generated by the chemical milling of aluminium aircraft parts. Chemical milling is used to remove metal from aluminium parts, such as curved sections of wing or fuselage that are difficult to machine with mechanical devices. The part is dip-coated with a film of rubber, and then a selected portion of the rubber is stripped away to expose the metal surface. Then the part is immersed in boiling NaOH that rapidly and uniformly dissolves the metal from the exposed surface. The dissolved aluminium accumulates in the etch tank as NaAlO₂, which must be discarded eventually. When the NaOH is removed from the solution by dialysis, the NaAlO₂ hydrolyses to Al(OH)₃ and NaOH. The Al(OH)₃ is recovered by filtration and sold as a pure product, and the released NaOH is returned to the etch tank along with the dialysed NaOH. Dialysis allows recovery of essentially all of the NaOH and completely eliminates the need for disposal of the waste etchant. An industrial installation of base dialysis has been operating successfully in a chemical milling plant in California since 1991.

See Colour Plate 48.

Further Reading

Donnan Dialysis

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Introduction

Donnan dialysis is a separation process that utilizes counterdiffusion of two or more ions through an ion-exchange membrane to achieve a separation. It can also be viewed as a continuous deionization process. For example, water softening can be done with a cation-exchange membrane. Hard water flows on one side of the membrane, and NaCl brine flows on the other side. Na⁺ ions from the brine diffuse across the membrane and cause the Ca²⁺ and Mg²⁺ ions to diffuse in the opposite direction. Donnan dialysis is usually performed as a continuous, countercurrent process so that a substantial portion of a cation from a dilute solution could be concentrated into a small volume. Differences in the volumes and concentrations of the two solutions can be exploited to achieve some interesting and useful separations.

Donnan dialysis can be used for changing compositions of process or analytical solutions, pollution control, and even deionization of a process stream. The deionization process, called ‘neutralization dialysis’, combines Donnan dialysis through both cation-exchange and anion-exchange membranes in one apparatus with H⁺ and OH⁻ ions exchanging for the cation and anion of a salt.

In the discussions that follow, the fundamental principles of Donnan dialysis will be presented, and some of its applications and capabilities will be described. The type of equipment and membrane arrangements appropriate for both Donnan dialysis and neutralization dialysis will be presented.

Background

The Donnan dialysis process is named after F. G. Donnan who in 1924 described the equilibrium that resulted when a semipermeable membrane separated two solutions of electrolytes. NaA on one side and KA on the other. The membrane he used was prepared by filling the pores of parchment paper with a gel of copper ferrocyanide, and he used ferrocyanide as the common anion A of the two salts. When the initial volumes and concentrations of the two salt solutions were the same, counterdiffusion of equal amounts of Na⁺ and K⁺ through the membrane led to an equilibrium condition where the two solutions had equal concentrations of NaA and KA. But when
initial concentrations were different, counterdiffusion of equal amounts of Na\(^+\) and K\(^+\) through the membrane produced solutions with equal ratios of Na\(^+\)/K\(^+\) on both sides of the membrane at equilibrium. This relationship of concentrations of the ions in the solutions on opposite sides of the membrane is called the ‘Donnan equilibrium’.

Before proceeding with the theory, it is useful to define some terms that are often used in discussions of modern polymeric ion-exchange membranes. First, an ‘ion-exchange membrane’ is a plastic film with fixed ioniically charged groups dispersed more or less uniformly within the film. Associated with the fixed charges are mobile charges of opposite sign called ‘counterions’. The counterions are free to exchange with other counterions in the adjacent solutions. When the membrane has fixed negative charges, e.g., sulfonic acid groups, it is called a ‘cation-exchange membrane’, and the counterions are cations. In the external solutions, mobile anions are associated with the cations, but in the membrane the charge balance is satisfied by the fixed negative charges. Therefore, anions tend to be excluded from the interior of the cation-exchange membrane. The ions with the same charge as the fixed charge in the membrane are called ‘co-ions’.

