549c Modelling the Micron- and Nano-Scale Trends in the Steady-State Concentration Profile of a Charged Solute Adjacent to a Membrane Surface

S.S. Vasan, R.W. Field, C.D. Bain, and Z.F. Cui

1. Background and identification of the problem

1.1 Micron-scale trends near a membrane surface

A membrane can partially or totally reject a solute depending on a number of factors such as steric and electrostatic interactions. ‘Concentration polarisation' refers to the accumulation of such rejected solutes in a thin layer near the membrane surface. The concentration of a solute varies across the thickness (typically a few microns) of the polarisation layer, therefore physical properties such as diffusivity, viscosity and density (which are concentration-dependent) vary as well. The rate of solute transport in the polarisation layer determines the overall performance of the membrane process, therefore the significance of concentration polarisation cannot be overemphasised. Not surprisingly, over one fifth of the publications in membrane science in the last 10 years has dealt with this phenomenon.

1.2 Nano-scale trends adjacent to a membrane

Within the polarisation layer, there is a nano-scale electrostatic depletion layer adjacent to the membrane surface (except when both the membrane surface and the solute are uncharged). The aforesaid physical properties are naturally affected in this depletion layer, as are other properties like the local pH, the extent of ionisation, etc. The depletion layer also influences the intermolecular and surface interactions (e.g. adhesion, affinity, and fouling) that may or may not be reversible.

1.3 The existing approach and its limitations

Due to the reasons mentioned above, it is of great importance to know the precise concentration profile of a solute in the micron-scale polarisation layer, as well as in the nano-scale depletion layer. Unfortunately, it has been the standard practice amongst membranologists to simply assume a steady-state concentration profile of the solute in the polarisation layer. Such arbitrary or empirical assumptions frequently turn out to be an incorrect representation of the micron-scale trends (of the polarisation layer), and completely ignore the nano-scale trends (of the depletion layer).

2. The performed work

This paper solves the aforesaid limitations by deriving a new analytical expression (given in 2.4 below) for the steady-state concentration profile of a solute adjacent to a membrane surface. Thus, it successfully resolves the microscopic and the nano-scale trends adjacent to a membrane, taking the finite ionic size into account.

2.1 The Maxwell-Stefan approach to modelling

In a multi-component mixture, the net force exerted on a given species is balanced by the friction it has with each of the other species. This force balance, given by the Maxwell-Stefan equation, is simplified in this paper to describe membrane processes such as ultrafiltration. The Maxwell-Stefan approach allows multiple driving forces (to be added to the chemical potential gradient), of which the electrostatic force is the most relevant to model the nano-scale trends adjacent to a membrane. In this paper, two electrostatic models are considered (as discussed below, in 2.2 and 2.3).

2.2 The Maxwell-Stefan-Gouy-Debye formulation

Most measurements of interfacial interactions probe the electrostatic potential at distances for which the potential is less than or equal to RT/F (where R is gas constant, T is temperature, F is Faraday's constant). Under these conditions, the electrostatic potential in the diffuse Gouy layer is described using the Gouy-Chapman and Debye-Hückel approximations. Combining this description with the Maxwell-Stefan approach gives the governing equation for the Maxwell-Stefan-Gouy-Debye model.

2.3 The Maxwell-Stefan-Derjaguin-Grahame formulation

A major drawback of the Gouy-Debye model (mentioned in 2.2 above) is its description of ions as point charges. This assumption would lead to significant errors when the nano-scale electrostatic depletion layer is comparable to the size of the macromolecule. To overcome this problem, this paper calculates the force between a sphere and a flat surface from the energy between two flat surfaces using the Derjaguin approximation. This force is then expressed using the Grahame equation, and incorporated into the Maxwell-Stefan force balance equation. This gives the governing equation for the Maxwell-Stefan-Derjaguin-Grahame model.

2.4 Solving to obtain an analytical expression

After appropriate scaling and simplifications, the two Maxwell-Stefan formulations (mentioned in 2.2 and 2.3) are solved analytically, in order to express the concentration C of a solute (say, a monoclonal antibody) at a dimensionless distance z from the membrane surface as follows:

$$C = C_b\left(1 - R_{obs}\left(1 - e^{Pe_{bl}(1-z) - Ne^{-Dez}}\right)\right)$$

where C_b is the bulk concentration, R_{obs} is the observed rejection of the solute by the membrane, and the terms De, Ne, and Pe_{bl} refer to dimensionless numbers – all of which are known or can be estimated as explained below.

3. Discussion

3.1 The dimensionless numbers Pe_{bl}, Ne and De

The boundary layer Peclet number (Pe_{bl}) is the ratio of the applied convection to the mass transfer coefficient (as interpreted by film theory). The electrostatics of the system is characterised by the Nernst (Ne) and Debye (De) numbers. The Nernst number (Ne) is a dimensionless zeta potential, which has different expressions depending on the approximation (Gouy-Debye or Derjaguin-Grahame) used. The Debye number (De) measures the polarisation layer thickness in terms of the Debye length.

