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Basic equations for desalination by reverse osmosis: a deduction based on the thermodynamics of irreversible processes

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ABSTRACT

The thermodynamics of irreversible processes is a useful tool for understanding and quantifying transport phenomena in dense membranes where the membrane structural parameters are not essential. Because of the existence of driving forces, the components within the solution are transported from one side of the membrane to the other by diffusion. The aim of this paper is to provide basic equations for reverse osmosis derived from a set of more general equations established for membrane transport which relates fluxes and driving forces, based on non-equilibrium thermodynamics.

Keywords: Thermodynamics of irreversible processes; Transport phenomena; Membrane; Reverse osmosis

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1. Introduction

The development of effective techniques for separating liquid and gaseous mixtures on an industrial scale has gained increased attention because of raised expectations concerning lower economic costs and greater environmental sustainability of separation processes. Many of these processes employ membranes technology. A membrane is a selective barrier between two solutions, one the feed solution (upstream side) and the other the permeate solution (downstream side). Separation is achieved because the membrane transports one component from the feed solution more readily than any other components.

The driving force exerted on each component of a mixture is the gradient of the electrochemical potential across the membrane. The electrochemical potential direction causes each component to move with an independent velocity from the feed to the permeate side; therefore, in the steady state, the compositions of the feed and permeate stream differ from each other.

In the case of desalination, membranes with dense non-porous surface layer 0.1–5 μm thick, and are generally supported by a synthetic polymeric material comprising a porous backing 100–500 μm thick [1,2]. The thin top layer is primarily responsible for the separation effect, while the supporting layer has little or no influence on the separation process. The supporting layer functions as a mechanical backing for the active membrane surface layer.

With membrane systems, two classes of membrane filtration are shown in Fig. 1. In dead-end filtration two streams are presented, the feed and permeate streams. This results in a constant concentration of each component over the surface of the membrane on the feed side as well as on the permeate side. In cross-flow filtration the incoming flow or feed stream is split into two streams, i.e., into the retentate or concentrate stream and into the permeate stream. The concentrate or permeate stream may be the product. The basic flow principle of cross-flow filtration is represented in various membrane separation modules, such as plate and frame modules, tubular modules, spiral-bound modules and hollow-fibre modules [1–3].

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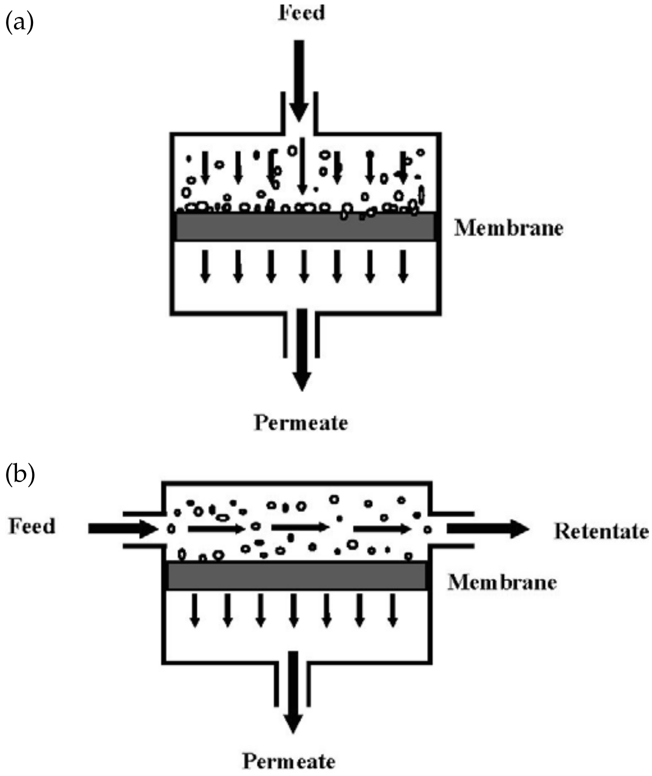

Fig. 1. Dead-end filtration (a) and cross-flow filtration (b).

When a semi-permeable membrane separates two solutions of the same solvent at different solute concentrations, the solvent flows from the more dilute to the more concentrated solution (osmosis) due to different values of the chemical potential on each solution. The increasing hydrostatic pressure in the concentrated solution produces a corresponding osmotic pressure difference in the solutions [1,2].