**Theory**

The Donnan equilibrium relationship is derived from thermodynamics. Under conditions of equilibrium the chemical potential \(\mu_i\) of any dissolved species \(i\) is the same in every phase present:

\[
\mu_i = \mu_0^i + RT \ln a_i
\]  

[1]

Here, \(\mu_0^i\) is the chemical potential of species \(i\) in the standard state, \(R\) is the gas law constant, \(T\) is the absolute temperature, and \(a_i\) is the activity of the particular chemical species \(i\) being considered. However, electrical potentials must also be considered when the chemical species are ionic, so the electrochemical potential \(\eta_i\) must be used to describe the equilibrium:

\[
\eta_i = \mu_0^i + RT \ln a_i + z_i F \theta
\]  

[2]

where \(z_i\) is the ionic charge, \(F\) is Faraday’s constant, and \(\theta\) is the electrical potential. When the two liquids, phase 1 and phase 2, are at equilibrium with the membrane, there is also equilibrium between the two liquid phases, and the electrochemical potential of any mobile species \(i\) in the two phases can be equated:

\[
\eta_{i1} = \eta_{i2}, \text{ or } RT \ln a_{i1} + z_i F \theta_1 = RT \ln a_{i2} + z_i F \theta_2
\]  

[3]

It should be noted that the \(\mu_0^i\) terms cancel because the same standard state exists in both liquid phases. But the co-ions are not free to move through the membrane that separates the two liquid phases, so there is no opportunity for their concentrations to change. Whenever salt concentrations on opposite sides of the membrane differ, there will be a potential difference across the membrane caused by the concentration difference. This potential difference, called the ‘Donnan potential’, \(E_{Don}\), is described by rearrangement of eqn [3]:

\[
E_{Don} = \theta_2 - \theta_1 = RT/z_i F (\ln a_{i1} - \ln a_{i2}) = RT/F \ln(a_{i1}/a_{i2})^{1/z_i} \]  

[4]

Since the Donnan potential acts on all mobile ionic species, the value of \((a_{i1}/a_{i2})^{1/z_i}\) is the same for all of the counterions in the system. In other words, the concentration difference of the co-ions causes an electrical potential that acts on the counterions.

As Donnan pointed out in his seminal description of the theory, a precise treatment of the equilibria would require the use of activities rather than concentrations of ions in the solutions. But the use of molar concentrations greatly simplifies the presentation of the theory, so that is the approach taken here. For the experiment described by Donnan where \(z_i = +1\) for both Na\(^+\) and K\(^+\) ions, the equilibrium written with concentrations would be:

\[
[Na^+]/[Na^+]_2 = [K^+]/[K^+]_2 \text{ or } [Na^+]/[K^+]_1 \quad [5]
\]

**Figure 1** illustrates the flow of ions in the approach to Donnan equilibrium. Two dilute salt solutions NaCl and KCl are separated a cation-exchange membrane, labelled C, which is permeable to the cations Na\(^+\) and K\(^+\) but impermeable to the common anion Cl\(^-\). The concentration difference of Na\(^+\) ions across the membrane provides a driving force for their diffusion through the membrane. There is no net flow of electric current through the membrane, so any net transfer of Na\(^+\) to the right must be balanced by transfer of an equivalent amount of K\(^+\) to the left. Those diffusive processes will occur until an equilibrium is established.

The equilibrium concentrations can be expressed in terms of the initial molar concentrations \(c_1\) of NaCl on the left and \(c_2\) of KCl on the right, \(x\) moles transported through the membrane (still the same for both cations) and the volumes \(V_1\) and \(V_2\) of the
Donnan potential forces $K^+$ ions to higher concentration.

Solutions, expressed in litres:

\[
\frac{(c_1 - x/V_1)}{(x/V_1)}/\frac{(x/V_2)}{(c_2 - x/V_2)} = \left(\frac{x}{V_2}\right)/\left(\frac{c_2}{V_2}\right) \tag{6}
\]

Solving this equation for $x$ yields:

\[
x = \frac{c_1 c_2}{(c_1/V_2 + c_2/V_1)} \tag{7}
\]

Donnan dialysis is particularly effective for recovery or removal of multivalent ions. The Donnan equilibrium for a divalent $Ca^{2+}$ ion and a univalent $K^+$ is described by the equation:

\[
\left(\frac{[Ca^{2+}]_1}{[Ca^{2+}]_2}\right)^{1/2} = \frac{[K^+]_1}{[K^+]_2} \tag{8}
\]

