SMALL-ANGLE X-RAY SCATTERING FUNCTIONS OF RODLIKE POLYELECTROLYTES IN AQUEOUS SOLUTIONS: THEORETICAL STUDY#

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#Dedicated to Prof. D. Dolar on the occasion of his 80th birthday

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Abstract

A theoretical study of small angle X-ray scattering on model rodlike polyelectrolytes containing a mixture of univalent (Li^+) and divalent (Sr^{2+}) counterions is presented. Scattering functions, based on the electron density contrast relative to solvent, were computed. The distribution of the excess electron density around the polyion was determined by numerical solving of the Poisson-Boltzmann (PB) equation within the cell model. For the systems containing only one kind of counterions analytical solutions of the PB equation were also used. Such a model can be applied to rigid polymeric entities with rodlike shape, the entities being either individual polymers or small constituents of otherwise flexible polymers. We studied the influence of both the polyion and its ionic atmosphere on the scattering function. As expected, the contribution of the polyion to the scattering function is significant while the contribution of the ionic atmosphere increases with increasing the fraction of strontium ions with a higher contrast in electron density against the solvent.

Introduction

Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) methods are very powerful experimental tools for studying the structure of macromolecular particles in solution. The aid of theoretical model calculations, which can be compared with the experimental data, is of a great importance for the interpretation of experimental results. There exist a variety of theoretical methods for building up a macromolecular particle and for calculating its small angle scattering function. The so-called MULTIBODY method[1] approximates the macromolecule by a large number of small spheres ("finite elements"), each of them having an arbitrarily chosen value of the contrast in electron density against surroundings. This model allows for building up a particle of arbitrary shape, size and internal structure, and as such, it serves for the calculation of the scattering function $I(q)$ and its Fourier transform, i.e. the pair distance distribution function $p(r)$, for an "isolated" particle.[1] The main disadvantage of this method is its inability to treat the interactions between individual macromolecules. Particularly usable are the analyticaly tractable models with adjustable geometric parameters, which may be fitted to reproduce the experimental scattering function, thus revealing the structural informations about the scattering objects in the solution, i.e. of colloids and polymers.[2] When analytical expressions are not available due to the complexity of the model, Monte Carlo simulations may be a valuable tool for determining the scattering function.[3,4]

Special concern is adressed to polyelectrolytes in solution where the polyion is surrounded by ionic atmosphere containing counterions and, optionally, ions of the added salt. Since the ionic atmosphere is often highly ordered, it may function as another "effective" particle with a certain scattering contrast against the solvent, and hence as a source of X-ray and neutron small-angle scattering. The structure of the polyion together with its ionic atmosphere is rather complicated; it is determined by the interplay of the hard core effects, short-ranged nonelectrostatic interactions, and electrostatic interactions among all charged species in the solution. It follows, that the above mentioned multibody method cannot be applied in treating the scattering of an "isolated" object consisting of the polyion and its ionic atmosphere. A special issue is the distribution of the ions within the atmosphere, which is mainly governed by electrostatic forces between the polyion and the counterions. Assuming no other forces are acting and that there is no interaction between individual polyions, the distribution of ions can be obtained by solving the Poisson-Boltzamann (PB) equation. The PB equation is very difficult to solve if the backbone of the polyion is flexible. However, in the case of rigid, rodlike polyions, the PB equation is simplified, since cylindrical symmetry may be introduced in the system, and may be solved within the frame of the cell model.[5] The problem is that the amount of such rigid systems, available for experimental studies, is rather limited. In most of the models studied so far, *e.g.* polystyrene sulfonates (PSS), the backbones of the polyion chains are at least partly flexible.[6]

SAXS is based on the contrast in electron density between the solute and the solvent; hence ions of heavy elements (*e.g.* strontium, caesium, iodine) produce much greater scattering intensities than light elements (*e.g.* lithium, sodium). For this reason, the individual contributions of polyion and counterions to the overall scattering intensity depend on the structure of polyion chain and on the type of counterions forming the ionic atmosphere. For example, many carbohydrate polyelectrolyte backbones have a very low electron density contrast against the solvent.

In such a case, the scattering of counterion cloud becomes a leading term which makes such compounds very suitable for experimental studies of ionic atmosphere without perturbations caused by the polymer backbone.