If a pressure greater than osmotic pressure is applied to the concentrated solution, the process of osmosis can be reversed. In which case, the solvent is transported through the membrane from the more concentrated solution into the less concentrated solution. This process is called reverse osmosis (RO). Generally, RO employs spiral-bound modules and is mainly applied to dilute aqueous solutions to produce purified water or to concentrate a solution by removing water. In this instance, the top layer of the membranes is made on a hydrophilic material (cellulose acetate, composite aromatic polyamides or polysulphones). In RO, the membrane is in contact with the liquid phase. In the case of desalination of sea water, pressures in the range of 80–100 bar are applied to the feed side, while in the case of brackish water the pressures range from 15 to 40 bar. In both cases, the permeate side is kept at ambient pressure.

The basic equations of RO have been established according to different theoretical models, including the solution-diffusion model and the finely porous capillary model [1,4]. The aim of this paper is to provide basic equations based on the thermodynamics of irreversible processes. The RO equations are derived from more general equations for membrane transport, which relate fluxes and driving forces [2,5–7]. The results are very useful in the study of electrokinetic phenomena [5,6].

2. Theory

2.1. Transport equations in the thermodynamics of irreversible processes

In the following discussion flux equations derived from the thermodynamics of irreversible processes (TIP) consider the membrane as a black box, so no information is required about the structure of the membrane system. In irreversible processes, free energy is dissipated continuously while entropy is increased internally, so that entropy production can be expressed as the summation of the product of conjugated fluxes (J_i) and forces (χ_i) [6,8]:

$$\frac{\mathrm{d}S_{\text{int}}}{\mathrm{d}t}=\sum_{i=1}^{n}J_i\chi_i \tag{1}$$

The dissipation function Φ is defined by the product of thermodynamic temperature T and entropy production:

$$\Phi=T\frac{\mathrm{d}S_{\text{int}}}{\mathrm{d}t}=T\sum_{i=1}^{n}J_i\chi_i \tag{2}$$

The flows refer not only to the transport of mass but also to the transfer of heat and electrical current. These parameters are usually expressed relative to the fixed membrane as a reference frame. Not far from equilibrium, it can be assumed that each flux is linearly related to the forces

$$J_i=\sum_{j=1}^{n}L_{ij}\chi_j, \qquad i=1,2,....n \tag{3}$$

where L_{ij} are the phenomenological coefficients, called cross or coupling coefficients when $i\neq j$, which, according to Onsager [6,8], are equal ($L_{ij}=L_{ji}$) and may be either positive or negative.

Before dealing with expressions for the fluxes of different components across membranes, it is necessary to introduce the electrochemical potential [6], which, for a charged species i in a liquid phase, is given by

$$\tilde{\mu}_i^{\ell}(T,P,\chi_i)=\mu_i^{\ell}(T,P,\chi_i)+z_iF\phi \tag{4}$$

where z_i is the valence, F is the Faraday constant (96,500 coulomb/mol), ϕ is the electrical potential and $\mu_i^\ell(T,P,\chi_i)$ is the chemical potential:

$$\mu_i^\ell(T,P,\chi_i)=\mu_i^{\ell,o}(T)+RT\ln a_i+V_i(P-P^*) \tag{5}$$

assuming that the partial molar volume of component i, V_i, is independent of the pressure P and P^* being the standard pressure. The activity of the i component in the liquid mixture is expressed as $a_i=\gamma_i X_i$ where X_i is the mole fraction and γ_i is the corresponding activity coefficient (for ideal solutions γ_i equals 1). The chemical potential of component i, $\mu_i^{\ell,o}$ in its standard state is a function of temperature only.

The driving forces across a membrane are the electrochemical potential gradients so if the membrane thickness is d, we can write

$$\chi_i=-\Delta\tilde{\mu}_i/d=-(V_i\Delta P+z_iF\Delta\phi_m+RT\Delta\ln a_i)/d \tag{6}$$

where $\Delta\phi_m$ is the electric potential difference across the membrane (membrane potential).

2.2. Basic equations for the transport in membranes

We shall consider the case in which a homogeneous ion-exchange membrane of uniform thickness separates two well mixed aqueous solutions of a binary electrolyte at equal temperature and different concentrations, with gradients of applied electric potential and pressure. Apart from the membrane, there are three components: two ionic species of the binary electrolyte (1, cation; 2, anion), and the solvent (3) (in our case water). In this case, $n = 3$ in Eq. (3) and there are three flux equations and nine coefficients.

