V.L. Poliakov

Institute of Hydromechanics of the NAS of Ukraine, Kyiv
E-mail: v.poliakov.ihm@gmail.com

The effect of liquid bound by microparticles (ions) on the membrane selectivity

Presented by Corresponding Member of the NAS of Ukraine O.Ya. Oliinyk

Notion "critical concentration" was introduced for membrane processes, and a formula was proposed to calculate it. A mathematical problem of steady-state convective-diffusive mass transfer within the layer of concentration polarization was formulated and exactly solved, taking into account the hydration of microparticles (ions). For numerous examples, analyses were performed to estimate the effect of hydration and mass transfer parameters on the concentration of suspended microparticles at the membrane surface and its selectivity for uniform impurity.

Keywords: *membrane, microparticle, impurity, hydration, concentration, selectivity, diffusion, mass transfer, concentration polarization.*

The most important indicator of the ability of porous membranes to separate a finely dispersed or dissolved impurity from a liquid containing it and thus obtain a permeate or concentrate with desired properties is selectivity [1-3]. It generally and in relative units (percentage) characterizes the distribution of the initial impurity between the products of membrane separation. The selectivity limit is 1 (100 %) and corresponds to the ideal separation of a two-component physical system. It is impossible to achieve such a separation because of the heterogeneity of the impurity and the structure of the pore space of the membrane. Nevertheless, it is possible to achieve a high selectivity of the membrane action, as a rule, due to the reasonable choice of its type and characteristics. Under certain conditions, liquid films can be one of the reasons for the decrease in membrane selectivity. They usually form on the surface of microparticles (small colloids, macromolecules, ions) and actively interact with them at the molecular level. The thickness of such a liquid film is often comparable to the size of a microparticle — collector, a pore. The liquid enclosed in a film has anomalous properties, for example, an increased viscosity [4]. This fact is indirectly confirmed by the data of experimental studies of a gel-like deposit that accumulates when suspensions are filtered through granular media of a rapid filter [5]. The indicated thickness of the aforementioned film can vary within very large limits under the influence of various external factors. Accordingly, the set of microparticles can be

both strongly and weakly hydrated. Here and below, their hydration, as well as any hydrophilic solid surfaces, is understood as the process of formation of a liquid film physically associated with them.

Below, the behaviour of only those microparticles that are commensurate with the membrane pores will be considered in detail. Then two characteristic situations can occur. In the first case, the microparticle, previously retained at the entrance to the membrane pore, now freely passes into it due to the thinning of its surface film. In the second situation, the microparticle loses its ability to penetrate inside the membrane due to the binding of an additional amount of liquid. If there are many such particles, then in both situations described, a significant change in their selectivity should be expected.

During the operation of membranes of various types, an impurity accumulates in the immediate vicinity of their working surface. It is here, in the diffusion boundary layer, that the degree of microparticle hydration can decrease much due to the intense interaction between them. As a result, a very sharp deterioration in the quality of the permeate occurs. The purpose of this research is a theoretical assessment of the specified effect of dehydration of a homogeneous impurity on the efficiency of separation of a fine suspension (solution) by micro- and ultrafiltration (when using reagents), reverse osmosis. At the same time, it is still assumed that the concentration of microparticles near the membrane surface is insufficient for their structuring. Therefore, a deposited layer is not formed. The following condition for the penetration of a microparticle into a membrane pore is of fundamental importance for the analysis performed below by analytical methods

$$r_h < \chi_p \, r_p \tag{1}$$

where r_h, r_p are the radii of a hydrated microparticle and pore, the empirical coefficient χ_p is less than 1 and, according to [6] is equal to 1/3. Condition (1) applies to the entire membrane if its pore space has a regular structure and is formed by many identical cylindrical pores. In the case of an irregular porous space, equivalent dimensions should be used. The second basic position here is the law of hydration, which establishes the relationship between the degree of hydration of microparticles and the content of impurities in the liquid. It will be generalized for

