

On boundary layers and the attenuation of driving forces in forward osmosis and other membrane processes

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Abstract

Concentration polarization refers to the emergence of concentration gradients at a membrane/solution interface resulting from selective transfer through the membrane. The link between this natural consequence of permselectivity and the attenuation of driving forces across the active layer of the membranes themselves is explored for a range of selected membrane processes. Common features are highlighted through use of the boundary layer Peclet number. It is shown for the first time that one of the unique features of forward osmosis (FO) is that owing to the reverse salt flux there is a maximum Peclet number. There are two paradigmatic approaches for modelling flux, one uses the overall driving force (in which case allowance for osmotic effects are expressed as additional resistances) and the other uses the net driving force across the separating layer or fouled separating layer. In FO the effective driving force, even in the absence of fouling, is limited by concentrative and dilutive concentration polarization and by reverse salt diffusion. Having expressed these as additional resistances, their relative importance is established. Comments on other forms of polarization, such as so-called temperature polarization, are included. An interesting link is made between the temperature polarization coefficient and its FO equivalent.

Key words: concentration polarization; pervaporation; forward osmosis; membrane distillation; temperature polarization

Highlights:

Proof that there is a limiting Peclet number in forward osmosis

Quantification of the relative resistances in forward osmosis

Unified equation for forward osmosis

Introduction of Osmotic Difference Reduction Coefficient (ORC) to parallel TPC

1. Overview

It an issue in honour of Professor Tony Fane it is appropriate there is a contribution analysing the influence of boundary layer mass transfer upon performance. Trained as a chemical engineer Tony has brought these skills and many others to the field of membrane science and technology, and has contributed from the early days when the whole of the membrane field could be classed as an emerging technology. His first contributions to Journal of Membrane Science and to Desalination, though not his first contributions to membrane science, were respectively on membrane surface pore characteristics and flux through ultrafiltration membranes, and factors affecting flux in crossflow filtration [1,2]. Herein we do not link directly with these papers but concentrate upon various aspects of transport phenomena and include diverse processes such as forward osmosis (FO) and membrane distillation (MD). As early as 1978 he was instrumental in introducing into the field of MD the concept of Temperature Polarisation Coefficient (TPC) which, as we note later, has been a most influential concept [3].

In the next section we start by examining concentration polarization effects in ultrafiltration and pervaporation and introduce the dimensionless Peclet number. This term was used most effectively by Wijmans et al [4] in their analysis to explain why boundary layer effects are much more severe in pervaporation than in ultrafiltration. We note *en passant* that they refer in their abstract to "... is dominated by boundary layer effects (concentration polarization)" and this is mentioned to emphasize that the phenomena of concentration polarization relate to a boundary layers and we advance our analysis when we link it to the rich literature on transport phenomena as exemplified by Zydney's [5] analysis of the stagnant film model for concentration polarization in membrane systems.

Having introduced previous work that used the Peclet number, the equations of Forward Osmosis are developed with Peclet numbers for the draw and feed sides. The overall driving force is not manifest across the membrane due to four adverse effects. These are fouling (which is not considered in this paper), concentrative concentration polarization on the feed side, dilutive concentration polarization on the draw side and reverse salt diffusion. The main objective of the paper is to show that there is a maximum Peclet number to mitigate the effects of concentration polarization. Comment is also made on the two paradigmatic approaches for modelling flux; one uses the net driving force across the separating layer or fouled separating layer and the other uses the overall driving force. In the latter case, allowance for osmotic effects are expressed as additional resistances. By developing the latter approach, the question "Where is the attenuation of the driving force in FO greatest?" is addressed. Lastly there is a digression on the meaning of 'polarization' and polarization coefficients and the concept of Osmotic Difference Reduction Coefficient (ORC) is introduced to parallel TPC.

2. Introduction to Concentration Polarization in Ultrafiltration and Pervaporation

For both microfiltration and ultrafiltration (UF) the separation is achieved through a basic sieving mechanism, with rejection of molecules whose size is greater than that of the pores. Due to concentration polarization the concentration at the membrane surface is elevated above that of the bulk feed and, as noted in a seminal paper by Bhattacharya and Hwang [6], this can cause a substantial reduction in separation factor and flux. They developed a generalised approach relating the modified Peclet number to concentration polarization occurring in the boundary layer and showed that it was applicable to a wide range of membrane processes including reverse osmosis, ultrafiltration, gas separation and pervaporation. The reason they referred to J/k_{bl} as the modified Peclet number was because they wanted to distinguish it from the conventional Peclet number. Now the fundamental definition of the Peclet number is:

$$Pe = \frac{\text{Convective fluid velocity}}{\text{Diffusive velocity}}$$

and one needs to distinguish between the bulk convective velocity outside of the boundary layer (taken to be the crossflow velocity), U , and the convective velocity within the boundary layer perpendicular to the membrane surface. The latter is generated by the total membrane flux and is taken herein to be equal to the volumetric flux, J . The conventional Peclet number would use U and the modified or boundary layer one uses J . The Peclet number used herein is the modified Peclet number that is also referred to as the boundary layer Peclet number. Both the conventional Peclet number and the modified Peclet number are important because the former plays a role in determining the concentration polarization boundary layer thickness and the latter characterizes the boundary layer mass transfer coefficient.

Herein a lumped parameter approach is taken to the modelling of the concentration boundary layer and it is assumed that a constant value k_{bl} characterises the boundary layer mass transfer coefficient. However this is recognised to be an approximation because the boundary layer thickness is not constant [6]. However this is justifiable on the basis that the models combine a straightforwardness of application to a range of membrane processes, with the production of insightful results. Those interested in fundamental approaches should consult Romero and Davis [7]. As this special issue is in honour of Tony Fane it is also appropriate to mention a recent paper [8] which includes an interesting mass transfer analysis in section 3.4 of that paper albeit not an analysis involving Peclet numbers.

