Enrichment of higher charge density subspecies of random polyelectrolyte copolymer in complex coacervate

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Mixing pH-adjusted solutions of oppositely-charged polyelectrolytes results in the formation of polyelectrolyte complexes. We explore the spontaneous liquid-liquid phase separation which results in a polymer-rich phase coexisting with a polymer-poor phase, known as complex coacervation, in the context of the complexation of a strong polyelectrolyte charged at every monomer and a weak one, randomly charged. Herein we focus in the effect of added monovalent salt, and the question of the partitioning of each of the monomers (positively charged, negatively charged and neutral) in the two phases. With the use of quantitative phase microscopy, solution NMR and inductively coupled plasma mass spectrometry, we establish a quantitative phase diagram, tie lines for the monomers, and salt partition in stoichiometric and off-stoichiometric ratios.
Our main result exhibit the enrichment of the dense phase by the weak polyelectrolyte's higher charge density subspecies. This self-organized partitioning may have implications in the phase separation of proteins revealing how post-translational modifications that alter the charge density may controlling the partitioning inside versus outside dense droplets.

Keywords:
complex coacervate, phase separation, quantitative phase microscopy, NMR

References:

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Acknowledgements:
We acknowledge funding and support from the Max Planck Partner Group program and the FORTH Synergy Grant.