For selective membrane, positively charged (anion exchange membrane), the anions will be transported more easily and so inside the membrane there will be an excess of anions over cations, and therefore the anion flux through the membrane will be greater than the cation flux: $J_2 > J_1$. Thus, we can write

$$J_2=J_2^*+J_2^{**} \tag{7}$$

where J_2* is the excess of anionic flux compared with the salt flux, due to the electric charge of the membrane and J_2** is the anionic flux in correspondence with the salt flux.

For a generic binary electrolyte the stoichiometric formula is

$$A_{v_-}C_{v_+}=A_{z_+}C_{z_-} \tag{8}$$

where A and C represent, respectively, anion and cation, and v_i (i = + or −) are their stoichiometric numbers in the formula, according to the valences z_i (i =+ or −). So, every molecule of salt transported through the membrane implies the transport of $z-$ion-gram of the anion and $z+$ ion-gram of the cation. The electric neutrality of the salt requires that

$$\nu_-z_-+\nu_+z_+=0 \tag{9}$$

For the salt flux, J_s:

$$J_S=\frac{J_1}{\nu_+}=\frac{J_2^{**}}{\nu_-}\Rightarrow J_2^{**}=\frac{\nu_-}{\nu_+}J_1 \tag{10}$$

and so, for the total anionic flux

$$J_2=J_2^*+\frac{\nu_-}{\nu_+}J_1 \tag{11}$$

and, according to the previous expressions for the different fluxes, Eq. (2) can be rewritten as

$$\begin{aligned}\frac{\Phi d}{T}&=-\sum_{i=1}^{3}J_i\Delta\tilde{\mu}_i=\\&-\left(\frac{\nu_+}{\nu_+}J_1\Delta\tilde{\mu}_1+\frac{\nu_-J_1}{\nu_+}\Delta\tilde{\mu}_2+J_2^*\Delta\tilde{\mu}_2+J_3\Delta\tilde{\mu}_3\right)\end{aligned} \tag{12}$$

$$\Phi d/T=-J_s(\nu_+\Delta\tilde{\mu}_1+\nu_-\Delta\tilde{\mu}_2)-J_2^*\Delta\tilde{\mu}_2-J_3\Delta\mu_3 \tag{13}$$

where we have taken into account the electrically neutral character of solvent 3, so that $\tilde{\mu}_3 = \mu_3$. In addition, the electric neutrality of the salt leads to

$$\begin{aligned}(\nu_+\Delta\tilde{\mu}_1+\nu_-\Delta\tilde{\mu}_2)&=\nu_+\Delta\mu_1+\nu_-\Delta\mu_2\\&+F\Delta\phi_m(z_+\nu_++z_-\nu_-)=\nu_+\Delta\mu_1+\nu_-\Delta\mu_2=\Delta\mu_S\end{aligned} \tag{14}$$

where μ_s is the chemical potential of the salt.

Now, it must be taken into consideration that the net current through the membrane is due only to anions whose flux excess J_2* (ion-gram per unit area and time) multiplied by the charge of the ion-gram *(z_-F)* gives the electric current density

$$I=z_-FJ_2^* \tag{15}$$

So, the term corresponding to J_2* in Eq. (13) becomes

$$J_2^*\Delta\tilde{\mu}_2=I\frac{\Delta\tilde{\mu}_2}{z_-F} \tag{16}$$

On the other hand,

$$\Delta\tilde{\mu}_2 = RT\ln\frac{a_2^{(2)}}{a_2^{(1)}} + z_- F\Delta\phi_m \tag{17}$$

where the superscripts of the anion activities refer to solutions 1 and 2 in contact with the membrane. The difference of pressure term has not been taken into account, due to the small value of the solute partial molar volume. The membrane potential $\Delta\phi_m$ measurement may be accomplished by anion selective electrodes and therefore a nernstian contribution [9] of the electrode potential $\Delta\phi_N$ is incorporated in the direct measurement $\Delta\phi$ so that

$$\Delta\phi = \Delta\phi_m + \Delta\phi_N = \Delta\phi_m + \frac{RT}{z_- F}\ln\frac{a_2^{(2)}}{a_2^{(1)}} = \frac{\Delta\tilde{\mu}_2}{z_- F} \tag{18}$$

and Eq. (16) gives

$$J_2^* \Delta\tilde{\mu}_2 = I\Delta\phi \tag{19}$$

By combining Eqs. (13), (14) and (19), we can write

$$\Phi d/T = -J_s \Delta\mu_S - I\Delta\phi - J_3\Delta\mu_3 \tag{20}$$

which shows that the entropy production in our system, in the presence of an ion-exchange membrane, is the sum of the solvent flux, current flux and salt flux multiplied by their conjugated driving forces ($\Delta\mu_s$, $\Delta\phi$ and $\Delta\mu_3$, respectively).

