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Structure formation in polyelectrolytes induced by multivalent ions

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ABSTRACT

We review recent investigations of aqueous solutions of polyelectrolytes in presence of multivalent ions. In particular, we look into the interaction of di- and trivalent counterions with star polyelectrolytes and spherical polyelectrolyte brushes. In presence of monovalent ions these systems are dominated by the marked osmotic pressure of the confined counterions. Higher-valent counterions lead to a collapse of these structures and to precipitation if the counterion concentration is raised beyond the critical coagulation concentration. This effect can be used to switch the structure of star polyelectrolytes between an extended and a dense conformation. No overcharging occurs in these systems. This is in contrast to the behavior of bare colloids where overcharging in presence of multivalent ions is a common phenomenon. A precise monitoring of the coagulation kinetics shows that the repulsive interaction between spherical polyelectrolyte brushes can be finely tuned by addition of trivalent ions. All experimental data obtained so far are well-understood by theory, at least in a semi-quantitative fashion.

1. Introduction

Linear polyelectrolytes present a ubiquitous class of macromolecular materials [1]. Many biopolymers as e.g. DNA are polyelectrolytes while synthetic polyelectrolytes as e.g. poly(acrylic acid) have acquired technical importance for waste water treatment and other applications [2]. Immersed in water or solvents with a sufficiently high dielectric constant, the counterions may dissociate and the resulting behavior of aqueous polyelectrolytes solutions is determined in many respects by the translational entropy of the free counterions. Theoretical work starting in the fifties has led to a thorough understanding of the interaction of the resulting macroion and the dissolved counterions [3–5]. It is now well-understood that a certain fraction of the counterions have not full translational freedom, but remain strongly correlated to the macroion. This counterion condensation [6] can be regarded as the basis of the modern theory of linear polyelectrolytes. Its quantitative treatment in terms of the cell model [3] has met with gratifying success when compared to experimental data done by SAXS and SANS on rodlike linear polyelectrolytes [7–10]. The osmotic coefficient of a polyelectrolyte in aqueous solution, that is, the fraction of osmotically active counterions can be understood semi-quantitatively by the original cell model as well [11,12] and more recent theoretical models have taken into account the effect of finite length of the macroion [13,14]. Surveying the literature on linear polyelectrolytes one may say that in many cases experimental work was restricted to systems in presence of monovalent counterions.

If linear polyelectrolytes are densely grafted to a planar or curved surface, a polyelectrolyte brush results. These systems have been the subject of intense research during the last 20 years. Again most of the research on planar [15] and spherical systems [16] has been confined to monovalent counterions. Here theory demonstrates clearly that a great majority of the counterions will be confined within the brush layer [17,18] and the fraction of entrapped counterions increases as a function of charge density of the brush. Hence, in salt-free solutions the polymer chains of the brush layer will be stretched to nearly full length by the osmotic pressure of the confined counterions resulting in an osmotic brush. Raising the ionic strength of the system by adding a sufficient amount of salt will then lead to a salted brush. Here the polyelectrolyte chains are much less stretched and assume a conformation similar to that in a non-charged (neutral) polymer brush. These predictions are well borne out by experiments done on planar [19–21] and on spherical polyelectrolyte brushes (SPB) [22,23].

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Star polyelectrolytes may be envisioned as spherical polyelectrolyte brushes with a core of vanishing diameter. Hence, the theory of their behavior in solution is very similar to the ones of polyelectrolyte brushes and depending on the number of arms most of the counterions will be confined within the star polyelectrolytes. Recent advances in polymer synthesis have led to routes that allow us to obtain well-defined star polymers in larger amounts [24]. Thus, a number of recent experimental studies were directed towards a detailed understanding of the solution behavior of these systems [25–27] and much of this work has been reviewed recently [28,29].

Practically all theoretical approaches discussed so far present descriptions in terms of meanfield Poisson–Boltzmann approach: The counterions are treated as a continuous distribution of charge in space, there is no localization of charges in entities as ions. Hence, fluctuations and correlations in the positions of the counterions are dismissed. The valency of the counterions only enters on the Poisson–Boltzmann level and no new phenomena are to be expected when going from a monovalent to a di- or trivalent counterion. Thus, major theoretical approaches treating polyelectrolyte brushes are self-consistent field meanfield theories. The same holds true for the much-used Gouy–Chapman theory of double electrical layer formed by small ions near a charged surface which leads to DLVO-theory of the stability of charged colloidal particles [30]. Here the electrostatic repulsion between two charged plates in aqueous environment is calculated by use of the Poisson–Boltzmann approach which treats the cloud of ions as a continuous charge distribution, no fluctuations of this distribution or correlations among the counterions are taken into account.