As noted above, owing to concentration polarization the concentration at the membrane surface is elevated above that of the bulk feed. As shown elsewhere (e.g. [9]) the relationship is:

$$C_m = (C_b - C_p) \exp(Pe) + C_p \quad (1)$$

where Pe is the boundary layer Peclet number and is defined as J/k_{bl} . J is the volumetric flux through the membrane and k_{bl} is the boundary layer mass transfer coefficient. Now if intrinsic enrichment factor is defined as $E_0 = C_p/C_m$ one obtains Eq. (5) as derived by Wijmans et al [4] but at this stage it is simply noted that the concentration adjacent to the pores is elevated which for macromolecules will elevate the osmotic pressure. Thus the effective pressure difference across a pore is the bulk pressure difference (ΔP) less the osmotic pressure difference, $\Delta\pi$, where $\Delta\pi$ is the osmotic pressure difference between that at the feed side adjacent to the mouths of the pores and that on the permeate side.

In UF the osmotic pressure on the permeate side will be close to zero but that on the feed side at the entrance to the pores will be many times greater than that of the feed itself due to the elevation in concentration as given by Eq. (1). The term $\Delta P - \Delta\pi$ represents the driving force across the membrane *itself*. In the absence of any fouling, the following equation is often preferred to describe the volumetric flux, J .

$$J = \frac{\Delta P - \Delta\pi}{\mu R_m} \quad (2)$$

where R_m is the empirically measured membrane resistance and μ is the dynamic viscosity of the permeate. The inclusion of the dynamic viscosity of the permeate, μ , as a separate term (as opposed to its inclusion within R_m) is to be preferred because viscosity is temperature dependent. The separate term R_m is then a constant for a given structure. The reciprocal of the term μR_m is known as permeability but it is clearly temperature dependent. So if it is used the temperature at which it is evaluated must be given. If the flux of pure solvent is being measured then the term $\Delta\pi$ is zero, and ΔP is simply the transmembrane pressure, TMP.

An alternative to Equation (2) is to relate the flux to the overall driving force between the bulk fluid on one side and bulk fluid on the other side, and the sum of the resistances in between. With this approach one has to ascribe a resistance of the concentration polarisation layer, R_{cp} , and this gives:

$$J = \frac{\Delta p}{\mu(R_m + R_{cp})} \quad (3)$$

It was shown by Wijmans et al in an earlier paper [10] that the two expressions, (2) and (3) are thermodynamically equivalent with the concentration boundary layer impeding the flow of the solvent and thus “consuming” part of the overall driving force. Further consideration of these two alternative approaches is made in section 4.

It is now shown that dilutive and concentrative concentration polarisation have a common basis as first shown in the 1990's. The key work was by Wijmans et al [4] who presented a rigorous treatment of concentration polarization using the resistances-in-series model. The resulting general expression is valid for compounds that are enriched in the permeate as well as for compounds that are depleted in the permeate. An intrinsic enrichment factor was defined:

$$E_0 = C_p/C_m \quad (4)$$

where C_p is the concentration of the minor component in the permeate and C_m is the concentration of that component at the membrane surface. The intrinsic enrichment factor is large and positive for pervaporation where the minor component is enriched in the permeate but for reverse osmosis (RO) and ultrafiltration (UF) there is rejection of the minor component so E_0 is typically in the range 0.001 to 0.1 (i.e 90% to 99.9% rejection). The expression for the concentration polarization modulus (defined as C_m/C_b where C_b is the concentration of the component of interest in the bulk) is a useful measure of the extent of concentration polarization. This ratio is equal

$$\frac{C_m}{C_b} = \frac{\exp(Pe)}{1 + E_0[\exp(Pe) - 1]} \quad (5)$$

where Pe is defined as J/k_{bl} , J being the volumetric flux through the membrane and k_{bl} being the mass transfer coefficient describing diffusive transport in the boundary layer. The variation of the extent of concentration polarization with Pe and E_0 is shown in Figure 2 and Figure 1 gives a schematic to illustrate the concentration polarization phenomena. It should be noted that the concentration profiles depend on the value of C_p relative to C_b . Figure 3 clearly demonstrates why concentration polarization effects are more severe in pervaporation than in UF and RO. In pervaporation, the concentration of solute at the membrane surface is often one-tenth or less of the concentration in the bulk solution because of the huge dilutive concentration polarization effect and therefore the driving force across the membrane is greatly reduced compared with its nominal value.

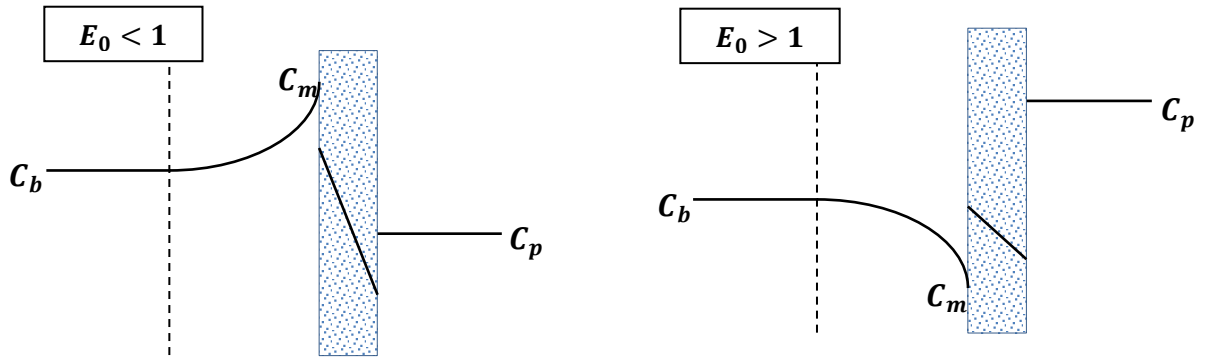


Figure 1 Schematic of the two types of concentration polarization phenomena. The type of concentration profile formed depends upon whether $E_0 < 1$ (the phenomenon is concentrative) or whether $E_0 > 1$ (the phenomenon is dilutive). Between the bulk feed solution (the region of constant C_b) and the membrane there is the mass transfer boundary layer - the region in which concentration is said to be polarized.

