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

Robert W. Field[a,*], Jun Jie Wu[b]

[a] *University of Oxford, Department of Engineering Science, United Kingdom*
[b] *Durham University, Department of Engineering, United Kingdom*

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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 paradigmic 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.

## 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 polarization 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 paradigmic 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 is expressed as additional resistances. By developing the latter approach, the question "Where is the attenuation of the driving force in FO

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[*] Corresponding author.
*E-mail address:* robert.field@eng.ox.ac.uk (R.W. Field).

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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 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, and 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:

$$C_m = (C_b - C_p)\exp(Pe) + C_p \tag{1}$$

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 ($\Delta P$) 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, $J$.

$$J = \frac{\Delta P - \Delta\pi}{\mu R_m} \tag{2}$$

where $R_m$ is the empirically measured membrane resistance and $\mu$ is the dynamic viscosity of the permeate. The inclusion of the dynamic viscosity of the permeate, $\mu$, 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 $\mu R_m$ 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 $\Delta P$ is simply the transmembrane pressure, TMP.

An alternative to Eq. (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 polarization layer, $R_{cp}$, and this gives:

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

It was shown by Wijmans et al. in an earlier paper [10] that the two expressions, Eqs. (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 concentration polarization and concentrative concentration polarization have a common basis as first shown in the 1990s. 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:

$$E_0 = C_p/C_m \tag{4}$$

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 equals:

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

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 Fig. 2 and Fig. 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 $C_b$. Fig. 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.

As shown in Fig. 2 the compounds that are enriched by the