Description of the Overall Mass Transport during Membrane Gas Separation

Endre Nagy*, Imre Hegedüs

[a]Affiliation Research Institute of Chemical and Process Engineering, University of Pannonia, Veszprém, Egyetem u. 10. Hungary
nagy@mukki.richem.hu

Concentration polarization has often been observed in membrane gas separation when there is an accumulation of the less permeable species and a depletion of the more permeable components in the boundary layer of the fluid phase as a result of high fluxes of solute and selectivity and low bulk diffusion. The theoretical prediction of the negative effect of the mass transfer resistance of the boundary layer is crucial in order to be able to calculate the separation efficiency of a gas separation. Models developed in order to describe the mass transport during gas separation enable the user to calculate under what operating conditions the best separation efficiency can be reached. Case study illustrates how these expressions can be applied for prediction of the separation efficiency of a membrane gas separation process applying rubbery polymer membrane. Comparing the theoretical data to that of the experimental it was proved that the model results are in good agreement with that of the experimental ones.

1. Introduction

The theoretical prediction of the negative effect of the mass transfer resistance of the boundary layer is crucial in order to be able to calculate the separation efficiency of a gas separation (Chou et al., 2013). The theoretical prediction of the mass transport, taking into account simultaneously both the mass transfer resistances of the polarization and the membrane layers, is necessary for a correct membrane design, since it is useless decreasing as much as possible the membrane thickness for increasing the flux if part of the transport resistance is in the feed boundary layer (Caravella et al., 2009). Several papers have analyzed the concentration polarization in gas permeation by both theoretically (Nemmani and Suggala, 2010) and experimentally (Park et al. 2008). It was shown that the convective velocity in the polarization layer is generally relatively high accordingly its effect of the mass transport must not be neglected. The main question to be answered is how the simultaneous effect of both the polarization and membrane layers can be exactly described in presence of not negligible convective velocity. This paper analyzes the simultaneous mass transport of the boundary and membrane layers in presence of convective plus diffusive flow in the boundary layer and diffusive one in the membrane.

2. Theory

It is assumed that there is diffusive and convective flow in the boundary layer and only diffusive flow exists in the dense, polymeric membrane layer. Under steady state, the gas concentration profiles of the more permeated component are illustrated in Figure 1 in the two layers. Due to the convective flow the concentration distribution can have convex shape in the boundary layer while that is linear in the membrane one.

2.1 Boundary layer mass transport
The mass balance equation of transported gases, through the boundary layer, for steady operation condition is (He et al. 1999):

$$J_i = -D_i \frac{dc_i}{dy} + \frac{c_i}{\rho}\left(J_i + J_j\right) \tag{1}$$

where J_i and J_j represent the mass transfer rate through the membrane, kg/m^{2}s; c_i is the concentration of component i in the boundary layer, kg/m^3, ρ is the density of the fluid, kg/m^3; D_i denotes the diffusion coefficient of component i;
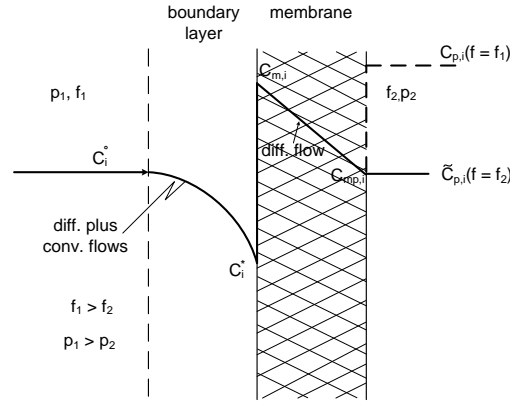

Figure 1: Concentration distribution and the important notations of the boundary and the membrane layer for gas separation

The boundary conditions according to Fig. 1 are as:

at $y = 0$ then $c_i = c_i^o$ (2a)

at $y = \delta$ then $c_i = c_i^*$ (2b)