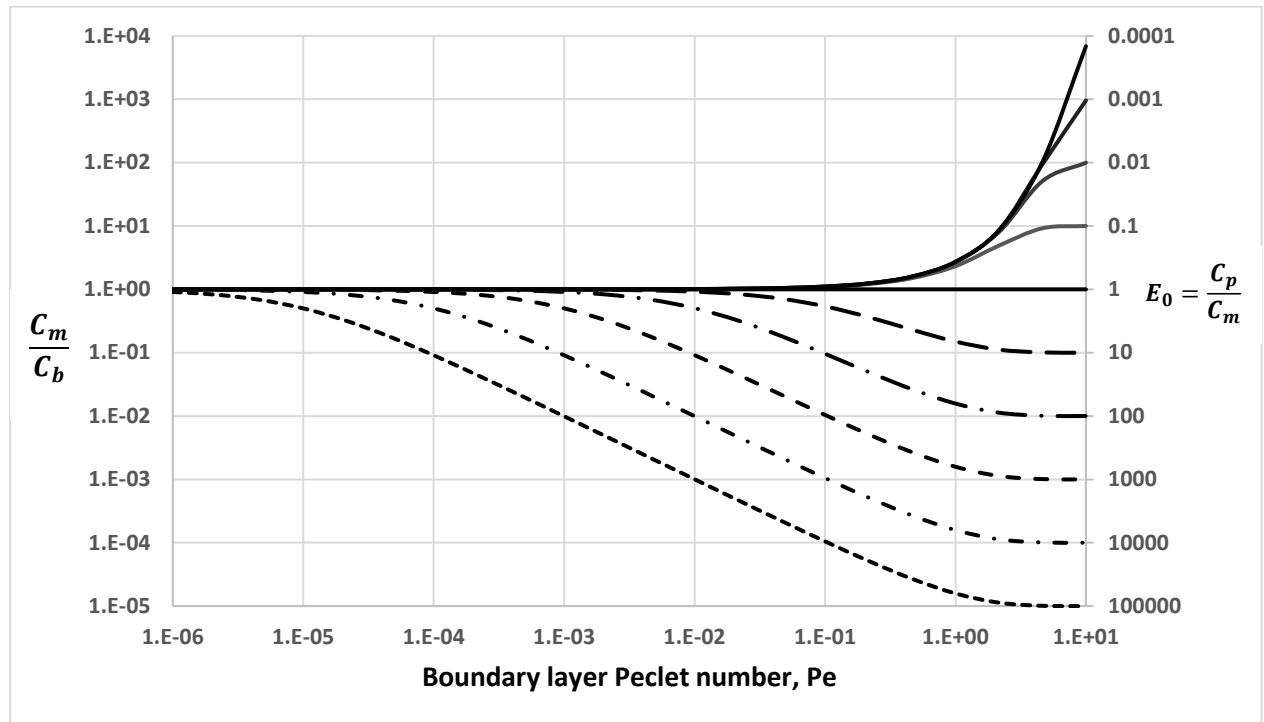


Figure 2: Concentration polarization modulus, C_m/C_b , as a function of Boundary layer Peclet number $Pe (=J/k_{bl})$ for a wide range of values of the intrinsic enrichment factor E_0 . Lines calculated from Eq. (5). The solid lines are for components that are rejected (i.e. the values of E_0 are less than unity) and there is concentration of these component in the concentration boundary layer. The dashed lines are for the components that are enriched in the permeate ($E_0 > 1$); there is dilution of these components in the boundary layer. Adapted from Wijmans et al [4].

As shown in Figure 2 the compounds that are enriched by the membrane ($E_o > 1$) are more affected by the resulting dilutive concentration gradients at a membrane/solution interface, resulting from selective transfer of the minor component (or components) through the membrane, than compounds that are rejected by the membrane ($E_o < 1$). Rejection gives rise to concentrative polarisation. To place the results in context one needs to establish typical values of Pe . Figure 3 shows that pervaporation (e.g. its application to the removal of VOCs from water using organophilic membranes) is strongly affected by concentration polarization at even low values of the Peclet number. The implication is that pervaporation systems should therefore be designed and operated to achieve excellent levels of boundary layer mass transfer.

