

Overall mass transfer rate's equations for separation by pervaporation of dilute aqueous solution

Endre Nagy

University of Pannonia, Research Institute of Chemical and Process Engineering
P.O.Box 158, 8201 Veszprém, Email: nagy@mik.vein.hu;

The negative effect of the stagnant concentration boundary layer on the mass transport through a membrane has been investigated for a long time. Experimental results have indicated that the liquid mass transfer boundary layer could affect the separation performance of the pervaporation system with Reynolds number as high as 10,000 (She and Hwang, 2006). It was proved that this layer can be a major limiting factor in various membrane separation processes (Bhattacharya and Hwang, 1997). Number of paper analyzed the effect of the concentration polarization and defined the well known equation to its prediction (e.g. Baker et al., 1997). Almost all earlier studies consider the mass transport equations in the boundary layer, only, defining its Peclet number ($Pe_L = v\delta_L/D_L$) and its effect on the outlet and interface concentration (Baker et al., 1997), but do not discuss the effect of the mass transport through the membrane layer and its back effect on the concentration polarization layer, consequently, its effect on the membrane separation. The membrane is regarded as a black box, there is inlet- and outlet mass transfer in that box, but how its mass transport properties affect the inlet and the outlet mass flows is not discussed, in most of these papers. This situation is illustrated by Fig. 1A, where concentration profiles are not given in the membrane layer. The inlet and outlet concentrations, the liquid concentration on the membrane feed surface as well as the liquid phase Peclet number, Pe_L are known in this treatment. During gas permeation or pervaporation, the driving force is the chemical potential difference, transmembrane pressure difference, etc. and consequently, depletion of the preferentially permeating components in the boundary layer takes place, due to its permeation through the membrane layer (Fig. 1B). Recently, several papers have investigated and modeled the mass transport during pervaporation of dilute organic compounds [She and Hwang, 2006, Bhattacharya and Hwang, 1997, Baker et al., 1997]. She and Wang (2004, 2006) defined specific mass transfer driving force based on the nonequilibrium thermodynamic formalism. They combined the concentration polarization equation with the solution-diffusion model of the membrane transport, taking into account the diffusive mass flow (J) in the membrane [$J = K(C_b - PC_p/H) = k_L(C_b - C_m) = k_m(C_m - PC_p/H) = Cv$, where K is the overall mass transfer coefficient, P is pressure of vapor, H is the Henry's law constant of species investigated, k_L and k_m are the mass transfer coefficient in the boundary layer and in the membrane, respectively, v is the convective velocity, C is the concentration]. Similar approach was applied by Olsson and Trägårdh (2001), Schafer and Crespo (2007) used also the

resistance-in-series model regarding the mass transport as diffusive one in both the boundary layer and membrane layer. Jiratananon et al. [17] have also combined the simple mass transfer equation ($J=k\Delta C$, k mass transfer coefficient for the boundary layer, ΔC denotes the driving force), given for the boundary layer, with the permeant convective mass transfer rate ($J=vC_p$) and obtained the J value for the boundary layer as given by Eq. (3). An important question that arises is that there is convective mass transport through the membrane or not during pervaporation of dilute volatile organic compounds through dense but plasticized (swollen) polymeric membrane. However, if you assume convective velocity in the concentration boundary layer then, according to the continuity law, it should also exist in the membrane structure. Another question is how the large water mass transfer rate can influence (increase) the transfer rate of the dilute organic compounds. Water transfer rate can one order of magnitude higher than that of the organic one (Garcia et al., 2008, Ten and Field, 2000, She and Hwang, 2006).

