New Method to Predict the Surface Tension of Complex Synthetic and Biological Polyelectrolyte/Surfactant Mixtures

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Electronic Supporting Information

Part 1: Experimental Details

Materials

Pure H_2O was generated by passing deionized water through a Milli-Q purification system (total organic content = 4 ppb; resistivity = 18 mΩ.cm). Poly(sodium styrene sulfonate) (NaPSS; 1 MDa; Aldrich) was purified by Amicon Ultra-15 Centrifugal Filter Units (30kDa molecular weight cut-off) in pure H_2O to give a stock solution of ~ 20000 ppm (determined by gravimetric analysis) free of low molecular weight impurities. Hydrogenous dodecyltrimethylammonium bromide (DTAB or hDTAB; Sigma; 99.9 %) was recrystallized twice in acetone, and each time the solutions were cooled over several hours to maximize the purity. Deuterated DTAB (dDTAB; Oxford Deuteration Facility) was kindly provided by Dr. R. K. Thomas and was used as received. DNA from salmon testes (Sigma Aldrich) was used as received. The DNA solutions all contained 10 mM NaBr (Merck; 99.99 %). The solvent for neutron reflectometry measurements was either pure D_2O (Euriso-top, Saclay, France or Sigma Aldrich) or a mixture of 8.1 % by volume D_2O in H_2O called air contrast matched water (ACMW).

Sample Preparation Methods

The solutions made all comprised 100 ppm polyelectrolyte (either NaPSS or DNA) with DTAB at various concentrations at 25 ºC. All NaPSS/DTAB mixtures were prepared in pure water and

all DNA/DTAB mixtures were made in 10 mM NaBr. A standard mixing[SI1] approach was used to ensure that the mixing of the oppositely charged components took place under reasonably well-defined conditions. These protocols were used to limit the formation of kinetically-trapped aggregates due to concentration gradients present during mixing.[SI2] To mix each solution, equal volumes of 200 ppm polyelectrolyte and double the intended concentration of DTAB were poured together simultaneously. The solution was then swirled gently for a few seconds. For measurements on fresh samples (turbidity, electrophoretic mobility and surface tensiometry), the mixtures were immediately transferred into cuvettes. For measurements on aged samples, fresh mixtures were transferred into 4 mL glass vials (UV-Vis spectroscopy and surface tensiometry) or 100-mL glass bottles (NR), in which they were left for the stated time. Afterwards, 1 mL of supernatant was pipetd from each vial (UV-Vis spectroscopy and surface tension) or 30 mL was pipetd from each bottle (NR) for immediate measurement. Care was taken not to agitate any precipitate that had sedimented on the bottom of the flask given that we have demonstrated previously that such agitation to the precipitate can redisperse enough surface-active material to result is a marked effect on the interfacial properties.[SI3] The only difference in the sample preparation of the DNA/DTAB mixtures was that to help the mixing of the components gentle magnetic stirring (300 rpm) was used during mixing. Where stated the supernatant of DNA/DTAB samples were centrifuged to remove the residual fine suspension of aggregates. A Hettich 22R centrifuge was used at 16000 rpm for 15 min. for the surface tension measurements and an Eppendrof 5804 R centrifuge was used at 11000 rpm for 15 min. for NR measurements.

UV-Vis Spectroscopy

The turbidity of NaPSS/DTAB and DNA/DTAB solutions was measured using a Perkin-Elmer Lambda 2 UV-Vis Spectrophotometer with a semi-micro quartz cell having a 1-cm path length. In each case the optical density of the samples was determined at 400 nm (O.D.$_{400}$). Measurements were carried out five minutes after mixing (fresh) or immediately after extracting the supernatant (aged). Since neither the polymer nor the surfactant has an adsorption band above 350 nm, the increasing O.D.$_{400}$ values indicate the formation of larger aggregates.

Electrophoretic Mobility

A Malvern Zetasizer NanoZ instrument was used to measure the electrophoretic mobility of the NaPSS/DTAB and DNA/DTAB complexes using the M3-PALS technique. All the measurements were performed at 25 °C. The standard error in the values of the electrophoretic mobility was around 10 %. Measurements were always performed on freshly mixed samples.