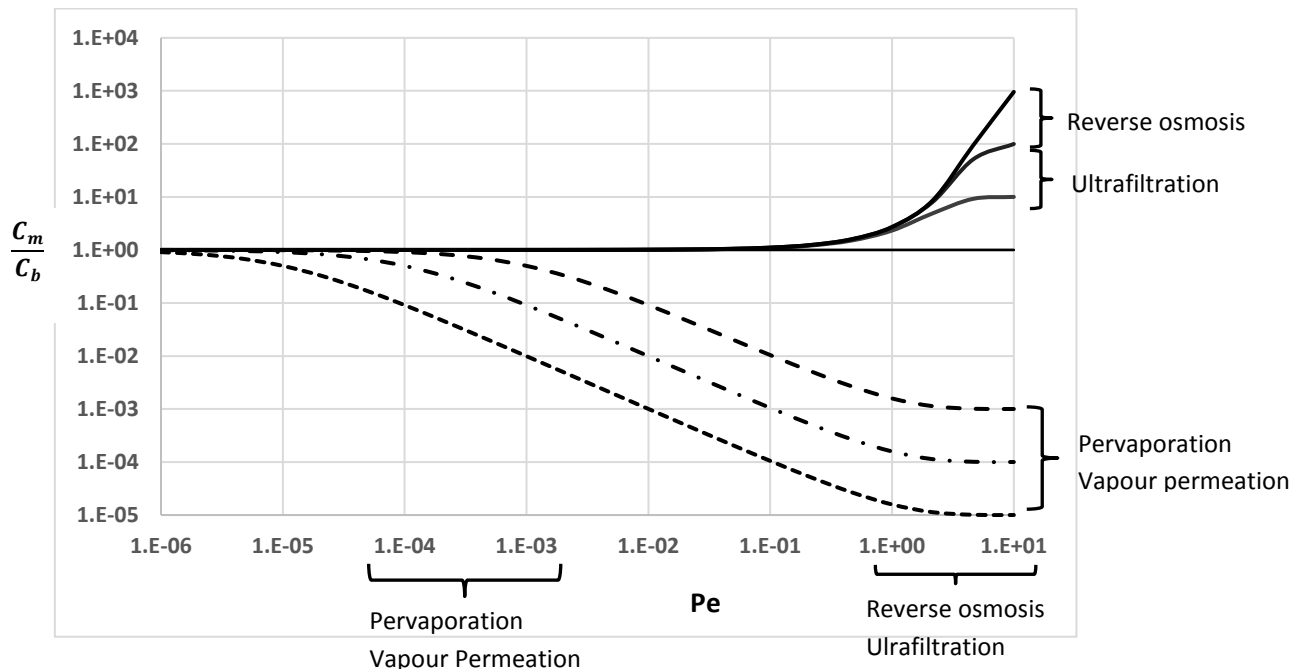


Figure 3: Illustration of the differing impact of concentration polarization depending upon the membrane process involved. For RO and UF the effect of concentration polarisation is concentrative; for pervaporation and vapour permeation (e.g. VOC recovery) it is dilutive and the effect is significant even at low values of the boundary layer Peclet number. Adapted from Wijmans et al [4].

3. Concentration Polarization in Forward Osmosis

In section 2 it was recalled that the effect of concentration polarization is much more severe in pervaporation than in ultrafiltration and reverse osmosis. Given that Forward Osmosis systems involve both dilutive and concentrative concentration polarization it is useful to undertake an equivalent analysis. In FO there is reverse salt diffusion i.e. diffusion of salt from the draw solution to the feed solution which is in the opposite direction to the main volumetric flux and as shown below there is not

an exact parallel with Figure 2

In a recent paper Field *et al* [11] presented a pair of equations relating flux, 'A', 'B' and the mass transfer coefficients k_{ca} and k_{sup} where the mass transfer coefficient, designated as k_{sup} , is the combined mass transfer coefficient for the support layer itself and the adjacent external mass transfer layer. The mass transfer coefficient for the support layer itself can be written as D/S where D is the diffusivity of salt in water (it has a moderate dependency upon concentration [12]) and S is the structural parameter, defined as the product of the support layer thickness and tortuosity over its porosity [13]:

$$S = t \cdot \tau / \varepsilon \quad (6)$$

$$\text{Thus} \quad \frac{1}{k_{sup}} = \frac{1}{k_{csup}} + \frac{S}{D} \quad (7)$$

where k_{csup} is for the channel adjacent to the support. For the channel adjacent to the active layer, its mass transfer coefficient is k_{ca} . Thus for the AL-FS orientation the expression is:

$$J_w = A \left[\pi_{ds} \exp\left(-\frac{J_w}{k_{sup}}\right) - \pi_f \exp\left(\frac{J_w}{k_{ca}}\right) \right] + B \left[\exp\left(-\frac{J_w}{k_{sup}}\right) - \exp\left(\frac{J_w}{k_{ca}}\right) \right] \quad (8)$$

For the AL-DS orientation:

$$J_w = A \left[\pi_{ds} \exp\left(-\frac{J_w}{k_{ca}}\right) - \pi_f \exp\left(\frac{J_w}{k_{sup}}\right) \right] + B \left[\exp\left(-\frac{J_w}{k_{ca}}\right) - \exp\left(\frac{J_w}{k_{sup}}\right) \right] \quad (9)$$

These equations are fully consistent for those for FO found elsewhere e.g. [14] but are presented in a manner which avoids the use of an overall mass transfer coefficient. Now Peclet numbers are introduced. For AL-FS, $Pe_{draw} = \frac{J_w}{k_{sup}}$ and $Pe_{feed} = \frac{J_w}{k_{ca}}$ whilst for AL-DS $Pe_{draw} = \frac{J_w}{k_{ca}}$ and $Pe_{feed} = \frac{J_w}{k_{sup}}$. Thus a unified relationship can be presented in Eq. (10). In moving from Equations (8) and (9) to Eq. (10) the opportunity has been taken to invert the terms in the second square bracket so that both of the terms in square brackets are positive. This format emphasizes that reverse salt diffusion reduces water flux.

$$J_w = A \left[\pi_{ds} \exp(-Pe_{draw}) - \pi_f \exp(Pe_{feed}) \right] - B \left[\exp(Pe_{feed}) - \exp(-Pe_{draw}) \right] \quad (10)$$

With AL-FS orientation $Pe_{draw} < Pe_{feed}$ and the converse holds for AL-DS. If the flux is 3 $\mu\text{m/s}$ and $k_{ca} = 10^{-5}$ m/s and $k_{sup} = 3 \times 10^{-6}$ m/s, $Pe_{feed} = 0.3$ and $Pe_{draw} = 1$ for AL-FS orientation

On the draw side, the concentration of the bulk draw solution is defined as C_{ds} and the concentration adjacent to the separating layer of the membrane as C_m . On the feed side, the concentration of the bulk feed solution is defined as C_f and the concentration adjacent to the separating layer of the membrane as C_i . The resulting expressions for the concentration polarization moduli are as follows.

$$\frac{C_m}{C_{ds}} = \exp(-Pe_{draw}) + \frac{B}{A\pi_{ds}} [\exp(-Pe_{draw}) - 1] \quad (11)$$

$$\frac{C_i}{C_f} = \exp(Pe_{feed}) + \frac{B}{A\pi_f} [\exp(Pe_{feed}) - 1] \quad (12)$$

The variation of the moduli with Peclet number is given in Figure 4. To determine the moduli one needs to estimate Pe_{draw} and Pe_{feed} and have knowledge of the membrane properties. Typical values were used for solid lines in Figure 4. It is seen that there is a sudden drop in C_m/C_{ds} and shortly this

will be associated with C_m approaching zero.

