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Reviewer report of the doctoral thesis

Author of the doctoral thesis: Anastasiia Murmiliuk

Title of the thesis: Multidimensional characterization of polyelectrolytes and interelectrolyte complexes in aqueous solutions

Reviewer: Dr. Radek Šachl

Polyelectrolytes are polymers containing one or more monomeric units that can dissociate in aqueous solutions, making the polymers charged. The degree of ionization can be regulated and used to influence the multipolymer structure into which polyelectrolytes self-assemble. Despite a big progress in the field during the last decades, there is still limited understanding of the relationship between the polymer structure, the charge of the monomeric units and the resulting nanoparticle structure and shape, making any bottom-up predictions extremely difficult. The presented dissertation by Anastasiia Murmiliuk represents a solid contribution to this field. It consists of 6 papers, out of which 5 are already published in impacted and well-recognized journals. Anastasiia Murmiliuk is the first author on two papers and the second author on the four remaining ones.

I would like to highlight two of these articles that seem to me the most interesting ones. In the first paper 'Quantitative prediction of charge regulation in oligopeptides'by Raju Lunkad et al the authors analyzed by both experiments and simulations the regulation of the overall charge on two short model peptides by pH. They showed that the ionization response is predominantly controlled by electrostatic interactions. A relatively good agreement between the experiments and simulations suggests that simulations can be used as an efficient tool to predict ionization behavior of short peptides. In the other publication 'Local pH and Effective pK…' by A. Murmiliuk published in ACS Macro Letters the authors analyzed the concept of a local pH in the proximity of a polyelectrolyte chain by comparing simulated and experimental titration curves. They conclude that pK_{eff} of an indicator attached to a polyelectrolyte chain is lower than that determined from the local pH.

Overall, I enjoyed reading the whole thesis and recommended it without any doubt for the defense.

Questions and comments:

- All papers: The presented thesis represents a highly multidisciplinary work which combines advanced experimental approaches with computer simulations. Considering that none of the published papers

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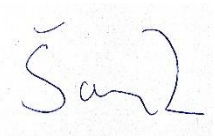
contains an Author contribution section, it would be helpful if the PhD applicant specifies her contribution to each paper.

- Paper I: Can the applicant make a qualified judge to which extent the simulations are applicable in predictions of the overall charge for more complex peptide structures and in the presence of other counterions?
- Papers IV-VI: Nanomaterials are often designed for targeted delivery and controlled release of drugs. Can the applicant make a qualified estimate in which manner the prepared nanoparticles would interact with lipid vesicles representing a simplified synthetic model of a cellular membrane?
- Paper IV and equation 2: Would not the change in the parameter *R* imply that the aggregation number of the micelles changes. Or in other words, cannot the authors reanalyse the fluorescence quenching data to get information about the micellar aggregation number and its dependence on the parameter beta (B. L. Bales and M. Almgren, J. Phys. Chem., 1995, 99, 15153–15162)?
- Paper V: In this paper, the authors mention the importance of a 'soft' micellar core for efficient drug delivery. In this context, I would like to ask how the softness of a micellar core can be measured and which parameter(s) would the applicant use to characterize the core-softness.

In conclusion, I would like to congratulate Anastasiia Murmiliuk to this excellent work!



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In Prague, 4th of February 2021