3.2 Transition from micron- to nano-scale trends

The electrostatic influence is negligible beyond the point of maximum solute concentration in the polarisation layer, which marks the transition from the nano-scale trends (described in 1.2) to the micron-scale trends (described in 1.1). This transition point, denoted as z_{max}, is given as:

$$z_{max}|_{Ne>0} = (\ln(DeNe/Pe_{bl}))/De$$

3.3 The significance of Pe_{bl}, Ne and De

Pe_{bl} (along with C_b and the R_{obs}) determines the maximum concentration in the polarisation layer, as well as the concentration profile from the bulk to the transition point. The electrostatic parameters (De and Ne) have no role in these. The concentration drops from its maximum value (at the transition point) as we go towards the membrane surface. The extent of this nano-scale electrostatic depletion is determined by Ne. The location of the transition point is strongly influenced by De (and sometimes by Ne/Pe_{bl} as shown in 3.2).

3.4 Gouy-Debye vs. Derjaguin-Grahame models

The finite size of the molecule prevents the molecule from approaching close to the membrane surface. The Gouy-Debye formulation models this repulsion by having a much larger Ne, i.e. a much larger effective surface potential is needed to give the same result as the excluded volume effect that has been ignored. Thus, the Derjaguin-Grahame formulation can be considered a way of offsetting the position of the wall without impinging upon the basic Gouy-Debye formulation (which neglects the finite size). In other words, the size of the molecule appears solely in a nano-scale change in the apparent position of the interface (membrane surface). This enables a way of comparing the offset position with the radius of the molecule, as a function of parameters such as the molecular size, charge and ionic strength.

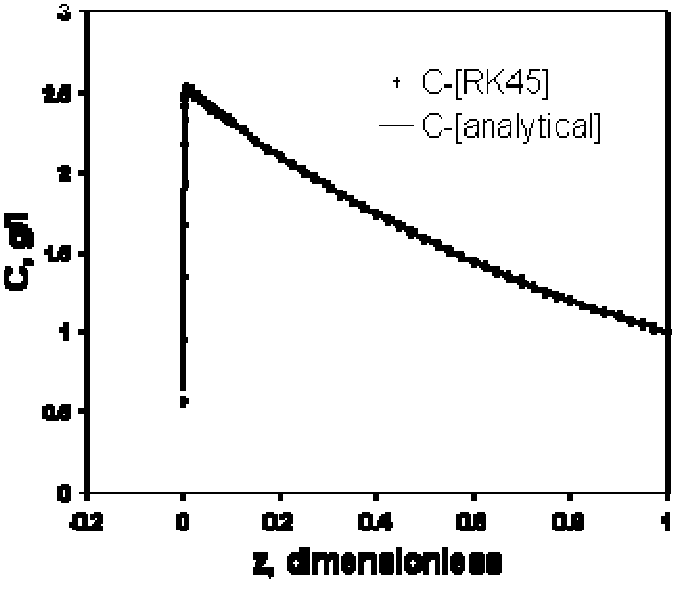

Figure 1 The concentration profile of a charged solute in the polarisation layer showing the micron- and nano-scale trends

(C_b = 1 g/l, De = 1000, Ne = 1.5 according to the Gouy-Debye formulation, Pe_{bl} = 1 and R_{obs} = 90%; z = 0 at the membrane surface and z = 1 at the bulk.)

4. Closing remarks

In this paper, the Maxwell-Stefan equation has been combined with the Gouy-Debye and Derjaguin-Grahame electrostatic models to express the concentration profile of a charged solute near a membrane surface in terms of the bulk concentration, the observed rejection, and the three dimensionless numbers (De, Ne and Pe_{bl}). This theoretically rigorous analytical expression (given in 2.4) would bring to an end the incorrect and unnecessary practice of assuming an arbitrary concentration profile, as well as enhance the fundamental understanding of the micron- and nano-scale trends, taking the finite ionic size into account. A sample plot of the concentration profile obtained from the Maxwell-Stefan-Gouy-Debye model (outlined in 2.1, 2.2 and 2.4) is shown in Figure 1. It can be seen that the analytical expression given in this paper has a very good agreement with the numerical (RK-45) solution of the exact model. The applications of this fundamental result are numerous -- it will be useful in many applications of membrane technology in the areas of healthcare, water environment, food, etc. Theoretical advances in the nano-scale understanding of membrane processes will also enrich the functional principles of bionanotechnology. A few applications of this paper will be illustrated in the conference.

Reference: S.S. Vasan, D.Phil Thesis, Trinity College, Oxford, 2005.