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On the Mechanism of Flexible Chain Polymer Ultrafiltration

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Abstract: The regularities of ultrafiltration (UF) of flexible chain polymers (FCP) differ from that of globular proteins (GP) which is manifested, in particular, in opposite dependences of retention coefficient (φ) on the applied pressure. According to one of the existing points of view this difference is caused by different influence of concentration polarization on these polymers and according to another by the deformation of polymer coils of FCP in longitudinal velocity gradients at the pore entrance. To settle this question we examined the behavior of globular proteins and dextrans under absolutely identical conditions, which was reached by UF of the mixture of these polymers in one experiment with separate registration of FCP and GP concentrations in permeate and bulk. As it follows from the experiments, one can make a conclusion that, at low pressures and also at low molecular masses (M), FCP molecules keep themselves as globular proteins i.e., as rigid spherical particles. However, with the increase in pressure and M, the transport of flexible chain molecules through pores of UF membrane begins to be determined by the mechanism of polymer chain uncoiling in longitudinal gradients.

Keywords: Flexible chain polymers, retention coefficient, applied pressure, concentration polarization, polymer chain uncoiling, longitudinal gradients

INTRODUCTION

It is known that the regularities of ultrafiltration (UF) of flexible chain polymers (FCP) differ from that of globular proteins—the major objects of

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UF separation. The principal difference in these polymers behavior is manifested in different dependences of the observed retention coefficient (φ)

$$\varphi = 1 - (C_P/C_B) \quad (1)$$

on the applied pressure (Δp). In eq. (1) C_P and C_B are concentrations in permeate and bulk respectively.

Thus, in the case of ultrafiltration of globular proteins as pressure increases and gel polarization regime is reached one can see the increase in retention ability, which is caused by modification of membrane surface by gel layer and therefore by decrease of effective pore sizes. In the case of ultrafiltration of flexible chain polymers one can see, in contrast, the monotonous decrease in retention coefficients up to zero φ values as applied pressure increases.

At the present time two general points of view on the cause of such dependence of FCP retention coefficient on Δp exist. According to one of them this effect is caused by concentration polarization (CP) which leads to the increase in solute concentration near the membrane surface and therefore to the decrease in φ values. At the same time, as the transport of polymer molecules from membrane surface to bulk is determined by diffusion, the boundary layer becomes enriched in molecules with high masses, which leads to the increase in molecular mass of solute in permeate with Δp.

According to another viewpoint the $\varphi(\Delta p)$ dependence for flexible chain polymers is determined by the deformation of polymer coils in longitudinal velocity gradients at the pore entrance and therefore by the decrease in effective sizes of macromolecules.

It is quite evident that the answer to this question has not only a scientific but a certain practical importance because these polymers are widely used last time for UF membrane characterization (see, for instance, (1–4)).

Therefore, the aim of the present work is the determination of the mechanism of FCP ultrafiltration. To settle this question we examined the behavior of globular proteins and dextrans under absolutely identical conditions. This was achieved by carrying out UF experiment with the mixture of these polymers in one experiment with separate registration of concentrations of flexible chain polymers and globular proteins in permeate and bulk.

PREVIOUS WORK

Protein Ultrafiltration

It is known that in the course of protein ultrafiltration, two regimes of concentration polarization depending on the applied pressure can be realized (5). In the region of low pressures (low filtration fluxes) the decrease in the observed retention coefficients with Δp rise, caused by the rise of solute concentration in

boundary layer can be seen (see below, eq. (2)). This is the so-called pre-gel regime of concentration polarization. As the applied pressure increases, the membrane surface is modified by gel layer which decreases all pore sizes by a constant ΔR value (the so-called gel regime of concentration polarization (Fig. 1)).

The reduction of pore sizes by gel layer leads to an increase in membrane retention ability which is manifested, particularly, in shifting of retention curves (i.e., φ(M) dependences) towards low molecular masses with an increase in Δp (Fig. 2).

Simultaneously with the growth of membrane retention ability the filtration flux ceases to depend on applied pressure reaching the so-called limiting flux value. The following Δp increase leads to further decrease in pore sizes i.e., to the following increase in protein retention coefficients.

