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Hydrodynamic and molecular characteristics of polyelectrolyte complexes between sodium dextransulfate and chitosan hydrochloride

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Abstract

Hydrodynamic and molecular characteristics of particles of polyelectrolyte complexes (PEC) between sodium dextransulfate and chitosan hydrochloride were studied by various physicochemical methods (high-rate sedimentation, viscosimetry, turbidimetry, and diffusion). As was shown, the complex formation is accompanied by increase in the average sizes with simultaneous changes in the shape of the particles of the investigated PEC. According to the proposed polycomplexes model, side by side aggregation of the taken macromolecules could cause disordering of adjacent helical parts of polyanion-matrix that facilitates the formation of sphere-like polycomplexes particles.

Keywords: Polyelectrolytes; Chitosan; Sedimentation; Chitosan hydrochloride; Polyelectrolyte complexes; Sodium dextransulfate; Hydrodynamic properties

1. Introduction

Earlier (Zezin & Kabanov, 1982), investigations of molecular weight and thermodynamic characteristics of water-soluble polyelectrolyte complexes (PEC), which were formed, mainly of two flexible-chain polyelectrolytes, showed that changes in the initial mixture composition caused corresponding changes in molecular parameters of the PEC.

Moreover, we showed (Alexandrova et al., 1989) that changes in the composition of the soluble PEC of sodium dextransulfate (SDS) and chitosan hydrochloride (CHC) significantly influenced intramolecular mobility of segments in the macromolecules that formed the complexes. Obviously, this phenomenon must be accompanied by changes in the structure and molecular parameters of the PEC.

In this work, hydrodynamic behavior of water-soluble PEC based on two semi-rigid-chain polysaccharides SDS and CHC (PEC_{SC}) in different aqueous media has been investigated for the first time.

2. Experimental

Low-molecular CHC with the average viscometric molecular weight $M_v = 1.8 \times 10^4$ and high-molecular SDS ('Farmacia', Sweden) with $M_v = 5 \times 10^5$ and sulfur content 17.4% were used in this work. CHC was prepared by acid hydrolysis of chitosan with $[\eta] = 4.0 \times 10^4$ dl/g in 1N HCl at 100 °C for 5 h. The polymer obtained was precipitated in acetone, washed with anhydrous acetone several times, and dried. CHC prepared in this way had $[\eta] = 0.57$ dl/g (in 0.2 M acetate buffer solution, pH 5.0).

PEC_{SC} were obtained by mixing together of aqueous or water–urea solutions of CHC and SDS at the ratio of the components in the range $Z = [CHC]/[SDS] = 1–10$ (measured in the initial mixture by base mol/l); as it had been described in Gamzazade and Nasibov (1995). Here parameter Z is the ratio between the numbers of all the units in the interacting chains independently of the fact, if they bear or not charged groups.

Intrinsic viscosities of PEC_{SC} solutions were measured at 25 °C by a modified Ubelohde viscometer with the capillary diameter 0.4 mm in the range of concentrations 0.2–0.7 g/dl. To attain isoionicity of the tested solutions, the latter were dialyzed against the used solvents.

The sedimentation coefficients (S_c) for PEC_{SC} samples were determined from high-rate sedimentation data obtained by means of a MOM 3170-5 analytical ultracentrifuge (Hungary). The changes of the sedimentation boundary were registered by the *Filpot-Swenson* optical system (Schlieren) in the range of PEC_{SC} concentrations 0.2–0.7 g/dl. Two-chamber cells (12 ml) with artificial boundary formation (synthetic boundary cells) were used in the experiments.

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Table 1
Hydrodynamic and conformational characteristics SDS and PEC_{SC} having various compositions (solvent: 4 M urea, pH 7.5, $I = 0.05$)

Z	$[\eta]$ (dl/g)	$S_{0w} \times 10^{13}$ s	$D_{0w} \times 10^{7}$ cm^2/s	γ	$m_{s\eta} \times 10^{-3}$ g/mol	$M_{SD} \times 10^{-3}$ g/mol	$(R^2_{ap})^{1/2}$ Å
SDS	1.44	5.82	0.85	1.19	505	596	515
0.11	1.37	6.08	0.70	1.31	457	700	628
0.17	1.26	6.69	0.63	1.45	464	788	684
0.33	1.11	7.47	0.54	1.65	480	996	812

The measurements were carried out at the rotation rate 60,000 rpm and temperature 20 °C. The tested solutions underwent to equilibrium dialysis before the measurements, and the dialyzates were used as the solvents.