However, an increase in the valency of the counterions leads to break down of the mean-field Poisson–Boltzmann approach describing the distribution of the electrical field and the mobile ions near a charged surface. The thickness of the double electrical layer becomes as small as the Bjerrum length and the multivalent counterions get strongly bound in the thin layer proximal to the surface. Furthermore, in this regime pronounced in-plane (two-dimensional) correlations in positions of heavily charged counterions may lead to the famous overcharging effect [31–33].

Small-angle scattering experiments done with X-rays (small-angle X-ray scattering, SAXS; small-angle neutron scattering, SANS) have been among the most important tools for the investigation of the spatial distribution of the counterions around their macroions. In case of SAXS counterions with strong scattering contrast as e.g. iodine ions can be used to determine this distribution [9]. In case of SANS the use of deuterated counterions has led to a quantitative comparison of the prediction of the cell model with the counterion distribution around DNA [7] and poly(styrene sulfonic acid) [8]. Anomalous small-angle X-ray scattering (ASAXS) uses the effect of anomalous dispersion of certain elements as e.g. rubidium, strontium or bromine to discern the spatial distribution of e.g. Rb^+ or Br^- counterions [34]. Up to now ASAXS has been applied only to a few systems as, e.g., rodlike polyelectrolytes [9,10], spherical polyelectrolyte brushes [35], and more recently to charged micelles [36–38].

All evaluations of experimental scattering data treat the counterions in terms of a structureless, continuous distribution that follows the symmetry of the macroion. Thus, these data treatments assume tacitly the validity of the meanfield approach for describing polyelectrolytes. As a direct consequence of this, the scattering intensity at high scattering angles will vanish as a well-defined power law. However, this cannot be correct anymore when considering that counterions present small but finite entities in which the charge is localized. SAXS- and SANS-experiments done at low angles may treat an ensemble of such counterions as continuous distribution inasmuch as the spatial resolution is low in this regime. Going to high scattering angles, on the other hand, increases the resolution to the point where a scattering experiment resolves the counterions as small spherical objects of a given scattering length. Hence, the scattering function of an assembly of counterions must tend to a constant value if the scattering angle is high enough. This effect has been seen directly in SAXS-experiments on rod-like macroions [9]. Moreover, simulations of systems of counterions bound to macroions at different strength have clearly shown under which conditions the meanfield approach may not be a suitable anymore [39]. These simulations have also demonstrated that scattering experiments and in particular ASAXS are uniquely suited to discern the effect of other deviation from the meanfield descriptions as e.g. the effect of fluctuations.

In the case of monovalent counterions the marked osmotic pressure of the counterions in the intra-molecular volume presents the dominant force that determines most of the observable quantities in solution as, e.g., the overall size of the macroions or the osmotic coefficient. The high osmotic pressure also suppresses the fluctuations effectively and meanfield theories lead to a correct description of the experimental observations. A different picture arises when replacing monovalent ions by concomitant number of multivalent ions: Now much less ions balance same change of the macroion and the osmotic pressure in the intra-molecular volume drops down by concomitant factor. Thus, multivalent counterions will replace monovalent ones inside the brush because of exponentially larger statistical (Boltzmann) probabilities to be found inside the brush, and the polyelectrolyte brush will shrink markedly because of drop in osmotic pressure. Now, more subtle effects as, e.g., correlations among the counterions and polyelectrolyte chains will become important terms. Given the large literature on branched polyelectrolytes and polyelectrolyte brushes, however, only a small fraction thereof has been devoted to investigations of the correlation effects introduced by multivalency.

Here we present a survey of recent results obtained by investigations of polyelectrolyte stars and polyelectrolyte brushes in presence of multivalent counterions. The limits of the validity of the meanfield approach are considered explicitly. In this context it is revealing to consider briefly the case of bare charged surfaces treated in terms of the well-known DLVO-theory. Here it will become apparent that correlation effects will lead to strong deviations from meanfield approaches already in case of divalent ions. Hence, electrostatic repulsion between colloids will be weakened considerably or suppressed altogether in these cases [40]. The entire discussion will demonstrate that multivalency may become an important basis for building up supramolecular structures from polymeric systems.

Overcharging effect is predicted theoretically and observed in real or/and computer experiments in the case when multivalent ions are adsorbed and make quasi-regular array on the planar or weakly curved surface (e.g. planar substrate, solid colloidal particles, charged dendrimers). Then, the correlations in the in-plane positions of the multivalent ions make it thermodynamically favorable that the net charge of the counterion's layer exceeds (in absolute value) the charge of the bare substrate [31]. In the polyelectrolyte star polymers and the SPB under consideration here there is a three-dimensional distribution of ions and oppositely charged flexible chains with definitely strong 3D correlation in their lateral positions. This leads to an effective net attraction which reduces the translational freedom of the counterions and the effect of osmotic pressure considerably. However, there is no obvious mechanism for the overcharging of the volume of the brush/star.

In the following, we first describe bare colloids in which multivalency leads to marked overcharging. Then polyelectrolyte stars and brushes are discussed where multivalent counterions do not lead to overcharging but to a strong change in structure.