Ultrafiltration of Flexible Chain Polymers

As distinct from ultrafiltration of globular proteins (Fig. 2), in the case of flexible chain polymers the monotonous and unrestricted (practically to zero φ values) decrease in retention coefficients with an increase in Δp can be seen (Fig. 3).

To explain the selective behavior of FCP and the distinction of this behavior from that of globular proteins, two points of view (two models) exist at present time.

Concentration Polarization Model

According to this model, the φ(Δp) dependence can be explained by the influence of concentration polarization on the observed retention coefficient. As flexible chain polymers are, as a rule, hydrophilic polymers, they do not

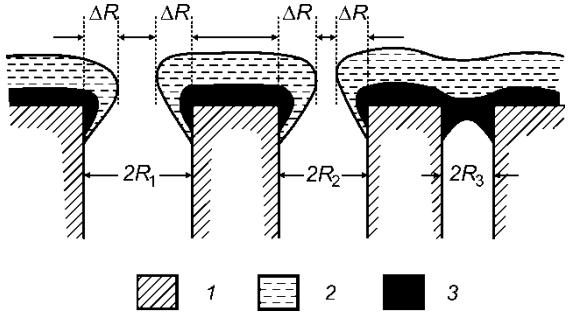

Figure 1. Formation of gel layer on UF membrane surface according to polarization-sieving model. 1–membrane material, 2–layer of reversible protein adsorption (gel polarization layer), 3–layer of irreversible protein adsorption (6, 7).

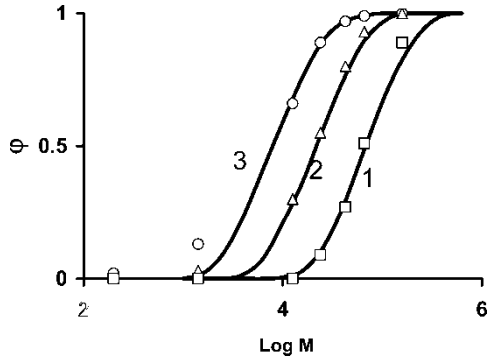

Figure 2. The shift of retention curves of membrane Omega-100 (Gelman) obtained in the process CP rise caused by pressure increase (Δp): 1–Δp = 0.2 bar, 2–Δp = 1 bar, 3–Δp = 2 bar. K = 1.1, where K is concentration rate i.e., the ratio of initial solution volume to the volume of concentrate (8).

form appreciable gel layers on membrane surface, as it takes place in the case of globular proteins, and the ultrafiltration of these polymers is going therefore in the pre-gel CP regime. Thus, to describe the dependence of the observed retention coefficient on UF flux eq. (2) obtained in the framework of stagnant film model can be used (5)

$$\varphi = \frac{\varphi_0}{\varphi_0 + (1 - \varphi_0)exp(J_V/k)} \tag{2}$$

where $\varphi_0 = 1 - C_W/C_B$ is a real retention coefficient, C_W is concentration near the membrane surface, J_v is filtration flux, and k is mass transfer

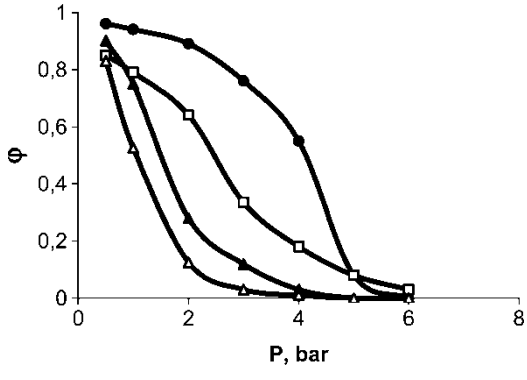

Figure 3. Dependences of retention coefficient on pressure obtained during ultrafiltration of 0.2% solution of: (●)–dextran T-70 on UPM-10 membrane, (□)–dextran T-70 on UPM-20 membrane, (▲)–polyethylene glycol on UAM-200 membrane, and (△)–dextran T-40 on UAM-200 membrane (9).

coefficient which characterizes the solute transport from membrane surface to bulk for different types of UF apparatus.

