Self-assembly of Charge-Containing Copolymers
at the liquid-liquid Interface

Felipe Jiménez-Ángeles,‡∥ Ha-Kyung Kwon,‡∥ Kazi Sadman,‡ Thomas Wu,‡
Kenneth R. Shull,‡ and Monica Olvera de la Cruz*,‡⁺,∥⁺,∥⁺

†Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States
‡Department of Chemistry
¶Department of Chemical and Biological Engineering
§Department of Physics
∥Both authors are first authors

E-mail: m-olvera@northwestern.edu
Phone: (847) 491-7801

Supporting Information
Figure S1: $^1$H-NMR spectra of PS-$b$-QVP0 (bottom) and PS-$b$-QVP37 (top).
Figure S2: $^1$H-NMR spectra of quaternized at fractions (a) 0.006, (b) 0.015, and (c) 0.038. P2VP homopolymers. Quaternization led to the appearance of a new peak at $\delta = 8.75$ ppm. The charge ratio was calculated by taking the integrated areas of peaks $a$ and $b$. 
Martini Model Potentials

Figure S3: Interaction energy potentials in the Martini force field between (a) identical beads and (b) disimilar beads; $w_p$, $C_x$, $P_4$, and $S_{cy}$ stand for the beads from water, chloroform, the polar groups in 2VP, and the aromatic rings in 2VP and in PS, respectively.

We employ the Martini force field to simulate block copolymers and homopolymers at the water chloroform interface. The copolymer is polystyrene-$b$-poly-2-vinylpiridine ($PS-b$-$P2VP$) with variable charge fraction $f_q$ and variable hydrophilic fraction $f_a$. The poly-2-vinylpiridine block is quaternized and acquires charge when it is in water ($PS-b$-$Q2PVP$). The charge fraction $f_q$ is equal to the degree of quaternization. The hydrophobicity and hydrophilicity of groups/molecules are mimicked by means of the Lennard-Jones potentials by assigning strong interactions between ‘similar’ molecules/groups and a weak interaction between ‘disimilar’ molecules/groups. In Figure S3 are shown the interactions between beads that represent similar and dissimilar molecules/groups. The interaction between ‘similar’ molecules, like the water-water and chloroform-chloroform, have a minimum below $1.5 \ k_B T$; the deeper the minimum the easier the similar groups aggregate. The minimum of the interaction between dissimilar molecules/groups is around and above $1 \ k_B T$. 


Figure S4: (a) Simulation box containing water and 2VP monomer forming two separate phases; the water phase consists of 508 water molecules and the 2-VP phase is made of 239 molecules. The system is simulated for 400 ns at $T = 298$ K and $P = 1$ bar. Periodic boundary conditions are applied in the three directions. (b) Equilibrium density profiles of water and 2VP calculated over the last 200 ns of the simulation. The monomer solubility is calculated from the 2VP density profile at the middle of the aqueous phase.

The monomer parameters are calibrated to match the experimental solubility of 2VP in water. To simulate the monomer dissolution in water we employ the simulation setup shown in Figure S4a. The two fluids are placed next to each other and are completely unmixed at $t = 0$. During the simulation some 2VP molecules go dynamically in and out from the aqueous phase. The density profiles converge to the curves shown in Figure S4b. The solubility is calculated from the equilibrium concentration of 2VP in water. We tested different combinations for the polar beads in our monomer model. The first natural combination was a non-polar backbone group using the STY bead from refs.\textsuperscript{1,2} and a polar
bead on the connecting ring bead. However, the solubility of the 2VP monomer can not be matched with the experimental value using a single polar bead in the aromatic ring. Hence, based on the fact that the dipole moment of 2VP is about 2.1 D, in our model we assumed the backbone and the connecting ring bead to be polar. We get the best match of the 2VP solubility when the polar groups in the 2VP model are taken as P4 beads. From the density profiles we wet a concentration of 2VP of 25 g/l in water while the experimental concentration is 27 g/l.
Copolymer Adsorption