In this paper we present a theoretical study of SAXS from the solutions of rodlike polyelectrolytes, containing the extended polyions surrounded by a mixture of uni- and divalent counterions. This model can be applied either to:

- Flexible polyelectrolytes (*e.g.* PSS), assuming that small subunits of such polymers are essentially linear. The calculations should then treat these small units by setting the degree of polymerization to a very low value (*e.g.* 10 monomer units) or
- Synthesized rodlike, rigid polyelectrolytes of arbitrary length; such as, for example, poly(p-phenylenes).[7]

The influence of both the polyion and the ionic atmosphere on the scattering function was studied as well as the influence of the composition of counterions. Presumably the scattering intensity will be higher with increasing content of strontium ions in the atmosphere.

Theory

Cell Model and Excess Electron Density. The polyelectrolyte solution is represented as an ensemble of cylindrical cells with radius R and length L. The chosen radius should reproduce the concentration of the polyelectrolyte, *i.e.* $R = \sqrt[3]{\frac{3V_1}{4\pi}}$, where V_1 is the average volume occupied by a single polyelectrolyte molecule in the solution. A cylindrical polyion of radius a and length $L = \nu b$, where b is the length of the monomer unit and ν the number of monomers, is fixed in the axis of each cell. Each monomer unit bears a single negative charge. The charge of the polyion, $-\nu e_0$, is supposed to be spread uniformly over its surface.

In the free volume of the cell are distributed uni- and divalent counterions such that the net charge of the polyion and its counterions is equal to zero. Only electrostatic forces are assumed to be acting. No interaction between individual cells is assumed within this model.

The distribution of the number densities $n_1(r)$ and $n_2(r)$ of the counterions around the polyion may be calculated from the solution of the Poisson-Boltzmann (PB) equation using the cell model.[5] The PB equation for the above model cannot be solved analytically. A numerical procedure must be applied.[8] However, in the special case when only one kind of counterions are present (*i.e.* only univalent or only divalent ions), there exists an analytical solution of the PB equation, yielding the following expression for $n_i(r)$[5,7]:

$$n_i(r) = n_i^0 \frac{B^2}{2r^2\kappa^2\cos^2(\frac{B}{2}\ln\frac{rF}{a})}, \tag{1}$$

where n_i^0 is the average density of the counterions in the cell and κ is the screening constant. B and F are integration constants which can be obtained by solving the following equations:

$$\arctan\frac{2}{B} = \frac{B}{2}\ln\frac{R}{a} - \arctan\frac{2(\lambda-1)}{B}, \tag{2}$$

and

$$F = e^{\frac{2}{B}\arctan\frac{2(1-\lambda)}{B}}, \tag{3}$$

where λ is defined as

$$\lambda = \frac{\lambda_B}{b}, \tag{4}$$

with λ_B being the Bjerrum length

$$\lambda_B = \frac{e_0^2}{4\pi\epsilon\epsilon_0 k_B T}. \tag{5}$$

With known $n_1(r)$ and $n_2(r)$, we can calculate the excess electron density (relative to solvent) within the cell. The number of the excess electrons $\Delta\varrho_1^c$ and $\Delta\varrho_2^c$ per counterion can be calculated by use of their crystallographic radii. The excess electron density of the polyion ($\Delta\varrho_{rod}$) may be calculated from its length and radius. Now we can write $\Delta\varrho(r)$ as

$$\Delta\varrho(r) = \left\{ \begin{array}{ll} \Delta\varrho_{rod} & 0 \le r \le a \\ n_1(r)\Delta\varrho_1^c + n_2(r)\Delta\varrho_2^c & a < r \le R \\ 0 & r > R \end{array} \right\}. \tag{6}$$

Scattering. The absolute scattering $I(q)$ may be written as[7]

$$I(q) = \frac{N}{V} I_0(q) S(q), \tag{7}$$

where $\frac{N}{V}$ is the number of the polyelectrolyte molecules per volume, $S(q)$ the structure factor reflecting the intermolecular interactions (here fixed at 1), $I_0(q)$ the scattering intensity of a single rodlike polyelectolyte molecule and q the magnitude of the wave vector.

