

SMALL-ANGLE X-RAY SCATTERING STUDY OF POLYELECTROLYTE SOLUTIONS#

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#This paper is dedicated to professor Davorin Dolar on the occasion of his 80th birthday

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Abstract

Small-angle X-ray scattering (SAXS) technique has been used to study solutions of salts of poly(styrenesulphonic) acid containing lithium, strontium, and a mixture of lithium and strontium counterions. Repulsive electrostatic interactions between the polyions lead to a decrease of scattering intensity at small values of the scattering vector q followed by a more or less pronounced interaction peak. The position of the maximum varies with polyion concentration and is strongly affected by the counterion charge. Addition of simple electrolyte to the solution causes an increase of the forward scattering; at sufficient concentration of added salt the peak vanishes and the behavior of the system becomes similar to the solution of neutral polymer.

Introduction

Understanding the properties of charged macromolecules in solution is important to a variety of problems in colloid science, biophysics, and engineering. Thermodynamic and structural behavior of polyelectrolyte solutions has therefore long been the subject of intense theoretical and experimental research. These solutions exhibit both chainlike properties and properties stemming from the electric charges borne by electrolyte groups. The structure of such solutions is thus affected by the steric effects as well as by the electrostatic and nonelectrostatic interactions between all particles in solution. Accumulation of counterions and other small ions around highly charged macromolecules in solution has been theoretically predicted a long time ago.^{1,2} Due to strong electric field of the macroions, a fraction of counterions is thought of as being condensed on the macroion.^{3,4} Counterion cloud around dissolved polyelectrolytes has been also studied experimentally by measurements of activity coefficients⁵⁻⁷, osmotic coefficients^{8,9}, and transport properties¹⁰ of polyelectrolyte solutions.

The phenomenon of counterion condensation has been also observed in small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) measurements.¹¹⁻²² These experiments have shown that scattering from polyelectrolyte solutions sensitively reflects the interaction between individual components in the solution. The scattering intensity can be considerably influenced by a solvation shell which is formed due to the interaction of the molecules of polar solvent with the charges on the polyion.^{11,12} Condensed counterions in the vicinity of the polyion may also contribute significantly to the scattering intensity. Using SAXS or SANS, the distribution of these localized counterions around various type of macroions involving protein molecules,¹³ ionic micelles,^{14,15} and cylindrical polyelectrolytes^{16,17} have been directly measured. On the other hand, 'free' counterions are irrelevant for the scattering at small angles and increase only the background scattering of the solvent. Of course, the scattering signal reflects not only the effects of interparticle correlations but also the effect of internal structure of polyions. In case of concentrated polyelectrolyte solutions, additional complications result from the overlap of polyion chains. The scattering pattern is thus determined by these combined and mutually dependent effects. They may give rise to a peak in the form of scattering intensity.¹⁸⁻²² This single broad peak, however, cannot be interpreted simply in terms of an ordering of the solution which would lead to oscillations in the polyion-polyion radial distribution function $g(r)$ or equivalently in its Fourier transform, i.e. in the static structure factor $S(q)$. In all cases, the position q_{max} of the maximum of the scattering intensity was found to increase with increasing concentration as $c^{1/2}$. Many theoretical studies have been addressed to the interpretation of this peak observed experimentally. For example, an effective potential model has been introduced to account for the Coulombic repulsion between macroions.²³ With this "correlation hole argument", the charged macromolecules were assigned to have an effective size, which was higher than the real geometric size to illustrate the hole of correlation produced by the Coulombic repulsion between the polyions. It was shown, for spherical as well as for rodlike macromolecular ions, that this effect produced a peak in the scattering signal. The same model was used to make an extension of theoretical treatment to long coiled charged macromolecules. The main conclusion drawn from theoretical studies was, that the maximum observed in the scattering intensity might have a different origin than a possible ordering due to long range Coulombic interactions. However, the existence of the maximum in the polyion-polyion static structure factor is not yet theoretically explained.

In this paper we report SAXS measurements of aqueous polyelectrolyte solu-

tions containing poly(styrenesulphonic) macroions and i) lithium, ii) strontium or iii) mixture of lithium and strontium counterions. In the next section, a detailed description of the experimental procedures is given. The experimental data obtained by SAXS are presented in the section Results and Discussion. The variation of the scattering intensity with the charge of counterions, the concentration of polyions and addition of salt is examined and discussed.

