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The effect of the concentration polarization and the membrane layer mass transport on membrane separation

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ABSTRACT

The negative effect of the concentration polarization layer on the membrane separation is well known. How the mass transport parameters of the membrane matrix, e.g. the solubility coefficient, membrane diffusion coefficient, membrane thickness, can affect the concentration profile of the boundary layer, and consequently, the separation efficiency is not investigated in detail yet. This article gives the suitable mathematical expressions, in order to predict the well known parameters as polarization modulus, enrichment factors, etc., taking into account the transport parameters for both the concentration boundary and the membrane layers, and analysis the concentration distribution and the polarization modulus. It has been shown that the transport properties of the membrane layer have significant effect on the concentration profiles of the boundary layer and thus, on the polarization modulus, enrichment factors, etc., as well. Thus, the well known equations, e.g. the polarization modulus, enrichment factor [see e.g. Eqs. (2) and (3)], could be regarded as approaches.

Keywords: Concentration polarization; Solubility; Pervaporation; Enrichment

1. Introduction

The negative effect of the stagnant concentration boundary layer on the mass transport through a membrane has been investigated for a long time. It was proved that this layer can be a major limiting factor in various membrane separation processes [1]. Two main types of the concentration polarization layers can be distinguished, namely the membrane separation can lead to an accumulation of the retained species (Fig. 1, continuous line) or a depletion of the preferentially permeating components in the boundary layer due to its permeation through the membrane, adjacent to it (Fig. 1, dotted line). The polarization can essentially reduce the overall efficiency of the membrane separation, it can severely limit flux and selectivity. Number of paper analyzed the effect of concentration polarization and defined the well known equation to its prediction [e.g. 1–8]. Almost all earlier studies [1–2] consider the mass transport equations in the boundary layer, only, defining its Peclet number [$\mathrm{Pe}_\mathrm{L} = \upsilon\delta/D$, see e.g. Eq. (1)], but do not discuss that in the membrane layer and its effect back to the concentration polarization layer and on the membrane separation. The membrane layer is regarded as a black box. As a consequence the important parameters as concentration polarization modulus, I, enrichment factor, E, intrinsic enrichment, E_o, etc. can not be calculated directly from the mass transport parameters. These parameters should be expressed by more general equation which involves

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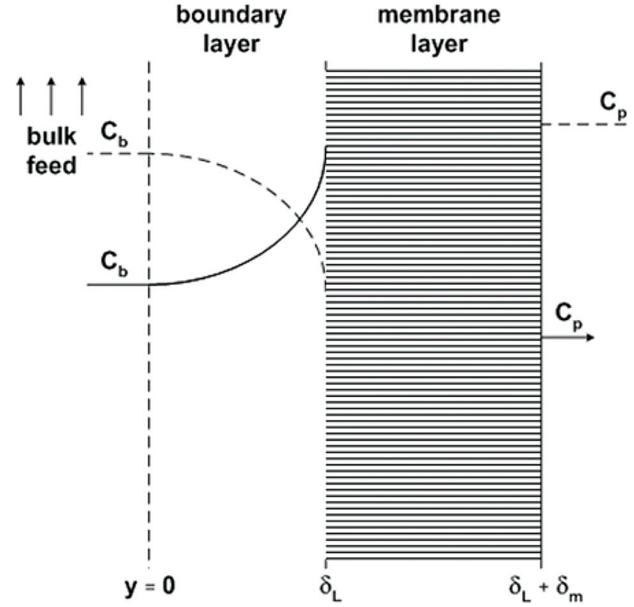

Fig. 1. Concentration profiles in the concentration boundary layer and membrane layer.

not only the Pe_L but also the membrane mass transport parameters as D_m and δ_m, H_m, as well.