Gravimetric Analysis

NaPSS/DTAB solutions (300 mL) were prepared in 500 mL glass bottles and were left to age and settle for one month. After this time 209 mL of the supernatant was transferred by glass pipet into a glass dish with known mass. It was dried through heating by steam from a water bath then was placed in a vacuum drier at 60 ºC for a few hours. The dish was removed warm from the vacuum drier and was placed to cool to ambient temperature in a desiccator (above dry calcium chloride) for 15 min. The heating and drying procedure was repeated for 3 or 4 cycles until constant mass was reached. This calculation takes the simplest approach of assuming an average stoichiometry of polyelectrolyte/surfactant in the precipitate of unity, i.e., all of the sodium counterions in the polyelectrolyte are replaced by dodecyl trimethyl ammonium ions.

Surface Tensiometry

The surface tension measurements were done using a home-built pendant drop apparatus. The experimental setup has been described elsewhere.[SI4] The pendant drop was created at the tip of a PTFE capillary which joined a gas-tight Hamilton syringe placed in a computer-controlled syringe pump. The drops were formed in a closed, temperature-controlled chamber with an internal size of $1 \times 2 \times 5$ cm. To avoid the evaporation of the pendant drop, the side walls of the chamber were covered with wetted filter paper. The applied experimental procedure was as follows: by turning on the syringe pump, a series of drops were formed at the tip of the capillary, thus ensuring the creation of a fresh surface. The time required for the formation of a pendant drop was approximately 1 s. After the formation of the third pendant drop, the syringe pump was stopped and the monitoring of the drop shape started (t = 0). A picture of the pendant drop was taken every ~2 s, and then the recorded sequential digital images were used for the calculation of the temporary surface tension values giving rise to the surface tension versus time function. The surface tension values were read after 30 minutes to describe the local surface equilibrium characteristic for the investigated state of the system (freshly mixed or aged).
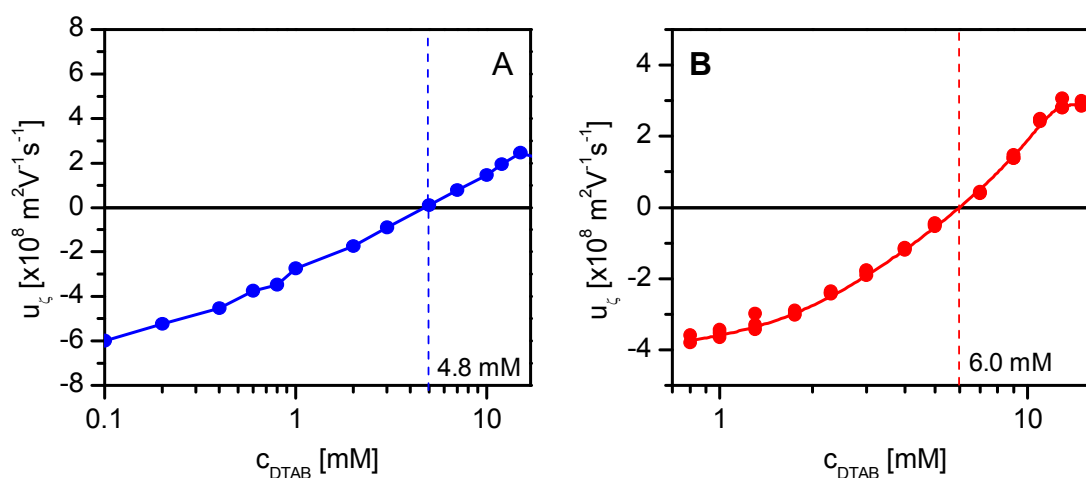
Neutron Reflectometry (NR)

NR measurements were performed on the horizontal neutron reflectometer FIGARO at Institut Laue-Langevin (Grenoble, France).[SI5] The time-of-flight instrument was used with a chopper pair giving neutron pulses with 4.0% $d\lambda/\lambda$ in the wavelength range $\lambda = 2$–30 Å. Data acquisitions were carried out at incident angles of 0.62° and 3.8°. Samples were left to reach steady state for around 2 hr prior to each measurement, and satisfactory matching of data from the two different

incident angles showed that the interfacial layers were not changing during the measurements. The neutron reflectivity profiles presented show the intensity ratio of neutrons in the specular reflection to those in the incident beam with respect to the momentum transfer, Q, defined by