Using this approach Goldsmith (10) showed for dilute solutions of blue dextran that the observed retention coefficient can be described by Eq. (2) with constant φ_0 values. In other words, molecules of dextran behaved themselves with Δp growth as rigid particles with constant values of real retention coefficient. A similar conclusion about the behavior of molecules of FCP as that of rigid particles was drawn, with the use of eq. (2) in works of Long et al. (11), Bil'dukevich and Kaputskii (12) and Mochizuki and Zydney (13).

It was concluded, as a result of these investigations, that molecules of flexible chain polymers in the process of ultrafiltration behaved themselves as globular proteins in the pre-gel CP regime.

Deformation Model

It is supposed in this model that in the course of ultrafiltration the uncoiling (deformation) of polymer molecules in longitudinal gradients at pore entrance takes place. As a result of decrease in molecule effective pore size decrease in real retention coefficient with Δp growth occurs.

According to the theory of polymer chain uncoiling (see, for instance, (14)) molecule deforms in longitudinal gradient after the critical value of this gradient (g_{cr}) is attained

$$g_{cr}\tau_0 = 1 \text{ (Deborah's criterion)} \tag{3}$$

where τ_0 is relaxation time of vector $\vec{h}$ (h is the end-to-end distance of polymer chain). In a general case we have:

$$\tau_0 = Z\frac{\eta_0[\eta]M}{R_0T} \tag{4}$$

where η_0 is solvent viscosity, $[\eta]$ is intrinsic viscosity of polymer, M is molecular mass, R_0 is universal gas constant, T is absolute temperature, and z is a constant, from which follows the dependence $g_{cr}(M)$ of the form

$$g_{cr} \sim M^{-1.5} \tag{5}$$

Eq. (5) is valid for constant g whereas in the course of ultrafiltration polymer molecule on its way to pore entrance moves into increasing longitudinal gradients. The analysis of the dynamics of individual chain at pore entrance performed on the basis of scaling analysis by Daoudi and Brochard (15) and by de Gennes (16) made it possible to obtain the expression for the so-called critical flux after the attainment of which polymer uncoiling ceases to depend on molecular mass distinctly

$$J_{cr} = \frac{k_BTf_{ef}}{\eta_0R^2} \tag{6}$$

where k_B is Boltzmann's constant, f_{ef} is effective (surface) porosity, and R is pore radius.

The apparent independence of critical flux on molecular mass is caused either by the fact that consideration in (15, 16) was, carried out for longitudinal gradients which, *a priori*, exceeding the maximum values of g_{cr} for the molecules under consideration, or by the peculiarity of the interaction of polymer coil with hydrodynamic flux in ultrafiltration. Thus, as the molecule moves to the pore entrance it arrives at successively increasing gradients until it reaches the critical one in which it is deformed[1]. Consequently the large molecule reaches its critical gradient earlier than a small one. Therefore, the time during which a molecule is deformed before it reaches the pore entrance is proportional to its molecular mass (relaxation time), which ensure the same deformation of molecules of different sizes.

The estimation of values of longitudinal gradient in ultrafiltration was carried out by Cherkasov et al. (17). By analyzing the experimental data on ultrafiltration of flexible chain polymers they showed that $g_{cr}\tau_0$ product calculated for maximal gradient (g^{max}) at pore entrance[2]

$$g^{max} = \frac{J_V}{Rf_{ef}} \tag{7}$$

coincides by an order of magnitude with Deborah's criterion (3), which indicates that data on ultrafiltration of flexible chain polymers can be interpreted from the standpoint of the theory of uncoiling of polymer molecules in longitudinal gradients.