For maintenance of electroneutrality in the system, the transport of $x$ moles of $Ca^{2+}$ ions through the membrane requires the transport of $2x$ moles of $K^+$ ions in the opposite direction. Thus the equilibrium is described by:

\[
\left(\frac{(c_1 - x/V_1)}{(x/V_1)}\right)/(c_2 - 2x/V_2) \tag{9}
\]

For $V_1 = 10$, $V_2 = 1$ and initial concentrations of $c_1 = 0.01$ and $c_2 = 1$, the value of $x = 0.095$ is calculated by eqn [9], which means that more than 95% of the calcium would be driven through the membrane. The effect of valence is even more dramatic when the $c_1/c_2$ ratio is much lower than the value used in this example.

**Comparison of Donnan Dialysis with Conventional Ion Exchange**

In many respects Donnan dialysis can be viewed as a continuous ion-exchange process. For instance, both processes can be used for the softening of water. In conventional ion-exchange softening, the ion-exchange resin beads are initially in the $Na^+$ form. When hard water flows through a column of the $Na^+$ form resin beads, $Ca^{2+}$ ions in the water exchange with $Na^+$ ions on the resin. When the supply of $Na^+$ ions on the resin approaches exhaustion, the flow of hard water is stopped, the resins are regenerated by passing NaCl brine through the column, and then the cycle is repeated. In contrast, water softening with Donnan dialysis is a continuous process. The $Na^+$ ions for regeneration are always available in the solution on one side of the membrane, and the $Ca^{2+}$ ions are continuously removed from the feed stream. Both processes are effective for water softening. Donnan dialysis works best in a situation where a continuous flow is expected. Softening with a bed of resin beads can easily accommodate variable flow rates or even on/off operation. Since water softening is most often done in situations where flow rates fluctuate widely, the use of resin beads rather than membranes is the accepted practice.

If a particular exchange of ions can be accomplished by the cyclic process with ion-exchange resin beads or the continuous process with ion-exchange membranes, what factors might influence the selection of the membrane process over the conventional process? Because the membrane process is continuous, it operates at steady-state conditions everywhere in the dialyser. In cases where acid or base is used to drive the process, conditions of pH extremes can be avoided more easily with Donnan dialysis than with conventional ion exchange. Compared to membranes, ion-exchange beads offers a large surface area in a small volume, so the rates of mass transfer are faster with beads. But that large surface area can be a problem if components of the solution are subject to denaturation at surfaces where pH extremes exist. Donnan dialysis can be a much gentler process.

A major limitation to Donnan dialysis is that, like ion exchange, there is a need to add chemicals to recover or remove chemicals. Essentially the stripper solution in Donnan dialysis serves the same function as the regenerant solution in ion exchange. Donnan dialysis has the added limitation that osmotic water transport makes the recovered electrolyte more dilute.
than it would be in the spent regenerant of an ion-exchange process. However, Donnan dialysis has the advantages that it is continuous and does not require the rinse step after regeneration. If the application is one in which the stripper solution is already available and needs to have the transported ion in it, then the Donnan dialysis can be an advantageous process.

**Neutralization Dialysis**

Anion- and cation-exchange membranes can be combined into a single dialyser where both acid and base drive the transport of the cation and anion of a salt as illustrated in Figure 2. Since the hydrogen and hydroxyl ions that drive the transport are neutralized in the feed solution, the driving force for desalting can be maintained until almost all of the acid and base are consumed. Neutralization dialysis has been used effectively for desalination of aqueous solutions of organic compounds. Research has demonstrated that the flux of salt ions increases with acid and base concentration up to about 0.1 M. Above those levels there was little benefit in raising the acid and base concentrations.

It should be noted from Figure 2 that the membrane arrangement in neutralization dialysis is different from that in electrodialysis. Here there are four membranes in a repeating sequence, two anion-exchange membranes and then two cation-exchange membranes. It is a fortunate circumstance in neutralization dialysis that the acid only contacts cation-exchange membranes, because anion-exchange membranes are notoriously leaky to acids. Likewise, the two anion-exchange membranes that bound the base compartments resist leakage of base.

