Pressure Effects on Self-assembly in Mixtures Containing Zwitterionic Amphiphiles

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1. Two-dimensional Nanopatterns for Zwitterionic AB/S Mixture

In this supporting information 1, we provide supplementary SCFT calculations on two 2-dimensional nanopatterns for the zwitterionic AB/S mixture, where the chain architecture (scheme S1) for the lipid-like AB amphiphiles becomes more realistic by having the zwitterionic A block and the two branches of uncharged B and B' blocks. The requisite equation-of-state parameters, σ_j and $\bar{\varepsilon}_{ij}$, for the given mixture is identical to those used for the L system in Figures 1 to 4, and the two branches, B and B' blocks, have $N_B = 30$ for both. It is necessary for this amphiphilic chain to define the end-segment distribution functions q_A, q_B, $q_{B'}$, and their conjugate functions for A, B, and B' blocks, respectively. Those functions are determined by solving the modified diffusion equations with the probability for these three blocks to end at one junction. The 2-dimensional Poisson equation in eq 32 is solved via the iterative Gauss-Siedel method instead of directly solving the matrix equation.
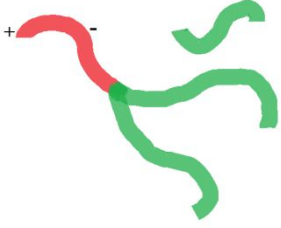
Scheme S1. Chain Architecture

The compositions for the mixture are set to have the dispersed phases, so that the hard-core volume fraction φ_c is chosen here to be $\varphi_c = 0.8$. The dielectric constant of the medium is set to 79.58. The following two nanopatterns are the packed cylinders of hexagonal (P6mm in plot *a* of Figure S1) or centered rectangular (C2mm in plot *b* of Figure S1) arrays. The latter one has C2mm symmetry but is a special case with the rectangular unit cell (a blue box) possessing the lattice parameter ratio $b/a = 2$. At T = 300 K and thus at $L_B = 0.7$ nm, the two nanopatterns are competing with each other. Of course, owing to packing efficiency, the hexagonally packed cylinders have the free energy slightly lower than
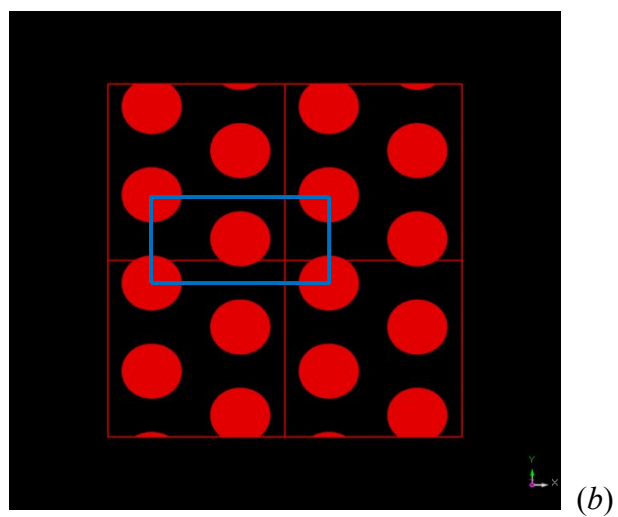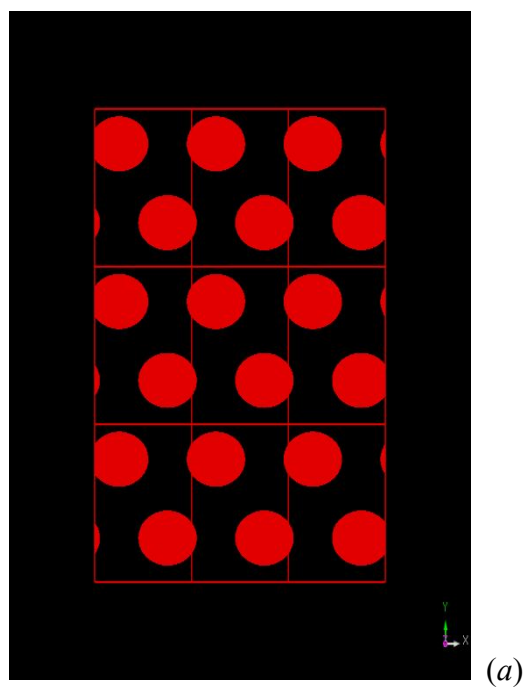
the C2mm patterns do.

(*a*)

(*b*)

Figure S1. Two nanopatterns, (*a*) P6mm and (*b*) C2mm, obtained for the 3-arm lipid-like amphiphilic systems.

2. **Pressure of Charged Hard Polyanion/Counterions Binary Mixture**

In this supporting information 2, let us give a stringent test of the formulated equation of state for a charged hard sphere chain system without non-bonded dispersion interactions. In our system of interest, there are negatively charged chains ($z_A = -1$) or polyanions with $N_A = 16$. In order to satisfy electroneutrality, there exist positively charged counterions P ($z_P = +1$) with $N_P = 1$. If their close packed volume fractions are denoted as φ_A and φ_P, then $\varphi_A z_A + \varphi_P z_P = 0$ or $\varphi_A = \varphi_P$. The equation-of-state properties of the given system was studied by Stevens and Kremer through Monte Carlo (MC) simulations. The mixture was treated in a primitive way as the background medium is continuous with $\varepsilon_0 = 106.8\varepsilon_{vac}$. In Figure S2, the simulated (osmotic) pressure is depicted as a function of overall packing density η. Pressure calculated using eqs 17 and 18 is also displayed in this figure. It is seen that the theoretical pressure is in excellent agreement with the MC results.
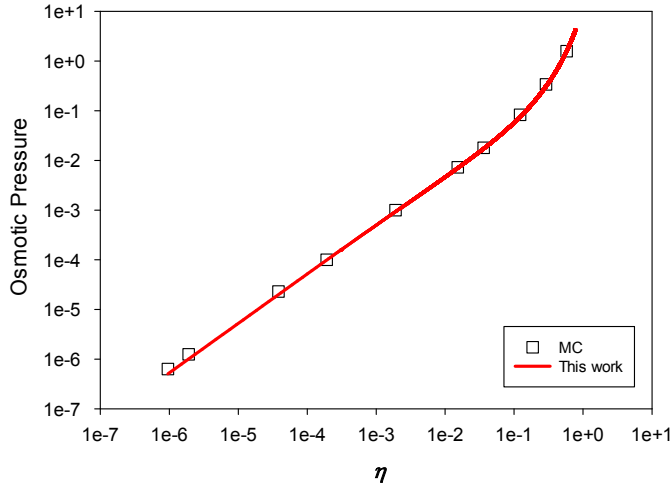

Figure S2. Comparison of osmotic pressure from MC simulation and from the theoretical equation of state for polyanion + counterion mixture in a dielectric medium with $\varepsilon = 106.8\varepsilon_{vac}$, while non-bonded dispersion interactions are absent.