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Approximation for modelling electro-osmotic mixing in the boundary layer of membrane systems

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ABSTRACT

A Computational Fluid Dynamics (CFD) model is used to compare the reliability and accuracy of the Helmholtz–Smoluchowski (HS) approximation against a one-dimensional charge density distribution (CD) solution of an electro-osmotic perturbation in a 2D membrane channel for reverse osmosis (RO). Electro-osmotic flow within the boundary layer is induced via the placement of a pair of electrodes parallel to the membrane surface and perpendicular to the bulk flow. Although this electrode configuration results in a two-dimensional electric field, the HS approximation considers only the electric field in the direction tangential to the membrane and not the normal component. The effect of the normal component of the electric field (E_y) on the flow field in the CD solution is compared against the solution using the HS approximation and it is found that the effect of E_y is minimal. Greater agreement between the CD solution and the HS approximation is found at higher bulk solute mass fractions, such as typically found on the membrane surface in RO systems. The relationships between cross-flow velocity, perturbation velocity and mixing are explored.

1. Introduction

Membrane operations have emerged as an important industrial separation technique since the breakthrough achieved by Loeb and Sourirajan in the development of asymmetric cellulose acetate membrane for sea water demineralisation [1]. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes are widely utilised in water treatment and desalination operations. Hollow fibre and spiral wound membrane (SWM) modules are the most common commercially available membrane modules. The latter dominate for RO and NF due to their good balance between ease of operation, fouling control, permeation rate and packing density [2].

One of the major problems encountered in membrane modules is the concentration polarisation that causes a decrease in the flux of solvent through the membrane. Concentration polarisation occurs when, because of solute rejection, the convective mass transfer of solutes towards the membrane is initially faster than back-diffusion to the bulk. Concentration polarisation leads to an increase of the local osmotic pressure and may lead to precipitation and fouling [3–6]. Approaches for minimising the effects of concentration polarisation on membrane performance can be categorised into four groups—

1. boundary layer (or velocity) control,
2. eddy inducers/generators/promoters,
3. membrane material and/or surface modification, and
4. external (electrical or magnetic) fields.

Of these, approaches 1–3 only reduce but never mitigate the membrane/solute interaction. On the other hand, external fields (approach 4) can potentially lift the solute from the membrane surface, leading to its subsequent removal due to convection by the bulk flow [7]. The external field approach can be implemented independently of the velocity field and membrane materials. Importantly, this approach does not require eddy promoters inside the membrane channel in order to reduce concentration polarisation.

The application of an external electric field near a solid/liquid interface may result in the motion of liquid with respect to an adjacent charged surface. These associated effects are known as electrokinetic phenomena [8]. Electro-osmosis is an electrokinetic phenomenon where the bulk fluid moves relative to a charged surface due to an external electric field. It should be noted that electro-osmosis can only occur if there are charged species in the fluid that can respond to the electric field [7]. Thus, this approach is ideal for desalination and reverse osmosis (RO) water treatment because they involve salts and other charged species. As charge separation generally occurs at a solid-fluid interface (such as a membrane surface), a thin layer that contains a net electric charge is formed near the wall. This layer is known as the electric double layer [9]. The thickness of the electric double layer can be

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characterised by the Debye length (λ_D) which is the distance from the surface to the region where the electric potential is $\exp(-1)$ or 37% of the maximum (zeta potential, ζ) [10]. Electro-osmotic flow induced near a membrane surface could potentially disrupt the boundary layer, enhance mass transfer and, therefore, reduce the extent of concentration polarisation and increase permeate flux in membrane separation operations.

Recently, there is an increasing number of publications that utilise CFD as a tool for aiding with the understanding of hydrodynamics and mass transfer in membrane processes [11–20]. This reflects the potential of CFD as a valuable tool to improve the performance of membrane processes. Therefore, this paper uses a Computational Fluid Dynamics (CFD) model to simulate the effect of electro-osmotic instabilities on the hydrodynamics in a rectangular membrane channel, similar to those found in SWM modules.

One of the major limitations for the numerical simulation of electro-osmosis is the high computational effort required to solve the Poisson and Navier–Stokes equations at the scale of the Debye length ($\sim 10^{-9}$ m) when considering the dimensions of a typical membrane channel ($\sim 10^{-3}$ m). Large velocity gradients near the wall require a very fine mesh in that region in order to capture the velocity profiles [21,22]. One possible way to address the large computational requirements of numerical simulation is the adoption of the Helmholtz–Smoluchowski (HS) velocity equation, which is an artificial slip velocity implemented on a charged surface to simulate the effect of electro-osmosis on the velocity profile in a channel [9].

