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GENERAL ANALYSIS OF CONCENTRATION POLARIZATION IN SEPARATION OF MULTICOMPONENT MIXTURES BY BAROMEMBRANE METHODS

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A method for calculation of concentration polarization in separation of multicomponent mixtures by baromembranes with allowance for the mutual influence of the components in the process of molecular diffusion is described. Equations are derived for the concentration polarizations of binary and multicomponent mixtures under unsteady conditions.

Baromembrane installations (retroosmotic, ultrafiltration plants) operate either in a continuous regime, in which the initial mixture is pumped only once through series apparatuses with the concentrate and the permeate being removed continuously, or in a semicontinuous regime, in which the processed solution is circulated, the permeate is continuously selected, and the concentrate is removed from the system periodically until the required degree of saturation is reached. In the operation of semicontinuous-action plants, the composition of the initial mixture changes with time from some initial value to the required one.

The separation of liquid mixtures by baromembrane methods depends greatly on the concentration polarization, which consists of an increased permeate concentration near the membrane surface as compared to the flow core. In the general case, the adverse effects of this phenomenon comprise a decrease of the moving force, formation, in some cases, of a gel layer on the membrane surface, which leads to an abrupt increase in the hydrostatic resistance to transfer, and changes in the properties and separation characteristics of the membranes. Numerous theoretical studies of concentration polarization describe the behavior of binary mixtures consisting of a solvent and a permeate [1]. We investigate the regularities of concentration polarization in the case of separation of multicomponent mixtures under unsteady diffusion conditions in a pregel regime within the framework of a film model for a semicontinuous process.

We select a membrane element with respect to whose length and width the concentration of the initial mixture is constant, while the composition of the latter changes with time and is prescribed by some function. Assume that diffusion proceeds only along the normal to the membrane surface. At first we consider the concentration distribution of components in a diffusion layer for a binary mixture

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + v_0\frac{\partial c}{\partial x}\,, \tag{1}$$

$$c\,(l,\,t) = g\,(t)\,, \tag{2}$$

$$v_0\,c\,(0,\,t) + D\,\frac{\partial c\,(0,\,t)}{\partial x} = 0\,, \tag{3}$$

$$c\,(x,\,0) = c_0\,. \tag{4}$$

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Boundary condition (2) shows that the concentration of the initial mixture changes with time (increases in our case). Boundary condition (3) expresses the material balance near the membrane surface: the amount of permeate transferred to the membrane surface by convection is equal to that of the permeate carried away from the membrane surface by molecular diffusion (the membrane transmits only the solvent). Thus, boundary condition (3) mathematically formulates the origin and development of concentration polarization. Initial condition (4) indicates that the substance concentration at the initial moment is constant along the diffusion path. Equations (1)-(4) are derived under the assumption that the rate of solvent filtration through the membrane does not change with time.

The solution of Eq. (1) with boundary (2), (3) and initial (4) conditions is sought in the form

$$c(x, t) = \frac{D}{D - lv_0} g(t) \left(1 - \frac{x}{l}\right) + g(t) \frac{x}{l} + \exp\left(-\frac{v_0}{2D} x - \frac{v_0^2}{4D} t\right) v(x, t). \tag{5}$$

Substituting (5) into Eqs. (1)-(4), we arrive at

$$\frac{\partial v}{\partial t} - D \frac{\partial^2 v}{\partial x^2} = F(x, t), \tag{6}$$

$$v(l, t) = 0, \tag{7}$$

$$\frac{v_0}{2} v(0, t) + D \frac{\partial v(0, t)}{\partial x} = 0, \tag{8}$$

$$v(x, 0) = \varphi(x), \tag{9}$$

where

$$F(x, t) = \left(-\frac{\partial g(t)}{\partial t} \frac{D - xv_0}{D - lv_0} + g(t) \frac{lv_0}{lv_0 - D}\right) \times \exp\left(\frac{v_0 x}{2D} + \frac{v_0^2 t}{4D}\right);$$

$$\varphi(x) = \left(c_0 - g(0) \frac{D - xv_0}{D - lv_0}\right) \exp\left(\frac{v_0 x}{2D}\right).$$