The last equation can be rewritten in an alternative form, introducing a new set of driving forces, such as the electric potential difference ($\Delta\phi$), the hydrostatic pressure difference through the membrane (ΔP) and the osmotic pressure difference ($\Delta\Pi$).

The difference in chemical potential for the water in the membrane is

$$\begin{aligned}\Delta\mu_3 &= \left(V_3^{(2)}P^{(2)} + RT\ln\chi_3^{(2)}\right) - \left(V_3^{(1)}P^{(1)} + RT\ln\chi_3^{(1)}\right)\\ &= V_3\left[\left(P^{(2)} - P^{(1)}\right) + \frac{RT}{V_3}\ln\frac{\chi_3^{(2)}}{\chi_3^{(1)}}\right]\end{aligned} \tag{21}$$

which reduces to

$$\Delta\mu_3 = V_3(\Delta P - \Delta\Pi) \tag{22}$$

where $\Delta P = P^{(2)} - P^{(1)}$, and $\Delta\Pi$ is the difference of osmotic pressure between the solutions on both sides of the membrane [1,2,6], given by

$$\Delta\Pi = \frac{RT}{V_3}\ln\frac{\chi_3^{(2)}}{\chi_3^{(1)}} \tag{23}$$

In the case of diluted solutions, $\Delta\Pi = RT\Delta C_S$, with $\Delta\bar{C}_S = C_S^{(2)} - C_S^{(1)}$ being the difference in solute molar concentration through the membrane.

Using Eq. (5), the chemical potential difference may be expressed as

$$\Delta\mu_i = V_i\Delta P + \Delta\mu_i^{(c)} \tag{24}$$

where

$$\Delta\mu_i^{(c)} = RT\ln\frac{a_i^{(2)}}{a_i^{(1)}} \tag{25}$$

Hence, the chemical potential difference for the salt can be written as

$$\begin{aligned}\Delta\mu_S &= \Delta P\left(\nu_+ V_1 + \nu_- V_2\right) + \left(\nu_+\Delta\mu_1^{(c)} + \nu_-\Delta\tilde{\mu}_2^{(c)}\right)\\ &= \Delta P\left(\nu_+ V_1 + \nu_- V_2\right) + RT\ln\frac{\left[a_1^{(2)}\right]^{\nu_+}\left[a_2^{(2)}\right]^{\nu_-}}{\left[a_1^{(1)}\right]^{\nu_+}\left[a_2^{(1)}\right]^{\nu_-}}\\ &= \Delta P\, V_S + RT\ln\frac{a_S^{(2)}}{a_S^{(1)}}\end{aligned} \tag{26}$$

where $V_S = v_+V_1 + v_-V_2$ is the partial molar volume of the salt, whose activity is given by

$$a_S = (a_+)^{\nu_+}(a_-)^{\nu_-} \tag{27}$$

When we are dealing with diluted solutions, the activity a_s is equal practically to the molar concentration, C_s, and so in this case

$$\Delta\mu_S = \Delta P\, V_S + RT\ln\frac{C_S^{(2)}}{C_S^{(1)}} = \Delta P\, V_S + \Delta\mu_S^{(c)} \tag{28}$$

Alternatively, $\Delta\mu_S^{(c)}$ can be written by defining a mean logarithmic molar concentration, $\bar{C}_S$ as

$$\bar{C}_S = \frac{\Delta\Pi}{\Delta\mu_S^{(c)}} = \frac{C_S^{(2)} - C_S^{(1)}}{\ln\left[C_S^{(2)}/C_S^{(1)}\right]} \tag{29}$$

When the concentrations in solutions 1 and 2 are very close, then $C_S^{(2)}/C_S^{(1)} \cong 1$ and so

$$\ln\frac{C_S^{(2)}}{C_S^{(1)}} \cong 2\frac{\frac{C_S^{(2)}}{C_S^{(1)}}-1}{\frac{C_S^{(2)}}{C_S^{(1)}}+1} = 2\frac{C_S^{(2)}-C_S^{(1)}}{C_S^{(2)}+C_S^{(1)}} \tag{30}$$

which, from Eq. (29), finally gives

$$\bar{C}_S = \frac{C_S^{(2)}+C_S^{(1)}}{2} \tag{31}$$

This result allows us to affirm that, for ideal solutions with close concentrations, the mean logarithmic concentration is the arithmetic mean of the concentrations for the solutions on both sides of the membrane.

