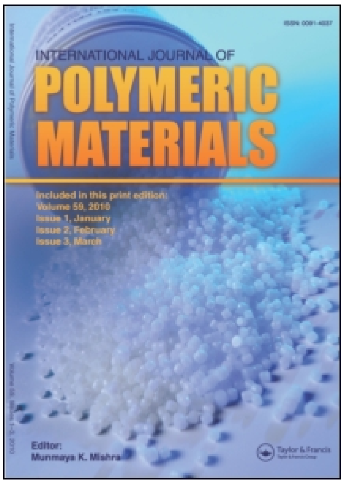

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Concentration Polarization in the Baromembrane Process

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Equations correlating the flows of the components and concentration polarization in baromembrane process are developed and discussed.

Keywords: Baromembrane process; mass transfer; component flow; concentration polarization; phenomenological equations

INTRODUCTION

For the analysis of the concentration polarization in the baromembrane process, the flows of the components in the limit diffusion layer and in the membrane are written in the form based on the phenomenology of the thermodynamic irreversible processes. The obtained equations of the connection between the flows show that the pressure change in the pre-membrane layer of the solution is not the outer factor, but the response of the system on the gradient of composition caused by the baromembrane process of separation. For the dilute solutions the integral equations of the mass-transfer are suggested and the calculations based on them are represented. They show that the negative effects of the concentration polarization are most abruptly

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displayed in the range of the dilute solutions and at high pressures, that correspond to conditions of common processes of the irreversible osmosis.

THEORY AND DISCUSSION

The concentration polarization, related to the change of the composition of the pre-membrane layer of the initial solution as compared with its composition in the volume is the inevitable consequence of the baromembrane process of the separation of the components. Consequently the concentration of the fast component in the pre-membrane layer becomes lower while that of the slow component increases. Therefore, the concentration polarization increases the flow of the slow component and decreases the flow of the fast component. This significantly changes for worse the quantitative and qualitative characteristics of the baromembrane process. The theoretical investigations [1–3] allow us to estimate qualitatively the effects of the concentration polarization, which significantly simplifies the problem (See Fig. 1).

In this study the approach based on the analysis of the flows in the limit diffusion layer is suggested [1,2] from the same positions of the thermodynamics of the irreversible processes, as in the analysis of the flows through the membrane. The flows of the components J_i (index "m" refers to the membrane and index "s"–to the solution of the limit diffusion layer). They are determined by the equations:

$$\begin{aligned} J_{is} &= -(D_i/RT)c_{is}(v_{is}\nabla P_s + RT\nabla \ln a_{is}), \quad x = -\delta_s, 0 \\ J_{im} &= -(L_i/RT)c_{im}(v_{im}\nabla P_m + RT\nabla \ln a_{im}), \quad x = -0, \delta_s, \end{aligned} \tag{1}$$

In which: c_i, v_i, and a_i–correspondingly the molar-volume concentration, partial-molar volume and activity of the component of solution in the limit diffusion layer and in the free volume of the membrane; D_i and L_i–coefficients of diffusion in the solution and transfer through the membrane; ∇_i–operator d/dx, where x–coordinate of the transfer, perpendicular to the surface of the membrane, ∇P_s and ∇P_m–gradients of the pressure in the limit