The experimental study of ultrafiltration of flexible chain polymers from this standpoint leads the investigators to different conclusions. Thus, Nguyen and Neel (19) who investigated the ultrafiltration of dextrans and polyethylene glycols came to the conclusion about the determining role of polymer uncoiling in ultrafiltration of flexible chain polymers. The same conclusion was reached by Cherkasov et al. (9) who investigated the ultrafiltration of dextrans by the method of differential diffusiometry. De Balman and Nobrega (20) using chromatography got the conclusion about the joint action of concentration polarization and polymer uncoiling on dextran ultrafiltration.

Thus, one can conclude that at the present time a wide spectrum of ideas about the mechanism of flexible chain polymer ultrafiltration exists. These ideas range from the complete identity between the ultrafiltration behavior of flexible chain polymers and globular proteins to the decisive role of polymer uncoiling in FCP ultrafiltration.

[1]Hence, the indispensable condition of the validity of eq. (6) is the existence in the hydrodynamic field at the pore entrance of longitudinal gradients exceeding the maximum value of g_{cr} for the molecules under consideration.

[2]The dependence of longitudinal gradient is of the extreme character with a maximum at a distance along the pore axis $x = 0.5R$ (18).

Therefore we made an attempt in the present study to determine the possible role of polymer uncoiling mechanism in flexible chain polymer ultrafiltration. To do this, we compared the UF behavior of dextrans with that of globular proteins in absolutely identical conditions. For this purpose we studied, with the use of gel chromatography, ultrafiltration of a mixture of proteins and dextrans with separate determination of concentrations of these polymers in permeate and concentrate at different pressures. In this way we were supposed to give an answer about the contribution of deformation mechanism to the ultrafiltration of flexible chain polymers.

It is necessary to mention that the principal advantage of this kind of investigation is the fact that the ultrafiltration of either proteins or dextranes is going on under absolutely identical conditions in one experiment, so the contribution of deformation mechanism, if it takes place in dextran ultrafiltation, can be easily revealed.

MATERIALS AND METHODS

All ultrafiltration experiments were performed with Omega-100 polyethersulfone UF membrane with molecular weight cut-off (MWCO) – 100 10^3 g/mol provided by PALL Corporation (Germany). Before experiments all membranes were held in distilled water for 10–12 hours and prior to use 100–150 ml of water was passed through the membrane to remove traces of preservative.

All filtration experiments were conducted with a 47 mm diameter stirred cell (stirring velocity (n ÷ (400–600) min^{-1}) with membrane area 12 cm^3. The trans-membrane pressure drop was set by nitrogen pressurization. The permeate flux was measured by weight method using electronic balance SVL 0.3 (Petroves, Russia) with an accuracy of ± 5 mg.

Water, buffer solutions, and solutions of proteins and dextrans had been prefiltered through 0.22 mcm pore size MFA membrane (Vladipore, Russia). The solutions of proteins, dextrans, and their mixtures were prepared by solution of previously weighted substances in 0.05M phosphate buffer solution + 0.1M solution of NaCl (pH = 6.6). Concentration of each protein in mixture was 1 mg/ml and that of each dextran 2.5 mg/ml.

Permeate and feed samples of volume 1 cm^3 were taken after filtration of 10 cm^3 of solution[3]. After this UF cell was refilled with a fresh solution, the pressure was increased and the next samples were taken. All experiments were conducted at room temperature (22 $\pm$ 2°C).

Permeate and feed samples were analyzed by HPLC using a column TSK 300 SW (Toyo Soda, Japan) at elution velocity 0.5 cm^3/min. The buffer solution mentioned above was used as eluent.

[3]Filtration of 10 cm^3 of solution through membrane with effective area of approximately 12 cm^2 is enough for filtration flux to reach the stationary regime. The following flux decrease is determined only by concentration growth according to (5).

For separate determination of protein and dextran concentrations in mixture we used spectrophotometer Uvicord–S (LKB, Sweden) with registration wavelength $\lambda = 280\,\text{nm}$ and differential refractometer RI 156 (Beckman, USA) both in linear range of concentration determination connected in series. Because dextrans do not absorb at wavelength 280 nm the retention coefficients of proteins were determined by the equation

$$\varphi_{\text{pi}} = 1 - \frac{h_{pi}^{ph}}{h_{fi}^{ph}} \tag{8}$$

where $h_{\text{pi}}^{\text{Ph}}$ and $h_{\text{fi}}^{\text{Ph}}$–heights of chromatographic peaks of permeate and feed at wavelength 280 nm respectively (Fig. 4) and i–ordinal number of protein or corresponding to this protein dextran fraction according to Table 1 (see below).