From Eqs. (20), (22), (28) and (29), it can be seen that

$$\frac{\Phi d}{T} = -\left[\frac{J_S}{\bar{C}_S}\Delta\Pi + J_3V_3(\Delta P-\Delta\Pi) + I\Delta\phi + J_SV_S\Delta P\right] \tag{32}$$

The total volume flux, J_v, is defined as

$$J_V = J_3V_3 + J_SV_S \tag{33}$$

and so Eq. (32) becomes

$$\frac{\Phi d}{T} = -\left[\left(\frac{J_S}{\bar{C}_S} - J_3V_3\right)\Delta\Pi + I\Delta\phi + J_V\Delta P\right] \tag{34}$$

The solute speed v_s in the membrane frame is given by $\left(J_S/\bar{C}_S\right)$ and the volume V for diluted solutions is equal to the partial mole volume number of solvent multiplied by its number of moles (n_3), so

$$n_3V_3 \cong V \Rightarrow C_3V_3 \cong 1 \tag{35}$$

where C_3 is the molar concentration of solvent, and the following equation can be derived

$$\frac{J_S}{\bar{C}_S} - J_3V_3 \cong v_S - \frac{J_3V_3}{C_3V_3} = v_S - v_3 = J_D \tag{36}$$

where v_3 is the speed of the solvent with respect to the membrane, and therefore J_D is the diffusive flux defined as the relative speed of the solute with respect to the solvent. Introducing the last equation in Eq. (34), it may be expressed as

$$\Phi d/T = -\left(J_D\Delta\Pi + I\Delta\phi + J_V\Delta P\right) \tag{37}$$

and according to Eq. (3), the corresponding phenomenological equations will be:

$$\left.\begin{aligned} J_V &= L_{11}\Delta P + L_{12}\Delta\Pi + L_{13}\Delta\phi \\ J_D &= L_{21}\Delta P + L_{22}\Delta\Pi + L_{23}\Delta\phi \\ I &= L_{31}\Delta P + L_{32}\Delta\Pi + L_{33}\Delta\phi \end{aligned}\right\} \tag{38}$$

2.3. *Basic equations for reverse osmosis*

In the case of non-charged membranes, $\Delta\phi = 0$ and $I = 0$, so that Eqs. (37) and (38) reduce to

$$\begin{gathered} \Phi d/T = -\left(J_D\Delta\Pi + J_V\Delta P\right) \\ \begin{cases} J_V = L_{11}\Delta P + L_{12}\Delta\Pi \\ J_D = L_{21}\Delta P + L_{22}\Delta\Pi \end{cases} \end{gathered} \tag{39}$$

with the following restrictions concerning the magnitude of the coefficients [8]:

$$L_{12} = L_{21},\ L_{11} \geq 0 \text{ and } L_{22} \geq 0,\ L_{12}\cdot L_{21} \geq L_{12}^2 \tag{40}$$

reducing the number of coefficients to three and indicating that, even if there is no difference in hydrodynamic pressure ($\Delta P = 0$), there is still a volume flux and, although the solute difference concentration is zero ($\Delta\Pi = 0$), there is still a solute flux when $\Delta P \neq 0$.

We can establish an alternative formulation for the phenomenological Eqs. (39) to deal with diluted solutions. From the expressions for the volume and diffusive fluxes Eqs. (33) and (36), it can be seen that

$$J_V + J_D = \frac{J_S}{\bar{C}_S}\left(1 + V_S\bar{C}_S\right) \tag{41}$$

For diluted solutions $\bar{C}_SV_S \ll 1$, and according to Eq. (39), we obtain

$$\frac{J_S}{\bar{C}_S} \cong J_V + J_D = \left(L_{11}+L_{12}\right)\Delta P + \left(L_{12}+L_{22}\right)\Delta\Pi \tag{42}$$

This equation, together with the first one in Eq. (39), offer a new formulation to describe the phenomenological behaviour of the membrane system:

$$\begin{cases} J_V = L_{11}\Delta P + L_{12}\Delta\Pi \\ J_S/\bar{C}_S = \left(L_{11}+L_{12}\right)\Delta P + \left(L_{12}+L_{22}\right)\Delta\Pi \end{cases} \tag{43}$$

where the fluxes corresponding to the volume and solute can now be directly measured.

