (mol/l)
- \( c_d \) equilibrated salt concentration on dialysate side in dialysis experiment (mol/l)
- \( c' \) corresponding concentration of solute in membrane adjacent to feed solution (mol/l)
- \( c'' \) corresponding concentration of solute in membrane adjacent to permeate solution (mol/l)
- \( C_b \) bulk concentration of solute (mol/l)
- \( C_M \) feed concentration of polyelectrolyte as charged monomer units (equiv./l)
- \( C_s' \) feed concentration of solute (mol/l)
- \( C_{s''} \) permeate concentration of solute (mol/l)
- \( J_s \) salt flux through the membrane (mol/m² h)
- \( J_v \) volumetric flux through membrane (m³/s or l/m² h)
- \( k_D \) mass transfer coefficient (m/s)
- \( L \) length of membrane flow channel (m)
- \( L_p \) membrane-averaged permeability coefficient for the solvent flux (l/m² h bar or m³/s Pa)
- \( \bar{L}_p \) local hydraulic permeability ((l/m² h)/(bar/m)) or (m³/s)/(Pa/m)
- \( p \) pressure of a corresponding solution in equilibrium with a point \( x \) in the membrane (Pa or bar)
- \( P \) pressure in external solution adjacent to membrane (Pa or bar)
- \( \Delta P_0 \) threshold trans-membrane pressure at which flux drops to zero (Pa or bar)
- \( [P] \) polyelectrolyte monomolar concentration in feed (mol monomer/l)
- \( P_s \) overall diffusive salt permeability of membrane (m/s)
- \( \bar{P}_s \) local diffusive salt permeability (m²/s)
- \( V_w \) molar volume of water (l/mol)
- \( x \) membrane coordinate, distance from membrane/feed solution interface (m)

Greek letters

- \( \Delta \) Difference between feed-side and permeate-side values of a physical quality
- \( \beta \) Donnan distribution coefficient, defined in Eq. (20). Ratio of salt concentrations between pure salt solution in equilibrium with solution of mixed salt and rejected polyelectrolyte with a common counter-ion
- \( \mu_W \) chemical potential of water in a particular solution
- \( v \) moles of ions per moles of salt
\( \pi \) osmotic pressure of a corresponding solution that would be in equilibrium with a point \( x \) in the membrane (Pa)

\( \Pi \) osmotic pressure of an external solution adjacent to a membrane

\( \sigma \) reflection coefficient for the partially permeable salt

\( \phi_p \) fraction of polyelectrolyte counter-ion behaving as unbound counter-ions

**Subscripts**

- \( b \): bulk solution
- \( d \): solution on dialysate side of membrane (dialysis)
- \( f \): solution on feed side of membrane (dialysis)
- \( i \): rejected solute
- \( M \): monomer
- \( s \): salt
- \( w \): water

**References**