Amplitude of the scattering of a single molecule in internal cylindrical coordinate system may be written as

$$A(q) = \int_{-\frac{L}{2}}^{\frac{L}{2}} dz e^{iq_z z} \int_0^R \Delta\varrho(r) r dr \int_0^{2\pi} e^{iq_r r\cos\varphi} d\varphi, \tag{8}$$

where $\Delta\varrho(r)$ is the excess electron density given by equation (6). The internal coordinate system is rotated for angle θ with respect to the wave vector $\vec{q}$. Amplitude of the scattering can now be written as

$$A(q) = L \frac{\sin\frac{q\cos\theta L}{2}}{\frac{q\cos\theta L}{2}} \int_0^R \Delta\varrho(r) J_0(q\sin\theta r) 2\pi r dr, \tag{9}$$

where J_0 is the Bessel function of the zeroth order. Intensity can be calculated as

$$I_0(q) = \mid A(q) \mid^2 . \tag{10}$$

In the solution, polyelectrolyte molecules can have all possible orientations. Therefore we have to average the value of $I_0(q)$ with respect to orientation. Averaging yields the following form of $I_0(q)$:

$$I_0(q) = \frac{1}{2}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \mid A(q,\cos\theta) \mid^2 d(\cos\theta) = \int_0^1 \mid A(q,a) \mid^2 da, \tag{11}$$

where $a = \cos\theta$ and

$$A(q,a) = L \frac{\sin\frac{qaL}{2}}{\frac{qaL}{2}} \int_0^R \Delta\varrho(r) J_0(qr\sqrt{1-a^2}) 2\pi r dr. \tag{12}$$

These two integrals have to be calculated numerically in order to get the scattering intensity.

Results and Discussion

A computer program for numerical solving of the Poisson-Boltzmann (PB) equation was developed. The numerical algorithm was mainly based on that proposed by Dolar and Peterlin in 1969.[8] The differential equations were integrated by the Runge-Kutta integrator of the fourth order.[9] Alternatively, analytical solution of the PB equation was used for the systems containing only one kind of counterions. Once having the solution of PB equation, the excess electron density was calculated. Another numerical routine was developed for the calculation of the scattering function according to equations (11) and (12). The integrals were evaluated using the trapezoid rule.

Pauling ionic radii $r_{Sr^{2+}} = 1.13$ nm, $r_{Li^+} = 0.60$ nm[10] were used for determining the excess number of electrons for counterions, yielding the values of $\Delta\varrho_1^c = 1.7$ electrons per ion for Li^+ and $\Delta\varrho_2^c = 34.0$ electrons per ion for Sr^{2+}. The radius and the length of the monomer unit were set to 0.475 and 0.251 nm, respectively, corresponding to polystyrene sulfonate (PSS) or similar polymers. Since it is known that the backbones of PSS and many other polymers are flexible,[6] the degree of polymerization was set to 10 monomer units, assuming that smaller polymers will more likely retain a rodlike shape. The excess electron density of the PSS polyion $\Delta\varrho_{rod}$ was calculated from the structure and dimensions of the monomer unit and yields 205 electrons/nm^3. In order to study the scattering of the ionic atmosphere separately from the scattering of the polyion, the value of $\Delta\varrho_{rod}$ was set to zero in some calculations. Such a case may be quite realistic and often met in practical work; some carbohydrate polymers, for example, may exhibit very low electron density contrast against the solvent (usually water). The concentration of monomer units was set to 0.008 moles per liter, corresponding to a solution of about 1.5% in polymer species. At such relatively low concentration, the effect of interactions between individual polyions is much less pronounced and affects the scattering function to a much smaller extent than at higher concentrations. This is in accordance with the apllied model, since it does not consider any correlations between macroparticles in the calculation of the scattering function. The composition of the ionic atmosphere was varied from pure Li^+ to pure Sr^{2+} in steps of 0.25 of mole fraction of either ion. The permitivity of the solvent was 78.39 corresponding to the aqueous solutions at the temperature 298.15 K.

In Figures 1 and 2 the scattering functions for ionic atmospheres are shown. The influence of the polyion was removed by putting $\Delta\varrho_{rod} = 0$. Figure 1 displays scattering functions of pure Li^+ (lower curve) and pure Sr^{2+} (higher curve) ionic atmosphere, with $\Delta\varrho(r)$ being calculated from the analytical solution of the PB equation, as outlined in equations (1)-(5). Same scattering functions are displayed on Figure 2, with the PB equation being solved numerically. Besides pure Li^+ and Sr^{2+}, mixtures of counterions are also considered (mole fractions 0.25, 0.50 and 0.75 of Sr^{2+}). It can be seen that the scattering functions for the ionic atmospheres containing only Li^+ or Sr^{2+} in Figures 1 and 2 are essentially equal, hence validating the numerical algorithm for solving the PB equation. As expected, higher content of strontium ion in the ionic atmosphere yields higher scattering intensities. Since lithium ions have a very small electron density contrast relative to water, the scattering intensity of pure lithium ionic atmosphere is very low.

