Initial Studies directed towards the Rational Design of Aqueous Graphene Dispersants

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1.1 Synthesis: Introduction

All reactants and reagents were purchased from either Sigma-Aldrich or Alfa Aesar and were used without further purification. Solvents used were purified by standard methods. Synthetic procedures were carried out under an atmosphere of dry nitrogen in dry solvents unless otherwise noted. Chromatographic purifications were performed using silica gel SDS (particle size 0.04-0.06 mm). Melting points were determined on a Sanyo Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were measured by Bruker Alpha FT-IR machine and absorption peaks ($\bar{v}_{\text{max}}$) are quoted in wave numbers (cm$^{-1}$). Deuterated chloroform (CDCl$_3$) was used as solvent unless otherwise stated to record the nuclear magnetic resonance (NMR) spectra. NMR spectra were acquired with a B400 Bruker Avance III 400 MHz or B500 Bruker Avance II+ 500 MHz spectrometers using TMS as an internal standard (0.00 ppm). Mass measurements were acquired with a Micromass Trio 200 spectrometer, using electrospray (ES), atmospheric pressure chemical ionization (APCI) or matrix-assisted laser desorption ionization (MALDI) techniques, as stated. A Carlo Erba EA 1108 Elemental Analyzer was used for determination of % levels of carbon, hydrogen and nitrogen.

1.2 Experimental Procedures

4-(Pyren-1-yl)butan-1-ol (3)$^1$

1-Pyrenebutyric acid (2) (300 mg, 1.0 mmol) was added to a three neck RBF (100 mL) which was then purged with dry N$_2$. The flask was cooled to 0 °C in an ice bath before borane-tetrahydrofuran complex (5.0 mL of a 1.0 M solution THF, Aldrich; 5.0 mmol) was added via syringe (CARE: this reaction occurs with the generation of hydrogen). The resulting reaction mixture was stirred for 10 minutes at 0 °C and then 10 minutes at room temperature. Additional borane-tetrahydrofuran complex (2.0 mL of a 1 M solution in
THF, Aldrich, 2.0 mmol) was then added via syringe and the reaction mixture brought to 60 °C overnight. The reaction was then allowed cooled to 20 °C before adding MeOH (7.0 mL) via syringe. The reaction was then allowed to stir at 20 °C for 5 hours after which time K$_2$CO$_3$ (200 mg, 1.5 mmol) was added in one portion. After a further period of 10 minutes at 20 °C water (3.5 mL) was added via syringe and the reaction mixture was extracted with DCM (2 × 15 mL). The combined organic extracts were washed with water (15 mL) then brine (15 mL), dried (MgSO$_4$) and concentrated in vacuo. The crude product was purified by column chromatography with a graded solvent system from 20% ethyl acetate in petroleum ether to 30% ethyl acetate in petroleum ether to afford the title compound (3) (157 mg, 0.6 mmol, 57% yield) as a colorless oil which crystallized on standing to afford the title compound as a colourless solid; mp 76-77 °C (lit.\textsuperscript{1}, 72.5-74.5 °C). δ\textsubscript{H} (400 MHz; CDCl$_3$) 1.33 (1 H, s, OH), 1.70 - 1.81 (2 H, m, C-C-H), 1.89 - 2.00 (2 H, m, C-C-H), 3.38 (2 H, t, J = 7.7, Ar-C-H), 3.71 (2 H, t, J = 6.4, O-C-H), 7.88 (1 H, d, J = 7.8, Ar-H), 7.97 - 8.07 (3 H, m, Ar-H), 8.09 - 8.14 (2 H, m, Ar-H), 8.17 (2 H, dd, J = 7.7, 2.1, Ar-H), 8.29 (1 H, d, J = 9.3, Ar-H) ppm; δ\textsubscript{C} (101 MHz; CDCl$_3$) 27.9, 32.7, 33.2, 62.8, 123.4, 124.7, 124.75, 124.82, 125.0, 125.1, 125.8, 126.6, 127.19, 127.22, 127.5, 128.6, 129.8, 130.9, 131.4, 136.6 ppm; m/z (MALDI-Dithranol) 274 ([M]+, 100%), 225 (45).