$$\frac{C_w}{C_i} = f_h(C), \tag{2}$$

where C_w, C_i are the volumetric concentrations of liquid bound by microparticles and non-hydrated microparticles; C is the volumetric concentration of hydrated microparticles, so that

$$C = C_i + C_w. \tag{3}$$

It follows from (2), (3) that

$$C_w(C) = F_h(C) = \frac{C f_h(C)}{1 + f_h(C)}. \tag{4}$$

Thus, the volumetric concentration of the liquid, bound at the membrane surface, C_{w0} will be

$$C_{w0} = C_w(C_{h0}) = F_h(C_{h0}), \tag{5}$$

where C_{h0} is the volumetric concentration of hydrated particles at the membrane surface.

If microparticles both in the absence and in the presence of surface films are justified to be considered spherical, then the radius and concentration of hydrated particles are related by the following relation

$$r_h(C) = r_i \sqrt[3]{1 + f_h(C)} \,, \tag{6}$$

where r_i is the radius of non-hydrated particles.

It should be emphasized that the impurity in suspensions is often substantially heterogeneous in practice. If it contains, among other things, a fraction of microparticles with sizes close to the (equivalent) pore diameter and their total volume is only a small part of the volume of the entire suspension, then the dehydration process will not noticeably affect the quality of the permeate. However, the selectivity of the membrane under certain conditions will seriously deteriorate with an increase in the number of such particles. For a reliable prediction of its change in the general case of a polydisperse impurity, first of all, it is necessary to choose such a hydration law that would correctly reflect the effect of the impurity concentration as a whole on the dehydration of the separated fraction. Then the form of law (2) does not change but C should be interpreted as the total volumetric concentration of the impurity. Therefore, it is necessary to perform mathematical modelling of the behavior of all impurity fractions in the layer of concentration polarization.

The critical concentration C_{cr} is of key importance for assessing the possible consequences of the initial hydration of an impurity (in the initial suspension or solution) and its subsequent dehydration in the indicated layer. With its development, a formal transition of the current concentration at the membrane surface C_{h0} through the value corresponding to the conditions under consideration C_{cr} is possible. This event will be accompanied by an abrupt change in the membrane selectivity in the corresponding direction. To calculate the marked value, a general formula is proposed

$$C_{cr} = f_h^{-1}(\chi_p^{\,3}\bar{r}_p^{\,3} - 1) \,. \tag{7}$$

If the law of hydration is linear so that,

$$f_h(C) = \bar{C}_{\max} - \sigma_h\, C \,, \tag{8}$$

then is received for C_{cr}

$$C_{cr} = \frac{1}{\sigma_h}(\bar{C}_{\max} + 1 - \chi_p^{\,3}\bar{r}_p^{\,3}) \,. \tag{9}$$

In the case of the exponential form of the law, namely,

$$f_h(C) = \bar{C}_{\max} e^{-\alpha_h C} \,, \tag{10}$$

will be true

$$C_{cr} = -\frac{1}{\alpha_h}\ln\frac{\chi_p^{\,3}\bar{r}_p^{\,3} - 1}{\bar{C}_{\max}} \,. \tag{11}$$

Here $\overline{r}_p = r_p / r_i$; $\overline{C}_{\max} = C_{\max} / C_0$ is the limiting relative volumetric content of bound liquid (in the absence of interaction between hydrated particles), C_0 is the initial volumetric concentration of hydrated microparticles; σ_h, α_h are empirical coefficients. The exponential and linear forms are fundamentally different. In the first case, complete dehydration of microparticles is achieved only asymptotically (at $C \to \infty$), and in the second case — at a finite value of C ($\overline{C}_{\max} / \sigma_h$).