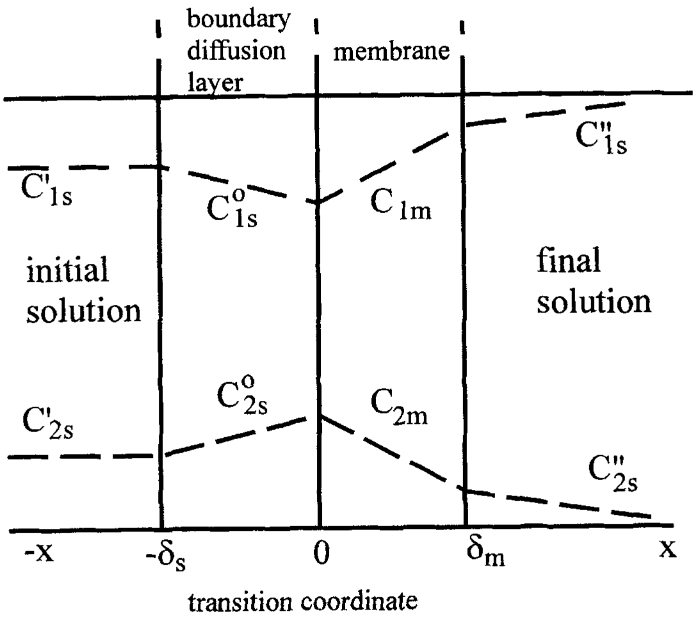

FIGURE 1 Scheme, explaining the effects of the comcentration polarization in baromembrane process. (1 – fast, 2 – slow component).

diffusion layer and the membrane corrspondingly. While considering further only the binary solution, from (1) taking into account the Gibbs-Duhem equation we obtain the equations of the bond between flows of the components

$$J_{1s}/D_1 + J_{2s}/D_2 = -\nabla P_s/RT$$
$$J_{1m}/L_1 + J_{2m}/L_2 = -\nabla P_m/RT \qquad (2)$$

Passing to the stationary state of the system, we have $\partial c_i/\partial t = 0$, $\nabla J_i = 0$ and $J_i =$ const. Integrating (2) at this conditions and taking into account the limit values : $P = P'$ under $x = -\partial_s$, $P = P^\circ$ under $x = 0$ and $P = P''$ under $x = \delta_m$, we obtain:

$$J_{1s}/D_1' + J_{2s}/D_2' = -\Delta P_s/RT$$
$$J_{1m}/L_1' + J_{2m}/L_2' = -\nabla P_m/RT \qquad (3)$$

where $\Delta P_s = P^{\circ} - P'$, $\Delta P_m = P'' - P^{\circ}$ – pressure changes in the limit diffusion layer and in the membrane correspondingly and $D_i' = D_i/\delta_s$, $L_i' = L_i/\delta_m$.

Molar flows of the components J_{is} and J_{im} may be expressed by the volume flow, J_v, common for the limit diffusion layer and the membrane

$$J_{is} = J_v(C_{is}'' - C_{is}') = J_v \Delta C_{is}, \quad J_{im} = J_v C_{is}'' \tag{4}$$

Then the analogs (3) will be

$$\begin{aligned} J_v(\Delta C_{1s}/D_1' + \Delta C_{2s}/D_2') &= -\Delta P_s/RT \\ J_v(C_{1s}''/L_1' + C_{2s}''/L_2') &= -\Delta P_m/RT \end{aligned} \tag{5}$$

Introducing the total pressure change $\Delta P = \Delta P_s + \Delta P_m = P'' - P'$ we obtain the united equation of bond between the flows.

$$J_v(\Delta C_{1s}/D_1' + \Delta C_{2s}/D_2'' + C_{1s}''/L_1' + C_{2s}''/L_2') = -\Delta P/RT \tag{6}$$

From (5) and (6) we express ΔP_s and ΔP_m by ΔP. If in the baromembrane process the components do not separate then $\nabla \ln a_{im} = 0$. From (1) follows, that this condition demands the equality

$$L_i v_{1m} = L_2 v_{2m} \tag{7}$$

Thus, the concentration polarization does not change the condition (7) of indivisibility of the components of the solution in the baromembrane process and the faster component is that, which has the higher factor $L_i v_{im}$. In the absence of separation of the components there is concentration polarization $\nabla \ln a_{is} = 0$, $\Delta c_{is} = 0$. Therefore according to (4) we have $J_{is} = 0$, according to (1) and (5) $-\Delta P_s = \nabla P_s = 0$. Thus the gradient of pressure in the limit diffusion layer is not the outer factor, but the response of the system to the gradient of composition, caused by the separation. Evidently, the gradient of pressure in the limit diffusion layer is determined by the difference not only of the coefficients of diffusion of the components, but also of their partial-molar volumes. This dependence is easy to establish stating $v_{is} = \text{const.}$ Then the first equation in (5) may be written down as

