Structure of Rod-like Polyelectrolyte-Surfactant Aggregates in Solution and

in Adsorbed Layers

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Abstract

Polyelectrolyte-surfactant aggregates (PES) have diverse sets of properties, which could be controlled by a wide range of parameters, both within the aggregates themselves and the surrounding environment. The large portfolio of applications amplifies the need to understand them. A particular system of polyelectrolyte-surfactant aggregate, polycetyltrimethyl vinylbenzoate, denoted $pC_{16}TVB$, which self-assembles in aqueous solution, is the main focus of the thesis. Its structure is the product of the balance between surfactant head groups – polyelectrolyte charge groups electrostatic interactions and surfactant tails – polyelectrolyte backbone hydrophobic interactions. At neutral solution pH, the structure is one of a core-shell cylinder, with the shell consisting of surfactant heads. The surfactant tails point toward the core center, while the polyelectrolyte also resides in the core, but remains close to the core-shell interface for charge neutralization. As the pH drops to 1.0, the balance is disrupted with the hydrophobic interaction being increasingly dominant while electrostatic interaction is reduced, and the structure transforms into a more commonly seen string-of-pearl, in which the polymer chain connects a series of spherical surfactant micelles. The solution properties are impacted accordingly, becoming viscoelastic while solubilizing 10 times more hydrophobic molecules.

Treating the $pC_{16}TVB$ aggregate as a whole, its adsorption onto oxide nanoparticles surfaces has been analyzed, extended from a previous flat surface adsorption work. Aided by hydrophobic dyes as molecular trackers, the adsorbed thickness has been proven to be a function of the surface curvature, with less curve surface adsorbs more material. The dye loading remains intact after the adsorption, enabling the use of the aggregate as a delivery vehicle for hydrophobic materials in aqueous solution. The resulting adsorption of $pC_{16}TVB$ aggregate onto SiO₂ surfaces has a core-shell sphere structure. Unlike for flat surfaces, in which the adsorption mechanism has been shown previously to consist of two main steps, with some dissociated surfactant molecules adsorbing head first via electrostatic attraction with the surface to create hydrophobic anchor points for further aggregate adsorption, the high bending energy cost and the low aggregate concentration (relative to the total sphere surface area) suspend the adsorption after the initial surfactant adsorption step.

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Chapter 1

Introduction and background

1.1 Background

For the last century, there has been considerable interest in understanding suspensions of colloid particles, mainly due to their extensive applications as thickeners in fabric and hair conditioners, foodstuffs, paints, cosmetics, and others.¹ These suspensions typically have multiple components, including different particle types and/or sizes, additives, and solvents. Among the components, polymers, typically characterized by their persistence length L_p and contour length L, are among the most common.¹ The presence of polymeric additives has almost limitless possible impact on fluid structure and interactions.²⁻ ⁷ Rods, expanded from the polymer chain models but with significant diameter D_r, have also been studied.⁸⁻¹⁴ Rod flexibility, characterized as the ratio between contour length and persistence length L/L_p, has been found to enhance depletion forces in a colloidal suspension.¹⁵⁻¹⁷

One system that often has the shape of a rod is polymer-surfactant (PES) aggregates in aqueous solution. These aggregates possess both the nanoscale structure of micelles and the larger length scales relevant in polymeric solutions. The specific interactions between the polymer and surfactant control the stability, structure and properties of the aggregates and solutions. The presence of PES aggregates alters both the bulk solution properties, and the interfacial properties, including those of the solid-liquid¹⁸⁻²¹ and liquid-liquid²²⁻²⁵ interfaces. Insoluble aggregates find applications in nanoscale templating^{26,27} while soluble aggregates

extend the general application of surfactants, control protein conformation and manipulate interfacial properties.²⁸⁻³⁰