To reliably assess the effectiveness of the membrane, first of all, it is necessary to know the concentration of suspended (unstructured) microparticles on its surface C_{h0}. Just here the concentration C reaches not just the maximum, but often a very large value (reverse osmosis) [7]. This may create preconditions for the formation of a layer of deposit, which already has the properties of a solid porous medium. Thus, the value C_{h0} can determine not only the quality of separation of the liquid-impurity system but also the performance of the membrane apparatus. It should be emphasized that the diffusion boundary layer stabilizes already at the beginning of the operating period [8]. Therefore, it is sufficient to use the steady-state model of convective-diffusion mass transfer for approximate calculations of the impurity concentration profile in it. Within this layer, both transport mechanisms play an equally important role [9]. The presence of a semipermeable flat or cylindrical surface in cross-flow technologies for the separation of liquid systems enhances the diffusion transfer of microparticles due to a sharp increase in shear stresses in the near-wall zone. It is important to note that the change in the flow of hydrated particles is balanced with the decrease in the liquid associated with them. Therefore, a special term appears in the basic equation of one-dimensional steady-state mass transfer that characterizes the intensity of the release of the bound liquid. The equation in relation to C_δ takes on the following form

$$\frac{d}{dz}[D_z(C_\delta)\frac{dC_\delta}{dz} + VC_\delta] - V\frac{dC_w}{dz} = 0. \tag{12}$$

Here, the dependence of the diffusion coefficient on their concentration, which is characteristic of especially small particles (macromolecules), is additionally taken into account [10]. At the boundaries of the considered boundary layer, traditional conditions are set, namely, [11]

$$z = -\delta_h, \ C_\delta = C_h; \tag{13}$$

$$z = 0, \ D_z(C_\delta)\frac{dC_\delta}{dz} + VC_\delta = VC_p; \tag{14}$$

where δ_h is the thickness of the separated layer, V is the constant rate of the liquid flow in the layer and the membrane, and C_p is the impurity concentration in the permeate. It is possible to get rid of the unknown quantity C_w in equation (12) by using expression (4). If an interlayer with completely dehydrated microparticles does not form in the vicinity of the membrane surface, then the concentration of bound water on it should be calculated using the formula (5). Therefore, integrating the equation (12) with the use of condition (14) gives

$$D_z(C_\delta)\frac{dC_\delta}{dz} + VC_\delta - V[F_h(C_\delta) - F_h(C_{h0})] = VC_p. \tag{15}$$

ISSN 1025-6415. Допов. Нац. акад. наук Укр. 2023. № 1

43

The solution of equation (15) under condition (14) is represented as the following inverse integral function

$$\frac{1}{V}\int\limits_{C_h}^{C_\delta}\frac{D_z(\xi)d\xi}{\xi-F_h(\xi)-C_p+F_h(C_{h0})}=\delta_h-z\,. \tag{16}$$

Then the concentration of the hydrated impurity on the membrane surface can be easily found by selection from the equation

$$\int\limits_{C_h}^{C_{h0}}\frac{D_z(\xi)d\xi}{\xi-F_h(\xi)-C_p+F_h(C_{h0})}=\delta_h V. \tag{17}$$

In the subsequent quantitative analysis, however, the same equation will be used, but already in a dimensionless form, namely,

$$\int\limits_{\bar{C}_h}^{\bar{C}_{h0}}\frac{\bar{D}_z(\xi)d\xi}{\xi-F_h(\xi)-\bar{C}_p+F_h(\bar{C}_{h0})}=Pe_\delta, \tag{18}$$

where the Peclet number Pe_δ is $\delta_h V/D_{z0}$; D_{z0} is the value of the coefficient D_z for the non-hydrated impurity; $\bar{C}_{h0,\,p}=C_{h0,\,p}/C_{00}$, C_{00} is the scale for impurity concentrations selected depending on the specific filtration conditions; $\bar{D}_z=D_z/D_{z0}$.

