

# V.N.18 Electrostatically Self-assembled Amphiplexes

Helmut H. Strey (Primary Contact),  
Theresa Cargioli  
Biomedical Engineering Department  
Stony Brook University  
Psych-A, 3<sup>rd</sup> floor  
Stony Brook, NY 11794  
Phone: (631) 632-1957; Fax: (631) 632-8577  
E-mail: Helmut.Strey@stonybrook.edu

DOE Program Officer: Arvind Kini  
Phone: (301) 903-3565  
E-mail: Aravinda.Kini@science.doe.gov

## Objectives

We are studying the electrostatic self-assembly of amphiplexes made from polyelectrolytes, oppositely charged surfactants, neutral cosurfactants, oil and water. Such complexes are fascinating because they spontaneously precipitate after mixing of the components in water to form long-range ordered materials. The main focus of this project is to gain a basic understanding of their phase diagrams, their material properties and mechanism of self-assembly. To enable the daunting task of measuring phase diagrams of a system with multiple components we are developing a setup for combinatorial x-ray scattering at beamline X6B at Brookhaven National Laboratories (Upton, NY) capable of determining several hundred structures per day. As this research progresses, we will also look into future applications of these materials for bioseparation, oil-recovery and water cleanup, drug and fragrance delivery, and fuel cell membranes.

## Technical Barriers

Many areas of technology are in urgent need of solid materials of well-defined porosity on the nano-scale. Our proposal addresses an important aspect of creating such materials using electrostatically driven self-assembly. Applications of this approach may be used for filters with so far unmatched size discrimination, molecular sponges that can soak up non-polar molecules, and mechanically strong fuel cell membranes. Not only would our materials perform better, but they will also be cheap and easy to manufacture since they are self-assembled from commodity chemicals.

## Abstract

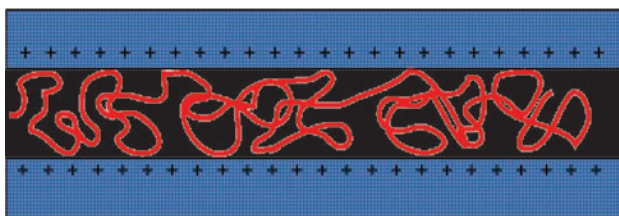
We are presenting the phase diagram of amphiplexes made from polyelectrolytes, oppositely charged surfactant, cosurfactant and oil at different salt concentrations. We find that at higher salt concentrations the amphiplexes can take up more oil, resulting in larger unit cell structures. We attribute this effect to the softening of the attractive interaction between the surfactant moieties. In addition, we are studying a model system for polyelectrolyte induced self-assembly of membrane stacks. We studied the lamellar spacing as function of membrane charge density as set by the ratio between DOTAB and DOPC and the salt concentration of the bathing solution. As predicted by theoretical models, the lamellar spacing decreases as the membrane charge density increases. Interestingly, at charge densities lower than 50% and 500mM NaAc we observed a coexistence of two lamellar spacings, one larger and one smaller than at lower salt concentrations. We will also report progress on the design and construction of a combinatorial material science X-ray scattering beamline at the NSLS at BNL.

## Progress Report

### 1. Membrane Assembly

We have been studying a model system of charged lipid bilayers and oppositely charged polyelectrolytes that aggregate into membrane stacks. This system serves as a planar model for the more complicated polyelectrolyte-surfactant amphiplexes with mostly curved interfaces. The intermembrane distance in within the stacks is measured by X-ray scattering as a function of charge density of lipid bilayer and polyelectrolyte, polyelectrolyte molecular weight, and salt concentration. In addition, we will study to what extent counterion release [1] is responsible for the polymer induced attraction using thermodynamic and electrochemical methods.

The simplest model system for the study of polyelectrolyte induced self-assembly is the assembly



**FIGURE 1.** Schematic picture and concept of oppositely charged polyelectrolyte induced bridging of two charged surfaces.