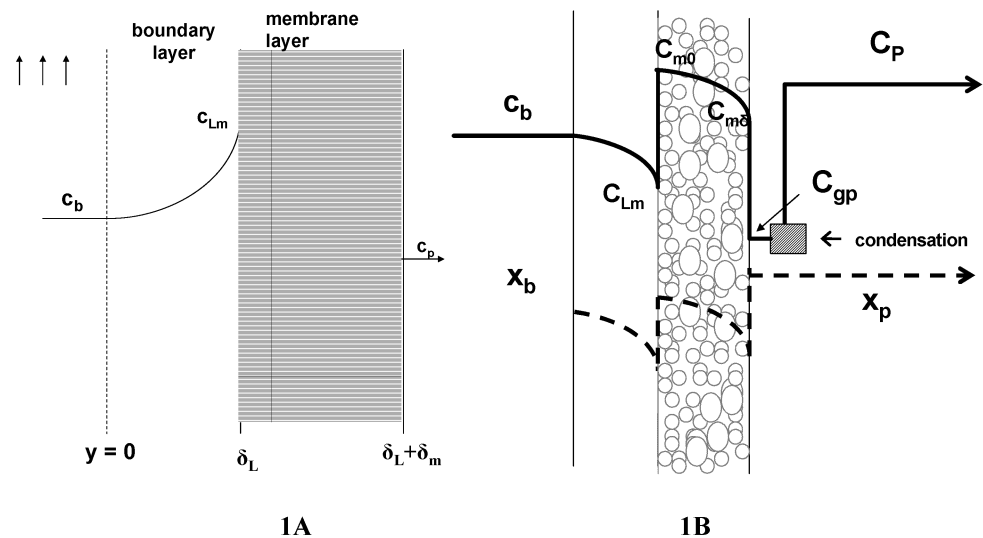


Fig.1 The concentration distribution and notations in the boundary and membrane layers; 1A: membrane layer is regarded as a “black box”; 1B: Concentration distribution for pervaporation

The main aim of this work is to discuss the basic equations of mass transfer rates, of the concentration profiles, of the ratio of convective and diffusive mass flows, etc. These equations should also take into account the mass transport parameters (convective velocity, diffusion coefficient, solubility) of both the concentration boundary layer and the membrane layer. The mass transfer equations should be defined as a product of a mass transfer coefficient and driving force, similarly to that used in the case of gas-liquid system.

1. Basic equations of the polarization model from previous works

At steady state, the mass transport rate in the boundary layer equals the amount permeated through the membrane (Baker et al., 1997, She and Hwang, 2006, Bhattacharya and Hwang, 1997):

$$vC - D_L \frac{dC}{dy} = vC_p \quad (1)$$

Applying the boundary conditions (at $y=0$ $C=C_b$), you can get the concentration distribution ($Y=y/\delta$):

$$C = (C_b - C_p) e^{Pe_L Y} + C_p \quad (2)$$

It is to note that Eq. (2) does not involve the effect of the membrane layer on the separation. It is obvious that the value of the outlet concentration, C_p can be essentially determined by the mass transport properties of the membrane layer. There is a lot of paper discussing this problem regarding the pervaporation process (She and Hwang, 2004, 2006, Jiraratananon et al., 2002). Typical equation for the mass transfer rate taking into account the mass transport in the membrane layer, as well, is developed by Jiraratananon et al. (2002):

$$J = \left(\frac{1 - (X_b / X_p)}{\exp(v_L / k_L) - 1} \right) (C_b - C_{Lm}) \quad (3)$$

2. Theory

The mass transfer will be defined in the presence of the membrane layer applying the well known boundary conditions defined by Eq. (1). The equation system given for the two layers (boundary and membrane layers) will be defined in an general form, as well, which involve the above case as well.

2.1 Mass transfer rate obtained with boundary conditions given in Eq. (1)

Differential equation system to be solved:

$$v_j \frac{dC}{dy} - D_j \frac{d^2C}{dy^2} = 0 \quad \text{where } j = L, m \quad (4)$$

where subscript L and m related to the boundary layer and membrane, respectively. The value of v_L is equal to the outlet convective velocity applied in Eq. (1).

