Journal of Engineering Physics and Thermophysics, Vol. 70, No. 6, 1997

CONCENTRATION POLARIZATION IN PIPE ULTRAFILTRATION

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A study is carried out to investigate unsteady concentration polarization in laminar ultrafiltration in a cylindrical channel as a function of the selective properties of the membrane.

In recent years ultrafiltration apparatus with pipe membrane elements and hollow fibers are widely used in the chemical, petroleum, food, biotechnology, and medical industries [1-3].

For determination of the optimal design and main parameters of ultrafiltration in pipe membranes and hollow fibers, it is necessary to have a clear understanding of the main mechanisms of the process.

In the literature there is no adequate theoretical description of ultrafiltration in axisymmetric membrane elements.

In the present article, on the basis of the semi-integral method suggested in [4], we consider concentration polarization in laminar ultrafiltration in cylindrical channels as a function of the selective properties of the membrane.

The convective diffusion equation is written in a cylindrical system with the assumption that in ultrafiltration the thickness of the diffusion boundary layer is much smaller than the radius of the pipe. Then, introducing the new variable $Y = R - r$ and taking only the main terms, we obtain the convective diffusion equation, which is written in dimensionless form as

$$\frac{\partial \theta}{\partial \tau} + u \frac{\partial \theta}{\partial \xi} - v \frac{\partial \theta}{\partial \eta} = \frac{1}{\mathrm{Pe}} \frac{\partial^2 \theta}{\partial \eta^2} \tag{1}$$

with the boundary conditions

$$\varphi V \theta_{\mathrm{w}} + \frac{1}{\mathrm{Pe}} \frac{\partial \theta}{\partial \eta} = 0 \ (\eta = 0) , \ \theta = 1 \ (\eta = \delta) ; \tag{2}$$

$$\theta = 1 \ (\xi = 0) , \ \theta = 1 \ (\tau = 0) . \tag{3}$$

In [5] it is shown that for a dynamic problem with a low transmembrane velocity and a parabolic velocity profile at the inlet to the cylindrical channel, the following expressions can be used for the velocity components:

$$u = (1 - 2V\xi)(4\eta - 2\eta^2) ; \ v = V(1 + \eta - 3\eta^2 + \eta^3) . \tag{4}$$

The following remark is to the point. Because Pe >> Re, the hypothesis of quasisteadiness can be used in consideration of a dynamic problem. This means that at a given moment each steady-state velocity distribution has its own concentration distribution.

Since the thickness of the diffusion layer is small, for a solution of diffusion problem (1)-(3), only the first terms can be taken in velocity distribution (4)

Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute of the Academy of Sciences of Belarus," Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 70, No. 6, pp. 902-906, November-December, 1997. Original article submitted January 3, 1996.

1062-0125/97/7006-0860$18.00

$$\frac{\partial \theta}{\partial \tau} + (1 - 2V\xi)\, 4\eta \frac{\partial \theta}{\partial \xi} = \frac{\partial}{\partial \eta}\left(V\theta + \frac{1}{\mathrm{Pe}}\frac{\partial \theta}{\partial \eta}\right). \tag{5}$$

Use will be made of the methods ordinary for unsteady-state problems when the unsteady-state distribution is preset proceeding from a solution of the steady-state problem

$$4\,(1 - 2V\xi)\,\eta \frac{\partial \theta}{\partial \xi} = \frac{\partial}{\partial \eta}\left(V\theta + \frac{1}{\mathrm{Pe}}\frac{\partial \theta}{\partial \eta}\right). \tag{6}$$

As follows from equation (6), in the immediate vicinity of the membrane surface, i.e., at $\eta \to 0$,

$$\frac{\partial}{\partial \eta}\left(V\theta + \frac{1}{\mathrm{Pe}}\frac{\partial \theta}{\partial \eta}\right) \approx 0. \tag{7}$$

is valid.