1-(4-Bromobutyl)pyrene (4)\textsuperscript{2}

CBr$_4$ (5.43 g, 16.4 mmol) and K$_2$CO$_3$ (2.70 g, 20 mmol) were added to a three neck RBF (250 mL) which was then purged with N$_2$. 4-(Pyren-1-yl)butan-1-ol (3) (3.59 g, 13 mmol) under N$_2$ was then taken up in dry DCM (62 mL) via syringe and injected into the reaction mixture, which was then cooled to 0 °C in an ice bath. PPh$_3$ (4.21 g, 16 mmol) in dry DCM (23 mL) was then added dropwise via syringe and the reaction mixture allowed to stir to room temperature for ~ 64 h. The crude product was purified by directly dry loading the crude material via DCM/silica onto a chromatography column and eluting with a 10%
DCM in petroleum ether solvent system to afford the title compound (4) (3.52 g, 10 mmol, 79% yield) as a colorless oil which crystallized on standing into a colorless solid; mp 73-74 °C (lit.,2 71-72 °C). δ_H (500 MHz; CDCl_3) 2.00 - 2.09 (4 H, m, C-C-H), 3.36 - 3.42 (2 H, m, Ar-C-H), 3.46 - 3.50 (2 H, m, Br-C-H), 7.87 (1 H, d, J = 8.5, Ar-H), 7.97 - 8.07 (3 H, m, Ar-H), 8.13 (2 H, d, J = 8.5, Ar-H), 8.18 (2 H, dd, J = 7.6, 3.5, Ar-H), 8.28 (1 H, d, J = 8.5, Ar-H) ppm; δ_C (126 MHz; CDCl_3) 30.2, 32.6, 33.6, 123.2, 124.7, 124.8, 124.9, 125.0, 125.1, 125.8, 126.7, 127.2, 127.3, 127.5, 128.6, 129.9, 130.9, 131.4, 136.0 ppm (three aliphatic carbons detected rather than four due to overlap as indicated by HSQC NMR spectroscopy) ppm; m/z (MALDI-Dithranol) 339 ([M(^81)Br + H]^+, 100%), 337 ([M(^79)Br + H]^+, 95), 227 (15).

_Sodium 4-(pyren-1-yl)butane-1-sulfonate (5)_3

Na_2SO_3 (4.48 g, 36 mmol) was added to a two neck RBF (250 mL) which was then purged with N_2. 1-(4-Bromobutyl)pyrene (4) (1.00 g, 3.0 mmol) was ground with a pestle and mortar before being taken up in portions into EtOH (6 × 10 mL) with sonication and injected into the reaction flask via syringe. Any remaining unsuspended material after sonication was added, as a slurry in EtOH (10 mL), against a flow of N_2. Water (54 mL) was then added via syringe and the reaction heated to 100 °C overnight. The crude reaction mixture was then concentrated _in vacuo_ and trituated with DCM (2 × 10 mL). The crude product was then recrystallized from an EtOH:water mixture (~1.3:1) (concentrating _in vacuo_) washing the filtered solid with ice cold water (10 mL) and DCM (10 mL). The partially purified material was then recrystallized one further time from an EtOH:water mixture (~1.3:1) (concentrating _in vacuo_ ) to afford the purified title compound (5) (604 mg, 1.6 mmol, 54% yield) as a colorless powder; mp >300 °C. δ_H (500 MHz; methanol- _d_4) 1.94 - 2.03 (4 H, m, C-C-H), 2.87 - 2.92 (2 H, m, SO_3Na-C-H), 3.35 - 3.41 (2 H, m, Ar-C-H), 7.90 (1 H, d, J = 7.9, Ar-H), 7.95 - 8.04 (3 H, m, Ar-H),
8.08 - 8.13 (2 H, m, Ar-H), 8.13 - 8.18 (2 H, m, Ar-H), 8.32 (1 H, d, \( J = 9.14 \), Ar-H) ppm; \( \delta_c \) (126 MHz, methanol-\( \text{d}_4 \)) 26.4, 32.3, 34.3, 52.7, 124.6, 125.9, 126.0, 126.1, 126.3, 126.4, 127.0, 127.7, 128.4, 128.6, 128.7, 130.0, 131.4, 132.5, 133.0, 138.1 ppm; 