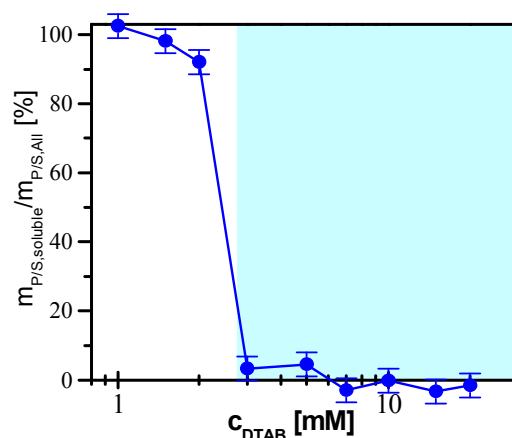$$Q = \frac{4\pi \sin\theta}{\lambda} \tag{1}$$

where θ is the incident angle. Samples of pure DTAB solution for the surface tension to surface excess calibration were measured in the isotopic contrast dDTAB/ACMW only at the lower incident angle. Samples for measurement of the interfacial composition of NaPSS/DTAB mixtures were made in the isotopic contrasts NaPSS/dDTAB/ACMW and NaPSS/dDTAB/D$_2$O; note that it would be usual to complement such samples with those comprising NaPSS/hDTAB/D$_2$O but we noted that the precipitate floated resulting in different surface properties. The data from the NaPSS/dDTAB/ACMW and NaPSS/dDTAB/D$_2$O isotopic contrasts were fitted using the structural model described in part 4. Samples for each measurement of the interfacial composition of DNA/DTAB mixtures were made in the isotopic contrasts DNA/cmDTAB/ACMW and DNA/dDTAB/ACMW, where cmDTAB is 4.4% dDTAB in hDTAB to give it a scattering length density matched to air. Data were recorded at the lower incident angle, and the scattering excesses measured for the two samples were used to solve uniquely the interfacial composition.

Part 2: Electrophoretic Mobility

Figure SI1. Electrophoretic mobility of freshly mixed (A) 100 ppm NaPSS/DTAB complexes and (B) 100 ppm DNA/DTAB complexes in 10 mM NaBr, each as a function of the bulk surfactant concentration. The vertical dashed lines mark the points of charge neutrality.