The solution of Eqs. (6)-(9) can be represented in the form of the series

$$v(x, t) = \sum_{n=1}^{\infty} T_n(t) X_n(x),$$

where

$$X_n(x) = \sin(\lambda_n x) - \frac{2D}{v_0} \lambda_n \cos(\lambda_n x)$$

are the eigenfunctions of the corresponding homogeneous problem, and the eigenvalues are found by solving numerically the equation

$$\tan(\lambda_n l) = \frac{2D}{v_0} \lambda_n .$$

Performing series expansion of $F(x, t)$ in the eigenfunctions $X_n(x)$, we obtain the Cauchy problem for determination of $T_n(t)$

$$\frac{dT_n(t)}{dt} + D\lambda_n^2 T_n(t) = f_n(t)\,, \tag{10}$$

$$T_n(0) = \frac{1}{J_n} \int_0^l \varphi(x) \left[\sin(\lambda_n x) - \frac{2D}{v_0}\lambda_n \cos(\lambda_n x)\right] dx = a_n\,, \tag{11}$$

where

$$J_n = \frac{l}{2}\left(1 + \frac{4D^2\lambda_n^2}{v_0^2}\right) + \frac{\sin(2\lambda_n l)}{4\lambda_n}\left(\frac{4D^2\lambda_n^2}{v_0^2} - 1\right) + \frac{D}{v_0}\left[\cos(2\lambda_n l) - 1\right].$$

The general solution of Eqs. (10) and (11) is written in the form

$$T_n(t) = a_n \exp(-D\lambda_n^2 t) + \int_0^t \exp\left[-D\lambda_n^2 (t - \tau)\right] f_n(\tau)\, d\tau\,,$$

where

$$f_n(\tau) = \frac{1}{J_n} \int_0^l F(x, \tau) \left[\sin(\lambda_n x) - \frac{2D}{v_0}\lambda_n \cos(\lambda_n x)\right] dx\,.$$

Thus, the complete solution of problem (1)-(4) is

$$\begin{aligned} c(x, t) = {} & \frac{Dg(t)}{D - v_0 l}\left(1 - \frac{x}{l}\right) + g(t)\frac{x}{l} + {} \\ & + \exp\left(-\frac{v_0}{2D}x - \frac{v_0^2}{4D}t\right)\left\{\sum_{n=1}^{\infty} a_n \exp(-D\lambda_n^2 t)\cdot\right. \\ & \left[\sin(\lambda_n x) - \frac{2D}{v_0}\lambda_n \cos(\lambda_n x)\right] + {} \\ & \left. + \sum_{n=1}^{\infty}\left[\sin(\lambda_n x) - \frac{2D}{v_0}\lambda_n \cos(\lambda_n x)\right] \int_0^t \exp\left[(-D\lambda_n^2)(t - \tau)\right] f_n(\tau)\, d\tau\right\}. \end{aligned} \tag{12}$$

while the time variation of the permeate concentration near the membrane surface ($x = 0$)

$$\begin{aligned} c(0, t) = {} & \frac{Dg(t)}{D - v_0 l} + \exp\left(-\frac{v_0^2}{4D}t\right) \times \left\{\sum_{n=1}^{\infty} a_n \left(-\frac{2D}{v_0}\lambda_n\right) \exp(-D\lambda_n^2 t) + {}\right. \\ & \left. + \sum_{n=1}^{\infty}\left(-\frac{2D}{v_0}\lambda_n\right) \int_0^t \exp\left[-D\lambda_n^2 (t - \tau)\right] f_n(\tau)\, d\tau\right\}. \end{aligned} \tag{13}$$

To characterize the concentration polarization in a multicomponent mixture, we use the generalized Fick equation to describe molecular diffusion of permeates from the membrane surface into the flow core:

$$M_i = -\sum_{k=1}^{n} D_{ik} \nabla c_k\,, \quad i = 1, 2, \ldots, n - 1\,, \tag{14}$$

or in matrix form

$$(M) = -[D](\nabla c)\,. \tag{15}$$

It follows from Eqs. (14) and (15) that the diffusion flow of the component is proportional to the concentration gradients of all independent components. The intervelation between the diffusion coefficients in Eqs. (14) and (15) and the diffusion coefficients in binary solutions is expressed by the relation

$$[D] = [B]^{-1} ,$$

where the elements of the matrix $[B]$ are determined as follows [2]:

$$B_{ii} = \frac{c_i}{D_{in}} + \sum_{k=1}^{n} \frac{c_k}{D_{ik}} , \quad i = 1, 2, \ldots, n - 1 ;$$

$$B_{ij} = - c_i \left[\frac{1}{D_{ij}} - \frac{1}{D_{in}} \right] , \quad i, j = 1, 2, \ldots , n - 1 , \ i \neq j .$$

Proceeding from Eqs. (14) and (15), Eq. (1) can be written on the form

$$\frac{\partial c_i}{\partial t} = \sum_{k=1}^{n-1} D_{ik} \frac{\partial^2 c_k}{\partial x^2} + v_0 \frac{\partial c_i}{\partial x} , \quad i = 1, 2, \ldots, n - 1 , \tag{16}$$

or in matrix form

$$\frac{\partial (c)}{\partial t} = [D] \frac{\partial^2 (c)}{\partial x^2} + v_0 \frac{\partial (c)}{\partial x} . \tag{17}$$