\( m/z \) (ESI\(^+\)) 697 ([M – Na + M]\(^+\), 15%), 337 ([M – Na]\(^-\), 100). (ESI\(^+\)) 743 ([M + M + Na]\(^+\), 30%), 383 ([M + Na]\(^+\), 100). HR \( m/z \) (ESI\(^+\)) \([\text{C}_{20}\text{H}_{17}\text{NaO}_3\text{S} + \text{Na}]^+\) requires 383.0694; found 383.0689; \( \bar{\nu}_{\text{max}}/\text{cm}^{-1} \) 3528br and 3475br (SO\(_3\)Na·H\(_2\)O), 3040 (Ar C-H), 2934, 2868 (C-H), 1621, 1603, 1586 (Ar C=C). \( \text{C}_{20}\text{H}_{17}\text{NaO}_3\text{S} \cdot \text{H}_2\text{O} \) requires C, 63.5; H, 5.1; S, 8.5; Na, 6.1%.; found C, 63.6; H, 5.1; S, 8.3; Na, 6.1%.
1.3 Figure S1. NMR spectra for PBBSA, (5)

(a) $^1$H NMR spectrum of (5) in CD$_3$OD.

(b) $^{13}$C NMR spectrum of (5) in CD$_3$OD.
2. rGO/EG Methodology

Initial PSA-rGO Study - Method

Dispersions of GO (GO synthesis in methods section, 1 & 2 mg/mL, 8 mL) and PSA (0-8:1 wt. GO) were mixed and bath sonicated (Elma P70H sonicator, 30 min). L-Ascorbic acid (7:1 wt. GO) was then allowed to dissolve into the dispersion before being heated to 80 °C for 72 h. The mixtures were subjected to bath sonication (15 min) and washing by centrifugation (Thermo Sorvall XTR, 15,000 rpm, 45 min). 75% of the supernatant was removed from each dispersion and replaced with an equivalent amount of DI water. This sonication-washing step was repeated 5 times after which the dispersions were filtered through fine wool to remove any remaining aggregates. Overall, 3 dispersions for each GO conc. and level of PSA were produced and the concentrations were measured by UV-Vis spectroscopy (Thermo Genesys 10s, 660 nm).

GO AND rGO

Figure S2: Optimization of PSA-rGO dispersions

Left: Absorption-over-length for the optimization study with PSA-rGO dispersions. Starting concentration of GO is fixed at 1 and 2 mg/ml, error bars correspond to the standard deviation from multiple measurements experiments. Middle: comparison between “A/l” absorption measurements taken at 660 nm comparing the efficiency of PSA against PBSA for rGO stabilization. Right: rGO concentration using a concentration of 10 mM for both PSA and PBSA, error bar are standard deviation taken for 18 and 5 measurements respectively.
Figure S3.

A. Images from initial PSA study, PSA-rGO dispersions before washing: A, 1 mg/ml initial GO concentration (left-right: 0:1, 1:1, 2:1, 3:1 4:1, 5:1, 6:1, 7:1, 8:1 PSA:GO wt. ratio.)
Figure S3 contd.
B. 2 mg/ml initial GO concentration (left-right: 0:1, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1 PSA:GO wt. ratio)
Figure S4. Raman spectra for GO and rGO flakes

Figure S5. Wide AFM of PBSA-rGO
Figure S6. Wide AFM of starting GO (left) and PSA-rGO (right)

Figure S7. XPS survey spectra for GO (left) and un-stabilized rGO (right)
Figure S8. High resolution C1 spectra of GO (left) and un-stabilized rGO (right) with multi-component peak fitting at fixed FWHM.
Figure S9. Raman 2D spectra of PSA-EG and PBSA-EG with fitting components at fixed FW.
Figure S10: Wide AFM micrographs of PSA-EG (left) and PBSA-EG (right).

[aggregate with flake heights > 8.0 nm have been disregarded in this analysis].
Determination of extinction coefficients

To determine the extinction coefficient for exfoliated graphene we first filtered the dispersion through 0.2 µm filter paper which was weighed before and after filtration. This filtrate was then used for TGA analysis (Fig S11: a and b). It was found that for the PSA dispersions approximately 23 % of the filtrate was graphitic and for the PBSA dispersions approximately 43 % was graphitic. Serial dilutions of the same dispersions were used to create Beer-Lambert plots of the concentration vs absorption over path length (Figure S11: c and d). The concentration was found using the filtered mass and the graphitic fraction. Using the absorption at both 660 nm and 750 nm we calculated the extinction coefficients for the 2 dispersions. We appreciate that the technique we have employed has not been rigorously tested, however our values for extinction coefficient fit very well with the current consensus for the extinction coefficients for exfoliated graphene dispersions from both the Coleman [5] and Texter [6].

