PRF#: **56803-ND6**
Project **Title: Computer Modeling of Threaded Surfactant Aggregates**
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The objective of this new direction (ND) project is to investigate using computer modeling the effect of threading of wormlike micelles formed by synthetic surfactants by polymers of different hydrophobicity and analyze the conformation of embedded polymers and (viscoelastic) properties of wormlike micelles. As wormlike micelles are actively used in oil recovery threading wormlike micelles by polymers may enhance their stability, the hypothesis that will be explored in the course of this project. Computer modeling results will be tested experimentally by the collaborator's group of Prof. Philippova. Being a new direction, this project will help the PI and the involved graduate student to gain experience in the new area of surfactant self-assembly.

During last year in a joint effort with our experimental collaborators we analyzed the effect of molecular weight of embedded polymer on the viscoelastic properties of wormlike micelles. We investigated incorporation of poly(4-vinylpyridine) (P4VP) of two different molecular weights into wormlike surfactant micelles of potassium oleate. We demonstrated that independently of molecular weight the polymer incorporates into the core-corona interface of the surfactant micelles (as shown in Figure 1) and does not alter the micelle structure or the micelle radius, but diminishes the packing density of surfactants.[1,2] One possible difference in system behavior is that longer polymer chains may initially adsorb on two different wormlike micelles (e.g. by different ends) and with time will bring these two micelles together to minimize contact between polymer and water, therefore forming a new cross-link, as shown in Fig.1a.

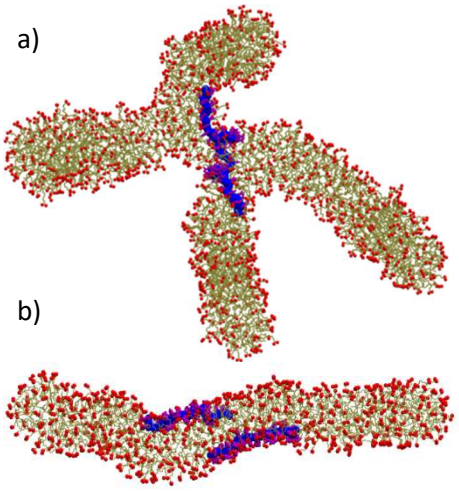


Figure 1. MD simulation snapshots of a) two wormlike micelles containing 487 and 426 potassium oleate each interconnected by embedded P4VP chain of 60 repeat units and b) two P4VP chain of 30 repeat units in wormlike micelle containing 497 surfactant molecules in 6 wt% of potassium chloride aqueous solution. The P4VP chain is shown in blue, oleate in olive with headgroups in red. Water, counter ions and salt are not shown for clarity.

Crosslinking of wormlike micelles by long polymers can enhance viscoelastic properties of the networks formed by wormlike micelles, as has been observed experimentally by our collaborators for a small concentration of added long polymers.[2] Further addition of polymer results in the shortening of micelles by micelle breaking at the "weak spots" located at the ends of polymer-containing sections, where the embedded polymer can contribute to micellar end-cap stabilization. To test this hypothesis we performed non-equilibrium molecular dynamics simulations by subjecting wormlike micelles with embedded P4VP chain(s) to shear deformation. As is shown in Figure 2, for both short and especially a longer embedded P4VP chain the wormlike micelle breaking indeed occurs in the vicinity of the boundary of P4VP-occupied and polymer-free sections, i.e. at "weak points". A longer polymer has a smaller fraction of "weak spots" resulting in

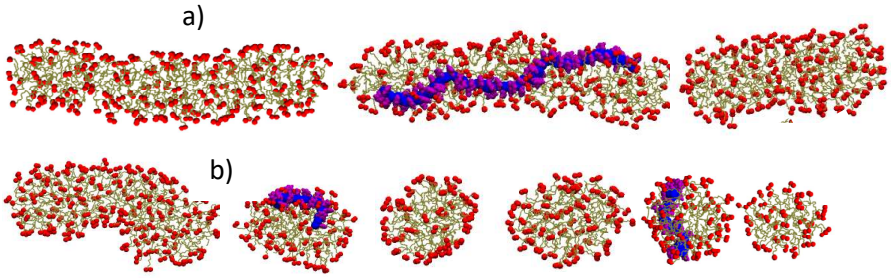
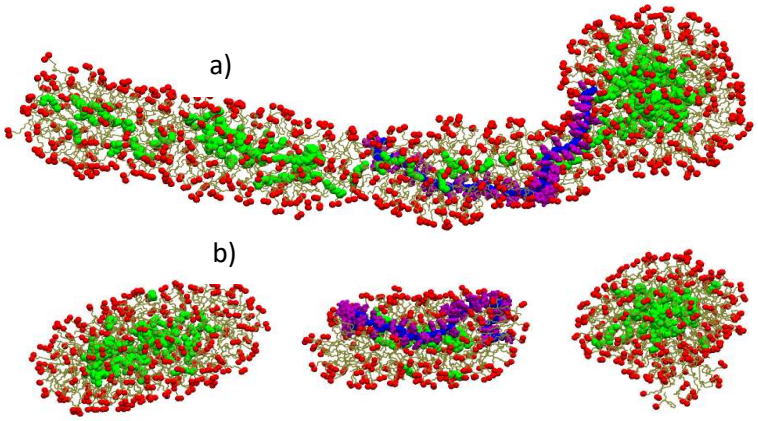