In the limit as the barrier layer of the membrane offers no resistance itself $C_m \rightarrow C_i$. In this limit the maximum flux can be obtained by solving the following equation:

$$C_{ds} - C_f \exp(Pe_{\text{draw}} + Pe_{\text{feed}}) = \frac{B}{A\beta RT} [\exp(Pe_{\text{draw}} + Pe_{\text{feed}}) - 1] \quad (13)$$

This places an upper estimate upon the maximum possible value of J_w . It can be calculated from the following equation:

$$(Pe_{\text{draw}} + Pe_{\text{feed}})_{\text{max}} = \text{LN} \left(\frac{C_{ds} + B/A\beta RT}{C_f + B/A\beta RT} \right) \equiv \text{LN} \left(\frac{\pi_{ds} + B/A}{\pi_f + B/A} \right) \quad (14)$$

From (14) it is clear that in FO mode with $k_{\text{sup}} \ll k_{\text{ca}}$, and with $C_d \gg C_f$ that

$$Pe \text{ (max)} = \text{LN} \left(1 + \frac{A\pi_{ds}}{B} \right) \quad (15)$$

The dashed lines in Figure 4 have $B=0$. The sudden drop in C_m/C_{ds} occurs as C_m approaches small values and in the limit zero. This places an upper estimate upon the maximum possible value of Pe for the draw side in FO mode, even if the feed side adjacent to the active layer had conditions that approached those of a perfectly stirred reservoir.

The expressions for the concentration moduli are more comprehensive than those presented in earlier works (e.g. McCutcheon and Elimelech [15]) because allowance has been made for the salt leakage. As shown in Figure 5 the relative contribution of the second term to the first can be significant on the feed side for both orientations. The plot does not include the corresponding ratio for the draw side as the influence of reverse salt diffusion on this side of the membrane is insignificant at realistic Pe – see Figure 4.

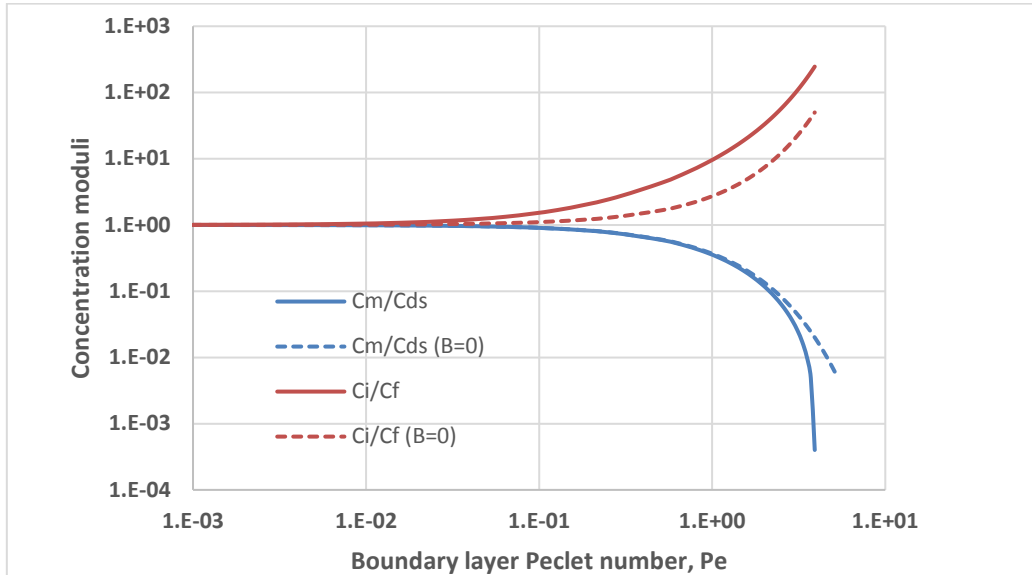


Figure 4: Variation of the concentration polarization moduli with boundary layer Peclet number. Solid lines drawn for $A = 2 \times 10^{-12}$ m/s per Pa; $B = 2 \times 10^{-7}$ m/s; $S = 350 \mu\text{m}$; $\pi_{ds} = 5 \text{ MPa}$; $\pi_f = 0.025 \text{ MPa}$.

Dashed lines are for same parameters except $B=0$.

This section has concentrated upon FO but the deduction that there is a maximum Peclet number to mitigate the effects of concentration polarisation in FO where concentration polarisation boundary layers are present on both sides of the membrane is also valid for pressure-retarded osmosis. This observation is made in the knowledge that Yaroshchuk [16] has recently claimed that for non-ideally semi-permeable supported membranes there could, under certain conditions, be no reverse solute diffusion and that correspondingly it would be technically possible to achieve unusually high power densities with a PRO process. It was envisaged that the power densities would exceed by one order of magnitude those previously achieved. However, the assumption that boundary layers can be neglected is, at best, highly problematic.