For example, the concentration modulus is given as a function of Pe_L (Eq. (1)) or the enrichment factor (Eq. (2)) also as a function of Pe_L and the intrinsic enrichment, E_o [2–4]. This last parameter ($E_o = C_p/C^*$) is also an unknown parameter.

$$\frac{C^* - C_p}{C_b - C_p} \equiv \frac{1/E_o - 1}{1/E - 1} = \exp\left(\frac{v\delta}{D}\right) \equiv \exp(\mathrm{Pe_L}) \qquad (1)$$

$$I \equiv \frac{C^*}{C_b} \equiv \frac{E}{E_o} = \frac{\exp(\mathrm{Pe_L})}{1 + E_o[\exp(\mathrm{Pe_L}) - 1]} \qquad (2)$$

The question is how enrichment factor and/or the intrinsic enrichment, the polarization modulus can be directly predicted by means of the two layer's transport parameters as β_m ($\beta_m = D_m/\delta_m$), β ($\beta = D/\delta$) and Pe_L ($Pe_L = \nu/\beta$). This article gives general equations for calculation of these parameters which equations make then possible the direct calculation of the polarization modulus and the enrichment factor, etc.

The mass transfer rate for the boundary layer, solving Eq. (1) with suitable boundary conditions (at $Y = 0$ $C = C_b$, at $Y \equiv y/\delta = 1$ then $C = C^*$) can be given as follows:

$$C = \left(C_b - C_p\right)e^{\mathrm{Pe_L}Y} + C_p \quad 0 \le Y \le 1 \qquad (3)$$

Pressure-driven membrane process as ultrafiltration is widely used for separation of macromolecules or colloidal particles from liquid. In this case when the permeate flux are larger than the diffusive flux in reversed direction (continuous line Fig. 1 in the boundary layer) the macromolecules starts to deposit on the membrane surface building a cake (gel) layer on it. In this article the fouling will not be discussed.

2. Theory

Let us look here at the pervaporation process. At steady state, the sum of the convective and diffusive flows, in the boundary layer equals the amount permeated through the membrane [3,4,8]:

$$vC - D\frac{\mathrm{d}C}{\mathrm{d}y} = vC_p \qquad (4)$$

where v is the convective velocity, D is the diffusion coefficient, C_p is the condensed, liquid permeate concentration. Eq. (4) is valid for both the increasing ($\mathrm{d}C/\mathrm{d}y > 0$, Fig. 1, continuous line) and decreasing concentration ($\mathrm{d}C/\mathrm{d}y < 0$, Fig. 1, dotted line) in the concentration boundary layer. Eq. (4) defines the overall mass transfer rate (the sum of the diffusion flow and the convective one in the left hand side of the equation) in the boundary layer and that on the permeate side of the membrane. We look for a general solution of the problem that involves Eq. (3) as well and also contains the case when there is a flowing phase on the permeate side of the membrane (for instance, this is the case of the sweep gas pervaporation). It was assumed in our models that only diffusive flow exists in the membrane phase, as this is the case for pervaporation process.

The following second order differential mass balance equations can be given for the concentration boundary layer and the membrane layer:

$$v\frac{\mathrm{d}C_L}{\mathrm{d}y} - D_L\frac{d^2C_L}{dy^2} = 0 \qquad (5a)$$

$$D_m\frac{d^2C_m}{dy^2} = 0 \qquad (5b)$$

where indices L, m denote the boundary layer and membrane matrix, respectively. The case when there is a convective flow in the membrane layer (e.g. membrane reactors) was discussed by Nagy and Borbély [7].