Obviously, at $C_{h0}>C_{cr}$ and, therefore, $r_h>\chi_h r_p$ the membrane in the case under consideration will completely retain a homogeneous impurity, even though $r_i<\chi_p r_p$. Therefore, the selectivity of the membrane concerning the impurity will be 100 %. As the concentration C_{h0} decreases to reach a critical value C_{cr}, the membrane loses its ability to separate the suspension (solution). The impurity entering the diffusion boundary layer will pass through it in transit and thus the selectivity of the membrane will drop to 0. The impurity concentration profile within the specified layer will quickly stabilize and C_{h0} equalize with C_{cr} and then remain invariant until a new change in technological conditions occurs. To prevent a mass breakthrough of microparticles through the membrane, it is necessary to correct in advance the parameters of the baromembrane process (pressure, flow rate, concentration) so that, as a result, the value C_{h0} determined from equation (18) will be less than C_{cr}.

Of interest is the time t_{cr} to reach the critical level of fluid contamination on the membrane surface $(C_{h0}=C_{cr})$. It can be easily estimated if the effect of impurity dehydration is neglected. Then it is justified to use the non-stationary equation of convective-diffusion mass transfer in the following form

$$\frac{\partial}{\partial z}[D_z(C_\delta)\frac{\partial C_\delta}{\partial z}+VC_\delta]=\frac{\partial C_\delta}{\partial t}\,, \tag{19}$$

Its approximate solution was obtained by replacing the local derivative in equation (19) with the expression

$$\frac{\delta_h-z}{\delta_h}\,\frac{dC_{h0}}{dt}\,,$$

which accurately reflects its behaviour at the boundaries of the concentration polarization layer. Then, taking into account the values of the impurity flow at its boundaries, as well as the initial condition

$$t = 0, \quad C_{h0} = C^0;$$

the following simple formula is derived for t_{cr}

$$t_{cr} = \frac{\delta_h (C_{cr} - C^0)}{2V (C^0 - C_0)}. \tag{20}$$

The above calculation dependencies and equations are illustrated by several examples with initial data, which make it possible to evaluate the possible consequences of (de)hydration of a dispersed impurity for the separating effect of membranes of various types.

Fig. 1. Dependence $\bar{\alpha}_h \bar{C}_{cr} (\chi_p \bar{r}_p)$: *1* $-$ $\bar{C}_{max} = 10$; *2* $-$ $\bar{C}_{max} = 7$; *3* $-$ $\bar{C}_{max} = 5$; *4* $-$ $\bar{C}_{max} = 3$

The relative characteristic concentrations $\bar{C}_{cr}$, $\bar{C}_{h0}$ were the subject of numerous calculations. The ratio between them determines the efficiency of the separation of a liquid system. The selectivity of the membrane, due to the homogeneity of the impurity under consideration and the regularity of the pore space, can take only extreme values $-$ 0 at $C_{h0} > C_{cr}$ and 1 at $C_{h0} \leqslant C_{cr}$. The law of hydration is chosen in the form (10). First of all, using formula (11), the value $\bar{C}_{cr}$ in combination with c $\bar{\alpha}_h$ is determined as a function of the equivalent pore size of the membrane. In this case, the hydration potential varied (parameter $\bar{C}_{max}$). The critical concentration, in principle, can take any non-negative values. The spherical microparticles must be so small in the first limiting case $(C_{cr} = 0)$, that even at the maximum degree of hydration they freely penetrate the membrane. In particular, it will not be able to retain the impurity at $\bar{C}_{max} = 3$ if $\chi_p \bar{r}_p$ exceeds 1.587. In another limiting case $(C_{cr} \to \infty)$, mobile microparticles will not get inside the membrane due to their large size, even if there is no bound water on their surface at all. The calculation results of $\bar{C}_{cr}$ are shown in Fig. 1 in the form of a series of graphs of the generalized dependence of $\bar{\alpha}_h \bar{C}_{cr}$ on $\chi_p \bar{r}_p$.

