DIALYSIS AND DIFFUSION DIALYSIS

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Summary

Dialysis is a separation process in which a semipermeable membrane separates a source solution and a receiving solution, usually water. The membrane is selected to be permeable to source solution components that need to be removed but impermeable to another component that must be retained in the source solution. The best known application of dialysis is in the artificial kidney. That process is called hemodialysis, because a patient's blood is the source solution. The membrane for hemodialysis is usually made of a cellophane-like material, and the selectivity of that membrane is mainly based on the size of the diffusing components. A specialized dialysis process that utilizes ion exchange membranes is called diffusion dialysis. Anion exchange membranes are notoriously leaky to acids, and diffusion dialysis exploits that property of anion exchange membranes to separate acids from salts. The most common application of diffusion dialysis is recovery of acids from waste metal pickling solutions, the strong acid solutions that are used to remove oxide coatings from metal parts before they are painted, galvanized, or electroplated. Cation exchange membranes are leaky to bases, and that property is utilized to recover NaOH from aluminum etching solutions.
1. Introduction

Dialysis may be defined as the diffusion of soluble substances through a semi-permeable membrane from one solution into another (Zender 1946). To avoid the confusion of terminology often encountered in the literature, the two solutions separated by the membrane will be called the source solution and the receiving solution. Although dialysis with non-aqueous solutions is possible, this work will deal only with aqueous source solutions and water as the receiving solution.

Many readers will associate dialysis with the artificial kidney, which is by far the largest application of dialysis. Although kidney dialysis is not the focus of this technical presentation, that familiar process can be used to illustrate many of the important principles of industrial dialysis processes. The kidney dialyzer contains a thin plastic membrane, usually made of regenerated cellulose, which is permeable to salts and small organic molecules that constitute waste metabolites normally removed in the natural kidney. But the cellulose membrane is not permeable to larger blood components like antibodies, red and white cells, platelets, and proteins. When the patient's blood flows across one side of the membrane and water flows across the other side, the ions and molecules that can permeate the membrane will diffuse from the blood through the membrane and into the water under the influence of the concentration difference that acts as a driving force for diffusion.

If the receiving stream were just pure water, there would be problems of depletion of desirable salts and small molecules like glucose that easily diffuse through the membrane, and there would also be a buildup of water in the blood due to osmosis. Both of these problems are alleviated by the addition of salts and glucose to the receiving solution to eliminate the concentration difference of these vital components across the membrane. Another important function of the kidneys is to remove water from the body. That can be accomplished in the artificial kidney by application of a small negative pressure to the receiving solution.

An important characteristic of the cellulosic membranes used for kidney dialysis is that the rate of diffusion is determined primarily by the size of the diffusing species. As the size of the molecule increases, its diffusion rate decreases. Ion-exchange membranes have rather different diffusion characteristics than the cellulosics in that the diffusion rates are influenced by the electrical charge of the diffusing species.

Diffusion dialysis is a subset of dialysis in which ion-exchange membranes are utilized. Since ion-exchange membranes have an ionically charged polymeric structure, their discrimination between solutes is based on ionic charge as well as size. But hydrogen and hydroxyl ions, which actually make up the solvent that pervades the membrane, seem to permeate by a different mechanism that avoids the rejection of the charged polymer structure. Anion-exchange membranes transport acids while rejecting salts, and cation-exchange membranes transport bases in preference to salts.

Figure 1 illustrates diffusion dialysis for recovery of HCl from a solution also containing FeCl₂. The anion-exchange membrane is quite permeable to the Cl⁻ ions, but an equivalent amount of cations must also pass through the membrane to maintain
electroneutrality. Because of their double positive charge the Fe$^{2+}$ ions are strongly rejected by the membrane, but the protons pass through rather easily. Thus a useful separation of acid and salt is achieved.

Figure 1. Diffusion dialysis for recovery of HCl from steel pickling solution.

2. The Principle of the Process and Fundamentals

Transport in dialysis and diffusion dialysis is described by Fick's Law with concentration difference as the driving force.

 Flux = $U \Delta C$ \hspace{1cm} (1)

The mass-transfer coefficient $U$ can be viewed as the reciprocal of the resistance to diffusion. Since resistances are additive, the overall value for $U/(U_o)$ can be expressed in terms of the diffusional resistances of the membrane ($U_m$) and the liquid ($U_l$) in contact with it.

$1/U = 1/U_m + 1/U_l$ \hspace{1cm} (2)

Values of $U$, expressed in units of length time$^{-1}$, can be measured for a particular solute through a particular membrane in a stirred cell with the membrane separating the source and receiving solutions. With sufficient stirring the resistance of the liquid can be minimized so that the measured value of $U$ is essentially $U_m$. Solutes that permeate the membranes rapidly and are thus separable by dialysis have $U$ values on the order of 10$^{-4}$-10$^{-3}$ cm s$^{-1}$. Since solution velocities in commercial dialyzers are slow, $U_l$ might be a significant part of $U_o$.

A rough idea of the diffusive resistance in the boundary layer can be estimated by examining the elements of the equation for diffusive flux through a film of liquid,
Flux = \( D \Delta C / z \)  

(3)

where \( D \) is the diffusivity of the solute through the solvent, typically about \( 10^{-5} \, \text{cm}^2 \, \text{s}^{-1} \), and \( z \) is the thickness of the film of liquid through which diffusion occurs. Since the spacing between membranes in a commercial dialysis apparatus might be on the order of 0.1 cm, liquid film thickness \( z \) is likely to be about 0.01 cm. So \( D/z=10^{-3} \, \text{cm} \, \text{s}^{-1} \), which is like a \( U \) value for the liquid film, is of the same order of magnitude as the typical \( U \) values for dialysis membranes. This means that both the membrane and the liquid films in contact with it are likely to contribute to the resistance to diffusion in a real dialysis application, even at rather high solution velocities.

Transport of solvent through dialysis membranes can be significant. Osmotic forces will tend to transport solvent from the dilute solution to the concentrated solution. However, the diffusing species can drag along solvent, both in the solvation shell and by convection, in the direction opposite to that of normal osmosis. Moreover, osmotic pressures are caused by the concentration difference of non-diffusing species across the membrane, the values of which can be difficult to determine. Consequently, prediction of even the direction of solvent transport can be difficult in certain circumstances, and prediction of the rate of solvent transport is definitely challenging.

Bibliography and Suggestions for further study


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