Under certain conditions, this new set of equations can be modified to adopt a more simplified form. To undertake this modification, we shall take into account that a strictly selective membrane should only allow the transport of solvent, rejecting all solutes, so that $J_s = 0$ for any value of ΔP and $\Delta\Pi$. Therefore, from Eq. (42), we can state that

$$\left.\begin{aligned} L_{11} &= -L_{12} \\ L_{22} &= -L_{12} \end{aligned}\right\} \Rightarrow L_{11} = L_{22} = L_P \tag{44}$$

where L_p is the hydrodynamic permeability or water permeability of the membrane. Introducing this new parameter in the first Eq. (43) gives

$$J_V = L_P(\Delta P - \Delta\Pi) \tag{45}$$

and when $J_v = 0$, it follows that

$$(\Delta P)_{J_V=0} = -\frac{L_{12}}{L_{11}}(\Delta\Pi)_{J_V=0} = \Delta\Pi \tag{46}$$

A real membrane always allows the transport of certain amounts of salt, in which case the so-called reflection coefficient or Stavermann coefficient [7], σ, can be defined by

$$\sigma = \left(\frac{\Delta P}{\Delta\Pi}\right)_{J_V=0} = -\frac{L_{12}}{L_{11}} < 1 \Rightarrow L_{12} = -\sigma L_{11} = -\sigma L_P \tag{47}$$

This coefficient is a measure of the selectivity of the membrane and usually has a value of between 0 and 1. For an ideal semi-permeable or permselective membrane, $\sigma = 1$ and there is no solute transport, while for a not completely semi-permeable membrane, $\sigma < 1$ and $\sigma = 0$ in the case of no selectivity.

The reflection coefficient can be interpreted with respect to the speeds of the solute (v_s) and the solvent (v_3) by defining it as follows:

$$\sigma = 1 - \frac{v_S}{v_3} \tag{48}$$

so that $\sigma = 1$ when $v_s = 0$ and $\sigma = 0$ if $v_s = v_3$. For example, the solute and solvent are transported with the same speed and the membrane shows no permselectivity and therefore no rejection of the solute takes place. Whatever the case, when $v_s < v_3$, then $\sigma < l$, while that $\sigma < 0$, if $v_s > v_3$, implies a transport rate of solute higher than that corresponding to solvent and indicating the presence of electric effects associated to the charge of the membrane.

The introduction of the reflection coefficient in Eq. (43) leads to the next expression for the volume flux:

$$J_V = L_P(\Delta P - \sigma\Delta\Pi) = L_P\left[(\Delta P - \Delta\Pi) + (1-\sigma)\Delta\Pi\right] \tag{49}$$

and for the salt flux

$$\begin{aligned} J_S &= \bar{C}_S\left[L_P(1-\sigma)\Delta P + (L_{22} - \sigma L_P)\Delta\Pi\right] \\ &= \bar{C}_S\left[L_P(\Delta P - \sigma\Delta\Pi) - L_P\sigma\Delta P + L_{22}\Delta\Pi\right] \\ &= \bar{C}_S\left[J_V - \sigma(L_P\Delta P - \sigma L_P\Delta\Pi) - L_P\sigma^2\Delta\Pi + L_{22}\Delta\Pi\right] \\ &= \bar{C}_S\left[J_V(1-\sigma) + (L_{22} - L_P\sigma^2)\Delta\Pi\right] \end{aligned} \tag{50}$$

which finally gives

$$J_S = \bar{C}_S(1-\sigma)J_V + \omega\Delta\Pi \tag{51}$$

ω is the osmotic permeability or solute permeability and is given by

$$\omega = \bar{C}_S L_P\left(\frac{L_{22}}{L_P} - \sigma^2\right) = \bar{C}_S L_P\left(\frac{L_{22}}{L_P} - \frac{L_{12}^2}{L_p^2}\right) = \frac{\bar{C}_S}{L_P}\left(L_P L_{22} - L_{12}^2\right) \tag{52}$$

Eq. (52) shows that the solute flux is formed by two contributions: one associated with the volume flux and the other associated with the osmotic pressure difference.