Integrating twice and using the first condition from (2), we can find the steady-state concentration distribution at the membrane

$$\theta = \theta_{\mathrm{w}}\,[1 - \varphi + \varphi \exp(-\,\mathrm{Pe}\,V\eta)]. \tag{8}$$

In view of Eq. (8) and physical considerations based on the boundary layer ideology, we can express the concentration distribution by the relation

$$\theta = \begin{cases} \theta_{\mathrm{w}}(\xi)\,[1 - \varphi + \varphi \exp(-\,\mathrm{Pe}\,V\eta)], & 0 \le \eta \le \delta(\xi); \\ 1, & \delta(\xi) < \eta \le 1, \end{cases} \tag{9}$$

where the unknown thickness of the diffusion boundary layer is obtained from the condition

$$1 = \theta_{\mathrm{w}}\,[1 - \varphi + \varphi \exp(-\,\mathrm{Pe}\,V\eta)],$$

i.e.,

$$\delta = \frac{1}{\mathrm{Pe}V} \ln \frac{\varphi \theta_{\mathrm{w}}}{1 - (1 - \varphi)\,\theta_{\mathrm{w}}}. \tag{10}$$

In order to find the unknown concentration at the membrane $\theta_{\mathrm{w}}(\tau, \xi)$, we use the integral mass balance equation. To do this, convective diffusion equation (1) is integrated across the boundary layer from 0 to δ and boundary conditions (2) are used. Then,

$$\frac{\partial}{\partial \tau}\int_0^{\delta} (\theta - 1)\, d\eta + \frac{\partial}{\partial \xi}\int_0^{\delta} u\,(\theta - 1)\, d\eta = V\,[1 - (1 - \varphi)\,\theta_{\mathrm{w}}]. \tag{11}$$

Substitution of velocity (5) and concentration (9) distributions into Eq. (11) gives

$$\frac{\partial}{\partial \tau}\int_0^{\delta} \theta_{\mathrm{w}}\,[1 - \varphi + \varphi \exp(-\,\mathrm{Pe}V\eta)] - 1)\, d\eta +$$

$$+ \frac{\partial}{\partial \xi}\int_0^{\delta} 4\,(1 - 2V\xi)\,\eta\,(\theta_{\mathrm{w}}\,[1 - \varphi + \varphi \exp(-\,\mathrm{Pe}V\eta)] - 1)\, d\eta = V\,[1 - (1 - \varphi)\,\theta_{\mathrm{w}}]. \tag{12}$$

Hence, upon integration with account of relation (10), we have

$$\frac{1}{\mathrm{Pe}V}\frac{\partial}{\partial \tau}\left[(\theta_{\mathrm{w}}(1 - \varphi) - 1) \ln \frac{\varphi \theta_{\mathrm{w}}}{1 - (1 - \varphi)\,\theta_{\mathrm{w}}} - 1 + \theta_{\mathrm{w}}\right] +$$

$$+\frac{1}{\mathrm{Pe}^2V^2}\frac{\partial}{\partial\xi}\left[4\,(1-2V\xi)\,(\theta_\mathrm{w}-1-[1-(1-\varphi)\,\theta_\mathrm{w}]\ln\frac{\varphi\theta_\mathrm{w}}{1-(1-\varphi)\,\theta_\mathrm{w}}-\right.$$

$$\left.-\frac{1}{2}\,[1-(1-\varphi)\,\theta_\mathrm{w}]\left(\ln\frac{\varphi\theta_\mathrm{w}}{1-(1-\varphi)\,\theta_\mathrm{w}}\right)^2\right]=V\,[1-(1-\varphi)\,\theta_\mathrm{w}]\,. \tag{13}$$

From physical considerations, an unsteady process can be considered as two limiting cases: absolutely unsteady and steady regimes.

Consider the steady-state regime of concentration polarization. From equation (13) we have

$$\frac{\partial}{\partial V\xi}\left\{4\,(1-2V\xi)\,(\theta_\mathrm{w}-1-[1-(1-\varphi)\,\theta_\mathrm{w}])\ln\frac{\varphi\theta_\mathrm{w}}{1-(1-\varphi)\,\theta_\mathrm{w}}-\right.$$

$$\left.-\frac{1}{2}\,[1-(1-\varphi)\,\theta_\mathrm{w}]\left(\ln\frac{\varphi\theta_\mathrm{w}}{1-(1-\varphi)\,\theta_\mathrm{w}}\right)^2\right\}=\mathrm{Pe}^2V^2\,[1-(1-\varphi)\,\theta_\mathrm{w}]\,. \tag{14}$$

Integration of Eq. (14) is impossible in the general case. Let us consider some particular cases.