Equations (16) and (17) differ from (1), which was written for a binary mixture, in its "coupled" form, i.e., the presence of nonzero cross coefficients in the matrix of real coefficients of multicomponent diffusion. Assuming $[D]$ to be a constant matrix composed of positive elements, we diagonalize $[D]$ using the modal matrix $[P]$ and the reciprocal modal matrix $[P]^{-1}$

$$[P]^{-1} [D] [P] = \begin{matrix} \ulcorner \mu_1 & & & & \\ & \mu_2 & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & \mu_{n-1} \lrcorner \end{matrix} = \ulcorner \mu \lrcorner .$$

After multiplying all terms of Eq. (17) by $[P]^{-1}$, we arrive at

$$\frac{\partial (\tilde{c})}{\partial t} = \ulcorner \mu \lrcorner \frac{\partial^2 (\tilde{c})}{\partial x^2} + v_0 \frac{\partial (\tilde{c})}{\partial x} ,$$

where $(\tilde{c}) = [P]^{-1} (c)$.

Having performed similar transformations of boundary and initial conditions (2)-(4), we obtain a system of equations for the concentration distribution of the components in a diffusion layer for a multicomponent mixture in the following form:

$$\frac{\partial \tilde{c}_i}{\partial t} = \mu_i \frac{\partial \tilde{c}_i}{\partial x^2} + v_0 \frac{\partial \tilde{c}_i}{\partial x} , \quad i = 1, 2, \ldots, n - 1 , \tag{18}$$

$$\tilde{c}_i (l, t) = \tilde{g}_i (t) , \quad i = 1, 2, \ldots, n - 1 , \tag{19}$$

$$v_0\tilde{c}_i(0, t) + \mu_i \frac{\partial \tilde{c}_i(0, t)}{\partial x} = 0\,, \quad i = 1, 2, ..., n - 1\,, \tag{20}$$

$$\tilde{c}_i(x, 0) = \tilde{c}_{0i}\,, \quad i = 1, 2, ..., n - 1\,. \tag{21}$$

Equations (18)-(21) are similar to (1)-(4); therefore, the solutions of (10) and (11) obtained above can be used to describe the behavior of the i-th component in "pseudoconcentrations." A transition from pseudoconcentrations to actual concentrations is accomplished by the equation

$$(c) = [P](\tilde{c})\,.$$

The concentration polarization for binary mixtures can be characterized by the ratio [3]

$$K = \frac{c_w}{c_b}\,,$$

which is valid provided that the concentrations of the permeate near the membrane surface and in the flow core do not change with time. In a semicontinuous regime of operation of baromembrane installations, the permeate becomes accumulated in the treated solution and, as a consequence, the substance concentration near the membrane surface changes. In this case, it is reasonable to introduce the following function to quantitatively describe the concentration polarization in separation of binary mixtures:

$$K(t) = \frac{g(t)}{c(0, t)}\,. \tag{22}$$

Generalizing formula (21) to the process of separation of multicomponent mixtures, we arrive at

$$K_i(t) = \frac{g_i(t)}{c_i(0, t)}\,, \quad i = 1, 2, ..., n - 1\,. \tag{23}$$

Relations (22) and (23) make it possible to evaluate the time variation of concentration polarization in the process of semicontinuous baromembrane-aided separation of binary and multicomponent mixtures and to find the conditions of gel layer formation over the membrane surface for separate mixture components. Moveover, to describe the mass transfer of multicomponent mixtures, one can employ experimental data on mass transfer for binary mixtures with allowance for direct mutual overlap of flows in diffusional transfer.

NOTATION

$c(x, t)$, concentration of the permeate at the point with the x-coordinate at the moment t; x, coordinate; t, time; D, molecular diffusion coefficient for a binary mixture; v_0, filtration length; l, diffusion path length; $g(t)$, concentration of the initial mixture; c_0, initial concentration of the initial mixture; $X_n(t)$, eigenfunctions; λ_n, eigenvalues, J_n, a_n, coefficients; M_i, flow of the diffusing i-th substance; D_{ik}, molecular diffusion coefficient for a multicomponent mixture; $[B]$, square matrix; $[P]$, modal matrix; $[D]$, (c), $(\tilde{c})$, matrices of the molecular diffusion coefficients in a multicomponent mixture of concentrations and pseudoconcentrations; $\tilde{c}$, pseudoconcentration of the i-th component; $\lceil \mu \rfloor$, diagonal matrix; c_w, c_b, permeate concentration near the membrane surface and in the flow core, respectively; i, j, k, component numbers.

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