SEPARATION OF SOLUTES WITH DIFFERENT DIFFUSIVITIES IN A HYBRID MEMBRANE CELL COMPRISING SEMI AND FULLY PERMEABLE MEMBRANES

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Abstract

A hybrid separation membrane cell comprising semi and fully-permeable membrane sections is employed to fractionate solutions containing a solvent and two solutes, namely BSA and dextran. The separation technique takes advantage of the difference between diffusivities of the solutes. The semi-permeable membranes are permeable to the solvent and impermeable to both solutes and the fully-permeable membranes are permeable to all components. Numerical simulations are used to understand the role of the physical mechanisms involved in the process and to determine the influence of the cell characteristics (e.g. number of sections), solute properties (e.g. diffusivities) and operational parameters (e.g., velocity of the solvent stream, velocity of the concentrate stream). For the solutes in study, BSA and Dextran, the separation depends also on the physical properties, like viscosity of the solution, and osmotic pressure of the solutes. These are concentration dependent properties and so they change along the cell. This numerical code is presently under development.

Introduction

In conventional pressure driven membrane fractionation processes, solutes with high diffusivities diffuse away from the membrane while the solutes with the low diffusivities remain concentrate near the membrane surface (concentration polarization phenomena). This phenomenon is usually considered undesirable since it may reduce the efficiency of the separation process (van Reis et al., 1997). However, the concentration polarization is a state of high separation between the solvent and the solute and between solutes with different diffusivities. Recently, Miranda and Campos (2007) presented a numerical study showing that it is possible to take advantage of the concentration polarization to improve membrane separation processes. They proved that solute purity and permeate velocity increase if hybrid cells, comprising semi and fully-permeable membrane sections, are used.
Hybrid membrane cells combine two types of membranes. These types of membranes with different properties are alternating in series. In the present study we show that the hybrid cell can be used to separate two proteins (BSA and dextran) with different diffusivities.

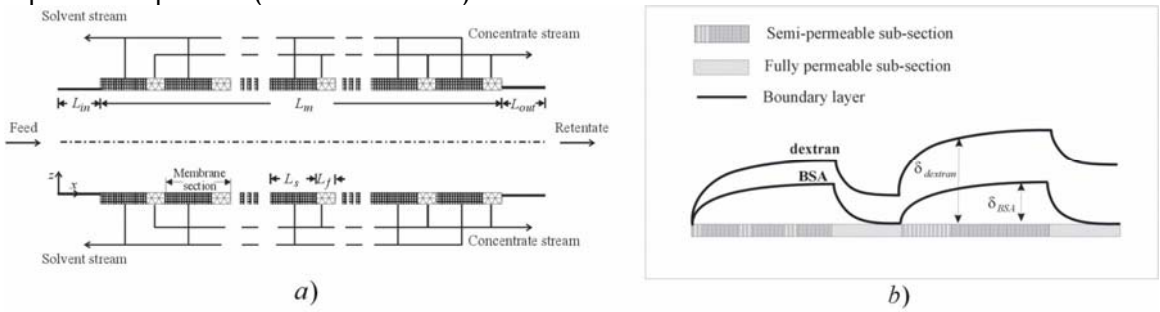

Figure 1 ñ a) Schematic representation of the hybrid cell; b) Mass boundary layers for a differential diffusivity process in a hybrid cell.

Figure 1 b) represents schematically the separation process. The cell combines semi-permeable membranes, permeable to the solvent and impermeable to both solutes and a fully-permeable membranes,

i.e., permeable to all the components. Two mass boundary layers are formed, one for each solute (BSA and dextran). The concentration near the membrane depends on the Peclet number of the respective solute. Since the fluid in the boundary layer of a semi-permeable membrane is removed in the contiguous fully-permeable membrane, the concentrate stream will be richer in the component with the lower diffusivity (BSA).

Concentration dependent properties bring additional problems to the efficiency of the separation process. Since concentration at the membrane surface is higher than the concentration in the bulk, solute diffusivity and solution viscosity change along the normal direction to the membrane. Because the molecular diffusivity decreases with increasing concentration, the fall of diffusivity in the vicinity of the membrane induce accumulation of solute in the boundary layer. Viscosity also increases with solute concentration and so it is higher in the vicinity of the membrane than in the bulk. The tangential velocity along the membrane decreases with this increase of viscosity inducing more solute accumulation near the membrane.
The hybrid cell in study is schematically represented in Figure 1a. It is a parallel plate cell with two kinds of membranes alternating along the walls: one semi-permeable (impermeable to the solutes and permeable to the solvent with resistance R_m) and another, fully permeable (permeable to both solutes and to the solvent and with a permeate velocity equal to Π_v^f). The distance between the walls of the cell is *H*, the width and length of the cell are *W* and *L* respectively. The feed stream (velocity V_0) is separated into three streams: a retentate stream and two permeate streams. One of the permeate streams crosses the semi-permeable membranes, and since it is almost pure solvent, it is called the solvent stream. The other one crosses the fully permeable membranes and since it is rich in the solute with the lower diffusivity, it is called the concentrate stream. The permeate streams are collected in two independent permeate chambers: the solvent chamber and the concentrate chamber. The mean velocity of the feed is V_0, the concentration of BSA and dextran at the inlet are C_{BSA}^{in} and $C_{dextran}^{in}$ respectively. The cell is divided into the inlet section, the outlet section and *n* membrane sections. Each membrane section includes a semi-permeable membrane sub-section and a fully permeable membrane sub-section.

