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Diffusion model of protein adsorption and effect of protein layer composition on water permeability for ultrafiltration membranes

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Abstract

The study of interrelation between kinetics of protein adsorption and flux of water through ultrafiltration membranes is of interest for understanding the influence of adsorption on ultrafiltration. A short model sketch of protein adsorption derived from complicated transport phenomena is presented. As quantitative criterion of protein adsorption the ratio of reversibility is proposed. This ratio describes the relative amount of adsorbed proteins that are reversibly arranged on the polymer surface. Ratio reversibility depends on chemical structure of membranes in sequence: polysulfone < polysulfoneamide (33% amide groups) < polysulfoneamide (47% amide groups) < aromatic polyamide. It is shown that protein adsorption mainly contributes to the deterioration of the water transport.

Keywords: Water permeability; Ultrafiltration; Protein adsorption; Polysulfone; Polysulfoneamides

1. Introduction

One of the most important points at issue in the theory of pressure-driven membrane processes is the behavior of solvent flux depending on both the membrane structure [1–5] and the interaction of solute (protein) with the polymer membrane matrix [6–10].

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It is a matter of common experience that the gel layer formation of proteins decreases essentially the rate of ultrafiltration (UF) [11–13]. Considerably less information has been obtained for the effect of protein adsorption on a membrane separation mechanism of protein solutions in biotechnology, food industry, pharmaceutic industry, etc.

Recently the authors of this report have formulated the principles and the mechanism of protein adsorption onto hydrophobic polymer surfaces [14, 15]. The proposed diffusion-kinetic model of adsorption also accounts for hydrodynamic aspects near the polymer surface [16].

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The purpose of the present study is the investigation of protein adsorption on the polymer surface of UF membranes as well as the determination of the influence of the protein layer on values of water fluxes under UF conditions.

2. Theoretical model

A water flux through a membrane contacted with a gel protein layer occurs as a result of the difference in applied pressure (Δp) and osmotic pressure ($\Delta \pi$) being determined by protein concentration gradient. Macroscopic translational movement of solvent is hindered by two consequent hydrodynamic resistances belonging to polarized gel layer and UF membrane, respectively. Such being the case, the expression for volume flux of water can be written in the rather simple form [17]:

$$J_w^v = \frac{\Delta p - \sigma \Delta \pi}{R_G + R_M} \quad (1)$$

where

σ = dimensionless reflection coefficient, which varies from 0 for an absolutely nonselective membrane to 1 for an absolutely selective membrane
J_w^v = volume flux of water ($cm^3/cm^2 \cdot s$)
R_G = hydrodynamic resistance for the boundary gel layer ($Pa \cdot s/cm$)
R_M = hydrodynamic resistance for the membrane ($Pa \cdot s/cm$).

For protein transport the situation is more complicated. In any point of the diffusion layer in contact with protein gel layer, or in the absence of the gel layer, with the polymer surface:

$$\frac{dC_s}{dt} = \frac{d\Sigma J_i}{dx} \quad (2)$$

where the sum of protein fluxes is determined by: a) transport from solution to polymer (or gel) surface (J_G); b) permeate flux (J_F); and c) back diffusion flux (J_D) emerging as result of concentration gradient of protein from gel layer to bulk solution

$$\Sigma J_i \equiv J_G - J_F - J_D \quad (3)$$

On the interface solution/membrane (or solution/gel protein layer) the boundary conditions of Eq. 2 are

$$\frac{dC_s}{dt} = \Sigma J_i \qquad \text{at } x = 0 \text{ (or } x = l_G) \quad (4)$$

and on the interface: boundary diffusion layer-bulk solution

$$C_V = C_V^0 \qquad \text{at } x = -\delta_D \quad (5)$$

In Eq. 3 for absolutely selective membrane JF is equal to zero and now initial continuity Eq. 2 has a more simpler form

$$\frac{dC_G}{dt} = \frac{dJ_G}{dx} - \frac{dJ_D}{dx} \quad (2a)$$

with boundary conditions, reflected in Eqs. 4a and 5

$$\frac{dC_s}{dt} = J_G - J_D \quad \text{at } x = 0 \ (x = l_G) \quad (4a)$$

The stationary regime of solvent transport realizes as the sequence of the gel deposit completion $dC_G/dt = 0$ from where equality $J_G = J_D$ follows (or $J_G = J_D + J_F$ for semipermeable membranes) that gives the completion of adsorption $dC_s/dt = 0$.