Let us introduce the υ convective velocity into Eq(1), then we can get as:

$$J_i = -D_i \frac{dc_i}{dy} + \frac{c_i}{\rho}\left(J_i + J_j\right) \equiv -D_i \frac{dc_i}{dy} + \upsilon c_i \tag{3}$$

with

$$\upsilon = \frac{J_i + J_j}{\rho}$$

or after differentiation of Eq(5), for the sake of more general solution, one gets as:

$$D_i \frac{d^2c_i}{dy^2} - \upsilon \frac{dc_i}{dy} = 0 \tag{4}$$

The solution of Eq(6) is (Nagy, 2012) ($Y = y/\delta$):

$$c_i = Ae^{Pe_iY} + B \tag{5}$$

Parameters A and B can be obtained by means of the boundary conditions given by Eqs(2a) and (2b). Accordingly the concentration distribution of component i will be as:

$$c_i = \frac{c_i^* - c_i^o}{e^{Pe_i} - 1}e^{Pe_iY} + \frac{c_i^o e^{Pe_i} - c_i^*}{e^{Pe_i} - 1} \tag{6}$$

The J_i mass transfer rate, namely the sum of the diffusive and the convective flow, at $Y = 0$, will be as:

$$J_i = -\frac{D_i}{\delta}\frac{dc_i}{dY} + \upsilon c_i = \upsilon \frac{c_i^o e^{Pe_i} - c_i^*}{e^{Pe_i} - 1} \equiv \beta\left(c_i^o - e^{-Pe_i}c_i^*\right) \tag{7}$$
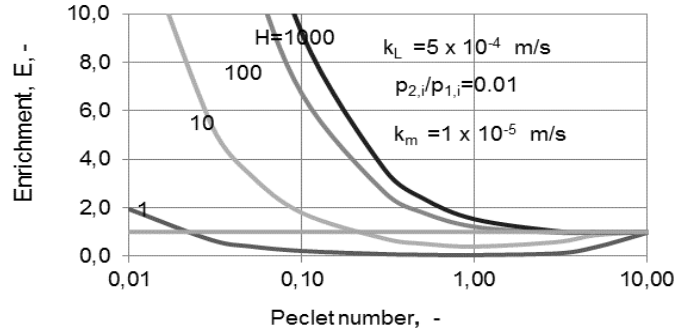
with

$$\beta \equiv k \frac{Pe_i e^{Pe_i}}{e^{Pe_i} - 1}$$ (8)

Figure 2: Enrichment as a function of the Peclet number (kL = 5 × 10-4 m/s; H = 10; km = 5 × 10-5 m/s; p2,i/p1,I = 0.01)

2.2 Mass transport through the membrane layer

The mass transport in non-porous, dense, polymeric structures following the solution-diffusion model has generally been applied for description of the gas transport (He et al. 1999). The steady state gas permeation rate is defined as:

$$J_i = \frac{D_{m,i} S_i}{\delta_m} \left(f_{1,i} - f_{2,i} \right)$$ (9)

where J_i is the permeation rate of the gas component, kg/m^{2}s; $D_{m,I}$ is the average effective diffusion coefficient, m^2/s; S_i is the solubility coefficient, kg/(m^{3}Pa); δ_m is the membrane thickness, m and $f_{1,I}$ and $f_{2,I}$ respectively the upstream and downstream fugacity, Pa. The S_i solubility coefficient is defined as the gas concentration in the polymer divided its fugacity as $S_i = c_{m,i}/f_i$. Eq(9) can be rewritten for ideal gas mixture as:

$$J_i = \frac{D_i S_i}{\delta_m} \left(p_{1,i} - p_{2,i} \right) \equiv \frac{D_{m,i} S_i}{\delta_m} \frac{RT}{M_i} \left(c_i^o - \tilde{c}_{p,i} \right)$$ (10)

where R is the gas constant, 8.314 m^{3}Pa/(mol K); T is temperature, K and c and $\tilde{c}$ are gas concentrations on the two sides of membrane (see Fig. 1), kg/m^3. The product of $D_i S_i = P_i$ is called as permeability with measure here as kg m/m^{2}s Pa (1 kg m/m^{2}sPa = 2.9 × 10^8/M$_i$ cm^3(STP) cm/cm^{2}s cmHg, where M$_i$ is the molecular weight of the i component in g/mol). Knowing the partial mass transfer rates [Eqs(7) and (10)], the overall mass transfer rate can easily be expressed applying the resistance-in-series model (Nagy, 2012).

3. Results and discussion

Important properties expressing the separation efficiency are the polarization modulus and the enrichment. Their values can be expressed easily from the model equations developed.