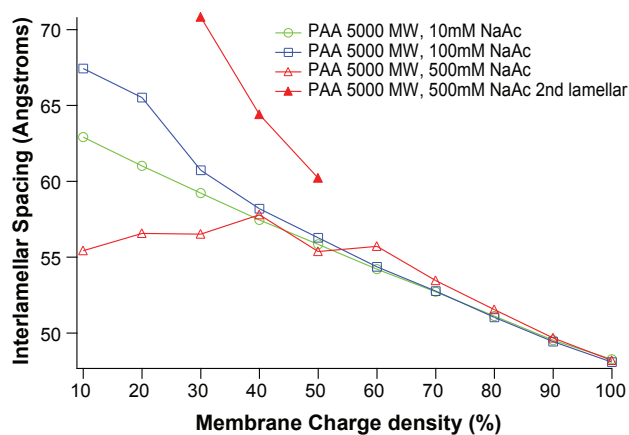
of charged lipid bilayers using oppositely charged polyelectrolytes. In our study we used different molar ratios of Dioleoyltrimethylammoniumpropane (DOTAP) and Dioleoylphosphatidylcholine (DOPC) complexed with different molecular weights of poly (acrylic acid) (PAA).

We investigated the effect of molecular weight of the polyelectrolyte and salt concentration (from 10mM to 500mM NaCl) on the polyelectrolyte layer thickness (this thickness is given by the lamellar repeat spacing minus the DOTAP:DOPC membrane thickness of 39Å [2]). The resulting repeat spacing are plotted in Figure 2 against the Membrane charge density.

As predicted by theoretical models [3-5], the lamellar spacing decreases as the membrane charge density increases. Interestingly, at charge densities lower than 50% and 500mM Na-Acetate we observed a coexistence of two lamellar spacings, one larger and one smaller than at lower salt concentrations. Further studies have to be performed to fully understand this system.

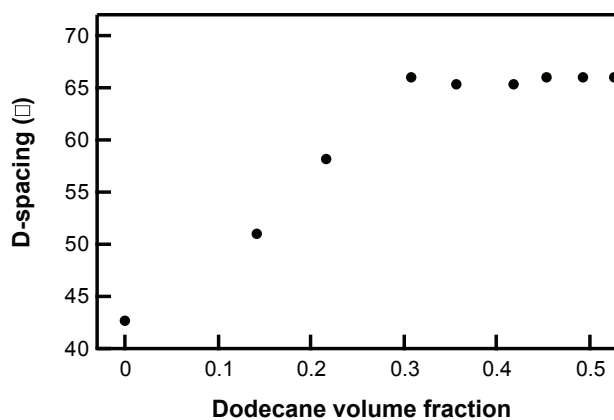
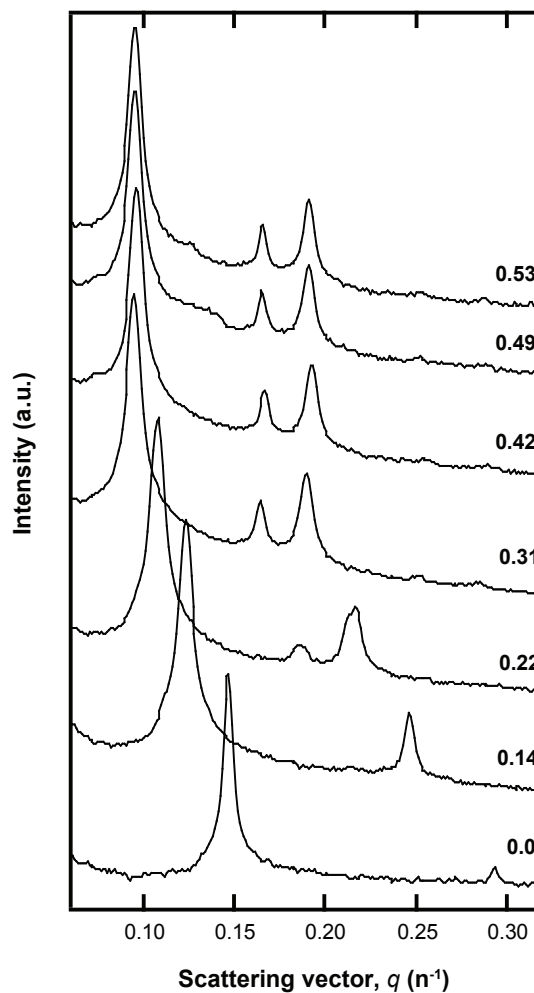
## 2. Polyelectrolyte – Oppositely Charged Surfactant – Cosurfactant – Oil Complexes

As model system we are studying microemulsions formed from copolymers of poly (acrylic acid – acrylamide), cetyltrimethylammonium chloride, alcohols of different chain length (e.g. 1-pentanol, 1-octanol), and dodecane. This system will be studied as function of composition (ratio between polyelectrolyte and surfactant is fixed by charge neutrality: for each surfactant charge there is one charged group on the polyelectrolyte chain), polyelectrolyte charge density, and salt concentration.