Eqs. (49) and (51) indicate that transport across a membrane is characterised by three transport parameters, which can be determined experimentally. The hydrodynamic permeability L_p can be obtained from Eq. (49) by experiments with pure water because in this case the osmotic pressure difference is zero and there is a linear relationship between the hydrodynamic pressure, ΔP, and the volume flux, J_v, while L_p represents the slope of the corresponding flux-pressure curve. The solute permeability ω and the reflection coefficient σ can be obtained from Eq. (51), which is rewritten for diluted solutions in the form:

$$\frac{J_S}{\Delta C_S} = \frac{\bar{C}_S}{\Delta C_S}(1-\sigma)J_V + \omega RT \tag{53}$$

In this way, by plotting $J_S/\Delta C_S$ vs. $\bar{C}_S/\Delta C_S$, the solute permeability ω may be obtained from the ordinate intercept and the reflection coefficient from the slope of the fitting straight line.

For an ideal semi-permeable membrane, Eqs. (49) and (51) become

$$J_V = L_P(\Delta P - \Delta\Pi)$$
$$J_S = \omega \Delta\Pi \tag{54}$$

The last equation is usually written as

$$J_S = K\frac{D_S}{d}\left(C_S^{(2)} - C_S^{(1)}\right) \tag{55}$$

where K is a characteristic coefficient of the system and D_s is the solute diffusion coefficient across the membrane, with a thickness d.

Eqs. (54) and (55) are used for membranes whose reflection coefficient is slightly lower than 1 and allow us to make predictions about the fluxes J_v and J_s across the RO membranes. As can be seen, J_v increases linearly with the applied pressure ΔP and takes a value of zero when $\Delta P = \Delta\Pi$ (osmotic equilibrium). Usually, under common working conditions, the salt flux is independent of the pressure difference established across the membrane. Fig. 2 illustrates this behaviour for a high-performance RO membrane (FT30, FilmTec), used with water containing 3.5% sodium chloride (which it is often used as a model for seawater) where the water flux product and the salt flux are shown vs. the applied pressure.

2.4. Two RO operative parameters

Permeate recovery rate and salt rejection — Permeate recovery, also called the conversion rate, is one of the most important parameters in the design and operation on RO systems [9], and can be defined in terms of the product water flow rate ($Q_v = J_V \cdot A$ where A is the active area of the membrane) and feed water flow (Q_f), as follows:

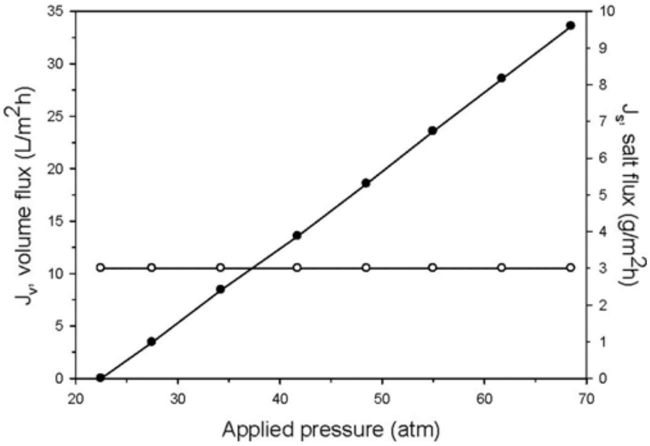

Fig. 2. Water (●) and salt (○) fluxes vs. applied pressure for high-performance RO membrane FT30 (Film.Tec) in water containing 3.5% sodium chloride.

$$R = \left(\frac{Q_v}{Q_f}\right) \times 100 = \left(\frac{Q_v}{Q_v + Q_c}\right) \times 100 \tag{56}$$

where $Q_c = Q_f = Q_v$ is the concentrate flow rate.