In this paper, a two-dimensional (2D) electric field is assumed to generate flow perturbations due to electro-osmotic effects, with the potential to enhance mixing within the concentration polarisation layer and lift the solute concentration from the membrane surface. Given that the HS approximation only takes into account the component of the electric field that is tangential to the charged membrane surface, it is unclear whether this approximation is appropriate for modelling electro-osmotic effects in membrane channels caused by 2D electrical fields. Moreover, the HS approximation implies that pressure gradients are negligible [9]. This means that the HS approximation shows no dependence on cross-flow velocity other than the flow velocity induced by the electric field. The applicability of the HS approximation for a system with cross-flow velocity is therefore unclear.

This paper compares the results from steady-state numerical simulations using the Helmholtz–Smoluchowski (HS) approximation of electro-osmosis against a more rigorous charge density (CD) solution in order to determine the reliability and accuracy of the HS approximation in membrane channels. The effect of cross-flow velocity on the accuracy and reliability of the HS approximation is therefore investigated. The effect of cross-flow velocity on the perturbation velocity flow regime and mixing are also assessed.

2. Basic concepts of electro-osmosis in membrane

Electro-osmosis refers to the movement of liquid in response to an applied electric field. The presence of co-ions (similarly charged ions) and counter-ions (oppositely charged ions) results in attraction and repulsion of ions in the vicinity of a charged surface. These phenomena, coupled with the random thermal motion of the ions, create an electric double layer (EDL). In order to neutralise the surface charge, there is an excess of counter-ions compared to co-ions, such that electroneutrality is not maintained within the EDL [9]. The inner most part of the EDL (adjacent to the surface) is known as the Stern layer (SL), while the outer layer (away from the surface) is known as the diffuse layer (DL). Fig. 1 illustrates the structure of the EDL.

Poisson's equation for electrostatics relates the spatial variation in the electric potential and the charge density, and is expressed in the following manner [8]:

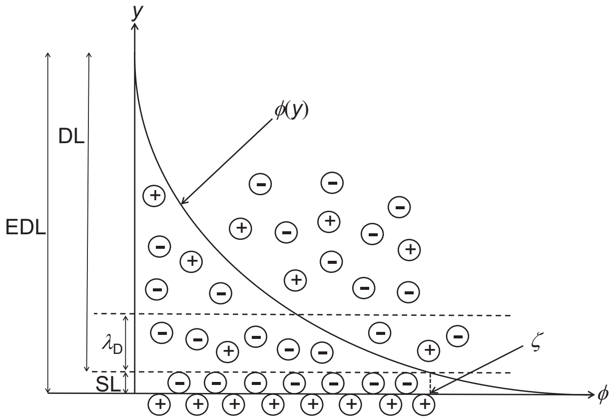

Fig. 1. Schematic of the electric double layer structure, illustrating the dependence of electric potential (ϕ) with distance from the surface (y), and indicating the relative sizes of the electric double layer (EDL), Stern layer (SL), diffuse layer (DL) and Debye length (λ_D).

$$\nabla^2\phi = \frac{-\rho_e}{\varepsilon} \tag{1}$$

where ϕ is the potential due to the double layer, ρ_e is the electric charge density and ε is the permittivity of the fluid. The electric charge density, ρ_e, can be expressed in terms of a Boltzmann distribution as follows [9]:

$$\rho_e = -2zen_o \sinh\left(\frac{ze\phi}{k_B T}\right) \tag{2}$$

where n_o is the ion concentration in the solution, z is the ionic valence, e is the charge of an electron, k_B is the Boltzmann constant and T is the temperature.

The system of Eqs. (1) and (2) can be linearised using the approximation $\sinh(a) \approx a$ for $\phi \ll \frac{k_B T}{e}$ (or 26 mV at room temperature) [9,23]. Assuming the electric potential is constant along the x direction, Eqs. (1) and (2) can then be reduced to the following equation:

$$\phi = \zeta \exp\left(\frac{-y}{\lambda_D}\right) \tag{3}$$

The CD solution in (3) used in this paper is the analytical solution of the 1D case of Eqs. (1) and (2), which gives an expression for the charge density in terms of normal distance from the wall.

For a symmetric monovalent electrolyte (such as NaCl), the Debye length can be calculated as [24]

$$\lambda_D = \sqrt{\frac{\varepsilon k_B T}{2e^2 n_o}} \tag{4}$$

Electro-osmotic effects can be introduced to the momentum transport equation in the form of an external force, to yield:

$$\rho\left(\frac{\partial \vec{v}}{\partial t} + \vec{v}\cdot\nabla\vec{v}\right) = -\nabla P + \mu\nabla^2\vec{v} + \rho_e\vec{E} + \rho g \tag{5}$$

where P, $\vec{v}$, μ, $\vec{E}$, ρ and g are the pressure, velocity, viscosity, electric field, density and gravitational acceleration respectively. For detailed descriptions of the electro-osmosis phenomenon, the reader may refer to the respective pertinent literature [9,23].

The electric field, $\vec{E}$, can be expressed as follows:

$$\vec{E} = -\nabla(\phi + \psi) \tag{6}$$

where ψ is the potential due to the external electric field [10,22].