Fig.2 Simulation snapshots of wormlike micelles with embedded P4VP chain of 60 repeat units (a) or two 30 repeat units (b) at steady state under shear deformation (1.67 ns^{-1} shear rate). The initial wormlike micelles contain the same number of potassium oleate surfactants, 498, with 6 % salt (potassium chloride) in both cases. The P4VP chain is shown in blue and purple oleate in olive with headgroups in red. Water, counter ions and salt are not shown for clarity.

higher zero-shear viscosity and elastic plateau modulus as was observed experimentally.[2] Therefore, to obtain a hybrid network with higher viscoelasticity it is necessary to employ longer polymer chains. Our findings that an increased MW of macromolecules permits formation of longer hybrid micelles and enhances their rheological properties are of obvious importance for fundamental understanding of polymer-surfactant interactions and the development of new industrial formulations based on hybrid polymer-wormlike surfactant micelles.



As wormlike micelles are actively used in oil recovery applications, we further progressed in our studies and started to investigate what effect the embedded polymer may have on encapsulation of oil (octane) into wormlike micelles. We found that the presence of polymer does not prevent oil encapsulation (Figure 3a). Furthermore, polymer presence may even partially stabilize or at least results in formation of large size droplets containing oil under flow, as the breaking of wormlike micelles occurs predominantly at weak spots, i.e. at the boundary of polymer-containing regions.

Figure 3. a) Simulation snapshots of a wormlike micelle with embedded polymer P4VP (60 repeat units) and encapsulated oil (105 octane molecules) and b) steady state condition at a shear rate of 1.67 ns^{-1}. Polymer is shown in blue and purple, oil in green. The wormlike micelle contains 497 potassium oleate molecules and thequeous solution contains 6 % salt (potassium chloride). Salt and water are not shown for clarity.

Working on this project has stimulated the PI to learn more about current research in the area of surfactant self-assembly. Thus, in 2018 the PI attended the annual meeting of the European Colloid and Interface Society to learn about new developments and research directions in the area of surfactant self-assembly. This also provided opportunity for the PI to develop contacts with researchers working in the field. This project also has had a positive outcome for the professional development of graduate students who took PI's class on "Introduction to Soft Matter" where some of the results obtained in this project were used to illustrate surfactant self-assembly and interactions with oil. The graduate student working on the project has learned both coarse-grained and atomistic molecular dynamics simulations in application to surfactant systems, which has expanded his knowledge of simulation techniques and surfactant system behavior. During last year he also has expanded his knowledge of computer simulation to non-equilibrium molecular dynamics from his studies of the effect of shear on wormlike micelle behavior with embedded polymer. Working on this project has also helped the graduate student to better understand the concepts of polymer science and apply mathematical models to analyze the system behavior. This project also has strengthened our collaboration with a leading experimental group and has allowed us to test stimulation models developed in the PI's group. Overall, the project has positively contributed to the professional development of the PI and graduate students from the PI's group in a new area of soft matter physics

Publications:

1. A. L. Kwiatkowski, H. Sharma, V. S. Molchanov, A. S. Orekhov, A. L. Vasiliev, E.E. Dormidontova, O. E. Philippova, "Wormlike Surfactant Micelles with Embedded Polymer Chains" *Macromolecules*, 50 (18), 7299–7308, 2017

2. A. L. Kwiatkowski, V.S. Molchanov, H. Sharma, A.I. Kuklin, E.E. Dormidontova, O.E. Philippova "Growth of Wormlike Micelles of Surfactant Induced by Embedded Polymer: Role of Polymer Chain Length" *Soft Matter*, 14, 4792-4804, 2018