However, the main attention during the quantitative analysis of the membrane process is paid to the influence on the concentration polarization of the ability of mobile microparticles to hydration, as well as the diffusion and convective mechanisms of mass transfer. In this regard, the choice of the effective diffusion coefficient is of great importance. According to the recommendations [12], the following two-term expression is accepted for the relative value $\bar{D}_z$

$$\bar{D}_z (\bar{C}) = a_h \bar{r}_h^{-\frac{1}{3}} (\bar{C}) + b_h \bar{r}_h^{\frac{2}{3}} (\bar{C}). \tag{21}$$

Here, the first term describes molecular diffusion, and the second describes diffusion induced by shear stresses [13, 14]. The scale for D_z is chosen in such a way that
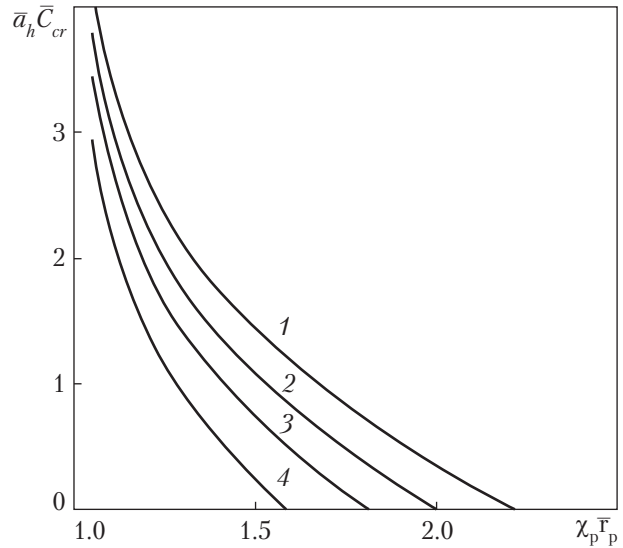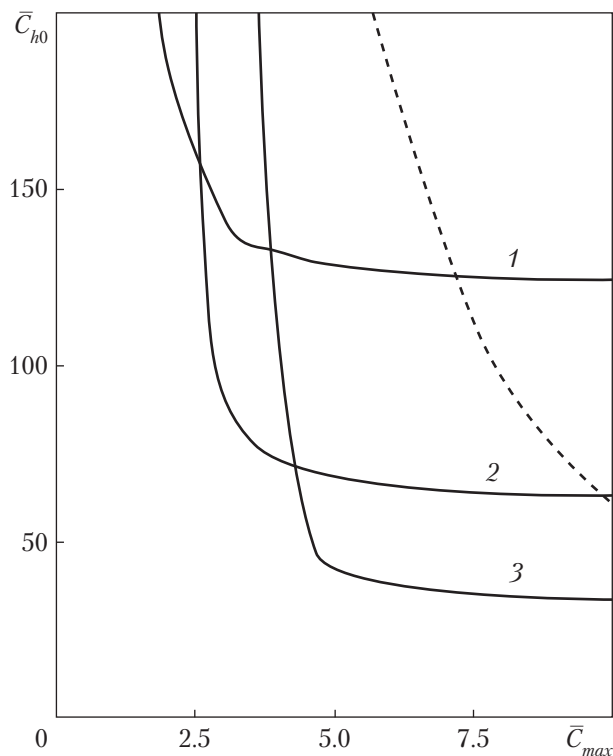
$$a_h + b_h = 1.$$

Fig. 2. Dependence $\bar{C}_{h0}(\bar{C}_{\max})$: $1 - \bar{\alpha}_h = 0.05$; $2 - \bar{\alpha}_h = 0.1$; $3 - \bar{\alpha}_h = 0.2$

Thus, the ratio between the coefficients a_h and b_h determines the relative contributions of each of the noted components to the diffusion mass transfer. Incidentally, molecular diffusion prevails with smaller microparticles, and the second component becomes essential for larger ones. Outside the layer of concentration polarization $\bar{C}_h = 1$ and hence

$$\bar{r}_h(1) = r_h(1)\big/ r_i = \sqrt[3]{1 + \bar{C}_{\max} \overline{e}^{\,\overline{\alpha}_h}} \ . \qquad (22)$$