On the other hand, the salt rejection coefficient of the membrane, S, shows the membranes capacity for rejecting salt and is defined as a percentage [10], as follows:

$$S = (1 - SP) \times 100 = \left(1 - \frac{C_S^{(2)}}{C_S^{(1)}}\right) \times 100 \tag{57}$$

where SP is the salt passage defined as the ratio of the concentration of salt on the permeate side of the membrane relative to the average feed concentration. For an ideal permselective membrane $C_s^{(2)} = 0$, and so $S = 100\%$, while for a completely non-selective membrane $C_s^{(2)} = C_s^{(1)}$ and so $S = 0$. The volume flux J_v increases with the applied pressure, ΔP, while the salt flux remains unchanged; $C_s^{(2)}$ decreases with ΔP and consequently S increases. Salt rejection coefficient is an important performance parameter in RO membranes since it determines the suitability of given membranes for various applications [10].

3. Conclusions

We report on the deduction-based non-equilibrium thermodynamics of basic equations for desalination in RO processes, giving the volume flux and salt flux through membranes. We started from the linear phenomenological equations for the transport established by TIP at not far from equilibrium conditions, relating generalized fluxes and driving forces. Afterwards, the equations were applied to the transport processes through a selective membrane in contact with two aqueous binary electrolyte solutions with the same electrolyte at different concentrations when differences in both hydrostatic pressure and electric potential are applied through the membrane. In this way, the phenomenological Eqs. (38) were obtained for the volume flux, the diffuse flux of solute respect to the solvent and electric current. These equations allow us a new formalization for the phenomenological behaviour of the membrane system in RO processes, described by Eqs. (43), giving the volume flux and salt flux as functions of applied pressure difference and osmotic pressure difference between the inlet and outlet streams.

Finally, these flux equations were transformed to present their habitual forms shown in Eqs. (49) and (50), which are utilized for the analysis and design of the RO desalination processes. These equations involve the transport coefficients (hydraulic permeability, L_p, and osmotic permeability ω) so as the reflection coefficient (σ) characterizing the non-ideal behaviour of the membranes. All these parameters can be determined experimentally.

4. Symbols

A — Active area of the membrane, m^2
a_i — Activity of component i
C_s — Salt concentration, mol/m^3
D_s — Solute diffusion, m^2/s
d — Membrane thickness, m
I — Electric current density, A/m^2
J_i — Flux of i-th component, mol/m^2 s
J_2^* — Excess of anionic flux with respect to salt flux, mol/m^2 s
J_2^{**} — Anionic flux in correspondence with the salt flux, mol/m^2 s
J_s — Salt flux, mol/m^2 s
J_1 — Cation flux, mol/m^2 s
J_2 — Anion flux, mol/m^2 s
J_3 — Water flux, mol/m^2 s
J_v — Volume flux, m^3/m^2 s
J_D — Diffusive flux, m/s
L_{ij} — Phenomenological coefficients linking flux J_i and generalized force χ_j, mol^2/J m s
L_p — Hydrodynamic permeability, m^3/m^2 s Pa
n_i — Number of moles of component i
P — Hydrostatic pressure, Pa
P^* — Standard pressure, Pa
Q_c — Concentrate flow rate, m^3/m^2 s
Q_f — Feed water flow, m^3/m^2 s
Q_v — Water flow rate, m^3/m^2 s
R — Conversion rate
S — Rejection coefficient of the membrane
S_{int} — Internal entropy, J/K
SP — Salt passage
T — Temperature, K
V_i — Partial molar volume of component i, m^3/mol
V — Volume, m^3
v_s — Solvent speed with respect to membrane, m/s
v_3 — Water speed with respect to membrane, m/s
v_+ — Stoichiometric numbers of cation in the salt formula
v_- — Stoichiometric numbers of anion in the salt formula
X_i — Molar fraction of component i
z_i — Valence of component I

Greek

$\Delta\phi_m$ — Membrane potential, V
$\Delta\phi_N$ — Nerstian contribution of the electrode potential, V
$\Delta\mu_s$ — Difference of chemical potential for the solute in the membrane, V
$\Delta\mu_3$ — Difference of chemical potential for the water in the membrane, V
ΔP — Applied pressure, Pa
$\Delta\Pi$ — Osmotic pressure difference, Pa
χ_i — Conjugate generalized force of the flux J_i, J/m mol
Φ — Dissipation function, J/s
ϕ — Electrical potential, V
γ_i — Activity coefficient of component i
μ_I — Electrochemical potential of component i, J/mol
$\Delta\mu_i^l$ — Chemical potential of component i in liquid phase, J/mol
$\Delta\mu_i^{1,0}$ — Chemical potential of component i in standard state, J/mol
σ — Reflection coefficient
ω — Osmotic permeability, mol/m^2 s Pa

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