Figure S5: Number density profiles of the water, chloroform, and copolymer beads near the chloroform-water interface. (a) $f_q = 0$, (b) $f_q = 0.1$, (c) $f_q = 0.2$, (d) $f_q = 0.4$. The profiles are shifted to set the crossing point of the water and chloroform profiles at $z \approx 0$. The left scale is for the water and chloroform profiles whereas the right scale is for the polymer beads and counterions. The line type and color is assigned as follows: black dotted line is for chloroform, light-blue dot-dashed line is for water, red dashed is for the ring beads (STY), blue solid line is for the polar groups (P$_4$), the green solid line is for the quaternized groups (Q$_a$), and the yellow solid line is for the counterions. The hydrophilic fraction is $f_a = 0.16$. 
Figure S6: Interfacial tension at the water-chloroform interface as a function of the number of adsorbed copolymers per unit area $\Gamma$ and for three different charge fractions. The hydrophilic fraction is $f_a = 0.16$.

Figure S7: Radial distribution function between the polymer charged $Q_a$ groups (black solid line) and between the polymer charged groups $Q_a$ and the counterions (dashed line). The profiles are calculated from the copolymer adsorbed at the water-chloroform interface. The copolymer charge fraction is (a) $f_q = 0.1$ and (b) $f_q = 0.4$. The hydrophilic fraction is $f_a = 0.16$ in both the cases.
Figure S8: Adsorption of a quaternized P2VP homopolymer (charge fraction of $f_q = 0.1$ and hydrophilic fraction is $f_a = 1$) at the chloroform-water interface. (a) Potential energy of the polymer-chloroform-water system during a 500-ns simulation run. The black line represents the instantaneous potential energy and the red line is the running average taken over intervals of 1 ns. Instantaneous snapshots of the system during the simulation time when the polymer is in the (b) chloroform phase at $t = 20$ ns and (c) adsorbed at the chloroform-water interface at $t = 220$ ns. Water is rendered as quick-surface representation in light blue; the chloroform beads are shown as gray dots and counterions. Close-up views of the polymer and the water and chloroform beads/molecules within a distance of 0.5 nm from the polymer, in (d) the polymer is in the chloroform phase and (e) the polymer is at the interface. Water beads and chloroform molecules are colored in light blue and gray, respectively. The polymer beads are colored as follows: the polar groups are in dark-blue, the quaternized groups in green, the ring beads in pink, and the counterions in yellow.
Figure S9: Number density profiles of the water, chloroform, and polymer beads near the chloroform-water interface. (a) $f_q = 0$, (b) $f_q = 0.05$, (c) $f_q = 0.1$, (d) $f_q = 0.2$, (e) $f_q = 0.4$, and (f) $f_q = 0.5$. The profiles are shifted to set the crossing point of the water and chloroform profiles at $z \approx 0$. The left scale is for the water and chloroform profiles whereas the right scale is for the polymer beads and counterions. The line type and color is assigned as follows: black dotted line is for chloroform, light-blue dot-dashed line is for water, red dashed is for the ring beads (STY), blue solid line is for the polar groups ($P_4$), the green solid line is for the quaternized groups ($Q_a$), and the yellow solid line is for the counterions. The hydrophilic fraction is $f_a = 1$ in all the cases.
Our model reveals the adsorption process of a polymer at the water-chloroform interface. In our simulations, the polymer and the counterions are initially placed in the chloroform phase. Due to the low dielectric constant in chloroform (strong electrostatic interactions) the counterions remain bound to the quaternized groups. The polymer adsorption is driven by Brownian motion and the adsorption time is in the order of hundreds of nanoseconds. In equilibrium the polar segments of copolymers ($f_q = 0, 0.1, 0.2, 0.3, \text{and } 0.4$) and homopolymers ($f_q = 0, 0.05, 0.1, 0.2, 0.3, 0.4, \text{and } 0.5$) are adsorbed at the water chloroform interface. The adsorption is accompanied by the release of counterions into the aqueous phase. Figure S8a shows the potential energy as a function of time from a 500-ns simulation. The polymer adsorption at the water-chloroform interface occurs at $t \approx 180$ ns which is seen as a step drop in the potential energy. After the 500-ns simulation at $T = 298$ K, the system is simulated at 350 K and re-equilibrated at 298 K. No further changes in the potential energy are observed after the polymer adsorption. The re-equilibration at $T = 298$ K leads to a similar potential energy as before the simulation at 350 K.