The corresponding value $\bar{D}_z$, taking into account (22), will be

$$\bar{D}_z(1) = a_h(1 + \bar{C}_{\max}\overline{e}^{\,\overline{\alpha}_h})^{-\frac{1}{3}} +$$

$$+ b_h(1 + \bar{C}_{\max}\overline{e}^{\,\overline{\alpha}_h})^{\frac{2}{3}}. \qquad (23)$$

To isolate the effect of impurity dehydration, it is advisable to supplement equation (18) with a formula. The indicated formula makes it possible to calculate $\bar{C}_{h0}$, provided that the amount of liquid initially bound by it does not change later. Then it follows from equation (15) that

$$\bar{C}_{h0} = \exp\frac{Pe_\delta}{\bar{D}_s(1)} \ . \qquad (24)$$

The measure of concentration polarization can be the concentration $\bar{C}_{h0}$, which is the highest in the entire region of the flow of a liquid system. The model parameters ($\bar{C}_{\max}$, $\bar{\alpha}_h$, a_h, Pe_δ) varied continuously or with a small increment over a broad range when calculating $\bar{C}_{h0}$. At the same time,
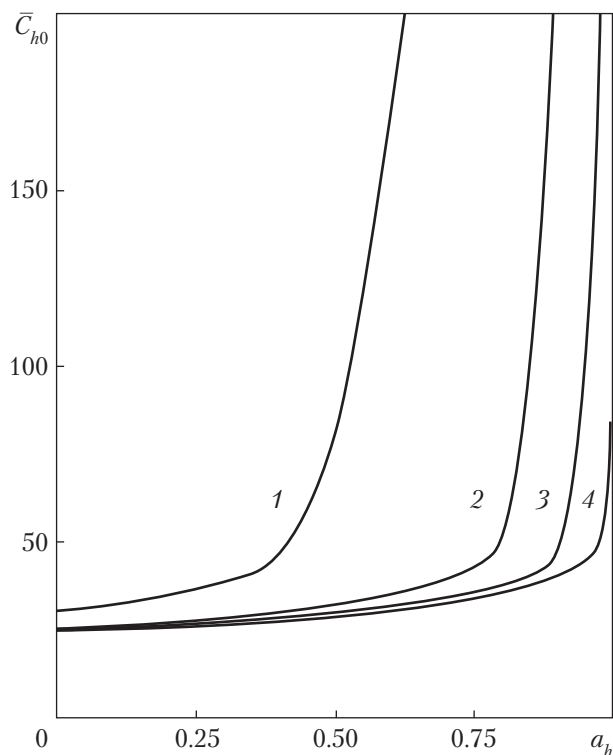

Fig. 3. Dependence $\bar{C}_{h0}(a_h)$: $1 - \bar{C}_{\max} = 3$; $2 - \bar{C}_{\max} = 5$; $3 - \bar{C}_{\max} = 7$; $4 - \bar{C}_{\max} = 10$

Fig. 4. Dependence $\bar{C}_{h0}(Pe_\delta)$: $1 - \bar{C}_{\max} = 3$; $2 - \bar{C}_{\max} = 5$; $3 - \bar{C}_{\max} = 7$; $4 - \bar{C}_{\max} = 10$