Figure S11: Determination of extinction coefficients

![Graph showing TGA analysis and Beer-Lambert plots for PSA and PBSA dispersions.](image)
3. Simulation Experiments

Molecular Dynamics Simulations

The adsorption free energy for each surfactant molecule transferring from bulk solution to the graphene surface was calculated by generating a potential of mean force (PMF), using molecular dynamics as implemented in the GROMACS software [7], version 5.0.4. For each molecule, the initial configuration consisted of an orthorhombic simulation cell (3.68 nm × 3.83 nm × 5.00 nm), with the graphene sheet positioned in the x-y plane at \( z = 0 \), the surfactant molecule placed in the centre of the cell and the remainder of the free space solvated with water. One water molecule was then selected at random and swapped for the Na\(^+\) counter ion. The simulation cell boundaries were periodic in all three dimensions, resulting in a graphene surface infinite in the \( x \) and \( y \)-dimensions.

Both the surfactant molecules and graphene sheet were modelled using parameters taken from the CHARMM force field [8-10] and the TIP3P model [11] was used for water. The full potential energy function and tables containing all the parameters are provided below.

The adsorption free energy was calculated using the umbrella sampling technique [12,13]. The initial configuration was minimized using the steepest descents algorithm. Then, the stabilizer molecule was pulled towards the graphene sheet using a harmonic potential with a force constant of 5000 kJ mol\(^{-1}\) nm\(^{-2}\) at a rate of 0.02 nm ps\(^{-1}\). This simulation was used to generate the initial configurations for all the umbrella sampling simulations, which were chosen on the basis of the \( z \)-component of the stabilizer centre of mass. Twenty simulations were performed for each stabilizer molecule, in the range \( z = 0.3 – 2.2 \) nm, with a spacing of 0.1 nm, employing a harmonic potential with a force constant of 2500 kJ mol\(^{-1}\) nm\(^{-2}\) to constrain the sampling. Only the \( z \)-coordinate of the stabilizer centre of mass was constrained by this potential, enabling the molecule to freely
rotate and translate in the $x$ and $y$ directions. Each simulation was performed for a total of 20 ns and only the forces from the final 19 ns of simulation time were used to generate the PMF. The PMF was obtained by integrating the forces required to keep the molecule at a given $z$-coordinate, saved every 0.1 ps, with the weighted histogram analysis method (WHAM) [14] using the GROMACS analysis tool, g wham [15]. The adsorption free energy was taken as the minimum value in the PMF after shifting the entire curve so that the free energy at $z = 2.2$ nm was equal to zero. The statistical uncertainty in the adsorption free energy was calculated using a bootstrapping resampling procedure with 100 bootstrap samples.

Additional 10 ns simulations of the stabilizer adsorbed to the graphene sheet were used to accurately obtain the total potential energy of interaction between the surfactant and the graphene sheet. In these simulations, the umbrella potential was removed. In the absence of this potential the stabilizer molecules only sampled the region around the global minimum in the PMF, due to the large adsorption free energies observed.

All simulations were performed in the canonical ensemble, with the graphene sheet held rigid for the duration of the simulation. The equations of motion were integrated using a leapfrog algorithm [16] and timestep of 1 fs. The long-range nature of electrostatic interactions was accounted for using the particle-mesh Ewald method (PME) [17,18] using a real-space cut off of 1.2 nm, a maximum Fourier grid spacing of 0.12 nm and 4th order interpolation, resulting in electrostatic energies accurate to approximately $5 \times 10^{-3}$ kJ mol$^{-1}$. Short-range, non-bonded, interactions were modified from 1.0 nm so that the potential tended smoothly to zero at 1.2 nm. A temperature of 298.15 K was regulated using the Nosé-Hoover thermostat [19,20] with a relaxation time constant of 1 ps. The geometry of TIP3P water was constrained using the SETTLE algorithm [21].
Summary of results from MD calculations