Recently it was shown that for polyethylene high density [18], siloxanecarbonate copolymers [19] and segmented polyetherurethanes "Vitur", "Biomer" [20] adsorption of proteins is formed by irreversible and reversible surface protein layers. Kinetics of adsorption is described by set of differential Eqs. 4a, 6–8

a) for irreversible adsorption layer, where interaction polymer/protein prevails

$$\frac{dC_{s1}}{dt} = k_{11}C_G(C_{s1}^{00} - C_{s1}^{*} - C_{s1}) - k_{12}C_{s1} - k_1^{*}C_{s1} \quad (6)$$

b) for transition of protein molecules from native condition to changed conformation condition (surface denaturation)

$$\frac{dC_{s1}^{*}}{dt} = k_1^{*}C_{s1} \quad (7)$$

c) for reversible adsorption layer of protein where protein/protein interaction prevails

$$\frac{dC_{s2}}{dt} = k_{21}C_G(NC_{s1} - C_{s2}) - k_{22}C_{s2} \quad (8)$$

where

C_{s1}, C_{s2} = protein concentrations of irreversible and reversible layers packed on polymer surface

C_s^{*} = concentration of protein molecules which has undergone a conformational transformation

k_{11}, k_{12} = adsorption and desorption rate constants in Eq. 6

k_1^{*} = rate constant of conformational transformation of irreversibly adsorbed protein

C_{s1}^{00} = limiting irreversible protein concentration

N = average number of active center per a molecule that has undergone conformational transformation.

At any moment, the mass balance on the polymer surface is described by the equality:

$$C_s = C_{s1} + C_{s2} + C_{s1}^{*} \quad (9)$$

In a concentration polarization layer, the formation of protein gel layer seems to be initiated by rather high values of pressure and of protein concentration.

On the whole, the transport model of protein adsorption is described by the set of Eqs. 6–9 and by the transport Eq. 2 with boundary conditions 4 and 5. Specifically, in absence of gel layer and $\sigma \approx 1$, boundary conditions are Eqs. 4a and 5.

3. Experimental

Polysulfone (PSU-70M) and polysulfoneamide (37% and 44% NHCO groups) were kindly presented by the Academy of Applied Biotechnology of Russia. Aromatic polyamide (Fenilon VPU-150) was presented by NPO Polymer Membrane Vladimir, Russia. The characteristics and details of the UF experiments in a rectangular flow cell were reported in previous work [21].

Registration of surface concentration for egg albumin (Commercial Mark "Poch" Polen) is performed by IR fourier spectrometer Brucker IFS-48 and ATR device Specac P/N 1100 with KRS-5 crystal (45°) using a special desorption procedure [16, 21].

The components of the 0.7% egg albumin phosphate buffer solution were of reagent grade. The rate of solution flow was 0.5 m/s and pressure difference 0.7 atm.

4. Results and discussion

Fig. 1 shows the kinetics curves of adsorption of egg albumin (EA) on polysulfone (PS) (curves 1, 1b) and polysulfoneamide (PSA) (curves 2, 2b) membranes. The chemical nature of polymers has a considerable effect on the total surface concentration of EA (curves 1a and 1b) and on ratio of reversibility (α_{rev}). The results of adsorption obtained by IR ATR technique are presented in Table 1.

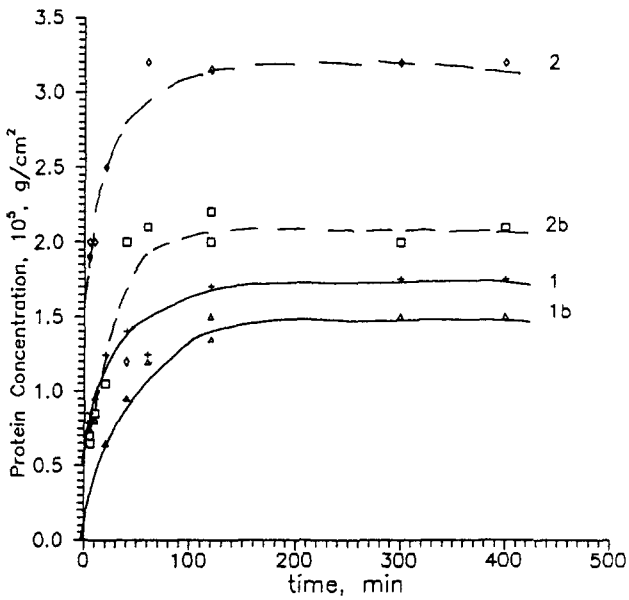

Fig. 1. Kinetics of protein adsorption. Total (1, 2) and irreversible (1b, 2b) adsorption of egg albumin on PS (1, 1b) and PSA-47% (2, 2b) membranes.

