THINK SIMULATION! Getting the chemistry right.

Technical basis for OLI membrane technology

An OLI white paper

This paper documents the approach that OLI has implemented to model the reverse osmosis membrane behavior.

A rigorous simulator for the reverse osmosis process

Summary

To model the transport mechanism inside the membrane, solution-diffusion approach has been incorporated. In the solution-diffusion model, it is proposed that transfer of ions and water through polymeric membranes occurs via a solution diffusion mechanism because of dissolution of permeates in the membrane materials [1]. The water flux through the membrane is a function of water permeability coefficient, hydrodynamic pressure difference and osmotic pressure difference across the membrane, whereas, the solute flux through the membrane is a function of solute permeability constant and solute concentration gradient across the membrane [2]. Molecular size of the ions strongly affect the transport characteristics of the ions due to the sieving action of the membranes. However, in water environment, different number of water molecules surround each cation and anion. Thus, the real radius of an ion is the one that considers the water molecules around it (i.e., the hydrated ion radius) rather than the absolute ionic crystal radius. Regardless of membrane type, the type of experiment, and the membrane configuration, the salt permeabilities are inversely proportional to the hydrated radii of the ions [3]. In OLI membrane model, permeability of ions has been correlated with their hydration numbers.

In general, the typical order of rejection of cations by reverse osmosis membranes follow Fe^{3+} > Ni^{2+} ≈ Cu^{2+} > Mg^{2+} > Ca^{2+} > Na^+ > K^+, and PO_4^{3-} > SO_4^{2-} > HCO_3^- > Br^- > Cl^- > NO_3^- ≈ F^- for anions [4]. The permeability of cations and anions calculated as a function of hydration numbers follow the typical trends. For some organics with same homologous group (i.e., alcohols, phenols, acids), the rejections have been correlated by calculating the topological parameters characterizing molecular structure [5]. For other neutrals, self-diffusivities relative to water have been used to correlate the permeability.

Commercial membrane manufacturers provide product specification sheet for each type of membranes. In addition to physical dimensions (i.e., membrane area), the product sheet also reports performance of the membrane (i.e., permeate flux, recovery and rejection percentage for NaCl or other solutes) at specific test conditions. User entered test conditions data are the key information for calculating the permeability coefficients of water and the test solute for the membrane element. These calculated permeability coefficients along with the above-mentioned correlations are used to estimate the permeability coefficients of other species present. The advantage of this method is that a reasonable and preferential order of permeabilities for the membrane regardless of membrane type can be correctly estimated.

In the current OLI membrane development, users can enter number of membrane elements per vessel and total number of vessels in the assembly. Alternatively, users can estimate total number of vessels required (or total membrane area) for a specific recovery. Concentration polarization is approximated using Peclet number and intrinsic enrichments [4]. Flow factor (sometimes referred as fouling factor) is estimated from the water activity reduction unless specified by the users. Users may specify feed side

pressure drop per element if available. There are options for conditioning the feed to a specific pH by choosing a pH acid titrant or base titrant.

Model Development

Water flux in RO membrane is a function of membrane permeability of water, applied pressure and the feed water osmotic pressure. According to solution-diffusion model, water flux can be calculated from the following equation.

$$J_w = AP_w(\Delta P - \Delta \pi) \quad \text{; For water} \tag{1}$$

$$J_{si} = AP_{si}(C_{si} - C_{pi}) \quad \text{; For } i = 2, n \text{ (water is not included)} \tag{2}$$

where J_w, P_w, ΔP, $\Delta \pi$ and A represent water flux through membrane, water permeability, membrane pressure gradient, osmotic pressure gradient and membrane area, respectively. J_{si}, P_{si}, C_{si} and C_{pi} represent species i flux through membrane, permeability, concentration at the membrane surface and concentration at the permeate side, respectively. It is to be noted that n represents total number of aqueous and ionic species in the system.

$$\Delta P = P_f - P_{pd} - P_p \tag{3}$$

where P_f, P_{pd} and P_p represent feed side pressure, pressure drop at the concentrate (residue) side and permeate pressure, respectively.

$$P_{pd} = 0.005Q_{avg}^{1.7} \tag{4}$$

$$Q_{avg} = \frac{Q_f + Q_c}{2} \tag{5}$$

where Q_f, Q_c and Q_{avg} represent feed, concentrate and average concentrate (residue) side flow rate, respectively.

$$\Delta \pi = \pi_{avg} - \pi_p \tag{6}$$

$$\pi_{avg} = \frac{\pi_f + \pi_c}{2} \tag{7}$$

where π_f, π_p, π_c and π_{avg} represent feed side osmotic pressure, permeate side osmotic pressure, concentrate (residue) side osmotic pressure and average concentrate (residue) side osmotic pressure, respectively.