The retention coefficients of dextrans in mixture were determined by an equation

$$\varphi_{\text{di}} = 1 - \frac{h_{pi}^{R} - K_i h_{pi}^{Ph}}{h_{fi}^{R} - K_i h_{fi}^{Ph}} \tag{9}$$

where h_{pi}^{R} and h_{fi}^{R} – heights of chromatographic peaks of permeate and feed with refractometric registration (Fig. 4), and coefficients K_i take into account the contribution of proteins to refractometric determination of dextran concentration. Coefficients K_i were determined by chromatograms of a mixture of the same proteins only with refractometric and spectrophotometric registration by equation

$$K_i = h_i^{R}/h_i^{Ph} \tag{10}$$

where h_i^{R} and h_i^{Ph}–height of corresponding peaks on chromatograms with refractometric and specrophotometric registration respectively (Fig. 4). The accuracy of concentration determination is within 5% error.

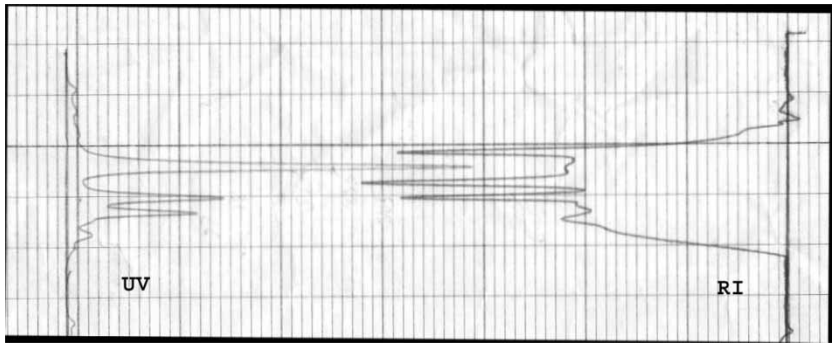

Figure 4. Chromatograms of protein-dextran mixture with ultraviolet (UV) and refractometric (RI) registrations.

Table 1. The principal characteristics of proteins and dextran fractions equivalent in effective molecular size

	Protein	$M_p \times 10^{-3}$, g/mol	$[\eta]_p \times 10$, cm^3/g	$D_p \times 10^7$, cm/s^2	$[\eta]_p M_p \times 10^{-5}$, cm^3/mol	$[\eta]_d M_d \times 10^{-5}$, cm^3/mol	$M_{hv} \times 10^{-3}$, g/mol	$M_c \times 10^{-3}$, g/mol	$D_d \times 10^7$, cm/s^2
1	CTG	24	32	9.5	0.77	0.77	8.4	8	10.1
2	OA	44	35	7.8	1.54	1.54	13.3	13	8.1
3	BSA	67	39	6.4	2.61	2.61	18.9	20	6.8

$[\eta]_p$–intrinsic viscosity of protein, $[\eta]_d$–intrinsic viscosity of dextran equivalent to protein by hydrodynamic volume, D_p – diffusion coefficient of protein, D_d–diffusion coefficient of dextran, M_{hv}–molecular mass of dextran calculated from hydrodynamic volume of equivalent protein and intrinsic viscosity of dextran with the use of eq. (13), M_c–molecular mass of dextran determined from the data of dextran HPLC calibration.

Globular proteins chymotrypsinogen (CTG), ovalbumin (OA), and bovine serum albumin (BSA) (Sigma, USA) and dextrans T-10, T-40, and T-70 (Pharmacia, Sweden) were used.

Calibration of chromatographic column was carried out with the use of dextran T-70 with a known molecular weight distribution (MWD) by the method of graphical fractionation and by correlation of integral dextran chromatogram with integral MWD function (21). Molecular weights of dextran fractions determined by this procedure are given in Table 1.