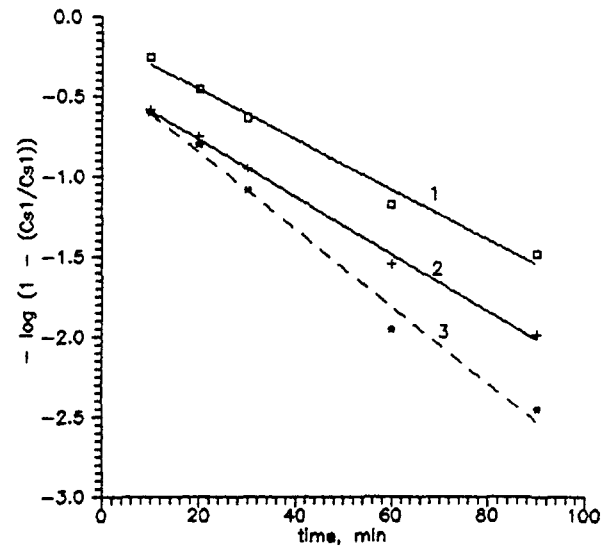

Fig. 2. Graphic solution of Eq. 10: 1 = PS, 2 = PSA, 3 = Aramid.

From Table 1 one can see that the ratio of reversibility is decreased by the increase of content of amide groups in membranes. This

Table 1
Equilibrium surface concentration of EA for UF membranes

Polymer	$C_s^{00}\,10^5$ (g/cm^2)	$C_{s1}^{00}\,10^5$ (g/cm^2)	α_{rev} *
Polysulfoneamide (47%) #	3.2	2.0	0.38
Polysulfoneamide (34%) #	2.0	1.35	0.33
Polysulfone "PSU-70M"	1.6	1.45	0.10
Aramid "Fenilon VPU-150"	0.63	0.28	0.55

* $\alpha_{rev} = C_{s2}^{00} / C_s^{00}$, $C_{s2}^{00} = C_s^{00} - C_{s1}^{00}$.
# mol percent of NHCO groups.

Table 2
Comparison of kinetic constants of adsorption (k_1^*) and of water permeation (k_w)

Membrane	$k_1^*\,10^3$ (s^{-1})	$k_w\,10^3$ (s^{-1})
Polysulfone	0.75	0.81
Polysulfoneamide (34% NHCO)	0.97	0.95
Aramid "Fenilon"	1.1	1.3

is likely due to interaction between the amid-containing surface and protein globules of egg albumin (EA).

In Fig. 2, the semilog transformations of above kinetic curves for the same membranes are presented. The achievement of limiting concentration C_{s1}^{00} is described by the kinetic equation

$$C_{s1} = C_{s1}^{00} [1 - \exp(-k_1^* t)] \quad (10)$$

which is the approximate solution of the set of Eqs. 6–9 in the kinetic range and at the condition that the bulk concentration C_v^0 is so high that $k_{11} C_v^0 >> k_1^*$ and $k_{11} C_v^0 >> k_{12}$. Calculations of effective constant k of irreversible adsorption are placed in Table 2.

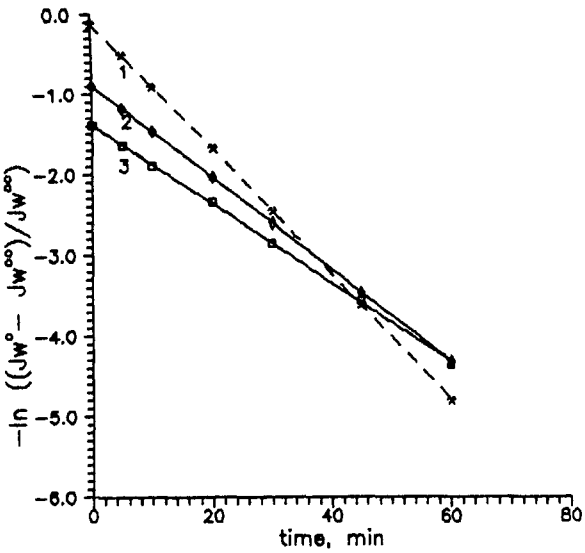

Fig. 3. Deterioration of water fluxes: 1 = Aramid, 2 = PSA, 3 = PS.