Wels van Hold parameter $\gamma = k_s/[\eta]$, which furnishes an opportunity to estimate the shape of the macromolecules, was determined from the dependence of S_c on c and $[\eta]$.

Diffusion coefficients $D_{c(0)}$ for PEC_{SC} particles were determined under static conditions by the method of dynamic light scattering with the use of a photon-correlation spectrometer, model 4300, of the firm 'Malvern' (GB) equipped with a digital correlator, model K 7023/96. A laser of the firm 'Spectraphysics' (Germany), model 124B, was used as the source of light. The angular dependence of the correlation function $g(\gamma) = 1 + \exp(-2Dk)$ (where $k = 4\pi\lambda \sin \nu/2$; λ is the wavelength of incident light in nm; ν is the angle of light scattering in degrees) for light scattered by macromolecules was studied in the range of angles from 30 to 120° and in the range of PEC_{SC} concentrations from 0.1 to 0.6 g/dl. Double extrapolation in accordance with *Zimm* method was carried out to determine $D_{c(0)}$ magnitude.

For the diffusion measurements, the tested solutions were dialyzed for 24 h followed by filtration through 22 μm filter 'Millipore' (France). The filtrate was collected into a previously dust-removed cylindrical cell of optically uniform glass with the volume about 3 ml. Extrapolation of D_0 measured in water to D_{0w} at infinite dilution was carried out with the use of adjustment for viscosity: $D_{0w} = D_0(\eta/\eta_w)$, where $D_0 = kT/f$ and $f = 6\pi\eta_0(R^2)^{1/2}$ (η_0 is the solvent viscosity and $(R^2)^{1/2}$ is the mean-square inertia radius).

Molecular weights of the polycomplex particles were calculated from *Swedberg* equation

$$M_{SD} = S_0RT/D_0(1 - \upsilon\rho_0)$$

where υ is the specific partial volume in cm^3/g and ρ_0 is the solvent density in g/cm^3.

The specific partial volume (υ) of polycomplex macromolecules was measured by the bottle method in the range of concentrations 0.1–0.6 g/dl followed by extrapolation to $c \rightarrow 0$ and calculated in accordance with the following equation

$$\upsilon = \upsilon_\beta[1/m_0 - 100/P(1/m_0 - 1/m)],$$

where υ_β is the picnometer water value, m_0 is the weight of the solvent in the picnometer in g, m is the weight of the solution in g, and $P = 100g\upsilon_\beta/m$ (g is the weight of the polymer sample).

3. Results and discussion

From general considerations one could assume that interaction between two semi-rigid-chain macromolecules, such as SDS and CHC, must lead to formation of highly asymmetrical particles resulting in increase of their average dimensions. This assumption was grounded on the data earlier obtained from the measurements of EPR-spectra of spin-labeled polycomplexes that indicated a rise in the kinetic rigidity of the chains with the increase of chitosan content in them (Alexandrova et al., 1989).

Actually, investigations of molecular parameters of PEC_{SC} particles showed that the complex formation causes a rise in their apparent dimensions (Table 1). This phenomenon is of special interest because, in accordance with the literature data, as a rule, complexing between synthetic flexible-chain polyelectrolytes causes compacting of the PEC particles resulting in decrease of their average dimensions (Charenko, Charenko, Kasaikin, Zezin, & Kabanov, 1979).

On one hand, increase of $(R^2_{ap})^{1/2}$ and decrease of D_0 with the rise in the chitosan portion of PEC_{SC} can be explained by the fact that, when the chitosan content is raised, asymmetrical chains of SDS-matrix polyanion are straightened, and the PEC_{SC} particles become still more elongated. However, on the other hand, the rise in asymmetricity of the particles must be accompanied by increase of $[\eta]$, and S_c magnitude must be practically unchanged. But, it is not so in this case. Hence, one can conclude that the changes in the magnitudes of the foregoing hydrodynamic parameters are not associated with the rise in asymmetricity of the particles during complexing between CHC and SDS.