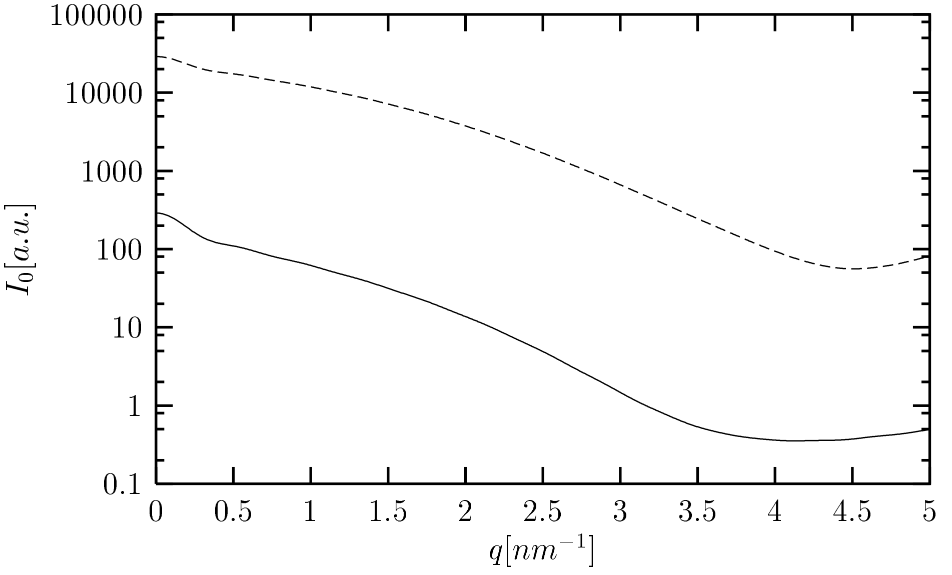

Figure 1: Scattering intensities of pure Li^+ (continuous curve) and pure Sr^{2+} (dashed curve) ionic atmosphere in logaritmic scale.

Figure 3 displays the scattering function for the polyion with $\Delta\varrho_{rod} = 205$ e^-/nm^3. Ionic atmosphere was removed by putting $\Delta\varrho_1^c = \Delta\varrho_2^c = 0$. Comparison between Figure 3 and Figures 1 and 2 reveals that the peak intensity brought about

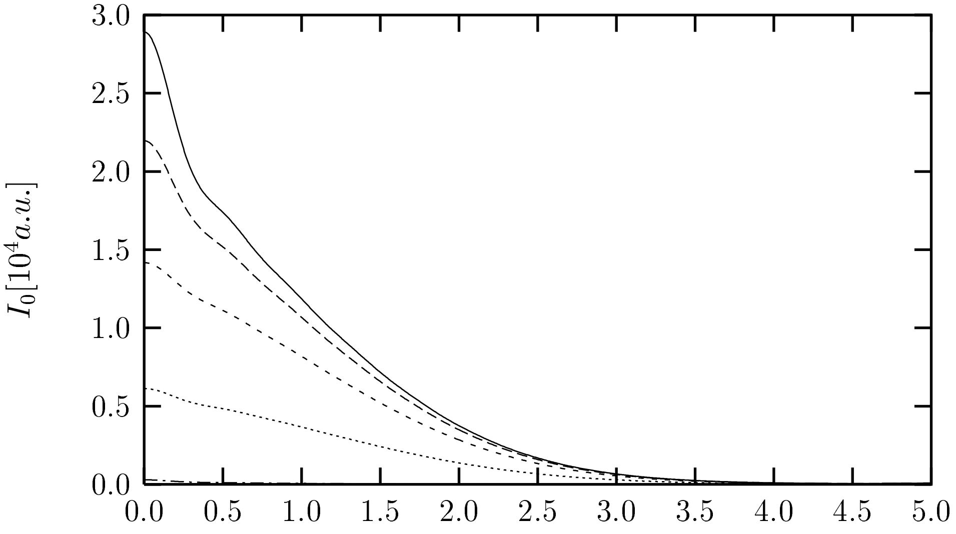

Figure 2: Scattering intensity of pure ionic atmosphere composing of different mixtures of Li^+ and Sr^{2+} counterions. Curves refer to the following fractions of Sr^{2+} ions, 1.00 (continuous line), 0.75 (long-dashed line), 0.50 (dashed line), 0.25 (dotted line) and 0.00 (dash-dotted line.