Experimental

Materials. Sodium Polystyrenesulfonate, NaPSS, (Poly[sodium 1-(4-sulfonatophenyl) ethylene]) with nominal weight of $\approx 70\,000$, and a degree of sulfonation 1.0, supplied by Polyscience Inc. (Warrington, PA), was used as the starting material. In order to remove the mechanical impurities and low molecular weight material, the solution of NaPSS was purified by ultrafiltration followed by dialysis against water. The conversion of NaPSS to HPSS was achieved by dialyzing the NaPSS solutions against 0.1 molal HCl and against pure water afterwards. The lithium (LiPSS) and strontium salt (SrPSS) were prepared by neutralization of the concentrated solution of pure HPSS with lithium carbonate (Li_2CO_3 , p.a. Merck) and strontium carbonate (SrCO_3 , p.a. Merck) until $\text{pH} \approx 5.5$. The solutions of SrPSS and LiPSS were concentrated, lyophilized and dried to constant weight in vacuum. Finally the solutions of concentrations varying from 1 to 6% were prepared by weighing and checked from optical density measurements at 261.5 nm with the estimate accuracy in concentration better than 0.5%.

Method. For the SAXS measurements an evacuated Kratky compact camera system (Anton Paar KG Graz, Austria) with a block collimating unit was used. It was attached to a conventional X-ray generator equipped with a sealed X-ray tube (Cu anode target type) operating at 35 kV and 35 mA. The samples were transferred to a standard quartz capillary for the Kratky camera (with an inner diameter of 800 μm and a wall thickness of 10 μm), placed in a thermally controlled sample holder, which was centered in the X-ray beam. The scattered X-ray intensities were measured with a linear position sensitive detector (PSD) (Mbraun, Garching, Germany) which sensed the intensity of the scattering pattern within the whole scattering range simultaneously. Measurements were carried out without a monochromator and without a β -filter. The contribution of the copper K_β line was taken into account in the numerical desmearing of the SAXS curves.

For each solution, five SAXS curves with a sampling time of 15,000 seconds

were recorded and subsequently averaged to ensure reliable statistics. After subtraction of the averaged solvent (water) file, the smeared data were corrected for instrumental broadening by numerical desmearing with the measured beam cross section profile and the wavelength distribution approximated by two discrete lines for K_α and K_β using a ratio of the intensities $I_{K_\beta}/I_{K_\alpha} = 0.3$. The result of these calculations is a smooth fit to the smeared data, a desmeared scattering function and also the pair distance distribution function $p(r)$. It is the Fourier transform of the scattering function:²⁴

$$I(q) = 4\pi \int_0^\infty p(r)[(\sin qr)/qr]dr \quad (1)$$

Above, q is the scattering vector defined as:

$$q = (4\pi/\lambda) \sin \Theta/2, \quad (2)$$

λ is the wavelength of the X-rays ($\lambda_{CuK_\alpha} = 0.154$ nm), Θ the scattering angle between the incident beam and the scattered radiation, and r is the distance between two scattering centers within the particle. For the numerical manipulations mentioned above the indirect Fourier transformation method (program ITP^{24,25} was used.

Results and discussion

In Figures 1 and 2 the SAXS scattering intensities of the solutions of different salts of poly(styrenesulphonic) (PSS) acid (HPSS) are displayed in the plots of intensity versus the scattering vector q . Figure 1 refers to the PSS with monovalent lithium counterions (LiPSS) whereas Figure 2 shows the SAXS intensities resulting for PSS having divalent strontium counterions (SrPSS).

In both cases the salt-free solutions with different polymer concentration ranging from 1% to 6% have been measured at 25° C. At the same conditions we examined the scattering of 2% PSS solution containing a mixture of Li^+ and Sr^{2+} counterions for different fraction of mono- and divalent counterions, respectively; the corresponding scattering curves are shown in Figure 3.