The salt concentration adjacent to the membrane surface is higher than the bulk solution concentration because reverse osmosis membranes preferentially permeate water and retain salt. Water and salt are brought toward the membrane surface by the flow of solution through the membrane. Water and a little salt permeate the membrane, but most of the salt is rejected by the membrane and retained at the membrane surface. Salt accumulates at the membrane surface until a sufficient gradient has formed to allow the salt to diffuse to the bulk solution [4]. The increase or decrease of the concentration at the membrane surface relative to the bulk solution concentration determines the extent of concentration polarization.

$$CP = \frac{e^{PK}}{1 + E_0(e^{PK}-1)} \qquad (8)$$

$$PK = {J_v \delta}/{D_v} \qquad (9)$$

where CP, PK, E_0, J_v, δ and D_v represent concentration polarization modulus, Peclet number, enrichment factor, typical flux through membrane, boundary layer thickness and typical diffusion coefficient, respectively.

$$C_{si} = C_{pi} + CP(C_{fi} - C_{pi}) \qquad (10)$$

where C_{si} and C_{fi} represent concentration at the membrane surface and feed side bulk concentration for the species, respectively.

The fouling factor is applied to membrane due to loss of permeability by compaction and scale fouling. Typically, a fouling factor less than 1.0 is applied depending on the membrane life. A correlation was developed for fouling factor which takes into account the water activity reduction at the membrane surface due to permeation relative to the fresh membrane under the test conditions.

$$FF = function\ (T_c, \pi_{avg}) \qquad (11)$$

where FF, T_c and π_{avg} represent fouling factor, concentrate (residue) side temperature and average concentrate (residue) side osmotic pressure, respectively.

The osmotic pressure, self-diffusivity and densities are calculated in OLI Systems' Mixed-Solvent Electrolyte (MSE) or Aqueous (AQ) framework.

Equations (1-11) constitute the solution of the RO membrane and are simultaneously solved to calculate J_w, J_{si}, C_{pi}, C_{si}, CP and FF.

Permeability Estimate

In a water rich environment, hydration numbers refer to the number of water molecules in the vicinity of the ion. Thus, real radius of an ion is the one that considers the water molecules around it (i.e., the hydrated ion radius) rather than the absolute ionic crystal radius. The water molecules that these hydration number pertain to presumably move together with the ions, and are sufficiently firmly attached to them by ion-dipole interactions and hydrogen bonding to constitute a fairly stable entity [6]. Stokes radii are calculated as a function of ionic limiting conductivities and charge of species. The Stokes radii are corrected to relate Van Der Waals ionic sizes [7, 8]. The hydration numbers are calculated as a function of corrected Stokes radii, ionic limiting standard molar volume and molar volume of water. Membrane specific permeation behavior found in open literature were analyzed and from the analyzed data, a correlation was developed for permeability as a function of hydration numbers. It is worth mentioning that regardless of membrane type, the type of experiment, and the membrane configuration, the salt permeabilities are inversely proportional to the hydrated radii of the ions [3]. However, for regressing the water permeability and key components (test solutes) permeabilities, a modified subset of equations (1-11) were formulated and simultaneously solved based on the

performance data provided. After calculating water and key components permeabilities, an update (but preserving the trend) in the aforementioned correlation was achieved, and the permeabilities of the rest of the ionic species were calculated from the updated correlation. The advantage of this technique is that a reasonable and preferential order of permeabilities for the membrane regardless of membrane type can be correctly estimated.

For some organics with same homologous group (i.e., alcohols, phenols, acids), the rejections were correlated by calculating the topological parameters characterizing molecular structure [5]. For other neutrals, self-diffusivities relative to water were used to correlate the permeability. These calculated permeabilities remain constant unless there is a change in temperature.

For more Information

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