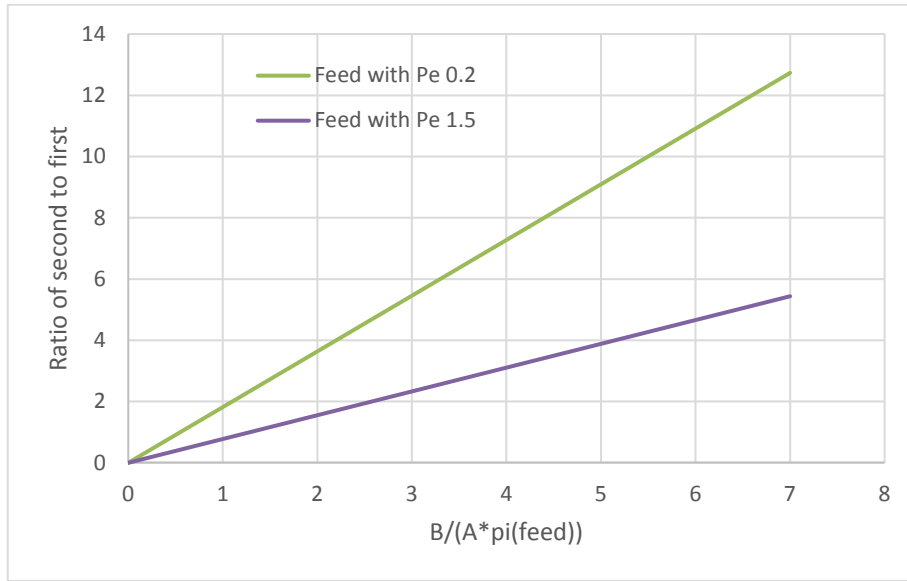


Figure 5: Variation of the second to the first term in Equation (12). The values of Pe have been chosen to give typical upper and lower bounds (1.5 and 0.2).

4. Relative Resistances in Forward Osmosis

Now in parallel to Eq. 3 the FO process is represented in Eq. (16) as having an overall driving force of $\pi_{ds} - \pi_f$ and four resistances. These are the membrane resistance R_m , the resistance due purely to concentration polarisation of the draw solution, R_{cpd} , the resistance due purely to concentration polarisation of the feed solution, R_{cpf} , and the additional resistance due to reverse salt diffusion.

$$J = \frac{[\pi_{ds} - \pi_f]}{\mu(R_m + R_{cpd} + R_{cpf} + R_{rsd})} \quad (16)$$

By using equations such as Eq. (17) the various terms can be established.

$$J = \frac{[\pi_{ds} - \pi_f \exp(Pe_{feed})] - \left(\frac{B}{A}\right)[\exp(Pe_{feed}) - \exp(-Pe_{draw})]}{\mu(R_m + R_{cpd})} \quad (17)$$

and

The reverse salt diffusion alters the concentrations at the interfaces and one might not conceive of it as an additional resistance but this model enables one to quantify the relative importance of the different contributions. The results (with the same values as those chosen for Figure 4) are shown in Figure 6.

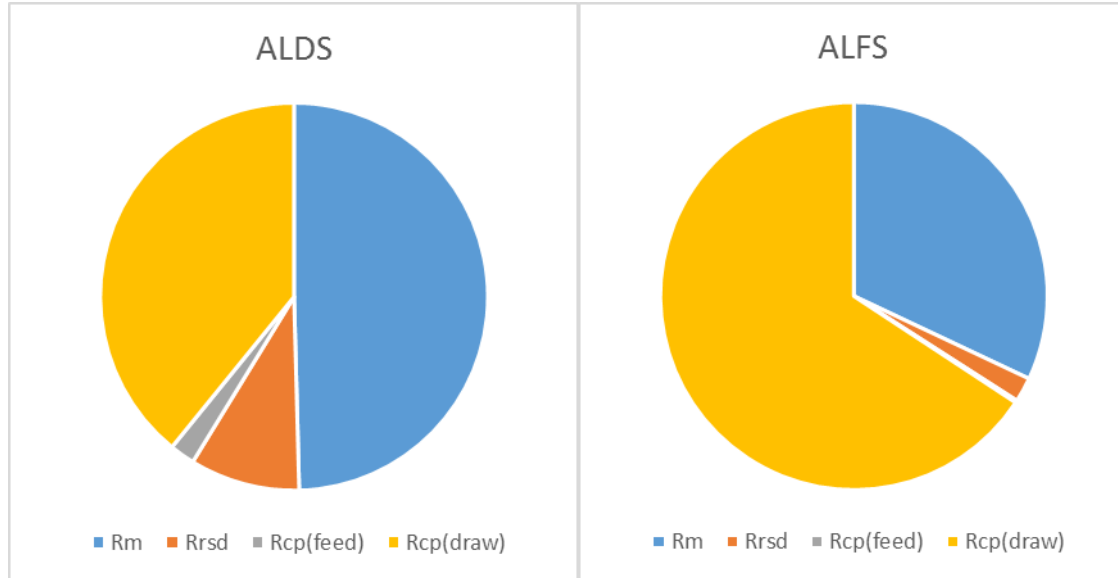


Figure 6: Illustration of the relative importance of the concentration polarization and reverse salt diffusion. Values calculated for $A = 2 \times 10^{-12}$ m/s per Pa; $B = 2 \times 10^{-7}$ m/s; $S = 350 \mu\text{m}$; $\pi_{ds} = 5 \text{ MPa}$; $\pi_f = 0.025 \text{ MPa}$.

As is well known, in the ALDS orientation the concentration polarization of the draw is reduced and thus $R_{cp(draw)}$ is reduced. In ALDS there is a higher concentration at the membrane surface and this leads to more reverse salt diffusion with the percentage contribution rising to 9%; in the ALFS orientation it was calculated to be only 2%. The contribution of $R_{cp(feed)}$ is very small in both cases.

5. Membrane Distillation and a digression on Polarization Coefficients

Outside science, polarization usually refers to how people think, especially when two views emerge that drive people into opposing camps. Within science, polarization is first met with regard to light, radiation, or magnetism moving in specific directions. Now when the concept of concentration polarization first emerged in the membrane field it was in the field of pressure driven membrane processes such as UF. With such processes one could identify a region of particular high concentration adjacent to the membrane and one of lower concentration in the bulk so there was a resonance between its use in membrane science and its use outside science. Indeed the 'gel' theory of ultrafiltration was popular in the early era [17] and here the concentrated region is considered to be a gel or close to a gel. Now with the recognition of dilutive concentration polarization probably first in dialysis, then in pervaporation and more recently in forward osmosis there has been a generalisation of what it means to have concentration polarization. Today the term refers to the emergence of concentration gradients at a membrane/solution interface resulting from selective transfer of some species through the membrane be it a minor species preferentially transferred (in which case there is dilutive concentration polarization) or if a minor species is preferentially retained it is concentrated within the mass transfer boundary layer. Whilst both are a natural consequence of permselectivity the link with the everyday use of the term polarized has been abandoned in order to have a unity of meaning within the field of membrane science.