To correlate the retention ability of proteins and dextrans with equal effective size of molecules we used the data of Meirles et al. (22) in which it is shown that in ultrafiltration, analogous to gel chromatography, the effective hydrodynamic volume (V_h) plays the role of an appropriate molecular size parameter

$$V_h \sim [\eta]M \tag{11}$$

According to these data in the course of exclusion chromatography macromolecules with different conformation but with equal V_h are eluted with equal volume of elution (V_{el}). This fact gave us the possibility to compare the retention coefficients of equivalent by elution volume proteins and dextran fractions as retention coefficients of macromolecules of different nature but equal in effective hydrodynamic sizes.

The principal characteristics of proteins and dextran fractions equivalent in effective molecular size are listed in Table 1.

The intrinsic viscosities $[\eta]_p$ and diffusion coefficients D_p of proteins were taken from literature data (23).

Diffusion coefficients and intrinsic viscosities of chromatographic dextran fractions were calculated by eqs. (13, 24):

$$\begin{aligned} D_d &= 7.7\ 10^{-5} M_d^{-0.478} \\ [\eta]_d &= 1\ 10^{-3} M_d^{0.5} \end{aligned} \tag{12}$$

To calculate the molecular mass of dextran chromatographic fraction with molecular size equivalent to the size of protein molecule (M_{cal}) the equation

$$[\eta_p]M_p = [\eta_d]M_d \quad (13)$$

based on the invariance of hydrodynamic volume of macromolecules was used.

As it follows from the data in Table 1, molecular weights of dextran fractions determined from column calibration data are practically equal to M_{hv} determined by eq. (13), which indicates the exclusive (sieving) character of chromatographic regime.

The pressure dependence of water filtration flux was linear up to 1 bar. A deviation from linear behavior of about 7% takes place at 1.5 bar, which is caused probably by a slight deformation of membrane selective layer under the influence of pressure (Fig. 5).

The dependence of filtration flux on pressure for the mixture of proteins and dextrans is also shown on this figure. It is seen that this dependence has an extreme character so that the flux at 1.5 bar is lower than the flux at 1 bar, which can be caused either by the above–mentioned membrane deformation or by consolidation of protein–dextran cake on the membrane surface.

RESULTS AND DISCUSSIONS

The retention curves (RC) of membrane Omega-100 determined with the use of globular proteins (solid circles) and dextrans (open circles) in mixture at different pressures are shown in Fig. 6. For data presentation in joined scale we ascribed to dextran fractions the molecular masses of globular proteins (M_{cal}) with the same value of effective hydrodynamic volume (see section Materials and Methods).

In the same figure the retention curves of this membrane determined with the use of dextrans in the absence of proteins (triangles) are also shown. One

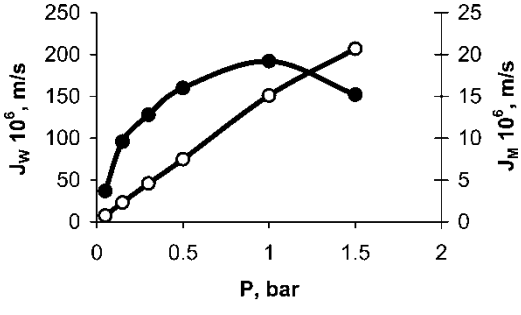

Figure 5. Dependencies of filtration flux on pressure obtained in: (○–J_W)–filtration of distilled water on Omega 100 membrane, (●–J_M)–ultrafiltration of a mixture of proteins and dextrans on the same membrane.