Part 3: Gravimetric Analysis

Figure SI2. Gravimetric analysis of 100 ppm NaPSS/DTAB mixtures to show the proportion of complexes which remain soluble or suspended in the bulk liquid of aged NaPSS/DTAB mixtures left for 4 weeks to equilibrate; the blue shaded area marks the phase separation region.
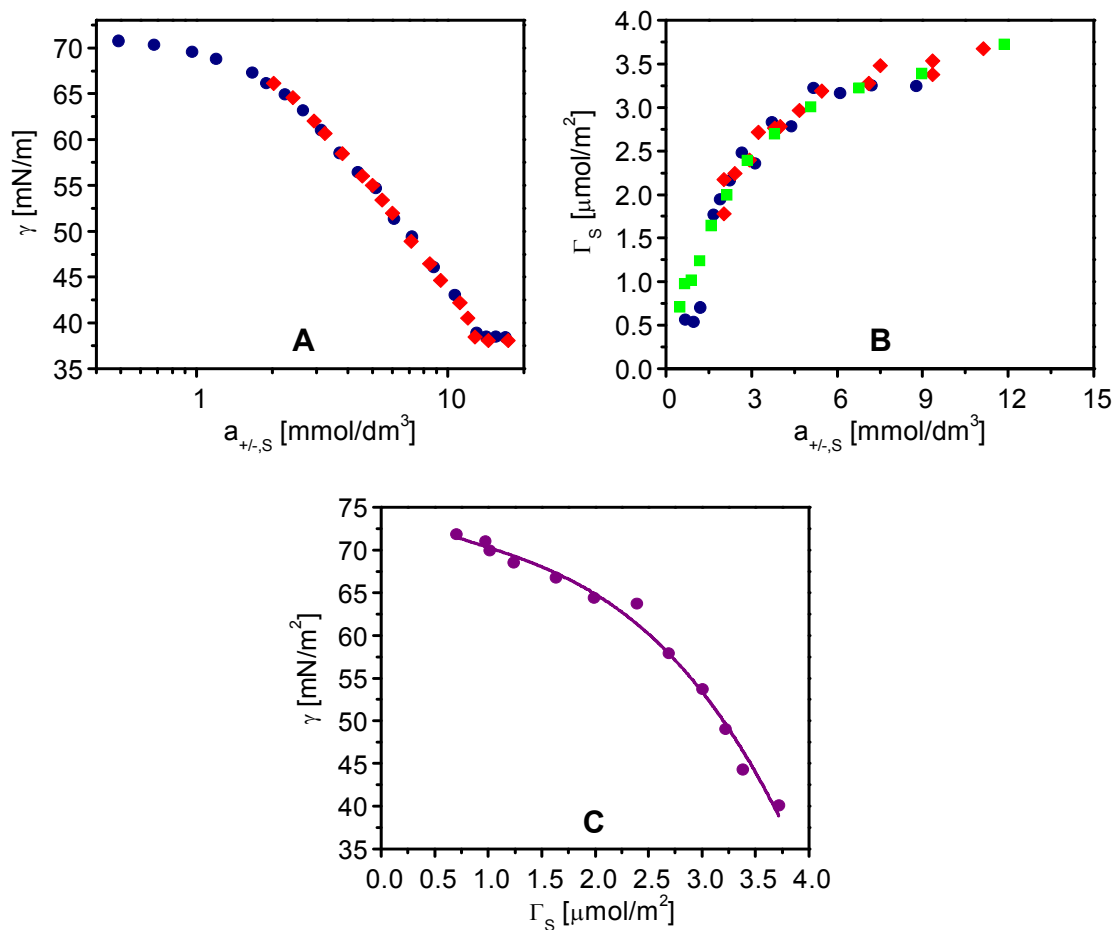
Part 4: NR Data Evaluation

(A) Pure DTAB

We need to relate the surface tension and surface excess for DTAB solutions in pure water and in 10 mM NaBr to calculate the surface tension from the measured surfactant surface excess of aged polyelectrolyte/surfactant mixtures using the approximation that they may be treated as depleted surfactant solutions after comprehensive precipitation had taken place. Measurements of the surface tension of DTAB solutions both in pure water and in 10 mM NaBr are shown in fig. SI3A. The isotherms, plotted in terms of the mean activity of the surfactant, are identical to within the experimental error, which means that the derived adsorption isotherms also coincide to within the experimental error (SI3B). Thus the relationship between the surface tension and surface excess of the surfactant is equivalent in pure water and in 10 mM NaBr, and only one calibration plot is required. The surface excess of dDTAB in ACMW was also measured directly using NR; see fig. SI3B. The NR data were fitted using Motofit[SI6] to a one-layer model to give

$$\Gamma_S = \frac{\sigma d}{b \, N_A} \tag{2}$$

where Γ_S is the surfactant surface excess, σ is the scattering length density and d is the thickness of the layer, b is the scattering length of dDTAB (286 fm) and N_A is Avogadro's number. These values are consistent with those derived from the isotherms yet the data have lower scatter. The

surface tension values in pure water (fig. SI3A) were interpolated using a third order polynomial function to generate the calibration plot between the surface tension and surface excess values measured using NR (fig. SI3B) shown in fig. SI3C. A third order polynomial function was then used to calculate the surface tension values shown in figs. 1B and 3B of the main text.

Figure SI3. (A) Surface tension isotherms of DTAB measured in H_2O (blue circles) and in 10 mM NaBr (red diamonds). (B) Surface excess of DTAB with respect to the bulk surfactant activity measured using NR (green squares) and converted using Gibb's equation from the surface tension data measured in H_2O (blue circles) and in 10 mM NaBr (red diamonds). (C) Calibration plot of surface tension to surface excess for DTAB solutions: interpolated surface tension values from panel A with respect to the surface excess data in panel B, and the resulting polynomial fit to these data (line).