$$J_v(\Delta\phi_{1s}/D_1{}'v_{1s} + \Delta\phi_{2s}/D_2{}'v_{2s}) = -\Delta P_s/RT \tag{8}$$

where $\Delta\phi_{is} = \phi_{is}{}'' - \phi_{is}{}'$, and $\phi_{is} = c_{is}v_{is}$ – volume fraction.

In binary system $\Delta\phi_{1s} = -\Delta\phi_{2s}$, therefore it follows from (8) that at $D_1v_{1s} = D_2v_{2s}$ the change of pressure gradient in the limit diffusion layer is equal to zero (or near zero) while the condition of $v_{is} = \text{const.}$ is not kept. Besides, the sign of ΔP_s is determined not by the outer change gradient of pressure $\Delta P < 0$, but by the relationship of factors D_iv_{is} of the components. So at condition $\Delta\phi_{1s} > 0$ (fast component) in situation of $D_1v_{1s} > D_2v_{2s}$ we have $\Delta P_s > 0$, and at $D_1v_{1s} < D_2 v_{2s} - P\Delta_s > 0$.

The equation of the connection (6) or (8) and (9) does not contain the simplification in statements and are convenient for the quantitative analysis of the experimental data, but they are in sufficient for the theoretical description of the flows. In particular, in the case of dilute solutions, the most important for the practice of baromembrane processes, the following conditions hold; $v_{is} = v_{im} = \text{const.}$, $\gamma_{is} = \gamma_{im} = \text{const.}$, $\phi_{1s}v_{2s} \gg \phi_{2s}v_{1s}$ in which γ_i – coefficient of activity. Therefore, it is necessary to obtain the integral equations of the flows, corresponding to differential ones in (1). Using $\phi_{is} = \phi_{is}{}'$ at $x = -\delta_s$, $\phi_{is} = \phi_{im} = \phi_{is}^{\circ}$ at $x = 0$ and $\phi_{im} = \phi_{is} = \phi_{is}''$ at $x = \delta_m$ is allows us to obtain

$$\begin{aligned} \phi_{1s}^0 &= \phi_{1s}e^{-J_{1s}V_{2s}/D_1'}\left[\frac{D_1'\Delta P_s\phi_{1s}'}{J_{1s}RT}\left(1 - e^{-J_{1s}V_{2s}/D_1'}\right) + 1\right]^{-1} \\ \phi_{1s}'' &= \phi_{1s}^0e^{-J_{1m}V_{2s}/L_1'}\left[\frac{L_1'\Delta P_m\phi_{1s}^0}{J_{1m}RT}\left(1 - e^{-J_{1m}V_{2s}/L_1'}\right) + 1\right]^{-1} \end{aligned} \tag{9}$$

For the calculation of all of the variables $J_{is}, J_{im}, \phi_{is}''\phi_{is}\phi_{is}^{\circ}\Delta P_m$ and ΔP_m on given $\phi_{is}{}'$ and ΔP and parameters D_i and L_i the Eq. (9) must be solved together with (3) and (4) or (4) and (5) taking into account the bonds $\phi_{1s} + \phi_{2s} = 1$, $\Delta P_s + \Delta P_m = \Delta P$. At not very high pressures, the implementation of the inequality $v_{2s}\Delta P/RT \ll 1$, is justified and by neglecting the pressure change gradient in the limit diffusion layer ($\Delta P_s = 0$, $\Delta P_m = \Delta P$) due to the equality $D_1 v_{1s} = D_2 v_{2s}$ we obtain from (9) a simpler, but less precise equations, in which $\Delta\phi_{is} = \phi_{is}'' - \phi_{is}'$:

$$\phi^0_{is} = \phi_{1s}'(1 - J_v \Delta\phi_{1s} v_{2s}/D_1' v_{1s}) = \phi_1'(1 - J_v \Delta\phi_{1s}/D_2') \qquad (10)$$

$$\phi_{1s}'' = \phi^0_{1s}(1 - J_v \phi_{1s}'' v_{2s}/L_1' v_{1s})/(1 + \phi^0_{1s} v_{2s} \Delta P/RT) \qquad (11)$$

