

Supplementary information for:
From microemulsion phase diagrams to
hydrophilicity and hydration controlled
adsorption: A dissipative particle dynamics
modelling study of phospholipid assembly in
bio oils

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Supplementary information

The supplementary information consists of additional DPD simulations details, the DPD conservative force parameter a estimation including the atomistic MD simulations details resulting in the cohesion energies and solubility parameters calculated from condensed phase

and *in vacuo* simulations of phosphatidylcholine, glycerol, octane, and water, see Table S1 for simulation system details. Additionally, Figure S1 presents data corresponding to the structural matching between atomistic MD and DPD simulations via radial density function (RDF). Figure S2 presents density profiles for DPPC and water adsorbed on surfaces with varying hydrophilicity λ .

Additional DPD simulations details

As discussed in the main manuscript, for the self-repulsion parameter a_{ii} for GLYS, TAIL, Water and the SURF beads a value of $25 k_B T$, derived from water isothermal compressibility at DPD particle density $\rho = 3$ is used. It is worth noting that a_{ii} should scale linearly with the degree of coarse-graining N_{CG} , with large N_{CG} corresponding to a steeper repulsive potential and more hard-sphere like behaviour. However, already at $N_{CG,limit} < 10$,¹ this approach causes solvent freezing. Because of this, compressibility matching is often disregarded in parametrization and instead, other parameters such as density and pressure are matched. Here we have $N_{CG} = 8$, which makes the choice $a_{ii} = 25 k_B T$ well motivated. For CHOL beads, $a_{ii} = 30$ is used to better reflect the charged nature and increased self-attraction resulting from the zwitterionic DPPC headgroup.

DPD conservative force parameter a estimation including the atomistic MD simulations details

The DPD conservative force repulsive parameter a for each DPD bead in the system was estimated based on fully atomistic molecular dynamics (MD) simulations corresponding to each bead component, including water, *in vacuo* and as condensed phase.

The cohesive energy E_{coh} for the DPD parametrization was determined from all-atom MD simulations using the CHARMM-C36 force field.² MD simulations were performed by the

Gromacs v2020.3^{3,4} simulation package. Separate condensed phase simulations consisting of 4000 molecules of phosphatidylcholine, glycerol, or octane, or 36000 molecules of water were carried out using the following protocol. First, the simulation box was energy minimized using steepest descent method for 5000 steps. This was followed by further relaxation in a two-step NVT simulation, first 0.05 ns with a time step of 0.001 ps followed by 1 ns using a time step of 0.002 ps at $T = 343.15$ K (velocity rescale thermostat,⁵ $\tau_T = 0.5$ ps). Then the density of the condensed phase was equilibrated during in NPT ensemble at $T = 343.15$ K (velocity rescale thermostat,⁵ $\tau_T = 0.5$ ps) and $p = 1.0$ bar (Berendsen barostat,⁶ $\tau_P = 2.0$ ps and compressibility of $4.5e^{-5}$ bar⁻¹) for 10 ns with a time step of 0.002 ps. The contributions to cohesive energy due to the non-bonded energy terms (Coulombic and Lennard-Jones contributions) were sampled in a 5 ns NVT ensemble simulation with a time step of 0.002 ns at $T = 343.15$ K (velocity rescale thermostat,⁵ $\tau_T = 0.5$ ps).

Single molecule gas phase / vacuum (*in vacuo*) simulations of the species targeted for parametrization, i.e. phosphatidylcholine, glycerol, octane, and water, were run in NVT ensemble using the exact simulation box dimensions of the condensed phase NVT run. This box size choice is to obtain the same system volume dependent contribution from the PME method used for electrostatic interactions; as the energies will be subtracted from each other, the PME size dependent contributions cancel out this way. Again, non-bonded energy terms were sampled during a for 5 ns NVT ensemble run with a time step of 0.002 ps at $T = 343.15$ K. E_{coh} was then calculated as the difference in non-bonded energies of the condensed phase and the *in vacuo* simulation. Notably, a reliable value of E_{coh} requires a well equilibrated condensed phase simulation. Finally, the solubility parameter can be obtained as $\delta = \sqrt{\frac{E_{\text{coh}}}{V_m}}$, where V_m is molar volume.

Initially, the DPD parameters were estimated based on the Hildebrand solubility parameters δ derived from the cohesion energy E_{coh} values. The non-bonded energies corresponding to each MD simulated system and the calculated E_{coh} and Hildebrand solubility parameter δ values have been tabulated in Table S1.