2.1. *Solution by literature boundary conditions of pervaporation (Model A)*

After integration of Eqs. (5a) and (5b), the concentration distribution of the boundary layer and the membrane layer layers can be given, respectively, as follows:

$$C_L = T_L e^{\mathrm{Pe}_L y} + Q_L \quad 0 \le y \le \delta \tag{6}$$

$$C_m = T_m y + Q_m \quad \delta \le y \le \delta + \delta_m \tag{7}$$

The well known boundary conditions with dimensionless space coordinates ($Y = y/\delta$) to determine the values of T_L, Q_L, T_m, Q_m parameters are as follows:

$$T_L + Q_L = C_b \quad Y = 0 \tag{8}$$

$$\upsilon Q_L = -\frac{D_m}{\delta_m} T_m \quad Y = 1 \tag{9}$$

$$H_m\left(T_L e^{\mathrm{Pe}_L} + Q_L\right) = T_m + Q_m \quad Y = 1 \tag{10}$$

$$-\frac{D_m}{\delta_m} T_m = \upsilon C_p \quad Y = 1 + \delta_m/\delta \tag{11}$$

where $\mathrm{Pe}_L = \upsilon\delta/D_L$

The value of υQ_L, in Eq. (4), is equal to that of the left hand side of Eq. (4). The last boundary condition, Eq. (11), defines that the outlet mass transfer rate and the membrane diffusion mass transfer rate should be equal to each other. Thus, the concentration on the interface of the permeate side is not defined, its value cannot be directly obtained by means of the above boundary conditions. In principle, its value should be equal to C_p, since concentration jump is not assumed on the outlet membrane interface. The values of υQ_L in Eq. (9), gives the overall mass transfer rate (the sum of the diffusive and convective flow) in the boundary layer, while H_m denotes the solubility of the transported compound in the membrane layer. If the solubility is negligible then the value of H_m should be equal to unit. The concentration distribution in both the boundary layer (Eq. (3)) and membrane layer (Eq. (12)) can easily be obtained by the use of Eqs. (6)–(11).

$$\begin{aligned} C_m = {} & \frac{\upsilon\delta_m}{D_m}(1 - Y)C_p + H_m\left(C_b - C_p\right)e^{\mathrm{Pe}_L} \\ & + H_m C_p \quad 1 \le Y \le 1 + \delta_m/\delta \end{aligned} \tag{12}$$

2.2. *A general solution of the concentration distribution (Model B)*

The boundary conditions of the ‘‘general’’ solution do not involve the transfer rate at $Y = 1 + \delta_m/\delta$ but defines the equality of the membrane and liquid concentration on the membrane interface, namely

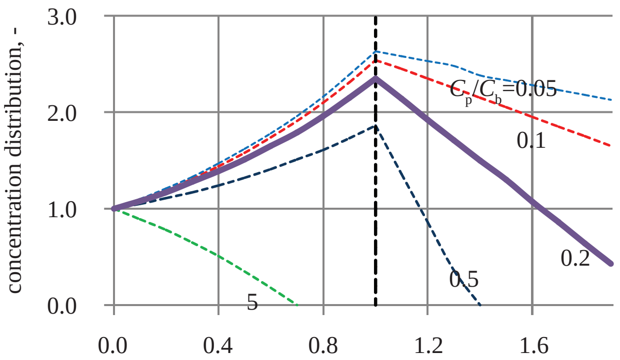

Fig. 2. Concentration profiles in the two layers applying the literature model (Model A), at different values of C_p. ($D_m = 1 \times 10^{-9}$ m^2/s; $D_L = 1 \times 10^{-8}$ m^2/s; $\delta = \delta_m = 1 \times 10^{-4}$ m; $H_m = 1$, $\mathrm{Pe}_L = 1$).

$$T_m\left(1 + \frac{\delta_m}{\delta}\right) + Q_m = H_m C_p \tag{13}$$

That means that the outlet concentration can be chosen freely. This can be the case of pervaporation applying sweep gas on the permeate side. By means of the sweep gas flow rate the outlet concentration, C_p, can be affected. Other important thing regarding the boundary condition of Eq. (13) is that the diffusive mass transfer resistance is neglected. This is mostly true due to the high diffusion coefficient of the vapor component. In this case, the boundary conditions used to the solution of Eqs. (6) and (7) differ from that of the literature solution (Eq. (8)–(11)) only by the fourth one, namely Eq. (13) is applied instead of Eq. (11). The parameter values (T_L, Q_L, T_m, Q_m) obtained for that case are listed in the Appendix.