(B) NaPSS/DTAB

First, a fit to the reflectivity profile of air/D_2O gave the measured scattering length density of D_2O (6.26×10^{-6} Å^{-2}) and a residual background of 5×10^{-7}, which were then constrained for all other measurements using D_2O.

Second, reflectivity profiles of 13.6 mM dDTAB/ACMW and dDTAB/D$_2$O were co-modeled to derive a structural model for the surfactant monolayer, which is necessary when fitting data in multiple isotopic contrasts over the whole Q range. A two-layer model was used comprising the surfactant chains above hydrated headgroups/counterions; a one-layer model did not result in satisfactory fits. The thickness of the top layer was fitted using a scattering length density of 7.00 x 10^{-6} Å^{-2}; scattering length = 246.53 fm; volume = 352 Å^3.[SI7] The volume fraction of the bottom layer was fitted using a constant thickness of 3 Å. The fit was constrained to preserve the same number of chains, headgroups and counterions, i.e., if the volume fraction were 100% the scattering length density would be 0.18 x 10^{-6} Å^{-2}; scattering length = 2.43 fm; volume = 133 Å^2 derived from that of the whole surfactant (485 Å^3 from ref. SI8) minus that of the chain (352 Å^3 from ref. SI7). A check was carried out that the inclusion of a dummy layer of hydrated NaPSS underneath the surfactant resulted in a fit of zero surface excess.
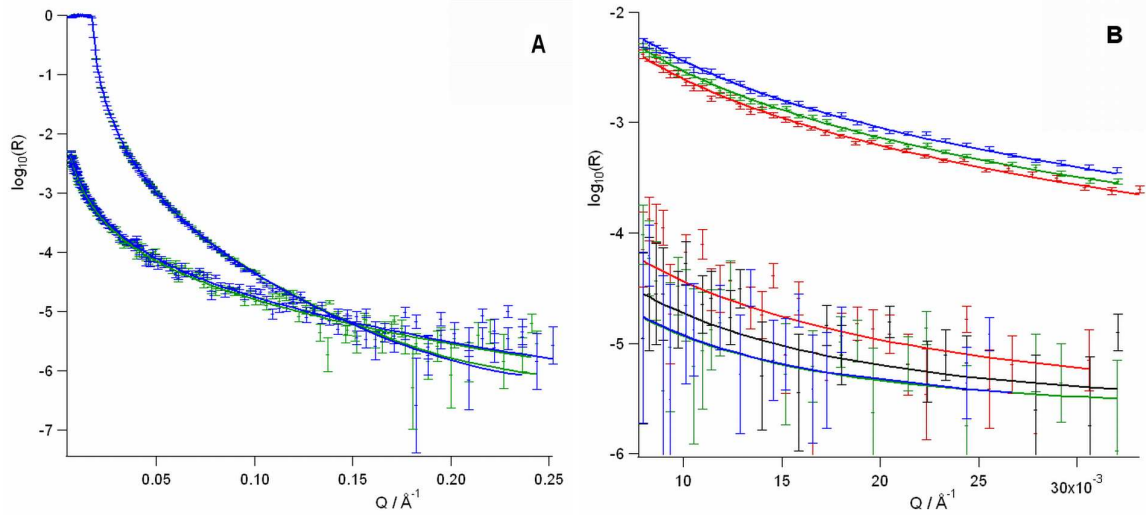
Third, reflectivity profiles of NaPSS/dDTAB/ACMW and NaPSS/dDTAB/D$_2$O were modeled using three layers: surfactant chains above hydrated headgroups/counterions above hydrated polymer. The polymer surface excess converged to zero for both bulk compositions measured, providing evidence that the system may be successfully treated as a depleted surfactant solution after the dynamic changes to the bulk phase behavior have finished. The surfactant surface excesses of 2.33 µmol m^{-2} for 3.5 mM DTAB and 2.46 µmol m^{-2} for 4.0 mM DTAB were used to calculate the surface tension of the mixture using the calibration plot in fig. SI3C, as shown as black crosses in fig. 1B of the main text. Fig. SI4A shows the reflectivity profiles and fits.