Let $\theta_\mathrm{w}\sim 1$. Then, it can be expressed in the form $\theta_\mathrm{w}=1+\varepsilon$. As a result,

$$\ln\varphi\,\theta_\mathrm{w}=\ln\varphi\,(1+\varepsilon)\,,\ \ \ln\,(1-(1-\varphi)\,\theta_\mathrm{w})=\ln\varphi\,(1-\varepsilon\,(1-\varphi)/\varphi)\,.$$

The logarithms are expanded into a power series in ε, and with accuracy to ε^3, we find from formula (14)

$$\frac{d\varepsilon^3\,(1-V\xi)}{dV\xi}=\frac{3}{2}\varphi^3\mathrm{Pe}^2V^2\left[1-\frac{\varepsilon\,(1-\varphi)}{\varphi}\right]. \tag{15}$$

Let $\varepsilon(1-\varphi)/\varphi \ll 1$ (this can be done since the selectivity of ultrafiltration membranes is high). The last expression is integrated under the obvious condition $\varepsilon=0$ at $\xi=0$

$$\varepsilon=\varphi\left(\frac{3}{2}\frac{V\xi\,\mathrm{Pe}^2V^2}{(1-V\xi)}\right)^{1/3}. \tag{16}$$

The radii of the pipes and hollow fibers used in laminar ultrafiltration are 10^{-3} and 10^{-4} m, the diffusion coefficient is 10^{-10} m^2/sec, and the transmembrane flow velocity is 10^{-5} m/sec. In this case for a pipe, $\mathrm{Pe}V \simeq 10^2$, and for a hollow fiber, 10. Since $\varepsilon < 1$, relation (16) is satisfied at $V\xi \ll 1$. Ignoring $V\xi$ in comparison with unity in the denominator, we find

$$\theta_\mathrm{w}=1+\varphi\left(\frac{3}{2}\,V\xi\,\mathrm{Pe}^2V^2\right)^{1/3}. \tag{17}$$

When the terms in equation (14) that contain logarithms are small in comparison with $\theta_\mathrm{w}-1$, for calculation of concentration polarization, we can use the relation

$$\frac{d}{dV\xi}\,[(1-2V\xi)\,(\theta_\mathrm{w}-1)]=\frac{\mathrm{Pe}^2V^2}{4}\,[1-(1-\varphi)\,\theta_\mathrm{w}]\,. \tag{18}$$

With the boundary condition $\theta=1$ at $\xi=0$, its integration gives the solution

$$\theta_\mathrm{w}=\left[1-\varphi-\frac{8}{\mathrm{Pe}^2V^2}\right]^{-1}\left[1-\frac{8}{\mathrm{Pe}^2V^2}-\varphi\,(1-2V\xi)^{(1-\varphi)\frac{\mathrm{Pe}^2V^2}{8}-1}\right]. \tag{19}$$

Formula (19) shows that in laminar ultrafiltration pipe flow, there exist two basically different regimes. The value of $(1 - \varphi)$ can be small or large in comparison with the complex $8/\mathrm{Pe}^2V^2$ that characterizes the relation between convective and diffusion mass transfer.

Consider the ultrafiltration regime

$$(1 - \varphi) << 8/\mathrm{Pe}^2V^2 . \tag{20}$$

As was shown above, in the case of ultrafiltration in a pipe and in a hollow fiber $\mathrm{Pe}V = 10 - 10^2$, condition (10) implies almost ideal selectivity of the membrane ($\varphi \cong 1$). Then, it follows from (19) that

$$\theta_{\mathrm{w}} = 1 + \frac{V\xi\,(\mathrm{Pe}V)^2}{4\,(1 - 2V\xi)}, \tag{21}$$

i.e., the dissolved compound concentration on the membrane grows continuously as the distance from the channel inlet increases.

Now, we take again equation (17), assuming $\varphi = 1$. Upon integration we obtain

$$\theta_{\mathrm{w}} - \ln\theta_{\mathrm{w}} - \frac{1}{2}(\ln\theta_{\mathrm{w}})^2 = 1 + \frac{\mathrm{Pe}^2V^2V\xi}{4\,(1 - 2V\xi)} . \tag{22}$$

If $\theta_{\mathrm{w}} >> \ln\theta_{\mathrm{w}}$, which was assumed in derivation of formula (19), relation (22) becomes Eq. (21).

The opposite case of $(1 - \varphi) >> 8/\mathrm{Pe}^2V^2$ is considered now. Under this condition, it follows from (19) that the dissolved compound concentration on the membrane increases rapidly with the distance from the channel inlet

$$\theta_{\mathrm{w}} = \frac{1}{1 - \varphi}\left(1 - \varphi\,(1 - 2V\xi)^{(1-\varphi)\frac{\mathrm{Pe}^2V^2}{8}}\right) \tag{23}$$

and reaches the limiting value $\theta_{\mathrm{w}} = 1/(1 - \varphi)$, which remains constant in the other part of the channel.