**FIGURE 2.** Poly (acrylic acid) layer thickness in membrane stacks assembled from PAA and a 1:1 mixture of DOTAP and DOPC as function of Debye screening length. The thickness is calculated from the X-ray lamellar spacing minus the bilayer thickness of 39Å.

Figure 3 shows how adding dodecane to aqueous complexes formed from polyelectrolyte – oppositely charged surfactants – cosurfactants affects the unit cell size of the resulting amphiphiles. In this example



**FIGURE 3.** Adding oil to a complex of polyelectrolyte-surfactant-cosurfactant (1:1 cetyltrimethylammonium chloride : poly (acrylic acid)) equilibrated in 100mM NaCl and 20% Pentanol saturation swells the unit cell size from 40Å to 65Å while adding up to 30% oil (dodecane) w/w.

swelling of the unit cell by almost 100% is achieved. Preliminary data suggests that by increasing the salt concentration we can expand the unit size to over 200Å. This will become important for applications in filtration where we would like to make materials with variable pore sizes.

### 3. Design and Construction of a Combinatorial Material Science X-ray Scattering Beamline at NSLS

Our amphiplex system and also many soft matter materials (e.g. personal care products, detergents, emulsions) consist of many different components. In order to optimize the structure and performance of these materials for specific applications the phase diagram has to be scanned as a function of composition. The difficulty with this approach is that, because of the enormity of the available phase space, often many thousand samples with varying compositions have to be investigated.

One possible solution to this problem is to scan through phase space using a combinatorial approach. This approach has been successfully employed in molecular biology, drug discovery and recently in material science [6]. We are developing a combinatorial material science X-ray scattering setup at the National Synchrotron Light source (NSLS) located at Brookhaven National Labs (BNL) for structure determination in soft matter systems. The development consists of a robotic liquid handling system commonly used in molecular biology using 96 or 384 well plates for the preparation of samples with varying composition.

We are in the process of designing a motorized stage that can hold up to 4 well plates and that will allow us in an automated fashion collect X-ray scattering data of up to 1536 individual samples in one run. We are also developing software that will analyze the 2-dimensional scattering data and fit the structures in batch. For that we chose to use python as a programming language because it is open-source and will allow us to create an open analysis platform for other X-ray scattering users. So far, we have developed the experimental protocols to prepare individual amphiplex samples in 96 well plates using a robotic system. The sample preparation requires several pipetting, mixing, and centrifugation steps. We already successfully reproduced phase diagram data that were determined without using a combinatorial approach.

### Future work

1. Finish the construction of the X-ray scattering stage so that we can more efficiently determine phase diagrams of our complexes.
2. We are working on ESAs that are compatible for skin-care products or foods. For that we quarternize chitosan and dextran to transform them into positively charged polyelectrolytes. We will then complex them with SDS or other negatively charged biocompatible surfactants. We will then determine the transport properties of these materials for applications in drug delivery.
3. We will determine phase diagrams of amphiplexes containing cross-linkable monomers (e.g. dicyclopentadiene). We then solidify these samples using second generation Grubb's catalyst. We will use EM and X-ray scattering to determine whether the structures stayed intact during the polymerization process. Such materials have great potential for applications in filtration and fuel cell membranes.

### References

1. P. Sens and J.-F. Joanny, "Counterion Release and Electrostatic Adsorption," *Physical Review Letters*, vol. 84, pp. 4862-4865, 2000.
2. J. O. Rädler, I. Koltover, T. Salditt, and C. R. Safinya, "Structure of DNA-cationic liposome complexes: DNA intercalation in multilamellar membranes in distinct interhelical packing regimes," *Science*, vol. 275, pp. 810-814, 1997.
3. I. Borukhov, D. Andelman, and H. Orland, "Scaling laws of polyelectrolyte adsorption," *Macromolecules*, vol. 31, pp. 1665-1671, MAR 10 1998.
4. A. V. Dobrynin, A. Deshkovski, and M. Rubinstein, "Adsorption of Polyelectrolytes at an Oppositely Charged Surface," *Physical Review Letters*, vol. 84, pp. 3101-3104, April 2000.
5. J.-F. Joanny, M. Castelnovo, and R. Netz, "Adsorption of charged polymers," *Journal of Physics: Condensed Matter*, vol. 12, pp. A1-A7, 2000.
6. Y. L. Dar, "High-throughput experimentation: A powerful enabling technology for the chemicals and materials industry," *Macromolecular Rapid Communications*, vol. 25, pp. 34-47, JAN 2 2004.