Figure S1 plots the RDF data calculated between the GLYS and TAIL and GLYS and CHOL atomistic detail equivalents in the MD simulations and the corresponding DPD beads in 50:50 binary mixtures of the components. For the atomistic detail MD simulations, the center of mass of the molecule species used as reference in RDF calculation. The data shows that the Hildebrand solubility parameters based approach described above functions well for extracting cross-interactions corresponding to the GLYS and TAIL beads as there are no hydrogen bonding or charged moiety interactions in these species. In particular, the DPD bead based RDF follows well the atomistic detail MD RDF, naturally with the coarse-graining smoothing the curve. However, for the zwitterionic CHOL bead, significant tuning of the DPD parameters is required as demonstrated by the variation of the DPD conservative force cross-interaction parameter a on the RDFs of Figure S1. The tuned parameter set used for the DPD production runs is presented in the main manuscript Table 1.

Table S1: Summary of the atomistic detail molecular dynamics simulations systems of phosphatidylcholine, glycerol, octane, and water including the calculated non-bonded energies of gas phase $E_{\text{NB,vacuum}}$ and condensed phase $E_{\text{NB,condensed}}$. Based on these, the DPD bead cross-interaction parameters, namely the repulsive parameters a , were derived from the calculated cohesive energies E_{coh} and Hildebrand solubility parameters δ . Atomistic detail molecular dynamics simulations model 1 molecule (vacuum) or N molecules (condensed phase) in a cubic box volume of $(l_{\text{box}})^3$.

Compound	DPD bead	N	l_{box} [nm]	$E_{\text{NB,vacuum}}$ [kJ/mol]	$E_{\text{NB,condensed}}$ [kJ/mol]	E_{coh} [kJ/mol]	δ
phosphatidylcholine	CHOL	300	4.27	-302.57	-163262.92	-241.63	19.24
glycerol	GLYS	300	4.28	-362.74	-12495.77	-55.58	9.19
octane	TAIL	180	3.68	16.14	-3834.20	-37.44	7.34
water	WATER	2165	4.01	-180.66	-88462.22	-146.22	15.63

Density profiles for DPPC adsorption on surfaces with varying hydrophilicity

Figure S2 presents density profiles calculated for DPPC and water adsorption on planar surfaces with hydrophilicity $\lambda = 0.2$ (comparable to polyethylene), $\lambda = 0.4$, and $\lambda = 0.8$

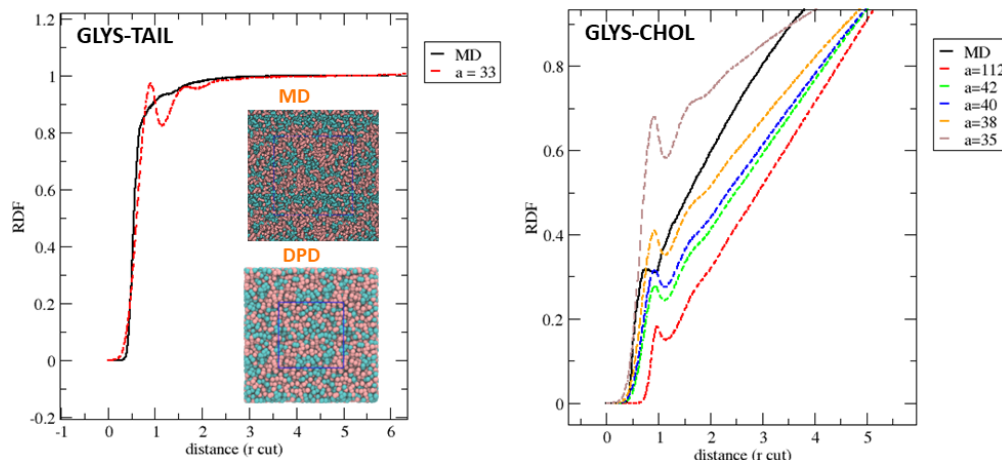


Figure S1: Radial distribution function RDF calculated between GLYS and TAIL (left panel) and GLYS and CHOL (right panel) DPD beads and the corresponding atomistic detail molecular dynamics simulation systems. The systems correspond to 50:50 binary mixtures. For the GLYS and CHOL bead pair, data for varying cross-interaction parameter a is presented to demonstrate the tuning. The example visualizations show GLYS – TAIL binary mixtures with GLYS/glycerol in cyan and TAIL/octane in pink in atomistic detail molecular dynamics (MD) and the DPD simulations.

(comparable to mica) in the DPD simulations. On hydrophilic surfaces corresponding to $\lambda = 0.8$, DPPC molecules interact directly with the surface with the hydrocarbon tails pointed towards the triglyceride solvent phase. The data shows that water adsorbs competitively with an increase in hydration number w corresponding to a decrease in the amount of adsorbed DPPC. On hydrophobic surfaces corresponding to $\lambda = 0.2$, DPPC adsorbs to the surface with the hydrocarbon tails facing the surface. Such adsorption of reverse micelles results in a thick, but patchy film on the surface. Additionally, the triglyceride solvent also shows some ordering at the adsorbent interface, with the tails of the triglyceride interacting with the adsorbent. Correspondingly, the triglyceride head groups can be expected to interact with the more hydrophilic substrates but here the DPPC adsorption masks the response. On surfaces of intermediate hydrophilicity corresponding to $\lambda = 0.4$, adsorption occurs as hemimicelles.