The boundary conditions to be applied are as:

$$\text{if } y=0 \quad \text{then } C=C_b \quad (5a)$$

$$\text{if } y=\delta \quad \text{then } SC_{Lm}=C_{m0} \quad (5b)$$

$$\text{if } y=\delta \quad \text{then } v_L C - D_L \frac{dC}{dy} = v_m C - D_m \frac{dC}{dy} \quad (5c)$$

$$\text{if } y=\delta_L + \delta_m \quad \text{then } v_m C - D_m \frac{dC}{dy} = v_L C_p \quad (5d)$$

The solution of the differential equation system by means of the above boundary conditions one can get the following equation for the boundary layer (it is well known from the literature) and for the membrane layer:

For the boundary layer ($0 \leq y \leq \delta$):

$$C = (C_b - C_p) e^{Pe_L y} + C_p \quad (6)$$

For the membrane layer ($\delta \leq y \leq \delta_L + \delta_m$):

$$C_m = \left\{ \left[S \left(1 - e^{Pe_L} \right) - \frac{v_L}{v_m} \right] C_p + S C_b e^{Pe_L} \right\} e^{Pe_m (y - \delta) / \delta_m} + \frac{v_L}{v_m} C_p \quad (7)$$

where

$$Pe_L = \frac{v_L \delta_L}{D_L} \quad Pe_m = \frac{v_m \delta_m}{D_m}$$

2.2 Mass transfer rate obtained by general boundary conditions

The differential equation system to be solved is identical with Eq. (4). The boundary conditions applied for the solution are partly identical with the above expression. For the solution should be used Eqs (5a) to (5c), as well as, the following condition instead of Eq. (5d), as the 4th boundary condition, at $y = \delta_L + \delta_m$:

$$\text{if } y = \delta_L + \delta_m \quad \text{then} \quad C_{m\delta} = S C_{gp} \quad (8)$$

The overall mass transfer rate, J , namely the sum of diffusive flow and convective flow, taking into account both layers, namely the concentration boundary layer and membrane layer, can be given as follows:

$$J = \beta_{tot}^0 \left(C_b - e^{-(Pe_L + Pe_m)} C_{gp} \right) \quad (9)$$

where

$$\beta_{tot}^0 = \frac{1}{\frac{1}{\beta_L^0} + \frac{e^{-Pe_L}}{S \beta_m^0}} \quad (10)$$

$$\text{with e.g. } \beta_m^0 = \frac{D_m}{\delta_m} Pe_m \frac{e^{Pe_m}}{e^{Pe_m} - 1} \equiv k_m Pe_m \frac{e^{Pe_m}}{e^{Pe_m} - 1}$$

The value of β_L^0 can be given similarly to β_m^0 . Details of the solution can be found in Nagy and Kulcsar's paper (2009) who investigated the effect of biochemical reaction on the mass transfer in a membrane reactor.

Applying the boundary condition given by Eq. (1), namely $J = v_L C_p$, one can give equation as follows.:

$$\beta_{tot}^0 \left(C_b - e^{-(Pe_L + Pe_m)} C_{gp} \right) = v_L C_p \quad (11)$$

If the above assumption is fulfilled then the mass transfer rate can be given as follows: (with applying $C_{gp} \Phi = C_{Lp}$: the vapor concentration, in g/m^3 or mol/m^3 differs

essentially from that of condensate; their mol- or mass fraction is generally identical to each other).

$$J = \beta_{\text{tot}}^{\circ} C_b \left(1 - \frac{\beta_{\text{tot}}^{\circ}}{\beta_{\text{tot}}^{\circ} + \Phi_{\text{VL}} e^{(\text{Pe}_L + \text{Pe}_m)}} \right) \quad (12)$$

The above equation gives the mass transfer rate involving the mass transport properties of the membrane layer as well and fulfill also the Eq. (1) used generally for pervaporation process.

3. Results

The model developed gives generally the mass transfer rate in a membrane layer where there is convection and diffusion in the layer. As a typical figure, the concentration distribution is plotted in Fig. 2 applying Eqs. (6) and (7). The outlet concentration of the transporting compound strongly depends on both the Pe_L and Pe_m numbers. The model can also be applied for the description of the pervaporation by means of Eqs. (6), (7) and (11). The model offers also possibility to describe of the mass transport in presence of chemical or biochemical reaction. In this lecture the pervaporation process will be discussed. Eqs. (3) and (12) will also be compared.