Figure S8b and S8c show, respectively, snapshots of the system when the polymer is away from the interface (in chloroform) and when the polymer is adsorbed at the interface. When the polymer is adsorbed at the interface the counterions are released into the aqueous phase. Close-up snapshots of the polymer when it is in the chloroform phase and at the interface are shown in Figures S8d and S8e, respectively. As we pointed out above, when the polymer is in the chloroform the counterions are bound to the polymer. In chloroform the polymer adopts a coil configuration in which the ring-beads are in contact with the chloroform and the polar groups form a core and have few contacts with the chloroform. At the interface, the counterions are released, and the rings at the water side open-up to allow the contact between the polar groups and the water beads. At the chloroform side the ring beads remain in contact with the chloroform and do not allow the contact between the polar groups and chloroform.

The density profiles of the polymer beads are shown in Figure S9. At all the charge
fractions from $f_q = 0$ to 0.5 we see that the ring beads (STY) are predominantly in the chloroform phase while the quaternized groups and the counterions are in the aqueous phase. As the charge fraction increases the distribution of the polar groups ($P_4$) is shifted towards the aqueous phase. This implies that the polymer penetrates more into the aqueous phase and disrupts more the interface as the charge fraction increases.
Varying $f_a$

Figure S10: Top view from the $xy$-plane and lateral view from the $xz$-plane of the aggregates of copolymer PS-b-P2VP at the water-chloroform interface. The hydrophilic fraction is (a,b) $f_a = 0.16$; (c,d) $f_a = 0.5$; (e,f) $f_a = 1$. The polar groups and the quaternized groups in the P2VP block are in dark blue and green, respectively; the counterions are colored in yellow; the hydrophobic backbone groups in the PS block are colored in red; the hydrophobic ring groups are not shown for clarity. The aqueous phase (snapshots from the $xz$-plane) is in transparent cyan and the water surface is at one-half of the bulk density, approximately. The charge fraction is $f_q = 0.2$ and the number of molecules per unit area is $\Gamma = 0.1125$ molecs./nm$^2$ in all the cases.
Figure S11: Typical configurations of the polymer aggregates in bulk chloroform. The hydrophilic fraction is (a) $f_a = 0.5$ and (b) $f_a = 1$. The polymers are initially dispersed in the chloroform at a density of $\rho_s = 0.006$ molecs./nm$^3$. The charge fraction is $f_q = 0.2$ in all the cases.

**Solvation Energy Calculation**

**Born Model**

The solvation free energy can be estimated using the Born equation$^4$ which represents the Gibbs free energy change by transferring one ion between two continuous media of dielectric constant $\varepsilon_1$ and $\varepsilon_2$, respectively. The Born equation is given by

$$
\Delta G_i = \frac{k_B T \ell_B}{2a} (1 - \frac{\varepsilon_1}{\varepsilon_2})
$$

where $\ell_B = z_i^2 e^2/(4\pi\varepsilon_1\varepsilon_0 k_B T)$, $z_i$ is the ionic valence, $e$ is the elementary charge, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\varepsilon_0$ is the vacuum permittivity, and $a$ is the ionic diameter. Since we are transferring two ions the total change of free energy is

$$
\Delta G_s = 2\Delta G_i
$$
The change of potential energy is calculated by assuming that in medium 2 the two oppositely charged ions are bound at their closest approach distance \( a \) whereas in medium 1 the ions are fully dissociated. The change in the potential energy by transferring two ions from medium 2 to medium 1 is

\[
\Delta U_s = \frac{k_B T \ell_B}{a} \left( \frac{\varepsilon_1}{\varepsilon_2} \right)
\]

(3)

The change in enthalpy is \( \Delta H_s \approx \Delta E_s = \Delta U_s \). The Gibbs free energy is related to the change of enthalpy \( \Delta H_s \) and entropy \( \Delta S \) by

\[
\Delta G_s = \Delta H_s - T \Delta S
\]

(4)

By combining Equations 1 to 4 we get

\[
T \Delta S = \Delta H_s - \Delta G_b = \frac{k_B T \ell_B}{a} \left( \frac{2\varepsilon_1}{\varepsilon_2} - 1 \right)
\]

(5)

**Molecular Simulations**

In molecular simulations the free energy of solvation can be calculated using the thermodynamic integration method\textsuperscript{5–7} which is represented by the following equation

\[
\Delta G = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda
\]