their basic values were: $\bar{\alpha}_h = 0.2$, $a_h = 0.5$, $Pe_\delta = 10$. Based on equation (18), the dependence of $\bar{C}_{h0}$ on the parameter $\bar{C}_{\max}$ was specified in the first series of examples for three values $\bar{\alpha}_h$ (Fig. 2). The graphs corresponding to them are shown by solid lines. At the same time, $\bar{C}_{h0}$ was determined without taking into account the dehydration of the impurity using formula (24). If its initial hydration is nevertheless taken into account, then the relationship between $\bar{C}_{h0}$ and $C_{\max}$, α_h is preserved. The curve corresponding to $\bar{\alpha}_h = 0.2$ and $C_w = const$ is given in Fig. 2 by a dotted line. Finally, in the absence of primary hydration, $\bar{D}_s$ no longer depends on $\bar{C}_{\max}$, $\bar{\alpha}_h$ and is equal to 1. Then the calculated value $\bar{C}_{h0}$ reaches $2.2 \cdot 10^4$ and, therefore, a dense layer of the deposit is necessarily formed.
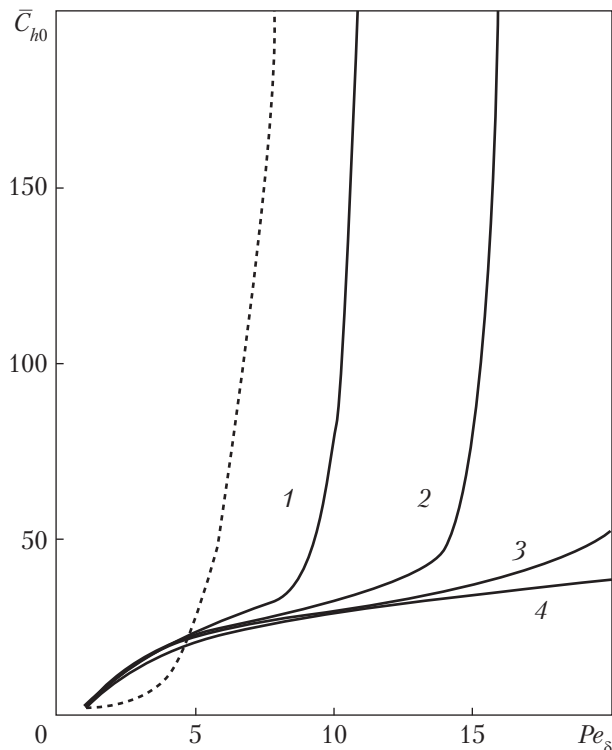
The desired concentration also demonstrates high sensitivity concerning the factors that determine mass transfer in the diffusion boundary layer. In the second series of examples, the coefficient a_h was used. As can be seen from Fig. 3, the molecular component of the diffusion mechanism turns out to be more significant under given operating conditions. The observed sharp rise in the calculated curves is explained by the fact that the hydration of microparticles weakens molecular diffusion. This, in turn, contributes to a more intense accumulation of impurities in the aforementioned layer and, as a consequence, the dehydration process. According to (22), the effect caused by dehydration, first of all, affects the indicated diffusion and therefore curve 1, calculated like all the others based on equation (18) and at a smaller $C_{\max}$, is located above the others.

Similarly, the value $\bar{C}_{h0}$ is related to the number Pe_δ, and, in essence, to the permeate velocity. Their increase means an adequate increase in convective mass transfer. In the final series of calculations, a change of Pe_δ from 1 to 20 was allowed. The curves presented in Fig. 4 indicate the danger of uncontrolled accumulation of suspended matter in the layer of concentration polarization with an excessive acceleration of the permeate flow with its subsequent deposition on the membrane surface. In addition, this figure also shows a dotted line curve that does not take into account the dehydration of the initially hydrated particles. Its significant discrepancy with other curves convincingly confirms the generally positive role of the impurity dehydration effect in membranous processes.

Thus, the processes of hydration and dehydration of dispersed and dissolved impurities, which provide changes in the size of microparticles up to ions, and their number in the diffusion bound-

ary layer, can have a noticeable effect on the separation of liquid systems by membrane technologies. Their reliable forecast makes it possible to adjust the operating conditions and thereby increase the efficiency of membrane devices.