3. Results and discussion

The concentration profiles obtained by the two models, namely the literature model (Model A) and the general one (Model B), are illustrated with Figs. 2 and 3. The essential difference between the results obtained is that in the case of Model A the C_p values are different from that of the C^*_{out} (it can easily be seen from Fig. 2; C^*_{out}denotes here the concentration of the transported component on the permeate side's interface of the membrane layer), while in the case of Model B it is obvious that $C^*_{out} = H_m C_p$ according to Eq. (13). The only exception is the curves obtained at $C_p/C_b = 0.214$ (continuous lines in Figs. 2 and 3), where $C^*_{out} = H_m C_p$ is also valid in the case of the Model A, as well. In principle, this value of C_p can be regarded as true solution, all other not. In this case, both

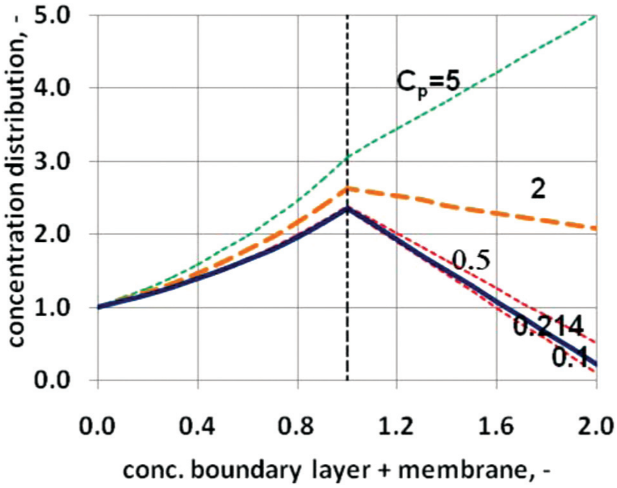

Fig. 3. Concentration profiles in the two layers at different values of C_p/C_b, applied the Model B. ($D_m = 1 \times 10^{-9}$ m^2/s; $D_L = 1 \times 10^{-8}$ m^2/s; $\delta = \delta_m = 1 \times 10^{-4}$ m; $H_m = 1$, $Pe_L = 1$).

models fulfill the boundary conditions given by Eqs. (11) and (13).

In Model A (Fig. 2), the permeate mass transfer rate is defined as boundary condition (Eq. (11)), thus, the concentration of C^*_{out} sharply decreases with the increase of C_p. Namely, the increasing value of C_p means increasing convective mass transfer rate and consequently, increasing diffusive transfer rate in the membrane matrix. This needs higher slop in the concentration distribution. Thus, for example at $C_p/C_b = 0.5$, the concentration in the membrane quickly reduces below zero. In Model B (Fig. 3), however, the C^*_{out} outlet concentration is equal to C_p but the mass transfer rate does not fulfill the condition given by Eq. (11).

From Eq. (12), the outlet concentration, on the membrane interface at the permeate side, can be given as:

$$C^*_{out} = -\frac{\upsilon\delta_m}{D_m}\frac{\delta_m}{\delta}C_p + H_m(C_b - C_p)e^{Pe_L} + H_m C_p \tag{14}$$

Replacing $C^*_{out} = H_m C_p$ into the left hand side of Eq. (14), one can get that value of C_p which correctly describes the concentration distribution in the case of model A, as well. Thus, one can obtain for the value of C_p as:

$$C_p = C_b \frac{e^{PeL}}{Pe_L\beta_L\delta_m/(\beta_m H_m \delta) + e^{Pe_L}} \tag{15}$$

Thus, the enrichment factor ($E = C_p/C_b$) can be given as:

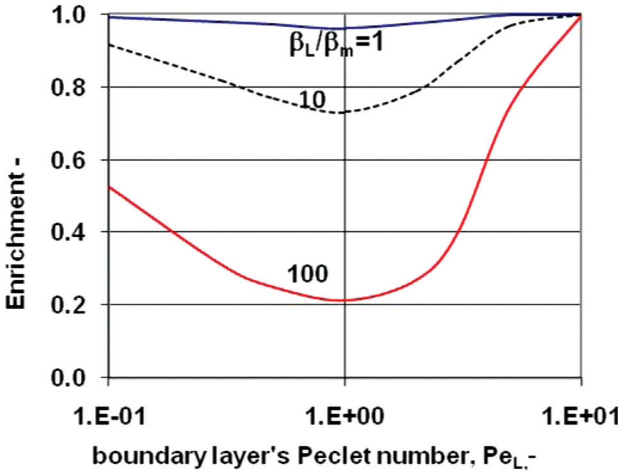

Fig. 4. Enrichment factor as a function of the Peclet number ($D_L = 1 \times 10^{-8}$ m^2/s; $\delta = \delta_m = 1 \times 10^{-4}$ m; $H_m = 10$).

$$E = \frac{e^{PeL}}{\xi + e^{Pe_L}} \tag{16}$$

where

$$\xi = \frac{Pe_L\beta_L\delta_m}{\delta\beta_m H_m}$$

Looking at Eq. (16), it is easy to see that the enrichment factor can directly be calculated by means of the mass transport parameters of the two layers. This was not possible applying the literature equations (see e.g. Eq. (2)). On the other hand, it can also be stated that the value of the enrichment can never be larger than unit that is $E \le 1$. In reality enrichment is larger, even it can be much larger than unit in pervaporation processes. Accordingly, the question arises whether the Eq. (16) is not correct or there is other reason for this anomaly. In the following we try to give an answer on this question accepting that Eq. (16) describes correctly the mass transport, obviously, under the given conditions. The polarization modulus can similarly be given:

$$I \equiv \frac{C^*}{C_b} = e^{Pe_L} + E(1 - e^{Pe_L}) \equiv \frac{e^{Pe_L}(\xi + 1)}{\xi + e^{Pe_L}} \tag{17}$$

The value of the intrinsic enrichment, E_o ($E_o = C_p/C^*$) can easily be obtained by means of Eqs. (16) and (17), namely

$$E_o = \frac{C_p}{C^*} \equiv \frac{E}{I} = \frac{1}{\xi + 1} \tag{18}$$

It is obvious from Eq. (18) that the value of the intrinsic enrichment is not larger than unit. This is also

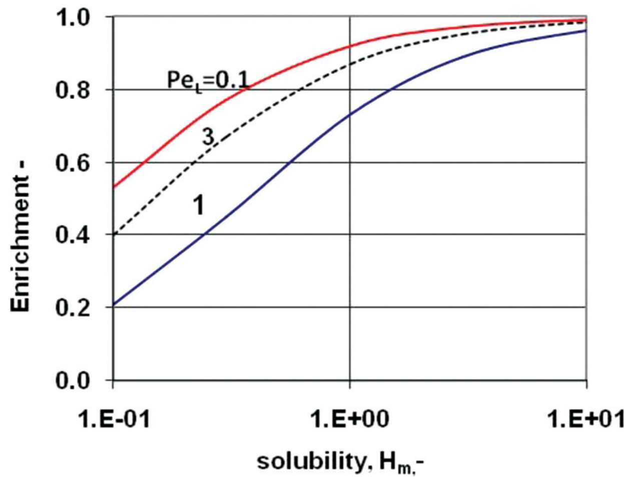

Fig. 5. The outlet concentration as a function of the solubility ($D_m = 1 \times 10^{-8}$ m^2/s; $D_L = 1 \times 10^{-8}$ m^2/s; $\delta = \delta_m = 1 \times 10^{-4}$ m).

