MODELLING THE EFFECTS OF COUNTERION CONDENSATION AND CHAIN STRUCTURE IN AQUEOUS POLYELECTROLYTE SOLUTION WITH ADDED SALT

Nikiforova K.V., *Victorov A.I.*
Saint-Petersburg State University
199034, St. Petersburg, Universitetskaya emb., 7–9

The demand for tailoring polyelectrolyte materials to specific applications has spurred growing interest in understanding how the structural features of polyelectrolytes govern the behavior of their solutions. The variational-filed theoretical framework [1,2] has recently been formulated for solutions that contain polyelectrolyte chains, counterions and salt additives, taking into account structural features of chains and free ions. For strongly charged chains, the effect of counterion condensation plays an important role [3], diminishing significantly the effective charge of the chain. This effect is modulated by the presence of salt in solution.

In this work, we applied the theoretical framework that reflects the structural details of a macromolecule and the effect of counterion condensation to describe structural and thermodynamic properties of polyelectrolyte solutions in presence of salt.

We consider different distributions of charged monomeric units along the backbone of polyelectrolyte chain, different hard-sphere diameters of the units and counterions, as well as the effects of chain elasticity and distribution of electrical charge inside the ions. The condensation of counterions on the chain is described applying the scheme proposed in ref. [4]. Calculated results are compared with computer simulation and experimental data on the osmotic coefficients for polyelectrolytes of different chemistry. We show that structural details of polyelectrolyte have a substantial effect on the structure of polyelectrolyte solution and that the model in its present form may provide reasonable description of the structure factors and osmotic pressure.

1. Shen, K., & Wang, Z. G., 2017. Electrostatic correlations and the polyelectrolyte self energy. J Chem Phys, 146(8). https://doi.org/10.1063/1.4975777

2. Budkov, Y. A., 2020. Statistical field theory of ion–molecular solutions. Phys. Chem. Chem. Phys., 22(26), 14756-14772. https://doi.org/10.1039/d0cp02432e

3. Manning G. S. Is the counterion condensation point on polyelectrolytes a trigger of structural transition? //The Journal of chemical physics. – 1988. – Т. 89. – №. 6. – С. 3772-3777. https://doi.org/10.1063/1.454899

4. Ermoshkin A. V., Olvera de La Cruz M. A modified random phase approximation of polyelectrolyte solutions //Macromolecules. – 2003. – Т. 36. – №. 20. – С. 7824-7832. https://doi.org/10.1021/ma034148p

Acknowledgements: We thank RSF (project No. 25-23-00040) for financial support.