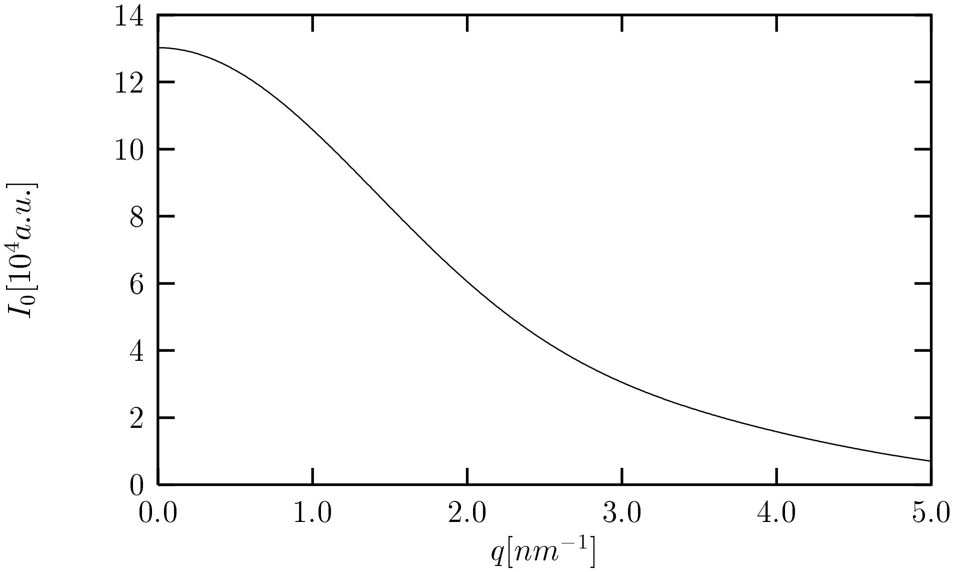

Figure 3: Scattering intensity for polyion. There is no ionic atmosphere.

by the polyion is about five times greater than the peak intensity brought about by the ionic atmosphere. In addition, the scattering pattern of the polyion differs qualitatively in comparison to that of the atmosphere (note an inflection in $I_0(q)$ for ionic atmospheres at $q \approx 0.4$ nm^{-1}).

Figures 4 and 5 display the scattering functions combining the influence of both the polyion and the ionic atmosphere. In the same way as before, the scattering

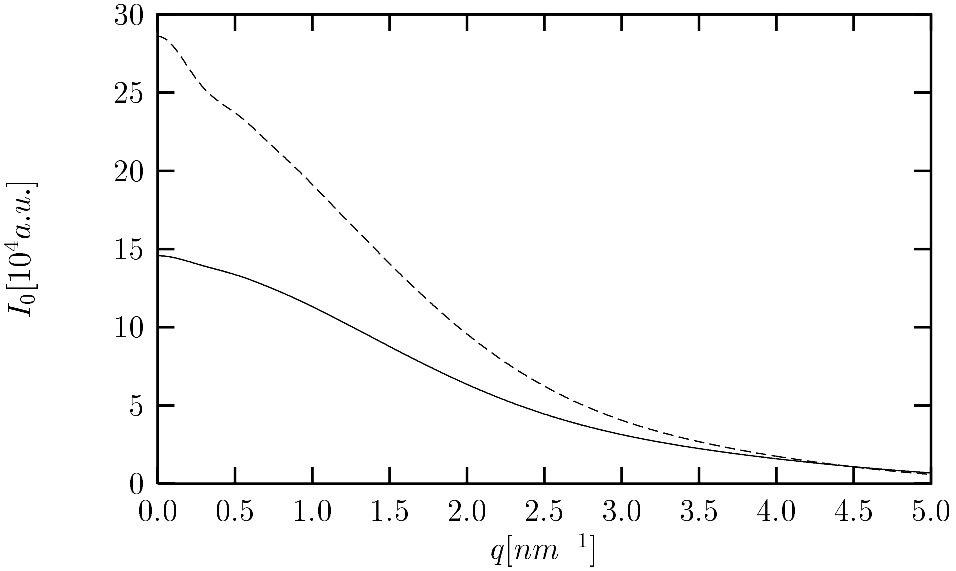

Figure 4: Scattering intensities of pure LiPSS (continuous curve) and pure SrPSS (dashed curve).