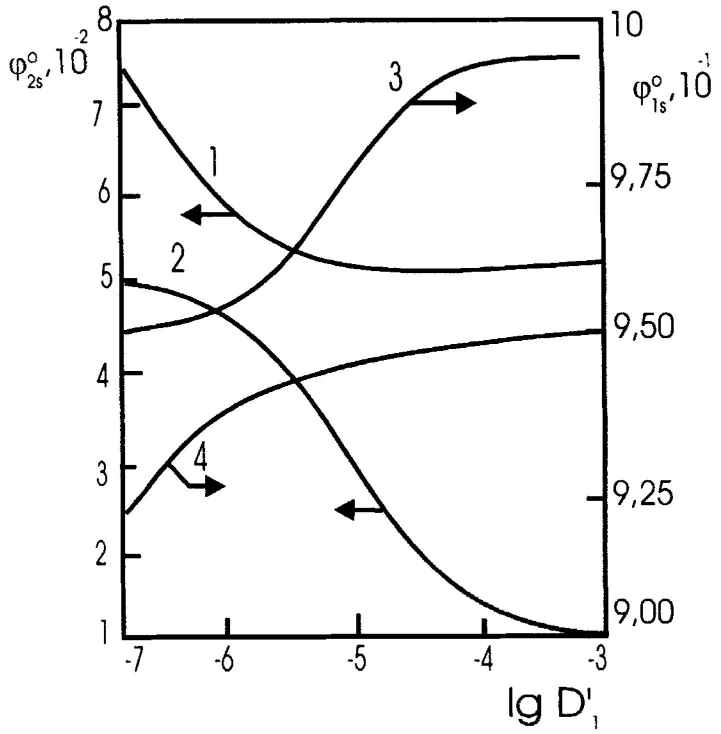

FIGURE 2 Calculated dependencies of the pre-membrane concentration of the slow (ϕ_{2s}^0) and quick (ϕ_{1s}^0) components from the coefficient of diffusion at $-\Delta P = 2$ mPa and $\phi_{2s}' = 0.01$ (curves 2, 4) and $\phi_{1s}' = 0.05$ (curves 1, 3).

Adding (10) and (11) by the equation of bond (5) in form

$$J_v(\phi_{1s}''/L_1'v_{1s} + \phi_{2s}''/L_2'v_{2s}) = -\Delta P/RT \qquad (12)$$

we have a system of algebraic equations for calculation of ϕ_{is}°, ϕ_{is}'' and J_v, on given ϕ_{is}', ΔP, D_i', and L_i'. Molar flows are calculated from (4).

Part of the calculations made on Eqs. (10–12) for the variant $L_i' = 10^{-3}, L_2' = 3\cdot10^{-8}\,\mathrm{m/c}$, $V_{1s} = 1\cdot8\cdot10^{-5}, V_{2s} = 6\cdot10^{-5}\,\mathrm{m^3/mol}$ are represented of the Figures 1 to 4.