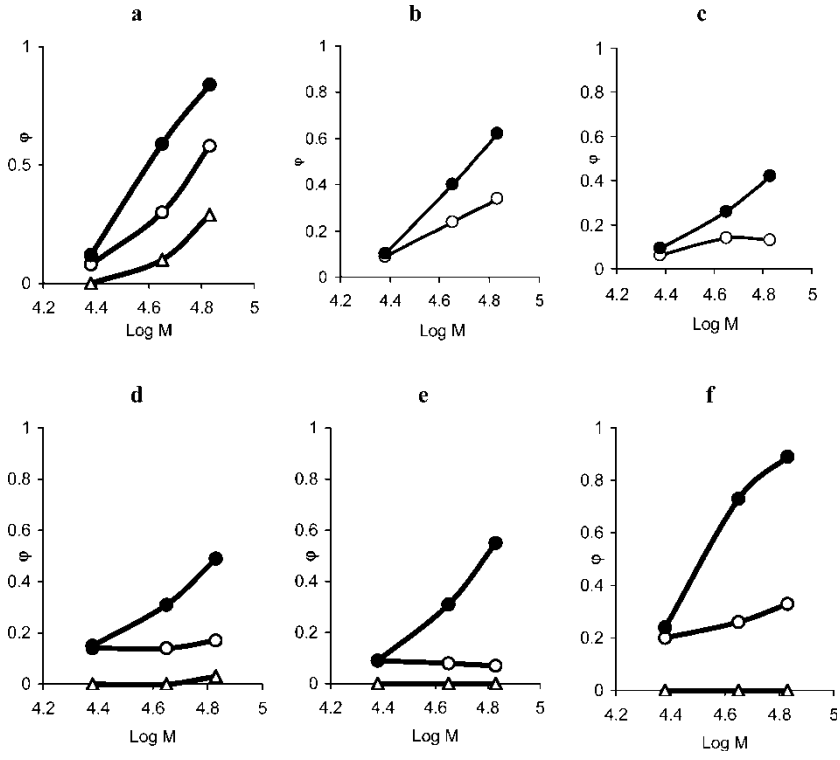

Figure 6. The retention curves of membrane Omega-100 determined with the use of globular proteins (solid circles) and dextrans (open circles) in mixture at pressures: a–0.05 bar, b–0.15 bar, c–0.3 bar, d–0.5 bar, e–1.0 bar, f–1.5 bar.

can see that although these curves repeat the form of RC determined by dextrans in mixture they are shifted to lower retention coefficients. The difference in retention curves position is caused by decrease in pore sizes either because of protein adsorption or by gel polarization of membrane surface (see Fig. 1).

As it follows from Fig. 6 at minimal pressure (0.05 bar) (Fig. 6a) the retention curves determined by proteins and dextrans in mixture are close to each other. Rather lower values of dextran retention coefficients, as related to retention coefficients of proteins, are caused evidently by higher intensity of diffusion transport of dextran molecules through membrane because for equal appropriate molecular size parameter diffusion mobility of flexible dextran molecules is by (4–6)% higher than that of proteins (Table 1).

As pressure increases up to 0.3 bar (Fig. 6c) one can see the decrease in retention coefficients of either proteins or dextrans which is caused, according to the existing concepts, by the influence of concentration polarization in pre-gel regime on the observed retention coefficients (Eq. (2)).

Thus, the close position of the retention curves determined by proteins and dextrans in mixture at 0.05–0.3 bar indicates that at low pressures the ultrafiltration of molecules of two types is governed by the same UF mechanism.

However, as pressure increases above 0.3 bar situation changes drastically (Fig. 6d–e). Retention coefficients of proteins increases with pressure rise, which is caused by decrease in pore sizes by gel layer (Fig. 1). Simultaneously one can see that the increasing divergence between retention curves determined with the use of proteins and dextrans takes place. Thus, if at pressures 0.05–0.3 bar these curves were rather close to each other i.e. dextrans kept themselves as proteins with equivalent molecular mass, as pressure rises above 0.3 bar the retention curves determined with the use of dextrans in mixture decreases approaching the RC determined with the use of dextrans in the absence of proteins (Fig. 6e). It is necessary to point out that at pressure 0.3 bar filtration flux of protein–dextran mixture begins to deviate from linearity tending to plateau value (to the value of limiting flux), which is caused by the transition of UF process to gel polarization regime.

