

# Ion Pair Formation and Counterion Condensation in Aqueous Electrolytes and Polyelectrolyte Solutions. Insights from Molecular Simulation

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## ABSTRACT

Polyion-counterion interactions play a relevant role in determining the stability and solubility of polyelectrolytes in aqueous solutions. These interactions are particularly strong for multivalent counterions, common in biological systems where the negatively charged biopolymer interacts with divalent and trivalent metal ions. The nature of the counterion in these systems, including its electrostatic charge and the short-range interaction with the binding site of the polyelectrolyte, appears to be as important as the location of the binding site in the backbone. Consequently, the binding between the polyelectrolyte charged sites and the counterions (counterion condensation) can exhibit a marked ion selectivity, resulting from a delicate balance between short-range (solvation) interactions characterizing the local environment and long-range (though partially screened by the presence of ions) electrostatic interactions, that leads to ion-pair association (when added-salt) and counterion condensation. The local environment around the charge species depends strongly on the solvent's properties, the ionic strength, as well as the state conditions, and therefore, it becomes significantly different from that characterized by a solvent as a continuum dielectric.

All these observations indicate that the chain conformation and the structure of the solution might depend on (a) the structure of the chain backbone and the distribution of charges of the polyelectrolyte, (b) the charge and concentration of the counterions as well as the presence of salts, and (c) the strength of the interactions between the solvent and both the polyelectrolyte and the counterions (solvation effects). Thus, it appears relevant to address explicitly not only the solvation effects, but also the electrostatic screening by the presence of the salt.

In this contribution we will address all these issues by molecular simulation of precisely defined models of aqueous (poly) electrolytes, discuss some recent developments on the molecular-based interpretation of the signature of ion pair formation in raw data from neutron diffraction with isotope substitution (NDIS), as well as propose a method to isolate the ion-pairing peak from the neutron weighted distribution functions and then measure its magnitude.

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