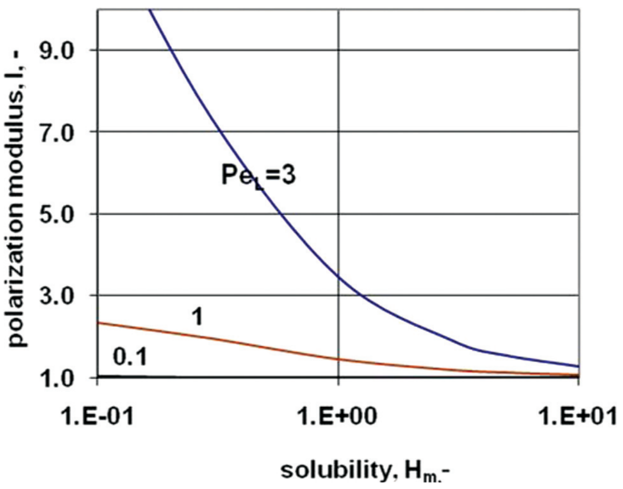

Fig. 6. The change of the polarization modulus as a function of the solubility coefficient ($D_m = 1 \times 10^{-8}$ m^2/s; $D_L = 1 \times 10^{-8}$ m^2/s; $\delta = \delta_m = 1 \times 10^{-4}$ m).

contradiction with literature data [4,8]. When one replaces the value of C* from Eq. (3), at $Y = 1$ into the right hand side of Eq. (2) one gets the same value for the polarization modulus, I, as it is given in Eq. (17). As it was mentioned, the value of E cannot be larger than unit, according to Eq. (16). Typical curves illustrate the change of the enrichment factor as a function of the Peclet number in the boundary layer (Fig. 4) at different values of the ratio of the diffusion mass transfer coefficients, namely β_L/β_m, where β_L and β_m are the mass transfer coefficient of the boundary layer ($\beta_L = D_L/\delta$) and membrane layer ($\beta_m = D_m/\delta_m$), respectively. The curves have minimum as a function of Pe$_L$, and tend to unit with both the increasing as well as decreasing Pe$_L$ number. During our calculation the thickness of both the boundary layer and membrane layer were kept to be constant, the membrane diffusion coefficient was changed according to the β_L/β_m values.

The effect of the solubility of the transported component is plotted in the next two figures (Figs. 5 and 6). The enrichment factor gradually increases with the increase of the H_m solubility. As can be seen, its value tends to unit, that is, it will not be larger than one. The polarization modulus calculated by Eq. (17) is plotted in Fig. 6. Its value decreases essentially with increasing solubility coefficient. It is also sensitive to the value of Peclet number. It is important to note that the value of the polarization modulus is always larger than unit. This is inconsistent with the reality where it value should be less than unit if the enrichment factor is larger than one. The question how can be given more suitable description of the mass transport through the pervaporation membrane matrix. Generally it is accepted, that only diffusion takes place in the dense polymer membrane. Our equations obtained by the two models accept this condition. For further analysis let us look the mass transfer rate trough the membrane layer, according to Baker [9]:

$$J = \frac{D_m}{\delta_m}\left(H_m C_m^* - H_p C_p\right) \tag{19}$$

where

$$\mathrm{H_m} = \left(\frac{\gamma_L \rho_m}{\gamma_m \rho_b}\right)_b; \quad \mathrm{H_p} = \left(\frac{\gamma_L \rho_m}{\gamma_m \rho_b}\right)_p$$