Neutralization dialysis competes with deionization with mixed bed ion-exchange resins which has lower capital cost. But neutralization dialysis has the advantage of being a continuous process that can be controlled by the flow rates and concentrations of the acid and base. Moreover, the feed solution is not exposed to such severe pH extremes as it would be in deionization with ion-exchange resins.

**Membranes for Donnan Dialysis**

Many ion-exchange membranes are manufactured for electrodialysis, and most of them would be potentially useful for Donnan dialysis. In addition, the Nafton® fluoropolymer cation-exchange membranes made by DuPont are uniquely suited to Donnan dialysis because of their ability to withstand severe thermal and chemical attack. Fluoropolymer membranes have been used to recover chromic acid, a strong oxidizing agent that attacks hydrocarbon-based membranes. Nafton® has been made as small tubules and fabricated into shell-and-tube dialysers.

The preparation of hollow fibres for use in analytical devices was reported in 1981. Low-density polyethylene was extruded into 300 µM i.d., 380 µM o.d. hollow fibres that were sulfonated with 10% chlorosulfonic acid in methylene chloride. A bundle of eight hollow fibres was inserted into a coiled tube and sealed with silicone rubber caulk.

Although many types of ion-exchange membranes have been used for Donnan dialysis, there seem to be no published studies comparing the performance of commercial membranes for Donnan dialysis or establishing criteria for desirable membranes. One would expect diffusional transport properties of the membranes to parallel those of electrodialysis. In Donnan dialysis, membranes with low electrical resistance would be expected to have low resistance to ion diffusion, and those with low electroosmotic water transport would be expected to have low osmotic water transport. Of course the membranes should be stable at the anticipated operating temperatures of the process and resist chemical attack by solution components. Experimental studies have established that, under typical hydrodynamic conditions, the major resistance to transport is in the boundary layer of the dilute solution rather than in the membrane; therefore, even some of the thicker commercial ion-exchange membranes could be candidates for use in Donnan dialysis.
Japanese researchers have made cation exchange membranes, specifically selective to the transport of uranyl ions, by forming a copolymer of 2,3-epithiopropyl methacrylate and 2-acrylamide-2-methylpropanesulfonic acid. They observed that the proportions of the monomers had a great effect on the ability of the membranes to transport uranyl ions. High transport was achieved when the 2-acrylamide-2-methylpropanesulfonic acid content was at least 34%, but very low transport occurred when that monomer comprised less than 21% of the membrane. By contrast, they found that the Selemion DLE membrane did not transport the uranyl ions under the same experimental conditions. The same researchers also made anion-exchange membranes of 2,3-epithiopropyl methacrylate–dodecyl methacrylate–methylacrylamide propyltrimethylammonium chloride terpolymer that selectively transported ferric oxalate complex anions from acidic ferric sulfate solution to a receiving solution containing sodium oxide. These studies suggest that the development of ion-specific membranes could lead to selective separations by Donnan dialysis that cannot be economically achieved by other methods.

The amount of membrane area required for a particular Donnan dialysis application depends on the mass transfer rates that can be achieved. However, the user should be cautious about relying upon mass transfer data obtained in stirred cells to design industrial systems, because the high shear rates obtained by stirring might not be achieved in a commercial dialyser. Results reported for Donnan dialysis of uranyl ions in a countercurrent dialyzer should offer realistic mass transfer coefficients for design purposes. AM-Fion C-103 cation-exchange membranes separated solutions of 0.01 M UO₂(NO₃)₂ and 2 M HNO₃. The solution compartments between the membranes were formed with 0.38-mm-thick woven screens of stainless steel. Uranyl ion fluxes were about 9 × 10⁻¹⁰ mol cm⁻² s⁻¹. The treatment rate was about 3 L h⁻¹ m⁻², and 96% of the UO₂(NO₃)₂ was recovered.