As the short comment on them, we should note only that sharply negative effects of the concentration polarization occur in the diluted solution and high pressures, that corresponds of parameters of widespread processes of the reverse osmosis. This products the higher

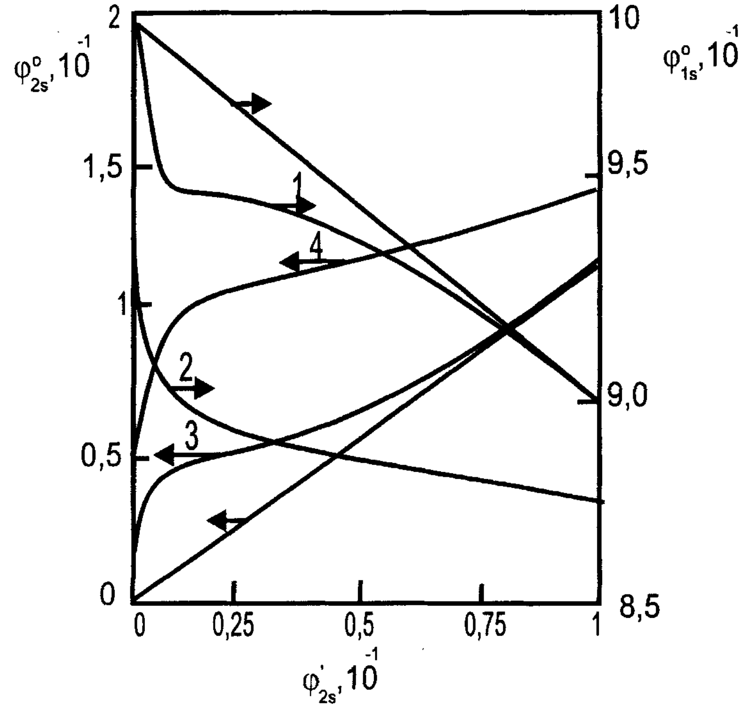

FIGURE 3 Calculated dependencies of the pre-membrane concentration of the components from the composition of the initial solution at $D_1' = 10^{-6}$ m/sec and $-\Delta P = 2$ mPa (curve 1, 3) and $-\Delta P = 5$ mPa (curve 2, 4). Straight lines correspond to the equality $\phi_1^0 = \phi_1'$ in absence of the concentration polarization.

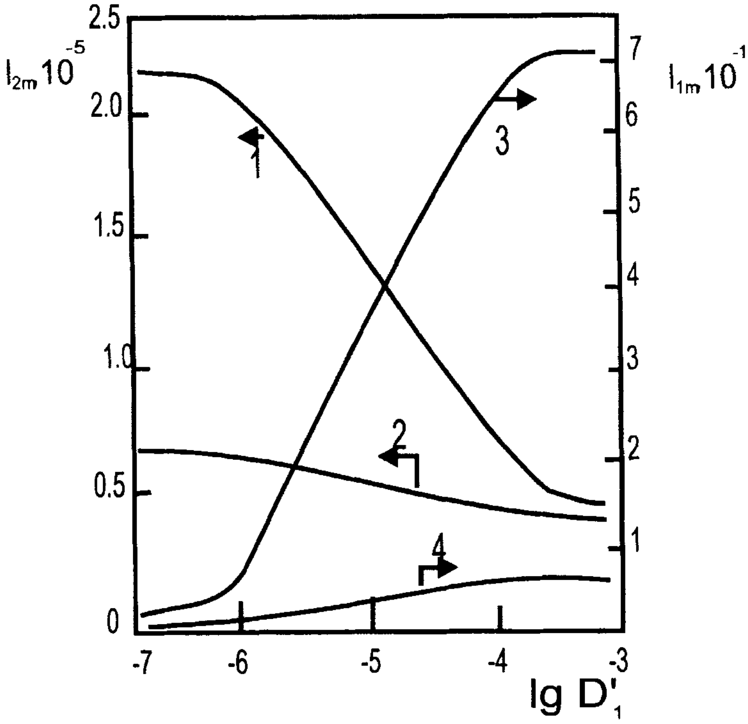

FIGURE 4 Calculated dependencies of the molar flows of slow (J_{2m}) and quick (J_{1m}) components trough the membrane, from the coefficient of diffusion at $-\Delta P = 2$ mPa and $\phi_{2s}' = 0.01$ (curves 2, 4) and $\phi_{2s}' = 0.05$ (curves 1, 3).

demands to the organization of the hydrodynamic regimes in corresponding membrane apparatus.

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