Equations and boundary conditions

The flow in the cell is described by Navier-Stokes equations. For a bi-dimensional cell, the dimensionless Navier-Stokes equations can be written for secondary variables (vorticity, ω and stream function, ψ):

$$\omega = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} \tag{1}$$

$$\frac{\partial \omega}{\partial t} + \left(v_x - 2\frac{\partial\, 1/\mathrm{Re}}{\partial x} \right)\frac{\partial \omega}{\partial x} + \left(v_z - 2\frac{\partial\, 1/\mathrm{Re}}{\partial z} \right)\frac{\partial \omega}{\partial z} = \omega\left(\frac{\partial^2\, 1/\mathrm{Re}}{\partial x^2} + \frac{\partial^2\, 1/\mathrm{Re}}{\partial z^2} \right) + \frac{1}{\mathrm{Re}}\left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial z^2} \right) + S \tag{2}$$

where *S*, is:

$$S = -2\left(\frac{\partial^2\, 1/\mathrm{Re}}{\partial x^2}\frac{\partial^2 \psi}{\partial z^2} - 2\frac{\partial^2\, 1/\mathrm{Re}}{\partial x \partial z}\frac{\partial^2 \psi}{\partial x \partial z} + \frac{\partial^2\, 1/\mathrm{Re}}{\partial z^2}\frac{\partial^2 \psi}{\partial x^2} \right) \tag{3}$$

Here ρ is the solution density (concentration independent). Viscosity, $\overline{\mu}$, was obtained by the following expression:

$$\overline{\mu} = \mu_A x_A + \mu_B x_B, \tag{4}$$

where, x_A and x_B are the fractions of BSA and dextran, respectively. The viscosity of the BSA

solution, μ_A, was taken from Gill et al. (1988) and the viscosity of the dextran solution, μ_B, from Field and Aimar (1993). The dimensionless stream function ψ is defined by:

$$v_x = \frac{\partial \psi}{\partial z}; v_z = -\frac{\partial \psi}{\partial x} \tag{5}$$

The mass transport equations were solved by the so-called ϕ method (Miranda and Campos 2001) based on the solution of the ϕ transport equations for each component:

$$\frac{\partial \phi_i}{\partial t} + \frac{\partial \phi_i}{\partial x}\left(v_x - \frac{\partial\, 1/\mathrm{Pe}_i}{\partial x}\right) + \frac{\partial \phi_i}{\partial z}\left(v_z - \frac{\partial\, 1/\mathrm{Pe}_i}{\partial z}\right) = \frac{1}{\mathrm{Pe}_i}\left(\frac{\partial^2 \phi_i}{\partial x^2} + \frac{\partial^2 \phi_i}{\partial z^2} + \frac{\partial \phi_i}{\partial x}\frac{\partial \phi_i}{\partial x} + \frac{\partial \phi_i}{\partial z}\frac{\partial \phi_i}{\partial z}\right) \tag{6}$$

where Pe_i is the Peclet number of component i (BSA or dextran):

$$\mathrm{Pe}_i = \frac{V_o H}{D_i} \tag{7}$$

and D_i is the molecular diffusivity of component *i* (BSA or dextran). The molecular diffusivity of the BSA solutions was taken from Leung and Probstein (1979) and the molecular diffusivity of the dextran is considered concentration independent. The equations were solved by finite differences methods and the general procedure is described by Miranda and Campos (2007).

The boundary conditions for concentration dependent properties are almost those for constant physical properties. The exceptions are conditions for the surface of the semi-permeable membranes:

$$v_x = 0;\ -v_z = \frac{\Delta P - \Delta \pi}{R_m V_0};\ \psi = -\frac{1}{2} + \int -v_z dx;\ \omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x};\ -\frac{\partial c}{\partial z} = v_z c;\ -\frac{\partial \phi}{\partial z} = v_z \tag{8}$$

The velocity boundary condition, for the semi-permeable membrane, involves the osmotic pressure difference ($\Delta\pi$) which is dependent on the concentrations of BSA and dextran. The following equation takes into account the non-linear concentration dependence of the osmotic pressure:

$$\Delta\pi = k_1^A C_A^{in} c_A + k_1^B C_B^{in} c_B + k_2^A C_A^{in} c_A^2 + k_2^B C_B^{in} c_B^2 + k_3^A C_A^{in} c_A^3 + k_3^B C_B^{in} c_B^3 \tag{9}$$

The values of k_1, k_2 and k_3 for BSA were obtained from Leung and Probstein (1979) and the values for dextran were obtained from G. Jonsson(1984).