The question is whether the values of the H_m and H_p can differ from each other or not. In the equations from (10) to (18), the equality of H_m and H_p was assumed. It might also be supposed, to my opinion, that the solubility on the permeate side can differ from that on the feed side of the membrane. According to the values of H_m and H_p defined after Eq. (19), the values of γ_m, for example, can differ on the both sides of the membrane. This might be confirmed e.g. by the well known Schroeder's paradox [10] or by several literature data (it is not discussed here in details). Accordingly, the membrane concentration on the permeate interface, C^*_{out} can be given by the following expression: $C^*_{out} = H_p C_p$. On the permeate side the vapor phase concentration can strongly differ from the liquid concentration, in measure of weight/volume. The solubility defines the dissolved amount of component in the membrane matrix as a function of its activity in the liquid phase or in the vapor phase. If one use concentration in weight/volume instead of weight fraction, the solubility may be essentially different on the feed

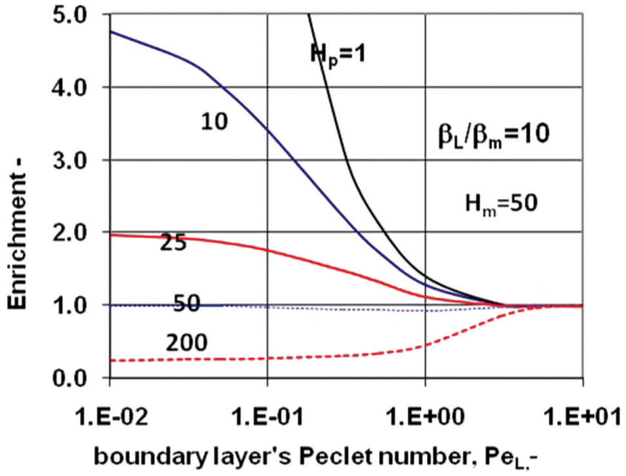

Fig. 7. Enrichment factor as a function of $\mathrm{Pe_L}$, at different solubility on the permeate side of membrane ($H_m = 50$; $D_m = 1 \times 10^{-9}$ m^2/s; $D_L = 1 \times 10^{-8}$ m^2/s; $\delta = \delta_m = 1 \times 10^{-4}$ m).

side (liquid phase) and the permeate side (vapor phase). This potential difference is expressed by applying H_p solubility on the permeate side. Taking into account that $H_m \neq H_p$ the enrichment factor can be expressed, as follows:

$$E = \frac{e^{\mathrm{Pe_L}}}{\xi + e^{\mathrm{Pe_L}} + \left(H_p/H_m - 1\right)} \tag{20}$$

Applying Eq. (18) we recalculated the enrichment factor at a constant value of H_m ($H_m = 50$) and at different values of H_p (Fig. 7) as a function of the $\mathrm{Pe_L}$ number. As can be seen the value of enrichment factor are strongly affected by the H_p values. With increasing $\mathrm{Pe_L}$ number enrichment factor decreases to unit, but with decreasing Peclet number its value tends to a limiting value and can have much higher value than unit. Similarly, the polarization modulus in Eq. (17) will also be less (not shown here) than unit according to the E value obtained by Eq. (20). Further analysis is needed to clarify the real effect of the variable solubility (and other effects as the variable diffusivity, the coupling of the two-component transport, etc.) on the separation efficiency.

4. Conclusion

The concentration polarization is affected not only by the external hydrodynamic conditions but on the mass transport process inside of the membrane layer. The membrane Peclet number, the solubility coefficient, the membrane thickness can strongly affect the concentration profile in the concentration boundary layer as well. The traditional models of the concentration polarization doe not contain the effect of the membrane mass transport parameters.