REFERENCES

1. Cherkasov, A. N., Zhemkov, V. M. & Mchedlishvili, B. V. (1978). On the influence of the ratio of particle and pore sizes on the selectivity of membranes. Kolloidn. Zhurn., 40, No. 6, pp. 1155-1160 (in Russian).
2. Mulder, M. (1999). Introduction to membrane technology. Moscow: Mir (in Russian).
3. Polyakov, V. S., Maksimov, E. D. & Polyakov, S. V. (1995). On the issue of modeling the process of flow microfiltration. Teor. osnovy khim. tekhnol., 29, No. 3, pp. 300-308 (in Russian).
4. Deryagin, B. V. & Churaev, N. V. (1971). New properties of liquids. Moscow: Nauka (in Russian).
5. Ojha, C. S. P. & Graham, N. J. D. (1993). Theoretical estimates of bulk specific deposit in deep bed filters. Water Res., 27, No. 3, pp. 377-387. https://doi.org/10.1016/0043-1354(93)90037-I
6. Dytnersky, Yu. I. (1986). Baromembrane processes. Theory and calculation. Moscow: Himiya (in Russian).
7. Zydney, A. L. & Colton, C. K. (1986). A concentration polarization model for the filtrate flux in cross-flow microfiltration of particulate suspensions. Chem. Eng. Commun., 47, pp. 1-21. https://doi.org/10.1080/00986448608911751
8. Lee, Y. & Clark, M.M. (1988). Modeling of flux decline during crossflow ultrafiltration of colloidal suspension. J. Membr. Sci., 149, pp. 181-202. https://doi.org/10.1016/S0376-7388(98)00177-X
9. Sethi, S. & Wiesner, M. R. (1997). Modeling of transient permeate flux in cross-flow membrane filtration incorporating multiple particle transport mechanisms. J. Membr. Sci., 136, No. 1-2, pp. 191-205. https://doi.org/10.1016/S0376-7388(97)00168-3
10. Shirazi, S., Lin, C.-J. & Chen, D. (2010). Inorganic fouling of pressure-driven membrane processes. A critical review. Desalination, 250, pp. 236-248. https://doi.org/10.1016/j.desal.2009.02.056
11. Kim, S. & Hoek, E. M. V. (2005). Modeling concentration polarization in reverse osmosis processes. Desalination, 186, pp. 111-128. https://doi.org/10.1016/j.desal.2005.05.017
12. Leighton, D. & Acrivos, A. (1987). Measurment of shear-induced shear-diffusion in concentrated suspensions of spheres. J. Fluid. Mech., 177, pp. 109-131. https://doi.org/10.1017/S0022112087000880
13. Leighton, D. & Acrivos, A. (1987). The shear-induced migration of particles in concentrated suspensions. J. Fluid. Mech., 181, pp. 415-439. https://doi.org/10.1017/S0022112087002155
14. Piron, E., Rene, F. & Latrille, E. (1995). A cross-flow microfiltration model based on integration of the mass transport equation. J. Membr. Sci., 108, pp.57-70. https://doi.org/10.1016/0376-7388(95)00141-4

В.Л. Поляков

Інститут гідромеханіки НАН України, Київ
E-mail: v.poliakov.ihm@gmail.com

ВПЛИВ ЗВ'ЯЗАНОЇ МІКРОЧАСТИНКАМИ (ІОНАМИ) РІДИНИ
НА СЕЛЕКТИВНІСТЬ МЕМБРАНИ

Стосовно мембранних процесів введено поняття критичної концентрації і запропоновано формулу для її визначення. Сформульовано і строго розв'язано математичну задачу усталеного конвективно-дифузійного масопереносу в шарі концентраційної поляризації з урахуванням гідратації мікрочастинок (іонів). На численних прикладах для однорідних домішок проаналізовано вплив параметрів гідратації і масопереносу на концентрацію завислих мікрочастинок на поверхні мембрани, її селективність.

Ключові слова: *мембрана, мікрочастинка, домішки, гідратація, концентрація, селективність, дифузія, масоперенос, концентраційна поляризація.*