3.1 Polarization modulus and enrichment.

The polarization modulus can be expressed in two ways: without taking into account the membrane properties and with the membrane mass transport properties. The first mode is often used in the literature. Accordingly, applying Eq(7) and the boundary for the permeate side [Eq(11)], one can get the

$$J_i = \upsilon c_{p,i}$$ (11)

polarization modulus from the equality of these expressions as (Avila et al., 2009):
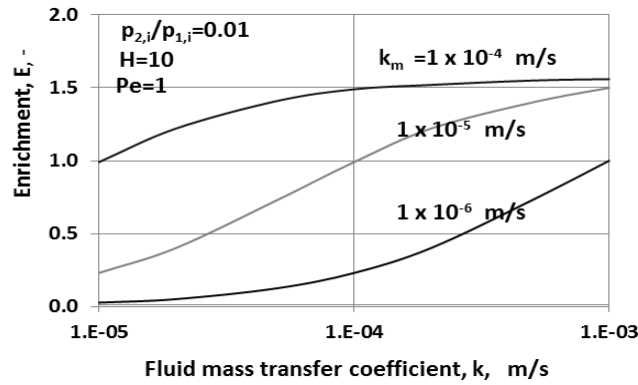
Figure 3: The effect of the k value on the enrichment factor at three different values of the membrane mass transfer coefficient, k_m.

$$I = e^{Pe_i} + E\left(1 - e^{Pe_i}\right) \tag{12}$$

where E is enrichment, $E = c_{p,i}/c_i^o$ while $I = c_i^*/c_i^o$. As it follows from Eq(12), one needs the enrichment factor for calculation of the value of I in this case or you need the value of I for calculation of E. This is the consequence of the fact that the membrane mass transport parameters are left without attention during the expression of the I value. Now let us express the polarization modulus and the enrichment factor taking into account the membrane properties, as well. Look at first the value of the enrichment factor. One can get the value of E from the equality of Eqs(7), (10) and (11) as:

$$E = \frac{e^{Pe_i}}{e^{Pe_i} - 1 + N + p_{2,i}/p_{1,i}} \tag{13}$$

with the N value (Nagy, 2010):

$$N = \frac{kPe_i}{k_m S_i} \frac{M_i}{RT} \equiv \frac{\upsilon}{k_m S_i} \frac{M_i}{RT} = \frac{\upsilon}{k_m H_i} \tag{14}$$

Similarly, the polarization modulus can be expressed by means of Eqs(7) and (10) as:

$$I = \frac{e^{Pe_i}\left(N + \dfrac{p_{2,i}}{p_{1,i}}\right)}{\left(\dfrac{p_{2,i}}{p_{1,i}} + e^{Pe_i} - 1 + N\right)} \tag{15}$$

As typical diagram, Figure 2 illustrates on the change of the enrichment as a function of the Peclet number at different values of the solubility coefficient, H. Note that the N value also changes, according to Eq(14), with the variation of the Peclet number due to the change in the convective velocity. As can be seen the E value strongly decreases with the increase of the Pe values, even below unit. With increase of the convective velocity the value of E can essentially be decreased. There should be a so called "optimal" value of convective velocity in order to get large permeation rate and even good separation factor. The expressions developed enable the reader to predict the "optimal" operating conditions. On the other hand, value of E can strongly be increased by the increasing value of H. How the boundary layer mass transfer resistance affect the enrichment is illustrated by Figure 3. The fluid phase mass transfer coefficient can significantly alter the separation efficiency. Its negative effect may be decreased with the increase of its value. This figure shows that if one can increase the k value than the enrichment will also increase, i.e. it dec decreases the effect of the polarization layer. Similarly, the higher value of the membrane mass transfer coefficient (k_m) can also improve the separation efficiency.
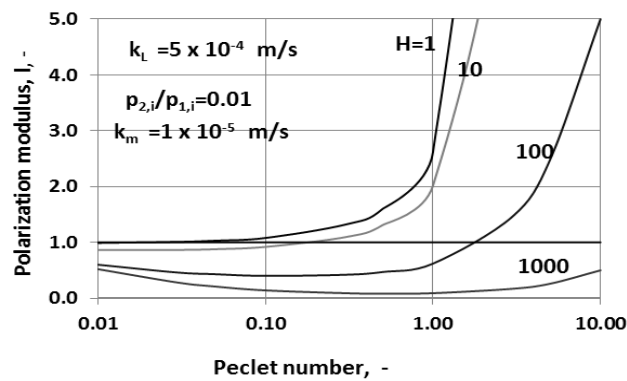
Figure 4. The change of the polarization modulus a s a function of the Peclet number at different H values ($k_L = 5 \times 10^{-4}$ m/s; $H = 10$; $k_m = 5 \times 10^{-5}$ m/s; $p_{2,I}/p_{1,I} = 0.01$).