Results and discussion

Numerical simulations were done for the separation of a BSA and dextran (BSA is the component with the lower diffusivity). Preliminary results for constant properties are presented in order to show the potential of this differential separation process. The physical properties, for BSA and dextran, were calculated for the inlet conditions. The operating conditions, supposing negligible osmotic pressure for both solutes, are in Table 3. The physical properties, for BSA and dextran are represented in Table 4.

Table 3 ñ Operating conditions and cell characteristics

V_0 (m/s)	H (m)	L_m (m)	ΔP_0 (Pa)	R_m	n	Π_v^f
0.5	0.001	0.1	10^4	$6.116 \Diamond 10^{10}$	8	10^{-4}

Table 4 - Physical properties of BSA and dextran.

	C^{in} (kg/m^3)	μ(kg/(m.s))	D(m^2/s)
BSA	10	0.009108	6.959×10^{-11}
Dextran	10	0.001181	10.5×10^{-11}

Figures 2 and 3 help to the physical understanding of the separation process. Figure 2 shows the flow field and the iso-concentration lines for the components in study. Since BSA has the lower diffusivity, its concentration is higher in the vicinity of the membrane. The streamlines of the fluid that leaves the cell through the fully-permeate sub-section cross a region rich in this component and poor in dextran. Therefore, the concentrate stream is richer in the component with the lower diffusivity (BSA).
For a better visualization, the concentrations of BSA and dextran along the line I-J (Figure 2) are represented in Figure 3 a). The cross-section represented by line I-J is crossed by all the fluid (see streamlines) that forms the concentrate stream. Along this cross-section, the concentration of the component with the lower diffusivity ñ BSA - is higher than the concentration of dextran. This pattern is maintained along all the trajectories of the fluid until it crosses the fully-permeable membrane (Figure 3 b)).

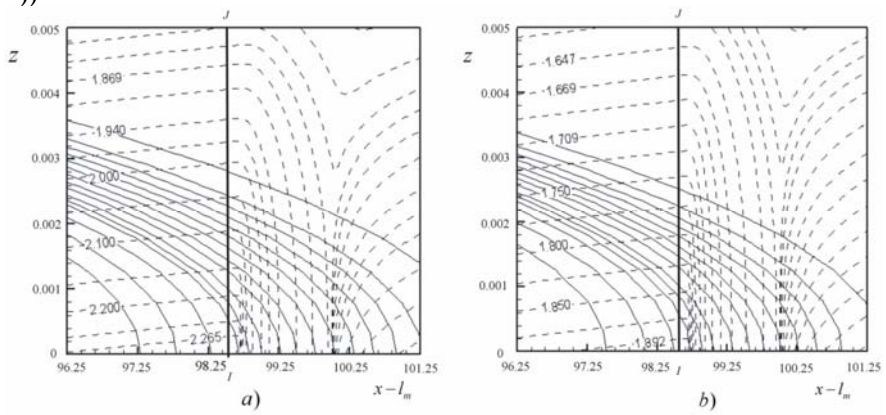

Figure 2- Streamlines and iso-concentration lines in the vicinity of the membrane at the end of the 8th section; a) for the component with the lower diffusivity - BSA; b) for the component with the higher diffusivity ñ dextran.

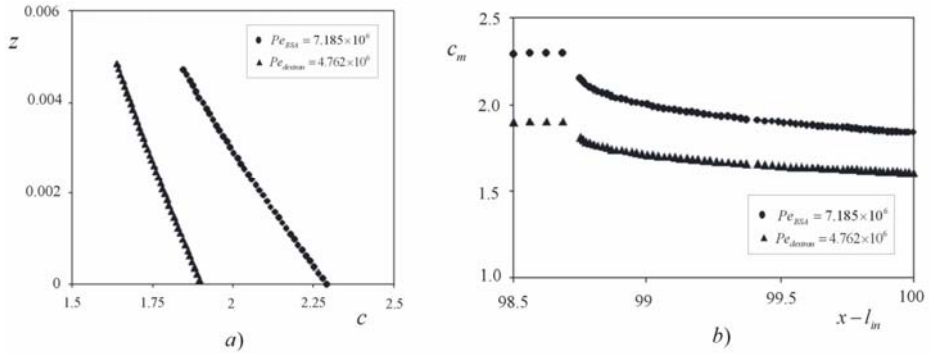

Figure3 ñ Concentration profiles: a) along z [x = 98.5]; b) along the fully-permeable membrane.

Figure 3 b) shows the evolution of the concentration in the last fully permeable sub-section (n=8), for each component in study.

Conclusions

A new membrane fractionation process based on the combination of hybrid membrane cells and differential diffusion of BSA and dextran was studied by numerical methods. The simulation data show

the potential of this new process. This new fractionation process needs to be further studied particularly the effect of the osmotic pressure of both solutes and the effect of the concentration on the physical properties (viscosity and molecular diffusivity).

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