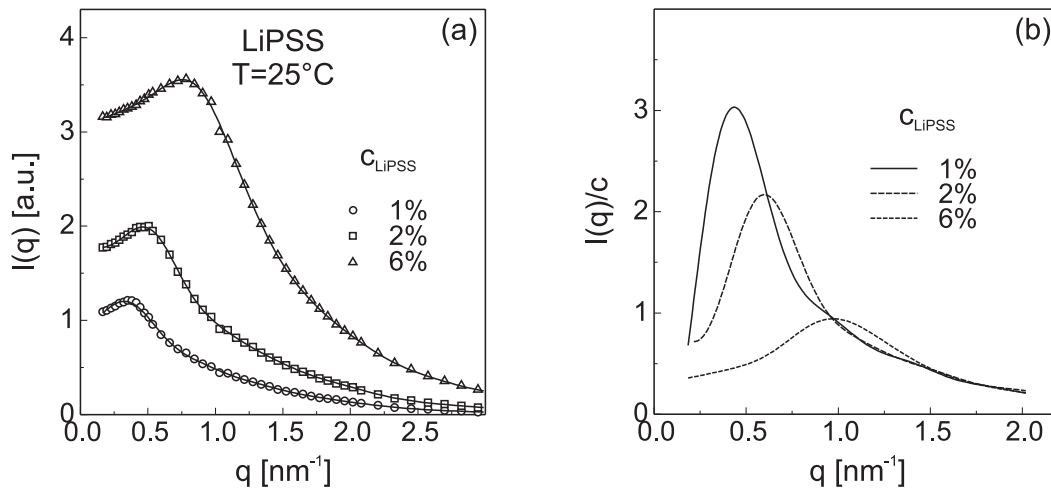


Figure 1: Experimental SAXS intensities of LiPSS (symbols) at various polymer concentrations (a) and desmeared scattering functions (b). Lines in (a) part represent the best fit to these curves as obtained by the desmearing routine.

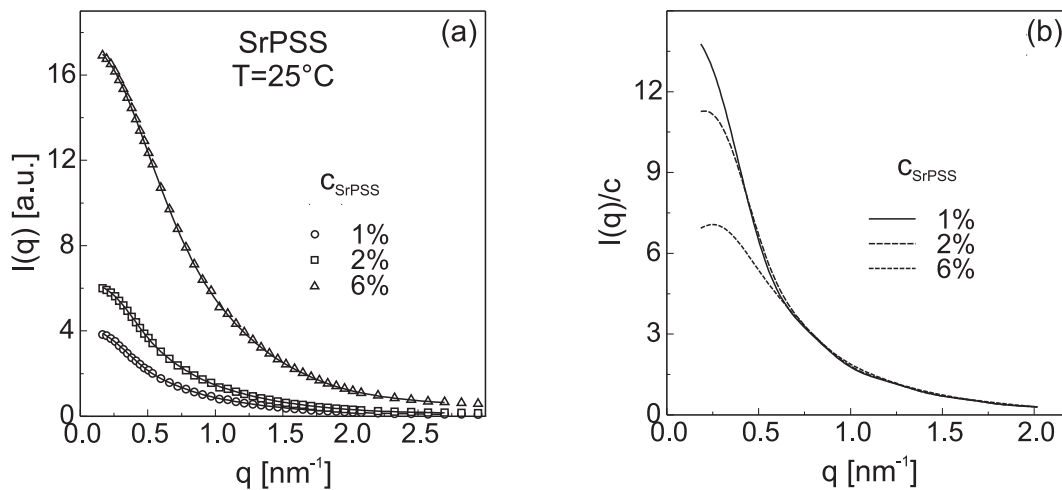


Figure 2: Experimental SAXS intensities of SrPSS (symbols) at various polymer concentrations (a) and desmeared scattering functions (b). Lines in (a) part represent the best fit to these curves as obtained by the desmearing routine.