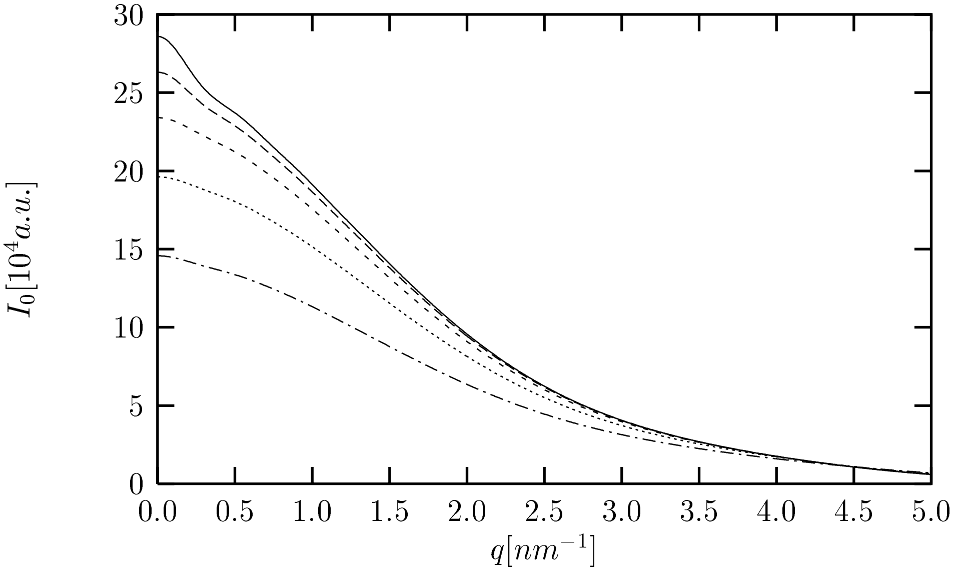

Figure 5: Scattering intensities for SrLiPSS. Ionic atmosphere is composed of different mixtures of Li^+ and Sr^{2+} counterions. Curves refer to the following fractions of Sr^{2+} ions, 1.00 (continuous line), 0.75 (long-dashed line), 0.50 (dashed line), 0.25 (dotted line) and 0.00 (dash-dotted line).

functions in Figure 4 utilize the analytical solution of the PB equation while those on Figure 5 are calculated on the basis of numerical solution of the PB equation. Similarly as seen in Figures 1 and 2, the intensity increases with the increasing content of strontium ions in the ionic atmosphere. A large part of the intensity now originates from the polyion. As a result, the overall scattering of the polyion and the pure lithium ionic atmosphere shows no big difference from that of polyion alone. The contribution of the lithium atmosphere with a very low contrast, namely, is lost in the strong scattering signal of the polyion. On the other hand, atmosphere of strontium counterions causes a significant raise of the scattering intensity refering to pure polyion. Consequently, the specific features being characteristic for the scattering of the pure strontium ionic atmosphere (Figures 1 and 2) can easily be recognized from the overall scattering function.

Conclusions

A theoretical study of small angle X-ray scattering on model rodlike polyelectrolytes was made. The scattering functions, based on the electron density contrast relative to solvent were computed. The distribution of the excess electron density around the polyion was determined by solving of the Poisson-Boltzmann (PB) equation within the cell model. The calculated scattering functions show that the scattering of the polyelectrolyte solution is originating from both the polyion and the counterions. The scattering intensity increases with the increasing content of strontium ions in the atmosphere around the polyion. While the scattering intensity caused by lithium ions alone is almost negligible compared with that caused by polyion, the contribution of strontium ions to the overall scattering is significant. This is due to much higher excess electron density of strontium than of lithium ion.

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Povzetek

V članku predstavljamo teoretsko obravnavo ozkokotnega rentgenskega sipanja na modelnih paličastih polielektrolitih, obdanih z mešanico enovalentnih (Li^+) in dvovalentnih (Sr^{2+}) protiionov. Izračunali smo sipalne funkcije, osnovane na kontrastu v elektronski gostoti med topljencem in topilom. Porazdelitev presežne elektronske gostote okrog poliiona smo dobili z numeričnim reševanjem Poisson-Boltzmannove (PB) enačbe z uporabo celičnega modela. Če je v ionski atmosferi le ena vrsta protiionov, je PB enačba tudi analitično rešljiva. Z opisanim modelom lahko obravnavamo iztegnjene, paličaste polimerne enote, ki so bodisi samostojni poliioni ali pa del fleksibilnega poliiona. Proučevali smo vpliv poliiona in ionske atmosfere na sipalno funkcijo. Pripevek poliiona je znaten, prispevek ionske atmosfere pa narašča z vsebnostjo visokokontrastnih stroncijevih ionov.