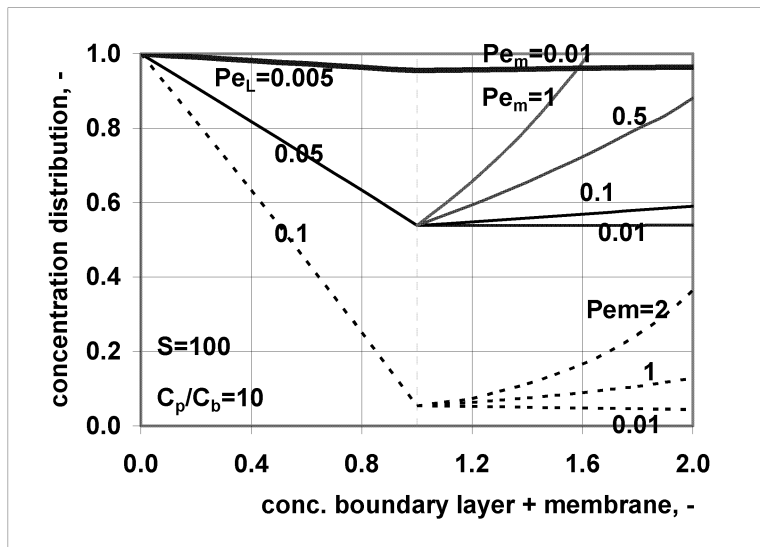


Fig. 2 Concentration distribution in the concentration boundary layer and membrane layer applying Eqs. (6) and (7). ($k_L = k_m = 1 \times 10^{-4} \text{ m/s}$; $\delta/\delta_m = 1$; $D/D_m = 1$)

4. Conclusion

The concentration distribution has been defined solving the differential equation system, Eq. (4) with boundary conditions, Eqs. (5a) to (5d). As can be seen, the Pe_m does not affect the concentration of the boundary layer (Fig. 2). The mass transfer rate has been also defined in a general form [Eq. (9)] with boundary conditions, Eqs. (5a) to (5c) and

(8). Applying Eq. (11) one gets the mass transfer rate for prevaporation which involves the membrane's mass transport parameters, as well.

Acknowledgement

We kindly acknowledge Hungarian Scientific Research Fund under Grants OTKA 63615/2006 for supported this work

References

- Baker R.W., Wijmans J.G., Athayde A.L., Daniels R., Ly L.H. and Le M., 1997, The effect of concentration polarization on the separation of volatile organic compounds from water by pervaporation, *J. Membrane Sci.*, 137, 159-172.
- Bhattacharya S. and Hwang S.-T. 1997, Concentration polarization, separation factor, and Peclet number in membrane processes, *J. Membrane Sci.*, 132, 73-90.
- García V., Pongrácz E., Muurinen E. and Keiski R.L., 2009, Pervaporation of dichloromethane from multicomponent aqueous systems containing n-butanol and sodium chloride, *J. Membrane Sci.* 326, 92-102.
- Jiraratananon R., Chanachai A. and Huang R.Y.M., 2002, Pervaporation of ethanol-water mixtures with chitosan/hydroxyethylcellulose (CS-HEC) composite membranes II. Analysis of mass transport, *J. Membrane Sci.*, 199, 211-222.
- Nagy E. and Kulcsár E., 2009, Mass transport through biochemical membrane reactor, *Desalination*, (in press)
- Olsson J. and Trägårdh G., 2001, Pervaporation of volatile organic compounds from water, I Influence of permeate pressure on selectivity, *J. Membrane Sci.*, 187, 25-37.
- She M. and Hwang S.-T., 2006, Effects of concentration, temperature, and coupling on pervaporation of dilute flavor organics, *J. Membrane Sci.*, 271, 16-28.
- She M. and Hwang S.-T., 2004, Concentration of dilute flavor compounds by pervaporation: permeate pressure effect and boundary layer resistance modeling, *J. Membrane Sci.*, 236, 193-202.
- Schafer T. and Crespo J., 2007, Study and optimization of the hydrodynamic upstream conditions during recovery of a complex aroma profile by pervaporation, *J. Membrane Sci.*, 301, 46-56.
- Ten P.K. and Field R.W., (2000) Organophilic pervaporation: an engineering science analysis of component transport and the classification of behavior with reference to the effect of permeate pressure, *Chem. Eng. Sci.*, 55, 1425-1445.