

## Detailed molecular dynamics simulation study of the phase boundary for complex coacervation between Poly(acrylic acid) and poly(*N,N*-dimethyl amino ethyl methacrylate)

D. G. Mintis,<sup>1</sup> D. Rigou,<sup>1</sup> V.G. Mavrantzas<sup>1,2,\*</sup>

<sup>1</sup>Department of Chemical Engineering, University of Patras & FORTH-ICE/HT, Patras GR 26504, Greece

<sup>2</sup>Particle Technology Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, Sonneggstrasse 3, Zurich 8092, Switzerland

(\*[vlasis@chemeng.upatras.gr](mailto:vlasis@chemeng.upatras.gr))

### Abstract

Under certain conditions, the complexation between oppositely charged polyelectrolytes at infinite dilution leads to the formation of a complex coacervate observed in the form of droplets where a polymer-rich (the coacervate) co-exists with a polymer-dilute phase (the supernatant) at thermodynamic equilibrium. Complex coacervates find numerous applications (e.g., in processed food, cosmetics and microencapsulation) due to the small surface tension they exhibit.

The motivation for the present study comes from the experimental work of Spruijt et al.<sup>[1]</sup> who used fluorescent labelled polyelectrolytes to compute the binodal composition of the complex coacervates formed between poly(acrylic acid) (PAA), and poly(*N,N*-dimethyl amino ethyl methacrylate) (PDMAEMA) of similar chain lengths. The mixtures were prepared at an overall monomer concentration of 0.11 M with 1:1 stoichiometric ratio of charged groups, and experiments were conducted at room temperature and pH=6.5. The aim of this study is to carry out all-atomistic Molecular Dynamics (MD) simulations to predict the binodal composition of such a complex coacervate between PAA and PDMAEMA at the same conditions. In our work, coacervation is studied as a function of salt concentration for PAA chains with length  $N = 20$  monomers and PDMAEMA with  $N = 17$  monomers, at ambient temperature and neutral pH. The generalized Amber force field (GAFF) with the RESP charge fitting scheme was adopted for both PAA and PDMAEMA.

Prior to the estimation of coacervate concentration at co-existence, two different sampling techniques, the Widom Test Particle Insertion method (WTPI) and the Bennet Acceptance Ratio method (BAR), were exploited to compute the excess chemical potential of two water models, SPCE and TIP3P, as a function of temperature ( $T = 300, 310, 320\text{K}$ ) for the purpose of validating their accuracy. It was observed that the BAR method accurately predicts the excess chemical potential for both (SPCE and TIP3P) models as a function of temperature whereas the WTPI fails; thus, for the subsequent calculations of the chemical potential of the complex coacervates, the BAR method was chosen. To determine the phase boundary of the complex PAA:PDMAEMA coacervate, an iterative procedure was followed which eventually leads to the determination of conditions (polyelectrolyte concentrations) for which the chemical potential of salt ions and solvent in the two phases (supernatant and coacervate) become equal. In our presentation, we will discuss the binodal composition of the PAA:PDMAEMA coacervates computed from this all-atom MD study, and how it compares with the experimental data of Spruijt et al.,<sup>[1]</sup> the mean-field model of Voorn and Overbeek,<sup>2</sup> and the coarse-grained simulations of Andreev et al..<sup>[3]</sup>

### REFERENCES

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