Table S1: Surfactant-graphene interaction energies (kJ mol\(^{-1}\)).

| Molecule | Total (kJ mol\(^{-1}\)) | PAH (kJ mol\(^{-1}\)) | -(SO\(_3^−\)) (kJ mol\(^{-1}\)) | -(CH\(_2\)) total (kJ mol\(^{-1}\)) | -(CH\(_2\)) mean (kJ mol\(^{-1}\)) |
|----------|-------------------------|-----------------------|-------------------------------|-----------------------------------|-----------------------------------|
| PSA      | −114.0                  | −93.5                 | −20.5                         | −                                 | −                                 |
| PBSA     | −134.4                  | −95.9                 | −16.3                         | −22.2                             | −5.6                             |

Surfactant-graphene interaction energies (kJ mol\(^{-1}\)). The total interaction energy is the sum of the interaction energies of the polyaromatic hydrocarbon (PAH). In cases where there is more than one substituent group (e.g. CH\(_2\) in the alkyl chains) both the total and the mean energy per group are reported.

Table S2: Energetics for the adsorption process.

| Molecule | \(\Delta A\) (kJ mol\(^{-1}\)) | \(\Delta U\) (kJ mol\(^{-1}\)) | \(-T\Delta S\) (kJ mol\(^{-1}\)) | \(z_{\text{min}}\) (nm) |
|----------|-------------------------------|-------------------------------|----------------------------------|--------------------------|
| PSA      | −52.5                         | −43.5                         | −9.0                             | 0.38                     |
| PBSA     | −72.3                         | −60.4                         | −11.9                            | 0.39                     |

Helmholtz free energy (\(\Delta A\)), internal energy (\(\Delta U\)) and entropy (\(-T\Delta S\)) contributions for the adsorption of surfactant molecules onto the graphene surface and the distance of the surfactant centre-of-mass from the sheet at the free energy minimum (\(z_{\text{min}}\)).
Non-bonded Interaction Parameters

In the CHARMM force field non-bonded forces are computed as the sum of electrostatic and Lennard-Jones 12-6 terms,

\[ V = \sum_{\text{non bonded}} \frac{q_i q_j}{4 \sigma_{ij}^6} + 4 \varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \]  

(S1)

where the cross parameters for unlike atoms, \( \sigma_{ij} \) and \( \varepsilon_{ij} \), are obtained from the Lorentz-Berthelot combining rules,

\[ \sigma_{ij} = \left( \frac{\sigma_i + \sigma_j}{2} \right) \quad \text{and} \quad \varepsilon_{ij} = \left( \frac{\varepsilon_i \varepsilon_j}{2} \right)^{\frac{1}{2}} \]  

(S2)

Non-bonded forces are not computed for atoms separated by fewer than three bonds within the same molecule. The full set of non-bonded interaction parameters used for the surfactant molecules are given in Table S3.

Table S3: Non-bonded interaction parameters used in this work.

| i    | \( \sigma_i \) (nm) | \( \varepsilon_i \) (kJ mol\(^{-1}\)) | \( q_i \) (e) |
|------|---------------------|---------------------------|--------------|
| C1   | 0.355005            | 0.29288                   | 0.000        |
| C2   | 0.355005            | 0.29288                   | −0.115       |
| C3   | 0.358141            | 0.23430                   | −0.180       |
| H1   | 0.242004            | 0.12552                   | 0.115        |
| H2   | 0.238761            | 0.14226                   | 0.090        |
| Na   | 0.243900            | 0.36585                   | 1.000        |
| O    | 0.302906            | 0.50208                   | −0.780       |
| S    | 0.374177            | 1.96648                   | 1.340        |

C1 – aromatic carbon (including graphitic carbon), C2 – aromatic carbon bonded to a hydrogen, C3 – aliphatic carbon, H1 – hydrogen bonded to aromatic carbon, H2 – hydrogen bonded to aliphatic carbon, Na – sodium cation, O – oxygen in a sulfonate group, S – sulfur in a sulfonate group.
**Bonded Interaction Parameters**