Since, in this case, only relatively slight increase in PEC_{SC} molecular weight is observed, the disclosed changes of S_c and $[\eta]$ depending on Z can be attributed to changes in the shape of PEC_{SC} particles, namely, to their curling up during complexing. Actually, parameter $\gamma = k_s/[\eta]$, [where k_s is the slope of the dependence $S_c = f(c)$] increases when Z is rising. At that, for PEC_{SC} with maximum chitosan content the parameter γ runs up to 1.65 that is typical for the conformation of impermeable clews of flexible-chain polymers. It permits us to assume that the decrease in $[\eta]$ of the polycomplex during chitosan attachment to SDS is caused by

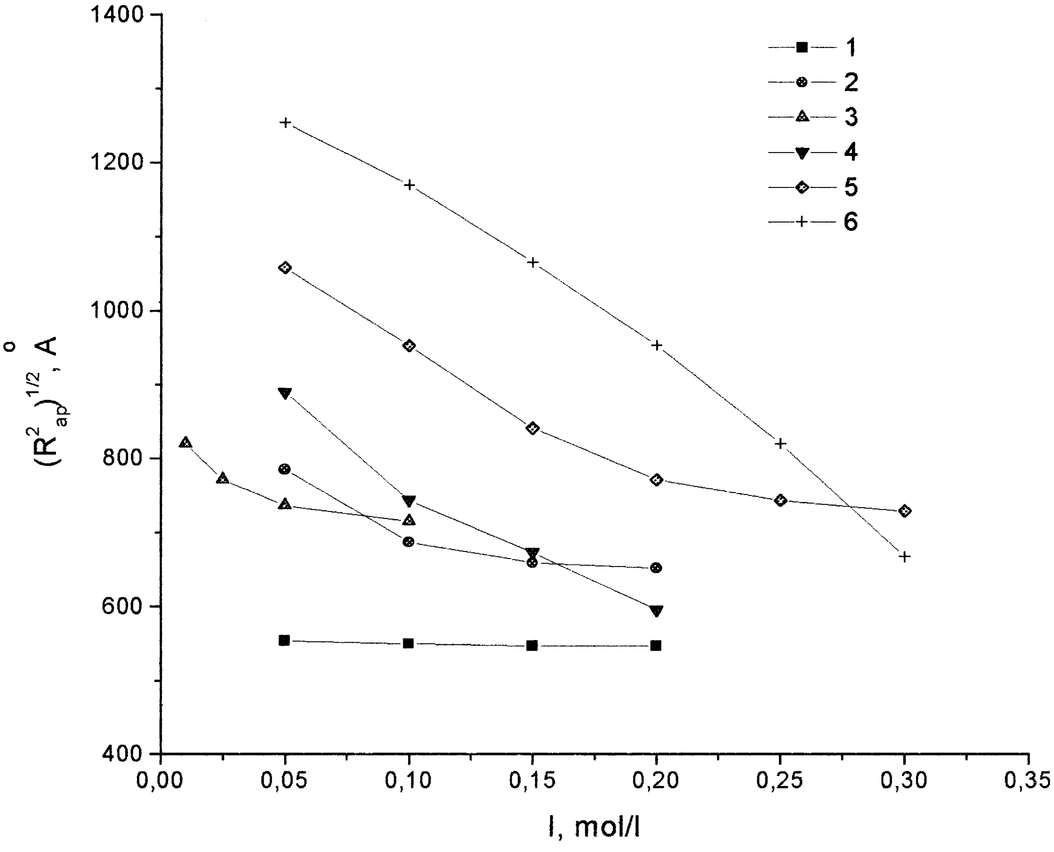

Fig. 1. Dependences of average apparent sizes of PEC_{SC} particles and SDS on ionic strength (*I*) in different solvents (concentration of $PEC_{SC} = 0.3$ g/dl, $Z = 0.33$). (1) SDS in aqueous solition of NaCl, (2) SDS in aqueous solition of NaCl with 4 M urea, (3) PEC_{SC} in aqueous solution of NaCl, (4) PEC_{SC} in aqueous solution of NaCl with 4 M urea, (5) PEC_{SC} in aqueous solution of LiCl, (6) PEC_{SC} in aqueous solution of LiCl with 4 M urea.

weakening of the hydrodynamic interaction of PEC_{SC} particles with the solvent, obviously, due to neutralization of the functional groups resulting in decrease of their hydrophilicity.

So from all the above-mentioned, one can conclude that the features of PEC_{SC} behavior and its conformational state in solutions are typical for flexible-chain polymers rather than rigid-chain ones.