Acknowledgement

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Symbols

C	liquid concentration, mol/m^3
C^*	liquid concentration at membrane interface on the feed side, kg/m^3
C^*_{out}	liquid concentration at membrane interface on the downstream side, kg/m^3
C_b	inlet liquid concentration, kg/m^3
C_p	outlet permeate concentration, kg/m^3
D	diffusion coefficient of the boundary layer, m^2/s
E	enrichment factor,–
E_o	intrinsic enrichment factor, –
H_m	solubility coefficient, –
H_p	solubility coefficient on the permeate side, –
I	polarization modulus, –
J	mass transfer rate, kgl/m^{2}s
Pe	Peclet number, –
y	space coordinate, m
Y	dimensionless space coordinate, –

Greek letters

β	mass transfer coefficient, m/s
γ	activity coefficient, –
δ	boundary layer thickness, m
δ_m	membrane thickness, m
ρ_b	density of the feed liquid, kg/m^3
ν	convective velocity in the boundary layer, m/s

Subscripts

L	liquid
m	membrane

References

[1] S. Bhattacharya and S.-T. Hwang, Concentration polarization, separation factor, and Peclet number in membrane processes, J. Membr. Sci., 132 (1997) 73–90.

[2] P.L.T. Brian, Mass transport in reverse osmosis, in: U. Merten (Ed.), Desalination by Reverse Osmosis, M.I.T. Press, Cambridge, USA, 1966, p. 181.

[3] M.H.V. Mulder, Basic Principles of Membrane Technology, Kluwer Academic, Dordrecht, 1991, pp. 416–464.

[4] R.W. Baker, J.G. Wijmans, A.L. Athayde, R. Daniels, J.H. Ly, M. Le, The effect of concentration polarization on the separation

of volatile organic compounds from water by pervaporation, J. Membr. Sci., 137 (1997) 159–172.

[5] L. Song, A new model for the calculation of the limiting flux in ultrafiltration, J. Membr. Sci., 144 (1998) 173–185.

[6] L. Song, Permeate flux in crossflow ultrafiltration under intermediate pressure, J. Colloid Interface Sci., 214 (1999) 251–263.

[7] E. Nagy and G. Borbély, The effect of the concentration polarization and the membrane layer mass transport on the membrane separation, J. Appl. Membr. Sci. Tech., 6 (2007) 1–8.

[8] R.W. Baker, Membrane technology and application, 2nd ed., John Wiley and Sons, Chichester, England, 2004, pp. 171–181.

[9] R.W. Baker, Membrane technology and application, 2nd ed., John Wiley and Sons, Chichester, England, 2004, pp. 36–42.

[10] M. Bass and V. Freger, Hydration of nafion and dowex in liquid and vapor environment: Schroeder's paradox and microstructure, Polymer, 49 (2008) 497–506.

Appendix

The concentration distribution obtained by the integration of Eqs. (5a) and (5b) can be given by Eqs. (6) and (7). The values of parameters, T_L, Q_L, T_m, Q_m can be obtained by the solution of the algebraic equations using the internal (Eqs. (9) and (10)) and external (Eqs. (8) and (13)) boundary conditions. They are listed below. From these all important parameters, namely overall mass transfer rate, concentration polarization modulus, enrichment, the concentration profiles in both the boundary and membrane layers, etc. can be calculated. For this prediction all important transport parameter, namely Pe_L, Pe_m, S_m, δ/δ_m should be known.

$$T_L = H_m \frac{C_b(\mathrm{Pe}_L \beta_L/\beta_m - H_m) + C_p}{\mathrm{DEN}} \tag{A1}$$

$$Q_L = H_m \frac{C_b e^{\mathrm{Pe}_L} - C_p}{\mathrm{DEN}} \tag{A2}$$

$$\mathrm{T_m} = \mathrm{H_m} \frac{\beta_L}{\beta_m} \frac{\mathrm{Pe_L}\left(\mathrm{C_p} - \mathrm{C_b e^{PeL}}\right)}{\mathrm{DEN}} \tag{A3}$$

$$Q_m = \left\{ C_p H_m \langle \xi + H_m (e^{\mathrm{Pe}_L} - 1) \rangle + C_b H_m \left(1 + \frac{\delta_m}{\delta}\right) \xi \right\} \frac{1}{\mathrm{DEN}} \tag{A4}$$

$$\mathrm{DEN} = H_m \left(e^{\mathrm{Pe}_L} - 1\right) + \xi$$