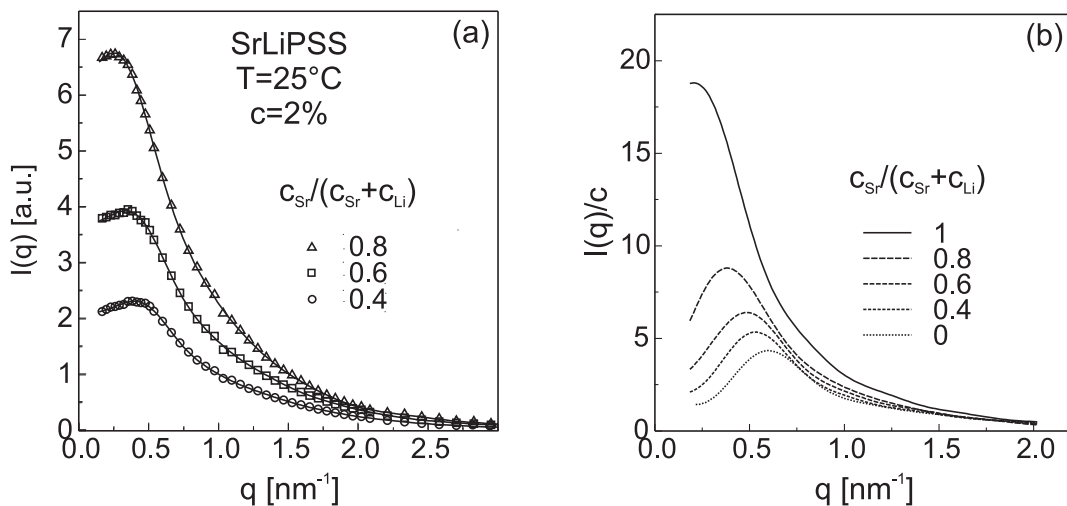


Figure 3: Experimental SAXS intensities (symbols) (a) and desmeared scattering functions (b) of PSS solutions containing a mixture of Li^+ and Sr^{2+} counterions at various fraction of divalent counterions. Lines in (a) part represent the best fit to these curves as obtained by the desmearing routine. The curves in the left figure are shifted by a constant factor to prevent a strong overlap.

The (a) parts of all figures represent the experimental scattering curves (symbols), i.e. the raw data not yet corrected for slit length and width smearing effects caused by the slit collimating optics of the Kratky compact camera, nor for K_β radiation. Only the corrections due to the background scattering were made by subtracting the scattering curves of the solvent from those of PSS solutions. The lines represent a fit to the experimental data as obtained by the indirect transformation procedure.^{24,25} The desmeared smoothed scattering curves corrected for instrumental broadening and K_β radiation^{24,25} are shown in (b) parts of the figures, where the scattering intensities are normalized to unit concentration by plotting I/c vs. q .

In the case of monovalent Li^+ counterions (Figure 1), the observed scattering function $I(q)$ is characterized by the similar features as found by SANS experiments on PSS salt-free solutions with sodium counterions,²⁰ these are: (i) a broad maximum for q values between 0.1 and 1 nm^{-1} , and (ii) a relatively weak scattering intensity in the small q regime. Both features stem from the polyion-polyion correlations, i.e they result from the interference effects between different chains. The position of the maximum is concentration dependent; with increasing concentration it shifts towards higher q values. The higher the concentration, the closer the distances, and consequently, because of the reciprocity law between the distances and scattering vector, the higher values of q . Figure 4 illustrates the law of this depen-

dence; as can be seen, the position q_{max} of the maximum of the scattered intensity increases linearly with $c^{1/2}$.¹⁸⁻²²

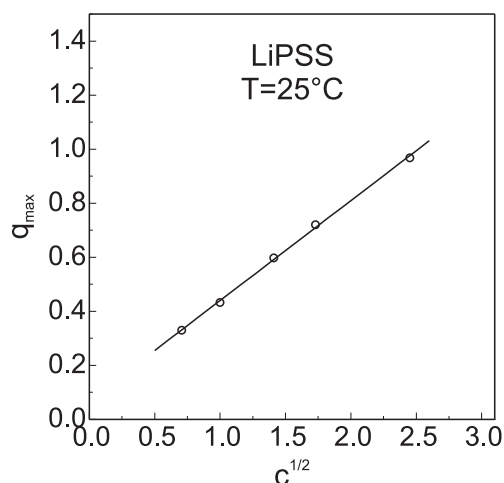


Figure 4: Plot of q_{max} values at different polyelectrolyte concentrations c as a function of the square root of c

It is known from the general SAXS theory^{26,27} that interparticle interference leads to a decrease of the scattering function at low angles. The curves in Figure 1(b) show all the features of the liquid type of concentration effects, i.e. a decrease of the scattered intensity at small angles with increasing concentration, and at larger angles the coincidence of the scattering curves normalized to unit concentration indicating no significant changes in the form (form factor) of the basic scattering objects upon concentrating the solution. The small values of $I(q \rightarrow 0)$ can be explained by the isothermal osmotic compressibility of polyelectrolyte solutions because the structure factor at zero angle $S(0)$ is directly proportional to the isothermal osmotic compressibility. The value of $S(0)$ decreases with increasing concentration indicating a lower osmotic compressibility of the system in the case of higher concentration. The effect of counterion charge on the polyion-polyion correlations is illustrated in Figure 2. Clustering of divalent counterions around the macroions is much more pronounced in comparison to the monovalent counterions thus giving rise to essentially different interactions between the macroions. As seen from Figure 2, the maximum in the scattering intensity is shifted towards lower q values that are even too small to be detected by the accessible q window. In any case, these results indicate a very strong effect of counterion charge on the correlations between the

macroions. Otherwise the effect of increasing concentration resembles that in the case of monovalent counterions; it is seen in the low q regime as a decrease of the normalized scattering intensity I/c upon concentrating the solution.