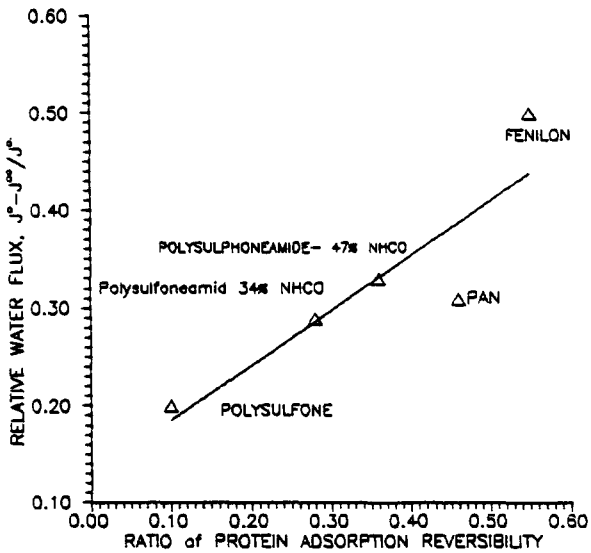

Fig. 4. Correlation between ultrafiltration water flux and protein ratio of reversibility.

In Fig. 3, the dependence of water fluxes on time is presented in semilog coordinates. Construction of kinetic curves in ln $[(J_w^v - J_w^{00})/J_w^{00}]$ vs. t coordinates gives the possibility to present the deterioration of water flux as

$$J_w^v = (J_w^0 - J_w^{00})\, e^{-k_w t} + J_w^{00} \qquad (11)$$

where k_w is the effective constant of the deterioration of water flux.

It is worth noting that the adsorption constants and k_w have about the same values. This equality shows that the reason of water transport deterioration is irreversible adsorption of protein (EA) under UF circumstances.

The comparison of ratio reversibility and relation $(J_w^0 - J_w^{00})/J_w^{00}$ is shown in Fig. 4. The linear correlation can be explained by the dual-mode mechanism of adsorption. The difference between initial and steady-state fluxes $(J_w^0 - J_w^{00})$ occurs mainly in accordance with protein layer formation, initiated by the reversible population of protein molecules. These results, as well as kinetic data (Figs. 1 and 3) testify interrelation between adsorption parameters and mechanism of UF rejection.

5. Conclusions

The development of the transport model of multistage adsorption of proteins (egg or albumines) on surfaces of UF polymer membranes (polysulfone, polyamidesulfone and aromatic polyamide) has been advanced.

Experiments were performed to study the kinetic mechanism of formation of protein layers reversibly and irreversibly adsorbed on surfaces. Registration of kinetic and structure characteristics were carried out using special plane-flow cell and FTIR ATR technique. All experiments showed existence of two-mode adsorption of albumin, namely reversible and irreversible surface layers.

The second purpose of this study was to determine the influence of adsorbed layers on the value of water fluxes occurred under UF conditions. For the separation of protein solutions by UF membranes, kinetic constants of irreversible adsorption correlate with effective constants of water deterioration fluxes.

As quantitative criterion of protein adsorption was proposed the ratio of reversibility determining a relative surface concentration of tightly immobilized macromolecules of protein. The ratio reversibility depends on the chemical structure of membranes. In sequence: polysulfone < polysulfoneamide (33% amide groups) < polysulfoneamide (47% amide groups) < aromatic polyamide.

Comparison of the ratio reversibility and the relation between initial and steady-state fluxes shows a satisfactory correlation.

6. List of symbols

C_s total surface concentration of protein, g/cm^2
C_{s1} protein concentration of irreversible adsorption layer
C_{s2} protein concentration of reversible adsorption layer
C_{s1}^{00} limiting surface concentration for C_{s1}
C_v^0 constant volume concentration of protein, g/cm^3
J_w^v volume flux of water, sm^3/cm^{2}s
J_w^0, J_w^{00} initial and limiting fluxes of water, g/cm^{2}s
J_D reverse diffusion flux of protein, g/cm^{2}s
J_F permeate flux, g/cm^{2}s
J_G protein flux to polymer surface, g/cm^{2}s
k_w effective constant of water flux deterioration, s^{-1}
k_{11}, k_{12} constants of irreversible adsorption and desorption, respectively, s^{-1} and cm^3/gs
k_1^* constant of change conformation for proteins, s^{-1}
k_{21}, k_{22} constants of reversible adsorption and desorption, respectively, s^{-1} and cm^3/gs
Δp difference of applied pressure, Pa
R_G, R_M hydrodynamic resistances for gel layer and membrane, respectively, Pa s/cm
t time, s
$\Delta\pi$ osmotic pressure, Pa
σ dimensionless reflection coefficient
PAN polyacrylonitrile [21]
PS polysulfone
PSA polysulfoneamide

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