In the CHARMM force field bond stretching and angle bending are treated with harmonic potentials (plus a Urey-Bradley term in certain cases) and torsional motions are accounted for using a cosine potential,

\[
V = \sum_{\text{bonds}} \frac{1}{2} k_r (r_{ij} - r_{eq})^2 + \sum_{\text{angles}} \frac{1}{2} k (\theta_{ijk} - \theta_{eq})^2 + \sum_{\text{Urey-Bradley}} \frac{1}{2} k_{ub} (u_{ik} - u_{eq})^2 + \sum_{\text{dihedrals}} k [1 + \cos(n \phi_{ijkl} - \phi_{eq})]
\]  

(\text{S3})

where \(r_{ij}\) is the distance between atoms \(i\) and \(j\), \(\theta_{ijk}\) is the angle between atoms \(i, j\) and \(k\), \(u_{ik}\) is distance between atoms \(i\) and \(k\) in the \(\theta_{ijk}\) angle, and \(\phi_{ijkl}\) is the angle formed between a plane defined by the atoms \(i, j\) and \(k\), and a plane defined by atoms \(j, k\) and \(l\), respectively. The parameters \(k_r\), \(k_\theta\), \(k_{ub}\) and \(k_\phi\), are the force constants for bond stretching, angle bending, the Urey-Bradley component and dihedral angle rotation. \(r_{eq}\), \(\theta_{eq}\) and \(u_{eq}\) are the equilibrium values of the bond distance, bond angle and Urey-Bradley 1,3-distance. \(n\) and \(\phi_{eq}\) are the multiplicity and angle at which the torsional motion passes through its minimum value. The full set of bonded interaction parameters used in this work is given in Tables S4 – S6.

**Table S4: Parameters for bond stretching.**

| \(i\)  | \(j\)  | \(r_{eq}\) (nm) | \(k_r\) (kJ mol\(^{-1}\) nm\(^{-2}\)) |
|--------|--------|-----------------|----------------------------------|
| C1/C2  | C1/C2  | 0.1375          | 255224.0                         |
| C1     | C3     | 0.1490          | 192464.0                         |
| C1     | S      | 0.1780          | 192464.0                         |
| C2     | H1     | 0.1080          | 284512.0                         |
| C3     | C3     | 0.1530          | 186188.0                         |
| C3     | H2     | 0.1111          | 258571.2                         |
| C3     | S      | 0.1807          | 154808.0                         |
| O      | S      | 0.1448          | 451872.0                         |
Table S5. Parameters for angle bending and the Urey-Bradley component.

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| i  | j  | k  | $\theta_{eq}$ (°) | $k_\theta$ (kJ mol$^{-1}$ rad$^{-1}$) | $u_{eq}$ (n) | $k_{ab}$ (kJ mol$^{-1}$ nm$^{-2}$) |
| C1/C2 | C1/C2 | C1/C2 | 120.0 | 334.7200 | 0.241 | 29288.0 |
| C1/C2 | C1/C2 | C3   | 120.0 | 383.2544 | 0.000 | 0.00000 |
| C1/C2 | C1/C2 | H1   | 120.0 | 251.0400 | 0.215 | 18409.6 |
| C1/C2 | C1/C2 | S    | 122.3 | 83.68000 | 0.000 | 0.00000 |
| C1/C2 | C3   | C3   | 107.5 | 433.4624 | 0.000 | 0.00000 |
| C1/C2 | C3   | H2   | 107.5 | 412.5424 | 0.000 | 0.00000 |
| C1/C2 | S    | O    | 98.00 | 711.2800 | 0.000 | 0.00000 |
| C3   | C3   | C3   | 113.6 | 488.2728 | 0.256 | 9338.69 |
| C3   | C3   | H2   | 110.1 | 221.7520 | 0.217 | 18853.1 |
| C3   | C3   | S    | 105.5 | 359.8240 | 0.000 | 0.00000 |
| C3   | S    | O    | 99.00 | 669.4400 | 0.000 | 0.00000 |
| H2   | C3   | H2   | 109.0 | 297.0640 | 0.180 | 4518.72 |
| H2   | C3   | S    | 109.0 | 410.0320 | 0.000 | 0.00000 |
| O    | S    | O    | 109.5 | 1087.840 | 0.245 | 29288.0 |
Table S6. Parameters for torsional rotation