In general, the scattering power of the sample is proportional to the contrast in electron density between the scattering objects (e.g. colloidal particles) and the solvent (background). In our case, the measured scattering intensity is originating from the macroions and the counterions. Unfortunately, the data are not on absolute scale for technical reasons, the ordinate axes being scaled in arbitrary units. In spite of that, we can make a relative comparison between the intensity scattered from the LiPSS and SrPSS solutions of the same concentration. The contrast in electron density of counterions against water can be estimated in good approximation by calculating the number of excess electrons per counterion using their crystallographic radii. For Li^+ we obtain approximately $2e^-/\text{ion}$ whereas for Sr^{2+} a value of 34 excess electrons per ion. By changing the counterions from Li^+ to Sr^{2+} the contrast is thus drastically changed; while the electron density of Li^+ is nearly matched by water, Sr^{2+} ions exhibit a strong contrast in aqueous solution thus giving rise to a strong increase of the measured scattering intensity. Hence, the scattering intensity measured for LiPSS solutions is governed by the scattering of the polyions, whereas the Sr^{2+} counterions considerably contribute to the scattering of SrPSS solution. The intensity scattered from the solutions containing mixture of monovalent Li^+ and divalent Sr^{2+} counterions (Figure 3) is therefore dependent on the fraction of both ions. It rises with increasing the fraction of Sr^{2+} ions with a much stronger contrast in electron density. In parallel, the position of the maximum of the scattering intensity systematically shifts toward lower q values, the actual values of q_{max} lying between the values for the pure LiPSS and SrPSS solutions.

Finally we turn our attention to the effect of the addition of simple electrolyte to the polyelectrolyte solution. By adding salt to the solution one enhances the effect of screening between charged particles. Changes in the measured intensity with concentration c_s of NaCl at fixed concentration of LiPSS are shown in Figure 5. The value q_{max} corresponding to the peak and the scattering function in the region $q > q_{max}$ remain practically unchanged with increasing c_s . As expected, addition of salt is reflected in the low q regime which is sensitive to the interactions between the polyions.

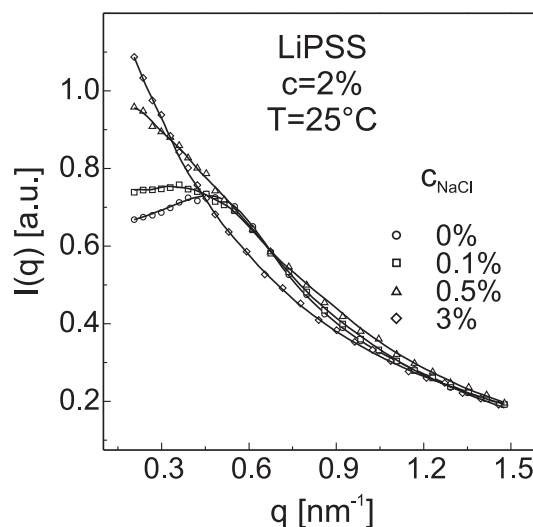


Figure 5: Experimental SAXS intensities of LiPSS (symbols) at various concentrations of NaCl

Increasing c_s causes a more pronounced screening of the repulsive electrostatic forces between the polyions which leads to an increase of the intensity at $q \rightarrow 0$. At sufficiently high concentration of NaCl the peak disappears, the scattering function becoming similar to that of a neutral polymer.

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Povzetek

Z metodo ozkokotnega rentgenskega sipanja smo obravnavali raztopine liti-jeve, stroncijeve, ter mešanice litijeve in stroncijeve soli polistirensulfonske kisline. Zaradi odbojnih elektrostatskih interakcij med poliioni se v območju nizkih vrednosti valovnega vektorja intenziteta sipanja zmanjša, zato se pojavi bolj ali manj izraziti "interakcijski" pik. Lega le tega se spreminja s koncentracijo polielektrolita ter je močno odvisna od naboja protionov. Ioni enostavne soli, ki jo dodamo raztopini polielektrolita, senčijo interakcije med poliioni. Intenziteta sipanja pri majhnih kotih se zato poveča; pri dovolj visoki koncentraciji dodane soli interakcijski pik izgine, obnašanje raztopine polielektrolita pa postane podobno raztopini nevtralnega polimera.