Solubility of highly charged anionic polyelectrolytes in presence of multivalent cations: Specific interaction effect

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Abstract. Studies performed on strong polyelectrolytes and on a weak polyelectrolyte, sodium poly(acrylate), show that their stability in presence of multivalent cations depends on the chemical nature of the charged side groups of the polymer. For sulfonate groups (SO$_3^-$) or sulfate groups (OSO$_3^-$) phase separation generally occurs in presence of inorganic cations of valency 3 (as La$^{3+}$) or larger and a resolubilization takes place at high salt concentration. The interactions of the polyelectrolyte with multivalent cations are of electrostatic origin and the phase diagrams are weakly dependent on the chemical nature of the polymer backbone and on the specificity of the counterions. For acrylate groups, (COO$^-$), the phase separation was observed with inorganic cations of valency 2 (as Ca$^{2+}$) or larger without resolubilization at high salt concentration. The phase separation is due to a chemical association between cations and acrylate groups of two neighboring monomers of the same chain. This chemical association creates a hydrophobic complex by dehydrating both monomer and cation. With organic trivalent cation, as spermidine $^+$H$_3$N(CH$_2$)$_4$NH$_2$$(CH$_2$)$_3$NH$_3^+$, where no chemical association occurs with the charged side groups COO$^-$ or SO$_3^-$ of the polyelectrolyte, similar phase diagrams were observed whatever was the polyelectrolyte with a resolubilization at high trivalent cation concentration.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.20.Qg Structure of associated liquids: electrolytes, molten salts, etc. – 83.70.Hq Heterogeneous liquids: suspensions, dispersions, emulsions, pastes, slurries, foams, block copolymers, etc.

1 Introduction

Anionic polyelectrolytes possess ionizable groups, which dissociate in aqueous media to give negatively charged polymer chains and positively charged counterions. The repulsion between charged monomers tends to expand the polymer chain. The high charge density on the polymer backbone produces a high electrostatic potential around it and a fraction of counterions are consequently located in the immediate vicinity of the polymer chain leading to a phase separation at low salt concentration, if counterions are multivalent. This precipitation of polyelectrolytes by multivalent salt, usually called “salting out”, has been studied for long time by several authors [1–13], but still remains poorly understood. The stability of the polyelectrolyte solution depends on the counterion valency and the characteristics of the polymer: nature of backbone (hydrophobic, hydrophilic, rigid, flexible), distance between charged groups, and nature of charged groups (carboxylate, sulfonate, sulfate, phosphate). Two types of phase diagram have been observed [2] namely the H-precipitation type (high critical salt concentration) and the L-precipitation type (low critical salt concentration). The H-precipitation occurs at high salt concentration threshold and weakly depends on the polymer concentration. The L-precipitation type appears at low multivalent salt concentrations, and the salt concentration needed for phase separation is proportional to polyelectrolyte concentration.

The present study addresses the nature of the specific interactions between highly charged polyelectrolytes and counterions, especially for L-type diagrams. Phase diagrams of different highly charged polyelectrolytes, in presence of different multivalent cations, were established. Two general mechanisms of precipitation were found, which depend on the nature of the charged groups and of the counterions. In the case of sodium polyacrylate, our interest was focused on calcium ion, for its broad range of applications, and on the cobalt ion which offers the advantage that its interaction with polyelectrolytes can be studied by absorption spectrometry.

More specifically, in Section 2 (theoretical consideration) the point on electrostatic condensation and chemical association are made. In this section we also recall the electrostatic model [9], introduced to describe solubility
of the sodium polystyrene sulfonate in presence of z-valent counterions, and we generalize this model when chemical association between counterions and charged groups of the polyelectrolyte can occur. In Section 3, experimental conditions are given. Section 4 is devoted to the presentation of different types of phase diagram obtained for a large variety of polyelectrolytes and of counterions. At the end of this section it appears that two types of mechanism are responsible of the precipitation: one is purely electrostatic and the other one is intimately related to a chemical association. In Section 5, entitled complexity between polyelectrolytes and multivalent counterions, we relate experiments, which allow us to determine the quantities and the types of complexes formed when chemical association occurs before phase separation. The understanding of the specific interactions between polyelectrolytes and counterions allows us to give a criterion to distinguish when electrostatic attraction or chemical association induces the precipitation. In Section 6, the phase diagram of sodium poly(acrylate) in presence of calcium chloride is described using a mean field approach presented in Section 2.

2 Theoretical considerations

For polyelectrolyte with a sufficiently high charge density along the backbone, some of counterions remain in the immediate vicinity of the charged cylinder representing the polyelectrolyte.

\[
[M^{z+}]_{\text{L}} = [M^{z+}]_{\text{bulk}} \exp(-z e \psi_{\text{local}}/kT).
\]

\(K_1\) is the first association constant (monocomplexation) between monomers and counterions and \(\psi_{\text{local}}\) is the local electrostatic potential of the polyelectrolyte. The quantity \([M^{z+}]_{\text{bulk}}\) is the bulk concentration. The local concentration is determined by solving the Poisson Boltzmann equations. This method was largely used for planar surfaces [24, 25]. Now having introduced the different associations between polyelectrolytes and counterions, we are interested in the limit of stability of polyelectrolyte solutions.

To describe solubility of the sodium polystyrene sulfonate in presence of z-valent counterions [8] the electrostatic model [9] was introduced. This model takes into account a short-range electrostatic attraction between negatively charged monomers (−1) and those carrying condensed multivalent counterions which are positively charged (z − 1). The following spinodal equation has been obtained:

\[
\frac{1}{NC} + \frac{\sigma^3}{1 - \varphi} + \frac{z \varphi^2}{2I} - 2(1 - f - f')f |V_{1z}| = 0.
\]

\(N\) is the degree of polymerization of the polymer, \(C\) is the number of monomers per unit volume, \(\sigma^3\) represents the volume of the monomer and \(\varphi = C \sigma^3\) is the volume fraction occupied by the polymer. The first term comes from the entropy of polymer and the second one represents the steric excluded volume. The third term corresponds to the electrostatic repulsion between monomers carrying an effective charge \(z \varphi^2\) and those carrying an effective positive charge of valency \((z - 1)\), due to the electrostatic condensation. The local attraction \(V_{1z}\) depends on the valency of the counterion and has the following form [9]:

\[
V_{1z} = -\frac{\pi(z - 1)^2 r_0^2}{\sqrt{8\pi l_B B}}.
\]