**Apparatus**

The equipment used for Donnan dialysis is similar to that used for dialysis and diffusion dialysis. Membrane shapes include sheets, tubes, and hollow fibres. Sheet membranes have been fabricated into spiral-wound devices, but the dominant configuration for flat membranes is the plate-and-frame arrangement used in electrodialysis. Thus any supplier of electrodialysis equipment is a potential supplier of stacks for Donnan dialysis. Since the major resistance to transport usually lies in the boundary layer of the dilute solution, equipment designers strive to achieve high shear in the feed solution. There is a major advantage to countercurrent flow of the feed and stripper solutions, because that configuration leads to maximum driving forces and maximum total transfer of the desired ions.

In a commercial dialyser, the simultaneous achievement of both high shear and countercurrent flow is difficult. High shear can be achieved by rapid stirring or by high flow rates, but the benefits of countercurrent flow can only be achieved if the residence time in the device is sufficient for a large fraction of the desired ion to be transferred through the membrane. As discussed below, studies of the effects of solution velocity on mass transfer rates show correlation with Vⁿ where the exponent n is always less than unity. This means that increasing the solution velocity through a dialyser of a given length always results in a smaller fraction of the solute being transferred through the membrane. Therefore, an increase in solution velocity requires an increase in path length to achieve the same fraction of transfer. (This Vⁿ relationship also applies to dialysis, diffusion dialysis, and electrodialysis.)

**Process Design and Control**

Most often the objective of Donnan dialysis is to both recover a target ionic species from a feed solution and raise its concentration. An increase in the concentration is achieved by the use of a small volume of a stripper solution with a diffusing ionic species that is higher in concentration than that of the target ionic species in the feed. A strip solution of about 1 M might be used with a typical 0.001 M feed solution. One might expect that a more concentrated strip solution would recover the target ionic species at a higher concentration, but stripper concentrations higher than 1 M do not seem to be beneficial. More concentrated strip solutions lead to osmotic dehydration of the gel structure of the membrane which reduces membrane permeability. Moreover, co-ion transport due to reduced Donnan exclusion at the higher concentrations allows loss of solutes from the receiving solution across the membrane, and osmotic transport of water through the membrane dilutes the strip solution.

The effects of hydrodynamics on mass transfer rates in Donnan dialysis have been studied by several researchers who correlated the data using the standard equation Sh = kScⁿReⁿ. The Sherwood number Sh = KD/h, Schmidt number Sc = μ/ρD, and Reynolds number Re = ρhV/μ are dimensionless parameters where K is the mass transfer coefficient, D is the diffusivity of the diffusing ionic species, h is
Table 1 Dimensionless parameters for correlation of mass transfer rates in Donnan dialysis through Nafion®

<table>
<thead>
<tr>
<th>Cation</th>
<th>Strip acid</th>
<th>k</th>
<th>m</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td>H₂SO₄</td>
<td>0.48</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>H₂SO₄</td>
<td>0.166</td>
<td>0.33</td>
<td>0.475</td>
</tr>
<tr>
<td>Na⁺, K⁺</td>
<td>HNO₃</td>
<td>0.201</td>
<td>0.4</td>
<td>0.62</td>
</tr>
</tbody>
</table>

the characteristic thickness or diameter of the conduit, μ is the solution viscosity, ρ is specific gravity, and V is solution velocity. The coefficient k, and the exponents m and n are used to correlate the data. The results of three studies are shown in Table 1, and some comments about the experiments follow.

Studies with CuSO₄ and NiSO₄ were done with the feed flowing inside a fluoropolymer membrane tube a few millimetres in diameter and with H₂SO₄ stripper flowing outside the tube. The correlation parameters apply to Re < 1000. The following observations were made in the studies with CuSO₄ and NiSO₄. Increasing the stripper concentration from 1 to 5 M did not improve mass transfer. Increasing the solution velocity of the stripper solution produced minor increases in mass transfer. The mass transfer rate was proportional to the metal ion concentration in the feed for concentrations below 2000 mg L⁻¹ and Re < 1000. Studies of NaNO₃ and KNO₃ feeds with HNO₃ stripping were done with a flat sheet fluoropolymer membrane in a stirred cell with 15° Re > 400.