The divergence between the retention curves determined with the use of proteins and dextrans in identical UF conditions points to the existence of an additional mechanism of flexible-chain polymer molecules transport through ultrafiltration membrane. Theoretically this additional transport can be caused by higher level of concentration polarization of FCP molecules as related to proteins. However, as it follows from Table 1, diffusion coefficients of dextrans with equal V_h which determine the CP level appeared to be even higher than that of globular proteins, which exclude this supposition.

Therefore, the only explanation of the observed divergence between UF behavior of proteins and dextrans under identical ultrafiltration conditions is the influence of deformation of flexible-chain molecules in longitudinal gradients at pore entrances which decreases their real retention coefficients.

As pressure increases up to 1.5 bar (Fig. 6f) one can see the increase in dextran retention coefficients which can be caused either by membrane deformation (see above, Fig. 3) or by consolidation of protein–dextran cake on membrane surface.

It is interesting to note that at pressure 1 bar when the maximal contribution of deformation mechanism to UF transport of flexible chain molecules takes place one can see a decrease of dextran retention coefficients with molecular mass, which correspond to theoretical dependence of critical gradients on M (Eq. (5)). This dependence can be demonstrated more clearly if we correlate the sieving coefficients ($S \equiv 1 - \varphi$) of proteins (S_p) and dextrans (S_d) of different molecular masses. The dependences of S_d/S_p ratio on M and p are shown in Fig. 7.

As is seen from this figure, the difference in sieving coefficients of two types of polymers increases with molecular mass. Thus, for the most low molecular protein (CTG) we do not see any difference in sieving coefficients, which can be explained by the fact that even at highest fluxes (highest

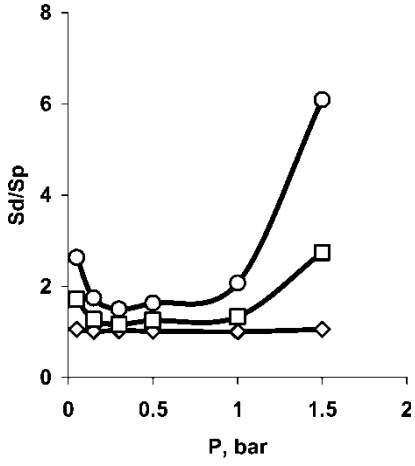

Figure 7. The dependence of ratio of sieving coefficients for the couple dextran–protein with equal hydrodynamic molecular volumes on applied pressure: (◇)–dextran–ChTG. (□)–dextran–OA, and (○)–dextran–BSA.

pressures) the values of longitudinal gradients are not sufficiently large to uncoil the molecules of low molecular dextran fraction.

However, as molecular mass increases one can see the increasing divergence between sieving coefficients of the two types of polymers. Thus, for instance, the sieving coefficient of most high molecular protein (BSA) appeared to be even twice lower than that of dextran fraction with the equal V_h. As pointed out above, this divergence in retention coefficients with M increase follows directly from the theory of polymer chain uncoiling (Eq. (5)).

It is necessary to note also the increase in (S_d/S_p) ratio for pressures below 0.3 bar. The increase in dextran transport as related to protein can be explained by relatively high diffusion transfer through membrane at $\Delta p \rightarrow 0$ caused by higher diffusion coefficients of dextranes as compared to proteins (Table 1).

Hence, on the basis of investigations carried out, one can come to a conclusion that ultrafiltration of flexible chain polymers is governed by two mechanisms. At low pressures and also at low molecular masses, molecules of these polymers keep themselves as molecules of globular proteins i.e., as rigid spherical particles and follow the regularities of stagnant film model of concentration polarization. The fact that this behavior of flexible chain polymers manifests itself either at low pressures of at low molecular masses follows directly from the theory of polymer chain uncoiling according to which polymer deformation is determined by the product of longitudinal gradient and molecular mass (see above, Deborah's criterion, (eq. 3).

However, with an increase in pressure and M, the transport of flexible chain molecules through pores of UF membrane begins to be determined by

the mechanism of polymer chain uncoiling, which is manifested in the increasing divergence between the retention coefficients of these polymers and globular proteins.

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