|   | i      | j      | k      | l      | $\phi_{eq}$ (°) | $k_\phi$ (kJ mol$^{-1}$) | n   |
|---|--------|--------|--------|--------|-----------------|--------------------------|-----|
| 1 | C1/C2  | C1/C2  | C1/C2  | C1/C2  | 180.0           | 12.97040                 | 2   |
| 2 | C1/C2  | C1/C2  | C1/C2  | C3     | 180.0           | 12.97040                 | 2   |
| 3 | C1/C2  | C1/C2  | C1/C2  | H1     | 180.0           | 17.57280                 | 2   |
| 4 | C1/C2  | C1/C2  | C1/C2  | S      | 180.0           | 12.97040                 | 2   |
| 5 | C1/C2  | C1/C2  | C3     | C3     | 180.0           | 0.962320                 | 2   |
| 6 | C1/C2  | C1/C2  | C3     | H2     | 0.000           | 0.008368                 | 6   |
| 7 | C1/C2  | C1/C2  | S      | O      | 0.000           | 0.016736                 | 6   |
| 8 | C1/C2  | C3     | C3     | C3     | 0.000           | 0.167360                 | 3   |
| 9 | C1/C2  | C3     | C3     | H2     | 0.000           | 0.167360                 | 3   |
|10 | C5     | C1/C2  | C1/C2  | H1     | 180.0           | 10.04160                 | 2   |
|11 | C3     | C3     | C3     | C3     | 0.000           | 0.269868                 | 2   |
|12 | C3     | C3     | C3     | H2     | 0.000           | 0.815880                 | 3   |
|13 | C3     | C3     | S      | O      | 0.000           | 0.962320                 | 3   |
|14 | H1     | C1/C2  | C1/C2  | H1     | 180.0           | 10.04160                 | 2   |
|15 | H2     | C3     | C3     | H2     | 0.000           | 0.920480                 | 3   |
|16 | H2     | C3     | C3     | S      | 0.000           | 0.041840                 | 1   |
|17 | H2     | C3     | S      | O      | 0.000           | 0.794960                 | 3   |
Adsorption of Multiple Surfactant Molecules

To study the cooperative adsorption of multiple surfactant molecules, simulations with higher concentrations were considered. In these simulations, a larger graphene sheet, periodic in the \( x,y \)-plane, was positioned at the bottom of a simulation box \( (z = 0 \text{ nm}) \) with dimensions of \( 5.16 \text{ nm} \times 5.11 \text{ nm} \times 7.5 \text{ nm} \). An aqueous solution, consisting of 25 randomly distributed surfactants and \( \text{Na}^+ \) counterions, and solvated with approximately 3600 \( \text{H}_2\text{O} \) molecules, was positioned on the surface. This setup allowed for a 3.5 nm vacuum gap at the top of the simulation cell, in order to prevent interactions between the solution and the opposite face of the graphene surface via the periodic boundary. The initial configuration for this simulation is shown in Figure S14a.

Surfactant molecules initially far from the surface displayed a propensity to aggregate and adsorb to the water-vacuum interface. In order to avoid this, the surfactants were first pulled towards the surface gradually, at a rate of 0.002 nm ps\(^{-1}\), using a harmonic potential with a force constant of 5000 kJ mol\(^{-1}\) nm\(^{-2}\) during a 1.5 ns simulation. The configuration at the end of this simulation is shown in Figure S14b. The final 40 ns of the simulation trajectory was used to calculate the density profiles of the components of the solution in contact with the graphene surface.
Figure S12: Aggregation of PSA

(a) depiction of the aggregation of PSA in the aqueous phase; (b) as with (a) but now indicating water of solvation; (c), (d) and (e) provides an indication of the various configurations taken up by single molecule of PSA with respect to the graphene surface.

Figure S13: Aggregation of PBSA

(a) depiction of the aggregation of PBSA in the aqueous phase; (b) as with (a) as but now indicating water of solvation; (c), (d) and (e) provides an indication of the various configurations taken up by a single molecule of PBSA with respect to the graphene surface.
Figure S 14: PBSA adsorption simulation study.

Snapshots from the multiple surfactant PBSA adsorption simulations for a) the initial configuration, b) after the surfactants have been pulled towards the surface using the harmonic restraining potential.
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