Since the flow rates in Donnan dialysis are normally rather low, one must be concerned with convective flow in the dialyser caused by density changes in the solutions as their compositions change. The use of excessively high acid concentrations in the stripper exacerbates the problem of changing densities. Osmotic transport of water into the acid stripper solution at the top of the solution compartment can cause substantial dilution of the acid, and the resulting density decrease allows the denser incoming stripper to stream downward through the diluted acid. The problem can be alleviated by mild pulsation of the solution at the top of the stripper side to improve mixing.

Applications

Although many industrial applications have been demonstrated in the laboratory and at the pilot scale, there appear to have been few industrial-scale applications of Donnan dialysis. Industrial applications have been mainly in recovering heavy metals from rinse waters of metal-finishing operations. One of the few descriptions of an industrial installation reports results of an experimental evaluation of a DuPont-made Nafion® hollow-fibre dialyser for metal recovery from rinse water in a Watts nickel electroplating process with 1 M H₂SO₄ as the stripper. With typical feed concentrations of up to 1 g L⁻¹, Ni²⁺ fluxes exceeded 20 g h⁻¹ m⁻² and the recovered Ni concentration exceeded 30 g L⁻¹.

An early application of Donnan dialysis with polymeric ion-exchange membranes was described in 1967. Multiple AMFion C-103C cation-exchange membranes were assembled in a plate-and-frame dialyser with solution compartments arranged so that the feed and strip streams could flow in a pattern that was countercurrent overall. This apparatus was used to recover UO₂(NO₃)₂ from a 0.01 M feed to a final concentration of 0.28 M with 2 M HNO₃ as the stripper and to 0.46 M with 2 M H₂SO₄ as the stripper. He also used a Donnan dialyser with AMFion A-104B anion-exchange membranes to remove acid from the UO₂(NO₃)₂ feed to improve the driving force for cation transport. Complexing agents, EDTA and DPTA, were used as strippers to separate Ag⁺ and Cu²⁺ ions. The Cu²⁺ ions formed such strong complexes that the free Cu²⁺ ion concentration in the stripper was low enough to maintain a driving force until virtually all of the Cu²⁺ ions were transported across the membrane.

The use of Donnan dialysis for water softening was reported in 1970. The process is illustrated in Figure 3. A brine of NaCl and hard feed water flow countercurrent. The diffusion of Na⁺ ions from the

![Figure 3](image-url)
brine causes a driving force for transport of Mg2+ ions from the feed into the brine. Countercurrent operation allows the large driving force to be maintained over the length of the membrane.

A hollow-fibre device has been used as a suppressor for ion chromatography. Compared to an ion-exchange column that is normally used to suppress conductance in the eluant, Donnan dialysis allowed more control over the conductivity and eliminated the need to regenerate the resins. Moreover, the resolution was improved by the use of Donnan dialysis.

The use of neutralization dialysis for desalination of cheese whey has been described.

**Conclusion**

Donnan dialysis can be used in many applications where ion-exchange beads are currently applied. The process might find a niche in water softening in a capacity range between that of home water softeners and the large-scale lime-soda softeners. Capital costs are higher for membranes than for resin beads, but the use of membranes offers the advantages of steady-state operation without the need for rinse-down, which produces large volumes of water that must be discarded. The capital cost of small-scale Donnan dialysis could be reduced by the availability of more ion-exchange membranes in hollow-fibre form that could be assembled into compact modules.

**Further Reading**


**Electrodialysis**

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Electrodialysis is a process in which ion exchange membranes in combination with an electrical potential difference are used to remove ionic species from an aqueous solution. The large scale industrial utilization of the process began about 30 years ago with the development of highly selective ion exchange membranes of low electric resistance arranged in a multicell stack.

Until the mid 1970s electrodialysis stacks were operated in a unidirectional mode, that is, the polarity of the electrodes was fixed. A significant step towards the efficient application of electrodialysis was the introduction of a new mode of operation referred to as electrodialysis reversal. In this operating mode the flow streams and the polarity in an electrodialysis stack are periodically reversed, which reduces membrane fouling and scaling. Costly and time-consuming membrane cleaning procedures are then unnecessary.

The main application of electrodialysis is the desalination of brackish water for domestic and industrial use. In Japan electrodialysis is also used on a large scale to concentrate sodium chloride from sea water for the production of table salt. More recently