In the field of MD there are other so-called polarization terms such as TPC and vapour polarization coefficient. One may ask how or whether these are related to the concentration moduli in Equations (11) and (12) or whether they are of a different nature. Putting it more controversially “Should the term Temperature Polarization Coefficient in the field of membrane distillation (MD) have been readily accepted?” Firstly, are any temperature profiles influenced by the flux of vapour through the membrane pores? Now it is certainly true that the permeate flux across the membrane in any MD system depends not only on the properties of the membrane (including pore size, pore size distribution, porosity and thickness of the membrane) but also on the heat transfer coefficients and the thermal conductivity of the membrane [18,19]. In the case of Direct Contact MD, the film heat transfer coefficients for both the feed side and the permeate side are important, as illustrated in Figure 7.

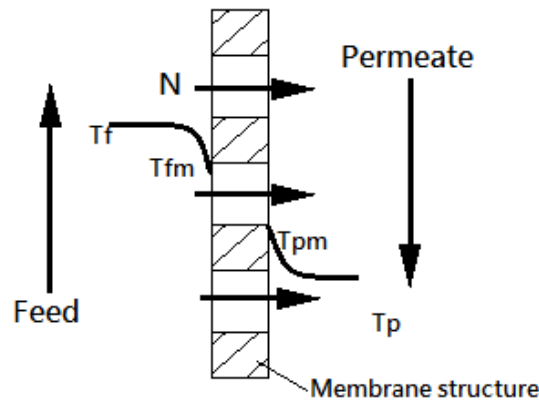


Figure 7 Schematic illustration of the transfer processes across a direct contact MD membrane. Source [20]

Consider a small section of a module. There are three expressions for the heat flux. The one for the membrane has two terms because there is heat conduction through the solid material as well as heat convection through the pores. Then there is one relating to the flow of heat to the membrane from the bulk feed and one for the flow of heat from the membrane to the bulk permeate. The flux through the membrane is N and the other symbols have their standard meaning.

$$Q = Q_c + N\lambda \quad (18)$$

$$Q = h_f(T_f - T_{fm}) \quad (19)$$

$$Q = h_p(T_{pm} - T_p) \quad (20)$$

The temperature across the membrane pores is $T_{fm} - T_{pm}$ which is less than the bulk difference $T_f - T_p$ and thus the driving force for transport is reduced. In order to give an indication of the significance the reduction the term temperature polarisation coefficient (TPC) was invented [3], where

$$TPC = \frac{T_{fm} - T_{pm}}{T_f - T_p} \quad (21)$$

Now this term is simply a temperature difference correction factor linking the readily measured temperature difference, $T_f - T_p$, to the actual temperature difference across the membrane pores, $T_{fm} - T_{pm}$. Building upon the work of Fane [3] others have suggested that as the transport of vapour is proportional to a difference in vapour pressure one should define a vapour pressure polarization coefficient, ϕ [21,22],

$$\varphi = \frac{\Delta p_{w,m}}{\Delta p_{w,b}} = \frac{P_{fm} - P_{pm}^o}{P_{fb} - P_{pb}^o} \quad (22)$$

where $\Delta p_{w,b}$ is the externally applied bulk driving force (i.e. bulk water vapour pressure difference) and $\Delta p_{w,m}$ is the water vapour pressure difference across the pores between the feed and permeate interfaces.

It cannot be said that a result of selective transfer of vapour through the pores has been the emergence of temperature gradients at a membrane/solution interface because in the absence of transport through the pores there would still be heat transfer across the membrane. Indeed from a simple development of an earlier analysis [20], which is appropriate for modest temperature differences across the membrane, it can be shown that TPC depends upon properties of the membrane, its thickness and the external heat transfer coefficients. Flux *per se* does not feature in the equation:

$$TPC = \frac{T_{fm} - T_{pm}}{T_f - T_p} = \frac{K_{eff}}{K} = 1 / \left(1 + \frac{k_o}{\delta U_L} + \frac{C\lambda}{\delta U_L} \right) \quad (23)$$

$$\text{where } U_L = \left(1/h_f + 1/h_p \right)^{-1} \quad (24)$$

It is suggested that there is no parallel with concentration polarization. Rather TPC captures the reduction in driving force; its resonance over the last 30 years stems from the fact that it straightforwardly draws attention to the fact that the actual driving force across the membrane is less than the nominal one. An appropriate link with FO is considered in the Discussion.

6. Discussion

Essentially the paper has considered two areas. Firstly there was the implicit comparison of concentration polarisation moduli as found in FO with those in UF and PV. An outcome of the FO analysis was the unified relationship in Eq. (10).

$$J_w = A[\pi_{ds} \exp(-Pe_{draw}) - \pi_f \exp(Pe_{feed})] - B[\exp(Pe_{feed}) - \exp(-Pe_{draw})] \quad (10)$$

where for AL-FS, $Pe_{draw} = \frac{J_w}{k_{sup}}$ and $Pe_{feed} = \frac{J_w}{k_{ca}}$ whilst for AL-FS $Pe_{draw} = \frac{J_w}{k_{ca}}$ and $Pe_{feed} = \frac{J_w}{k_{sup}}$.