The study results for the dependence of average sizes of PEC_{SC} particles on the solution ionic strength (*I*) and counterion nature confirm the assumption concerning the character of the conformational transformations in PEC_{SC}. The fulfilled measurements (Fig. 1) showed that the average dimensions of SDS macromolecules in aqueous solutions are practically independent of ionic strength (curve 1) indicating increased rigidity of this polymer chains. At the same time, the dependence is observed in water–urea solutions (curve 2). At that, the dependencies in these media are more pronounced for PEC than for 'free' SDS. Such a dependence of PEC_{SC} particle average dimensions on ionic strength indicates that the particles demonstrate some additional flexibility at complexing, obviously, as the result of disordering of some parts of SDS chains in PEC_{SC}.

Nature of low-molecular counterions present in the solutions remarkably influences the value of $(R_{ap}^2)^{1/2}$. The change of Na^+ for Li^+, under other equal conditions, causes a drastic increase of $(R_{ap}^2)^{1/2}$. Evidently, chaotropic properties and high dissociation constants of lithium salts prevent from intramolecular associative processes and, thus, promote electrolytic swelling of PEC_{SC} particles resulting in increase of their average dimensions. A rise in concentration of these counterions causes a remarkable decrease of $(R_{ap}^2)^{1/2}$, that is typical for flexible-chain polymers. It is of importance to

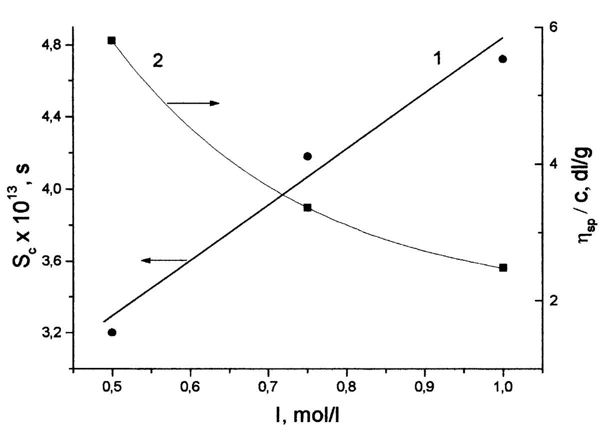

Fig. 2. Dependencies of sedimentation coefficients (1) and reduced viscosity (2) of PEC_{SC} solutions on ionic strength (*I*) ($Z = 0.17$, pH 7.5, $C_{PEC} = 0.3$ dl/g).

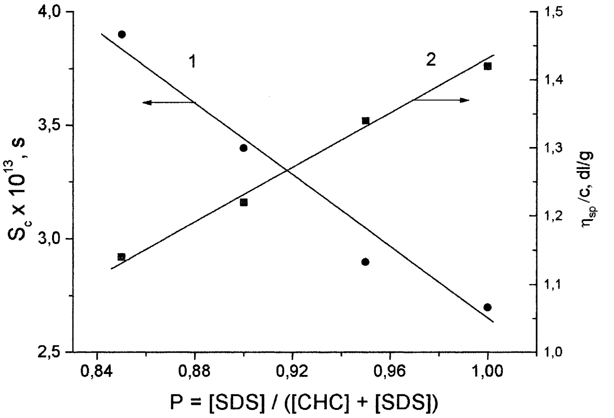

Fig. 3. Dependencies of sedimentation coefficients (1) and reduced viscosity (2) of PEC_{SC} solutions on relative content of SDS (*P*) (solvent: 4 M urea, 0.05 M NaCl, pH 7.5).

note that the observed dependencies of $(R^2_{ap})^{1/2}$ on ionic strength are in good agreement with the changes in other hydrodynamic characteristics (Figs. 2 and 3). Thus, simultaneous decrease of $[\eta]$ and increase of S_c can indicate compacting of PEC_{SC} particles with the rise in the solution ionic strength. Increase of CHC portion in PEC influences S_c and η_{sp}/c in the same way. Hence, one can conclude that the particle compacting occurs in this case as well.

In general, the complexing of the polymers under consideration can be described as electrostatic side by side aggregation of semi-rigid-chain macromolecules accompanied, obviously, by local increase in thickness and rigidity of the chain. At that, disordering (straightening) of the spiral (or folded) structure of the polyanion-matrix can take place in adjacent parts, resulting in appearance of a possibility for the macromolecules to take more advantageous, spherical, conformation. This assumption is in good agreement with the data on the complexing of protein molecules with linear polyelectrolytes, which is accompanied by considerable conformational changes, in particular, by decrease in the extent of protein molecule spirality (Mustafaev, Tsareva, & Evdakov, 1975).

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