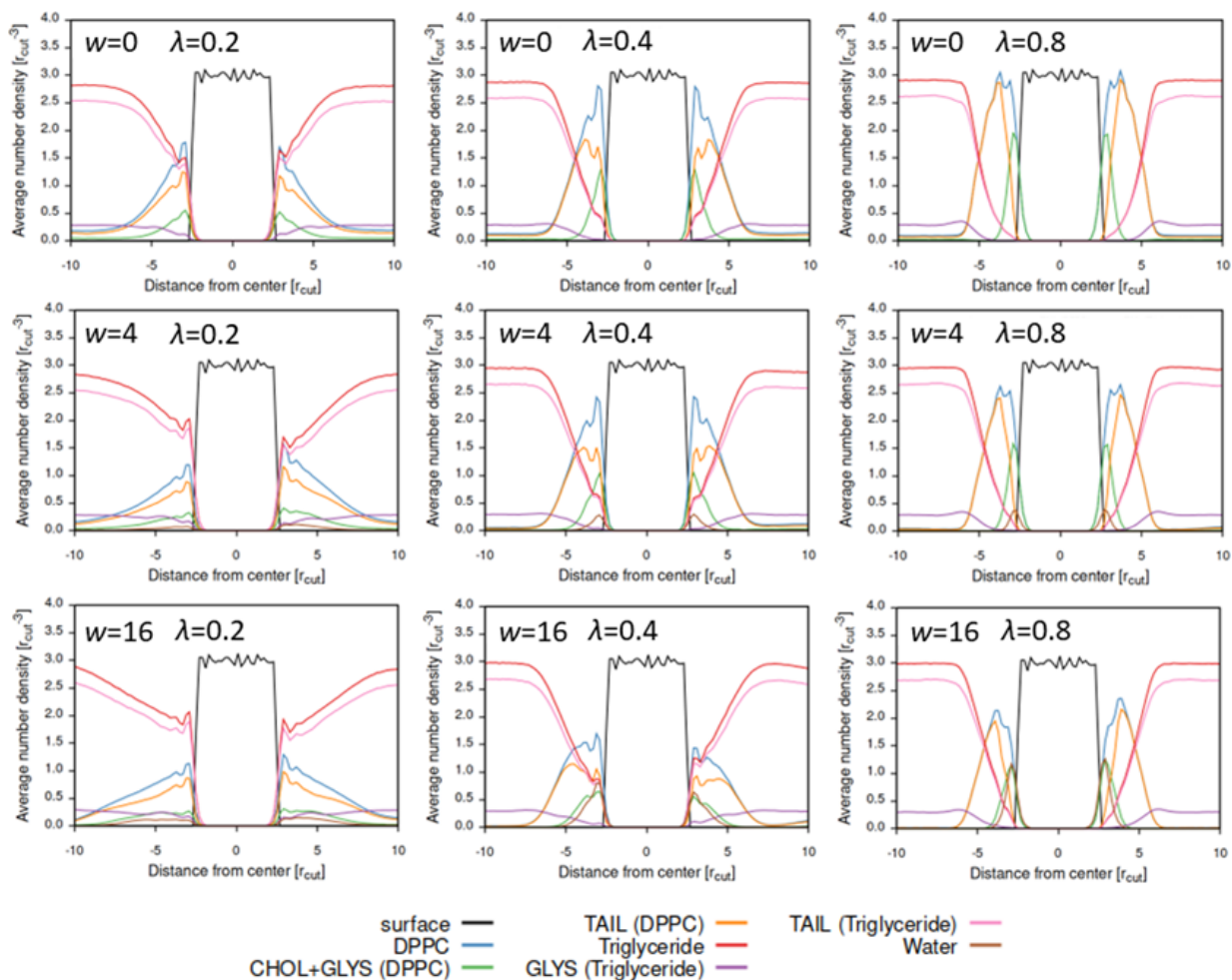


Figure S2: Density profiles for DPPC and water adsorption onto planar surface for different hydrophilicity λ and hydration number w values. Data presented corresponds to 100 mM DPPC in systems with surfaces corresponding to $\lambda = 0.2$ (comparable to polyethylene), $\lambda = 0.4$, and $\lambda = 0.8$ (comparable to mica) at hydration numbers $w = 0$, $w = 4$, and $w = 16$. The hydration numbers have been calculated as molar hydration numbers accounting that each DPD water bead is equivalent to 8 H_2O molecules.

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