(C) DNA/DTAB

A more direct approach was taken to derive the interfacial composition of aged DNA/DTAB samples in 10 mM NaBr. Reflectivity profiles were recorded at low Q in the isotopic contrasts DNA/cmDTAB/ACMW and DNA/dDTAB/ACMW with the former contrast only sensitive to DNA and the latter contrast sensitive to both DNA and surfactant. The scattering length density (σ) and thickness (d) of a single interfacial layer may be fitted at low Q with the product insensitive to details of a more complex model (as shown for another mixture in the Supporting Information of ref. SI9). The derived products of scattering length density and thickness were related to the interfacial composition through the solving of the following equations

$$(\sigma d)_1 = N_A \, b_{DNA} \Gamma_{DNA} \tag{3}$$

$$(\sigma d)_2 = N_A \left(b_{DNA} \Gamma_{DNA} + b_{dDTAB} \Gamma_{dDTAB} \right) \tag{4}$$

Figure SI4. (A) Neutron reflectivity profiles of 100 ppm NaPSS/DTAB/ACMW and NaPSS/DTAB/D$_2$O mixtures involving 3.50 mM (green) and 4.00 mM (blue) DTAB where the data with lower reflectivity at low Q involve the ACMQ subphase and the data with higher reflectivity at low Q involve a D$_2$O subphase. (B) Reflectivity profiles of air/ACMW (black) and 100 ppm DNA/DTAB/ACMW mixtures of 1.75 mM (red), 3.24 mM (green) and 6.00 mM (blue) DTAB where the data nearer the bottom of the figure involve cmDTAB and the data nearer the top involve dDTAB.

Fig. SI4B shows reflectivity profiles and the resulting fits of three bulk compositions of DNA/DTAB mixtures in the two isotopic contrasts as well as pure ACMW. The fitted values of σd are listed in the third column of Table 1. Note that when one quantifies very low scattering signals in ACMW it is necessary to correct for the scattering signal from subphase. It is insufficient simply to fit the background due to a positive contribution to σd which results from the statistical errors in the data and the fact that only positive values of the model are physically realistic. It is also insufficient to subtract the fitted reflectivity of the pure ACMW data from those of the mixtures as a positive contribution to σd remains, albeit smaller. Therefore we took the approach to subtract the fitted value of σd for pure ACMW from the fitted values of σd for the data recorded in the isotopic contrast DNA/cmDTAB/ACMW. Note that it is not appropriate to take the same approach for the data recorded in the isotopic contrast DNA/dDTAB/ACMW because the positive contribution to σd from statistical errors in the data is not linear. Nevertheless, it is quite clear that to within the error of the measurements there is no DNA at the interface of the supernatant of aged DNA/DTAB mixtures; one sample exhibited a slightly higher value of σd while the other two samples were slightly lower. The values of the

surfactant surface excess listed in Table 1 were used to calculate the surface tension of the mixture using the calibration plot in fig. SI3C, as shown in fig. 3 of the main text.

Table 1. The fitted values of σd before and after the correction described in the text and Γ for DNA/DTAB mixtures measured using NR.

Isotopic Contrast in ACMW	[DTAB] (mM)	σd (x 10^{-5} Å^{-1}) Before Correction	σd (x 10^{-5} Å^{-1}) After Correction	Γ (mol m^{-2})*
pure	0.00	1.073	0.000	0.00
DNA/cmDTAB	1.75	1.549	0.476	0.020
DNA/cmDTAB	3.24	0.811	−0.262	−0.011
DNA/cmDTAB	6.00	0.822	−0.251	−0.011
DNA/dDTAB	1.75	7.727	7.727	2.55
DNA/dDTAB	3.24	8.397	8.397	2.93
DNA/dDTAB	6.00	9.330	9.330	3.24

* The DNA surface excess was calculated per moles of base pairs of volume 1178 Å^3.[SI10]

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