Now, we consider unsteady filtration. From Eq. (13) we obtain the differential equation

$$\frac{\partial}{\partial V\tau}\left[(\theta_{\mathrm{w}\tau}\,(1 - \varphi) - 1)\ln\frac{\varphi\theta_{\mathrm{w}\tau}}{1 - (1 - \varphi)\,\theta_{\mathrm{w}\tau}} + \theta_{\mathrm{w}\tau} - 1\right] = \mathrm{Pe}V\,[1 - (1 - \varphi)\,\theta_{\mathrm{w}\tau}] . \tag{24}$$

It cannot be integrated in general form. Equation (24) will be analyzed in particular cases. For $\theta_{\mathrm{w}\tau} \sim 1$, i.e., $\theta_{\mathrm{w}\tau} = 1 + \varepsilon$, we can restrict ourselves to the initial powers of the series $\ln\varphi\theta_{\mathrm{w}\tau}$ and $\ln(1 - (1 - \varphi)\theta_{\mathrm{w}\tau}$ in ε. Then,

$$\frac{d\varepsilon^2}{dV\tau} = 2\varphi^2\mathrm{Pe}V\left[1 - \frac{\varepsilon\,(1 - \varphi)}{\varphi}\right], \tag{25}$$

Hence, assuming $\varepsilon(1 - \varphi)/\varphi << 1$, we find

$$\theta_{\mathrm{w}\tau} = 1 + \varphi\,(2\mathrm{Pe}VV\tau)^{1/2} . \tag{26}$$

If $(1 - \varphi)\theta_{\mathrm{w}\tau} << 1$, which, as is shown above, is valid when the condition $(1 - \varphi) << 8/\mathrm{Pe}^2V^2$ is satisfied, from equation (24) we obtain

$$\theta_{\mathrm{w}\tau} - \ln\theta_{\mathrm{w}\tau} = 1 + \mathrm{Pe}VV\tau . \tag{27}$$

In the case of $(1 - \varphi) >> 8/\mathrm{Pe}^2V^2$, we consider the stage of the process in which in expression (24) the term that contains logarithm is negligible in comparison with $\theta_{\mathrm{w}\tau} - 1$, i.e.,

$$\frac{\partial\theta_{\mathrm{w}\tau}}{\partial V\tau} = \mathrm{Pe}V\,[1 - (1 - \varphi)\,\theta_{\mathrm{w}\tau}] . \tag{28}$$

Integrating this differential equation with the condition $\theta_{w\tau} = 1$ at $\tau = 0$, we find

$$\theta_{w\tau} = \frac{1}{1 - \varphi} [1 - \varphi \exp (- (1 - \varphi) \mathrm{Pe} V V \tau] . \tag{29}$$

Now, we estimate the time τ_s required for the concentration polarization to attain a steady state in the case of ultrafiltration in pipes and hollow fibers. The time τ_s is determined from the condition $\theta_w = \theta_{w\tau}$. Then, from relations (17) and (26), (22) and (27), (23) and (29) we obtain

$$\tau_s \simeq \frac{1}{2} \left(\frac{3}{2} \mathrm{Pe} \xi^2 \right)^{1/3} , \quad \theta_w \sim 1 ;$$

$$\tau_s \simeq \frac{1}{4} \mathrm{Pe} V \xi , \quad (1 - \varphi) >> \frac{8}{\mathrm{Pe}^2 V^2} ;$$

$$\tau_s \simeq \frac{\mathrm{Pe} V \xi}{4 (1 - V \xi)} , \quad (1 - \varphi) << \frac{8}{\mathrm{Pe}^2 V^2} .$$

respectively.

The last formula is valid for channels with a moderate length.

The work was carried out with support from the Fundamental Research Fund of the Republic of Belarus.

NOTATION

$\xi = X/R$; $\eta = Y/R$, dimensionless longitudinal and transverse coordinates; $u = u_x/u_0$, $v = u_y/u_0$, dimensionless components of velocity vector; R, channel radius; u_0, mean velocity at channel inlet; $\mathrm{Re} = u_0 R/\nu$, Reynolds number; ν, kinematic viscosity; $\mathrm{Pe} = u_0 R/D$, diffusion Peclet number; D, diffusion coefficient; $\theta = c/c_0$, dimensionless concentration of dissolved compound; c_0, concentration of dissolved compound at channel inlet; θ_w, dimensionless concentration of dissolved compound on membrane; $V = V_f/u_0$, transmembrane velocity; φ, membrane selectivity; δ, thickness of diffusion boundary layer; V_f, filtration velocity. Subscripts: w, wall (membrane); s, steady.

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