However, extremely large k value is needed to reach significant improvement of this separation process. The polarization modulus is also an important factor during gas separation. During gas separation where the gas permeation unit, GPU is often relatively high, this boundary layer effect is almost always present. Eq(15) enables the reader to calculate its value by means of the mass transport parameters without knowing the value of enrichment. Its value is plotted in Figure 4 as typical values, as a function of the Peclet number. The parameters used for the calculation are the same as used in Figure 2. As can bee seen the I value can easily be higher or lower than unit, depending on the H and Pe values. The polarization modulus can firstly decrease with the increase of the Pe value then it starts to increase at higher values of Pe. Increasing solubility coefficient increases the mass transfer rate and accordingly, lowers the value of the polarization modulus. Generally it can be stated that the high value of convective velocity increases the concentration of the compound investigated in the polarization layer, and consequently decreases the separation factor as it is seen in Figure 2, as well. The model quality has been proven against experimental results taken from the literature in studies on separation (Sholes et al., 2010) and on drying (Wang et al., 1992). It was stated that the model can adequately describe the gas separation process (Nagy et al., 2013).

4. Conclusions

A new mass transport model is developed which enables the user to calculate separately both the enrichment factor and polarization modulus. It was proved that the solubility coefficient, the Peclet number, the external mass transfer coefficient can significantly affect the value of the enrichment factor. Models developed enable the user to calculate under what operating conditions the best separation efficiency can be reached. The adequacy of the medel was proved by experimental results.

Nomenclature

c	concentration, kg/m^3
c^o	bulk fluid concentration on the feed side, kg/m^3
c*	interface concentration, kg/m^3
c$_m$	membrane concentration, kg/m^3
c$_p$	permeate concentration at the feed side pressure and temperature, kg/m^3
$\widetilde{c}_p$	permeate concentration at the permeate side pressure and temperature, kg/m^3
D	diffusion coefficient of the boundary layer, m^2/s
D$_m$	diffusion coefficient of the membrane layer, m^2/s
E	enrichment factor (= $c_{p,i}/c_i^{*}$)
GPU	gas permeation unit, (= 7.6×10^{-12} m^3(STP)/(m^{2}sPa) = 7.6×10^{-7} m^3(STP)/(m^{2}satm)
H$_i$	distribution coefficient, (kg/m^3[polymer])/kg/m^3[gas]
J	convective +diffusive mass transfer rate, kmol/m^{2}s
J$_V$	volume transfer rate, m^3(STP)/(m^{2}s)
I	polarization modulus, (c_i^{*}/c_i^o),-
k	diffusive mass transfer coefficient for the boundary layer, (= D/δ), m/s

k_m diffusive mass transfer coefficient for the membrane layer, (= D_m/δ_m), m/s

M   molar weight, kg/kmol

N   constant defined in Eq(14), [$kPe/(k_m H_i) = \upsilon/(k_m H_i)$],-

p   pressure, Pa

P   permeability, barrer [1 barrer = 7.6 x 10^{-18} m^3(STP)m/(m^2sPa]

Pe   Peclet number (= $u\delta/D$),-

R   gas constant (R = 8314.5), Pa m^3/kmol K

S   solubility coefficient, kg/(m^3Pa)

S^* solubility coefficient ($S^* = SRT/M = H$), m^3(STP)/(m^3[polymer]atm)

T   temperature, ^{o}K

y   space co-ordinate perpendicular to the membrane interface, m

Y   dimensionless space coordinate, (= y/δ for boundary and y/δ_m for the membrane),-

Greek letters

β convective plus diffusive mass transfer coefficient for the boundary layer (Eq. 8), m/s

δ boundary layer thickness; thickness of the mass transport layers, m

γ activity coefficient

ϕ fugacity coefficient

ρ density, kg/m^3

υ sum of the convective velocities at the feed side pressure and temperature, m/s

ϑ $= \gamma_i M_i P_i^{sat} / \phi_i \rho_p RT$,-

Subscripts

i   ith component to be separated

m   membrane layer

p   permeate

Superscript

*   at liquid-membrane interface

sat   saturated

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