(6)

\( U(\lambda) \) is the potential energy of the system where the interaction of the particles of interest is coupled with the rest of system through the \( \lambda \) parameter. The \( \left\langle ... \right\rangle_{\lambda} \) symbols mean an ensemble average taken at certain constant value of \( \lambda \) between 0 and 1. To perform the integration method \( N_s \) identical systems are simulated at different values of \( \lambda \). Here we calculated the free energy of solvation of Na\textsuperscript{+} and Cl\textsuperscript{−} ions in water and in chloroform. We used the Gromos force field for the atomistic model\textsuperscript{8} with the SPC-E model of water and the
Martini force field for the coarse-grain system. In the Coarse grain simulations, chloroform phase is made of 1602 beads and the aqueous phase of 802 polarizable water beads. In the atomistic model the liquid chloroform is made of 1560 molecules and the aqueous phase is made of 2160 water molecules. The free energy calculations are performed using separated boxes of the two liquids. The thermodynamic integration (Eq. 6) is performed by generating equally spaced windows from $\lambda = 0$ to 1 with increments of 0.1. At each value of $\lambda$ the system is simulated for 2 ns.

The change of the total $\Delta E_s$ energy is calculated by combining the two liquids to form an interface like in Figure S4. The simulation is initiated by releasing the two in the chloroform phase and the system is simulated until the two ions diffuse into the aqueous phase. We track the total energy as a function of time. There is a clear decrease of the total energy when the ions enter into the water from the chloroform phase. We calculate the change of the total energy by taking the running average of the total energy at intervals of 50 ps. The total energy and the running average are shown in Figure S12.

![Figure S12: Total energy as a function of time from the (a) coarse-grain simulation and from the (b) atomistic simulation. The total change of energy is shown by the red parallel bars.](image)

The internal energy is equal to the total energy and $\Delta H_s \approx \Delta E_s$. The change in entropy is calculating Eq. (4).
Figure S13: (a) Association of two ions in chloroform and (b) ion solvated by four water molecules.
References

(1) Rossi, G.; Monticelli, L.; Puisto, S. R.; Vattulainen, I.; Ala-Nissila, T. Coarse-Graining Polymers with the MARTINI Force-Field: Polystyrene as a Benchmark Case. *Soft Matter* 2011, 7, 698–708.

(2) Vögele, M.; Holm, C.; Smiatek, J. Coarse-grained simulations of polyelectrolyte complexes: MARTINI models for poly(styrene sulfonate) and poly(diallyldimethylammonium). *J. Chem. Phys.* 2015, 143, 243151.

(3) Rowbotham, J. B.; Schaefer, T. Long-range Proton-Proton Coupling Constants in the Vinylpyridines. Conformational Preferences of the Vinyl Group and Molecular Orbital Calculations. *Can. J. Chem.* 1974, 52, 136–142.

(4) Paula, A. D. *Physical Chemistry*, 8th ed.; Oxford university press.: The address, 2006.

(5) Kirkwood, J. G. Statistical Mechanics of Fluid Mixtures. *J. Chem. Phys.* 1935, 3, 300–313.

(6) Hess, B.; Kuttner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *J. Chem. Theory Comput.* 2008, 4, 435–447.

(7) Berendsen, H.; Spoel, D. V. D.; Drunen, R. V. Gromacs: A Message-Passing Parallel Molecular Dynamics Implementation. *Comp. Phys. Comm.* 1995, 91, 43–56.

(8) Schuler, L. D.; Daura, X.; van Gunsteren, W. F. An Improved GROMOS96 Force Field for Aliphatic Hydrocarbons in the Condensed Phase. *J. Comp. Chem.* 2001, 22, 1205–1218.

(9) Marrink, S. J.; Risselada, H. J.; Yefimov, S.; Tieleman, D. P.; de Vries, A. H. The MARTINI Force Field: Coarse Grained Model for Biomolecular Simulations. *J. Phys. Chem. B* 2007, 111, 7812–7824.
(10) Yesylevskyy, S. O.; Schäfer, L. V.; Sengupta, D.; Marrink, S. J. Polarizable Water Model for the Coarse-Grained MARTINI Force Field. *PLOS Computational Biology* **2010**, *6*, 1–17.