From this it was deduced (Eq. (14)) that for given feed and draw solutions (and fixed A and B parameters) that there is a maximum value of the sum ($Pe_{draw} + Pe_{feed}$) and hence a maximum value of flux for given values of the mass transfer coefficients. In FO mode with $k_{sup} \ll k_{ca}$, and with $C_d \gg C_f$ the interesting finding was that the boundary layer Peclet number would have a maximum value given by:

$$Pe \text{ (max)} = \text{LN} \left(1 + \frac{A\pi_{ds}}{B} \right) \quad (15)$$

Secondly we considered the so-called polarization coefficients that are used in MD. Personally whilst noting the influence of the TPC term (and by implication its acceptance and usefulness) it is suggested that mass transfer and thermal boundary layers do not need new names just because they are being applied to membrane systems *unless* a feature special to membrane systems is being captured through use of the term. Both usages of the term concentration polarization do capture a feature unique to membrane systems and indeed Eq. (5) covers both concentrative and dilutive concentration polarization. Thus it would be perverse not to include the latter as well as the former within the framework of concentration polarization.

After 30 years it is unlikely that the term TPC will be renamed although in retrospect it is a pity that it was not labelled temperature difference reduction coefficient or TRC for short. Care in the definition of terms can often tease out subtleties that are important; we have in mind the evolution of the concept of a threshold flux [23] which is distinct from critical flux and sustainable flux. Here having reflected upon TPC for MD, it is suggested that for FO there is a parallel concept, namely that of Osmotic Difference Reduction Coefficient (ORC) might usefully be introduced where ORC is defined as:

$$\text{ORC} = \frac{J_w(\text{actual})}{J_w(\text{ideal})} = \frac{[\pi_{ds}\exp(-Pe_{\text{draw}}) - \pi_f\exp(Pe_{\text{feed}})] - \left(\frac{B}{A}\right)[\exp(Pe_{\text{feed}}) - \exp(-Pe_{\text{draw}})]}{\pi_{ds} - \pi_f} \quad (25)$$

Equation (25) takes into account the influence of reverse salt diffusion and represents the overall effect and, unlike the pie charts in Figure 6, this does not break down the losses to be attributed to the draw side and feed side boundary layers, and to that associated with the reverse salt diffusion. Rather ORC reflects the ratio of the actual outcome to the ideal outcome. If the 'Rm' sectors in Figure 6 were expressed as a fraction of the whole, then they would equate to the ORC values given by Eq. (25).

7. Concluding Remarks

Others [4,6-7] have previously shown that in expressing the effects of concentration polarization it is useful to introduce the concept of a boundary layer Pelet number which has also been defined in the past as the 'modified Peclet number'. Herein it was shown that the concentration polarization moduli in FO display slightly different characteristics to those derived for UF and PV. In particular, it was shown that owing to the reverse salt flux there is a maximum Peclet number in FO. In general, there is limit upon the sum of the Peclet numbers for the draw side boundary layer and for the feed side as given by:

$$(Pe_{\text{draw}} + Pe_{\text{feed}})_{\text{max}} = \text{LN} \left(\frac{C_{ds} + B/A\beta RT}{C_f + B/A\beta RT} \right) \equiv \text{LN} \left(\frac{\pi_{ds} + B/A}{\pi_f + B/A} \right) \quad (14)$$

In FO mode with $C_d \gg C_f$ and assuming that the lower mass transfer coefficient on the support side dominates (i.e. $k_{\text{sup}} \ll k_{\text{ca}}$) then

$$Pe(\text{max}) = \text{LN} \left(1 + \frac{A\pi_{ds}}{B} \right) \quad (15)$$

Secondly through a simple analysis it was shown that one can express the effects that attenuate the driving force in terms of additional resistances. Whilst this is not novel, to the best of our knowledge it has been applied to FO for the first time. In reflecting upon the true essence of TPC, which as discussed above does not reflect polarization *per se*, the equivalent term for FO was developed. Just as TPC represents a ratio of the actual to the ideal driving force so it is suggested that for FO the concept of Osmotic Difference Reduction Coefficient (ORC) might usefully be introduced where ORC is defined by Eq. (25).

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omenclature		
A	'A' parameter for water flux	m/s per Pa
B	'B' parameter for salt flux	m/s
C	solute concentration or Parameter used in Eq. (23) and defined fully in [20]	kg/ m ³ OR kg/ m. s K
D	diffusion coefficient	m ² /s
E_0	enrichment factor	
h	heat transfer coefficient	W/m ² K
k	mass transfer coefficient	m/s
K and K_{eff}	actual and overall MD mass transfer coefficients as used in [20]	kg/ m ² s K
k_o	thermal conductivity of membrane matrix	W/ m K
J	volumetric flux	m/s
N	mass flux across MD membrane	kg/ m ² s
P^0	saturated vapour pressure	Pa
Q	heat flux	J / s
R	resistance	m ⁻¹
S	structural parameter	m
t	thickness	m
T	temperature	K
U_L	heat transfer coefficient defined in Eq. (24)	W/m ² K
β	van 't Hoff factor	
δ	membrane thickness in MD analysis (consistent with nomenclature in [20])	m
ε	Porosity	
λ	latent heat of vaporization	J / kg
μ	dynamic viscosity	Pa.s
π	osmotic pressure	Pa
τ	tortuosity	
ΔP	transmembrane pressure difference	Pa
ΔT	difference in temperature	K
$\Delta \pi$	osmotic pressure difference across membrane	Pa
Pe	boundary layer (modified) Peclet number	
ORC	Osmotic difference Reduction Coefficient	
TPC	Temperature Polarisation Coefficient	
Subscripts		
b	bulk	
bl	Boundary layer	
c	convection	
ca	channel	
cp	concentration polarisation layer	
csup	channel on support side	
ds	draw side (bulk)	

f	feed (bulk)
fm	membrane surface on feed side
m	membrane OR Membrane surface
p	permeate side (bulk)
pm	membrane surface on permeate side
rsd	Reverse salt diffusion
sup	support side
w	water
Superscripts	
0	Pure water

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