Previously, a unique PES material has been synthesized in our laboratory. The structure of the aggregate of a cationic surfactant, cetyltrimethylammonium $C_{16}TA^+$, and an anionic polymer, polyvinylbenzoate, pVB, at the condition of neutral solution pH has been proposed in previous work,³¹⁻³⁶ and shown in Figure 1.1. The PES aggregate, denoted pC_nTVB , exists as a cylinder of surfactants with the polyelectrolyte chain trapped in the core; the radius is determined by the surfactant tail length, which is several nanometers for typical C_nTAB , with 12 < n< 18, while the length by the polyelectrolyte, varying from 80nm to hundreds of nanometers. Each aggregate contains, on average, one to two polymer chains which maintain the structure and are located at the interface between the aggregate core and the aqueous bulk.³² At a 1:1 molar ratio of surfactant molecules to charge groups on the polyelectrolyte, these aggregates are rod-like in aqueous solution with low surface charge and minimal interparticle interactions.^{31,32,35} This leads to structural stability against changes in temperature (up to 50°C),^{32,33} concentration (600 mg/ml or above),³⁷ ionic strength (up to 300mM of NaCl or similar levels of other monovalent and multivalent salts)³⁵ and when adsorbed irreversibly at solid-liquid interfaces.³⁸⁻⁴¹ Freeze-drying (lyophilization) and re-suspension do not alter the aggregate properties, and neither does long-term storage. This structure has been confirmed by nuclear magnetic resonance (NMR), small angle neutron scattering (SANS), static light scattering (SLS) and dynamic light scattering (DLS), among other techniques.



Figure 1.1: The proposed $pC_{16}TVB$ aggregate structure at neutral pH and 1:1 molar ratio of VB⁻:C₁₆TA⁺.

1.2 Thesis objectives

This thesis aims to improve the knowledge of the inter- and intraaggregate interactions of various commonly encountered colloidal species, such as surfactants, polymers, and metal oxide nanoparticles. In the case of the $pC_{16}TVB$ aggregate, this knowledge consists of understanding i) the aggregate structures in different solution conditions, which change the properties of the individual surfactant and polymer components, how they interact with each other, and with the surrounding solvents, ii) the ability of the aggregate to solubilize different hydrophobic dyes, or the interactions of the aggregate with small molecules and iii) the ability of the aggregate to adsorb onto oxide nanoparticles, or the interactions of the aggregate with larger particles.

In aqueous solution, the equilibrium structure of $pC_{16}TVB$ has been proposed previously to be a semi-flexible rod. In chapter 3, scattering techniques have been used to provide direct evidence of the structure, in particular, the distribution of various components within. Aided by the deuteration of the surfactant molecules, contrast matching data indicates a core-shell cylindrical structure, with the shell made up of surfactant head groups, while the polymer chain resides in the core and most likely assumes a worm-like chain conformation.

Chapter 4 further explores the local effects of the solution conditions on the interactions between the surfactant molecules, the polymer chain, and the solvent molecules. By lowering the solution pH, the electrostatic attraction between the surfactant molecule and the polymer chain decreases, while the hydrophobicity of the same chain increases. Together with the neutralization of a large fraction of the VB⁻ groups which act as counterions, the new balance of interactions in the system suggests that the structure reverts to "string-of-pearl", or "necklace", a more commonly observed conformation for this type of system. In a necklace structure, a numbers of spherical micelles are connected by the polymer chain, with gaps between adjacent spheres. Although not necessarily involved in the structure formation, the protonated carboxylic groups introduce more hydrogen bonds into the system, which plays a major role in inter-aggregate interactions and network formation.

In chapter 5, the macroscopic effects provided by lowering the solution pH, illustrated by experimental evidence from small angle neutron scattering, static light scattering, dynamic light scattering, nuclear magnetic resonance, and potentiometry via surfactant sensitive electrode, are consistent with the proposed necklace structure. The cross section remains the same, while the hydrodynamic diameter doubles, in agreement with the expected drop in micellar packing factor and the very little dissociation of surfactant molecules from the aggregate during

the cylinder-sphere transition. The exposed segments of the polymer chain, which reside in the gaps between the spheres, have also been detected. Hydrogen bonding capacity manifests in the dependence of the hydrodynamic diameter on temperature and PES aggregate concentration, and the network structure in the viscoelastic solution at low pH. All structural transformations can be reversed with the addition of a strong base to return the solution pH to neutral.

In the next two chapters, chapter 6 and chapter 7, the aggregate is treated as a whole, and its interactions with other particles become the focus. In chapter 6, hydrophobic dyes, including pyrene and Nile Red, solubilize onto these PES aggregates. The solubilization starts at very low aggregate concentration, while the solubilizing power, which is already high at neutral pH, could be improved by a factor of ten at acidic conditions, a major advantage for the potential use of the aggregate as a solubilizing agent. Using the solubilized dyes to track the location of PES aggregate, the adsorption of the aggregate onto TiO_2 and SiO_2 nanoparticles is analyzed. The adsorption has no effect on the location of the solubilized dye molecules inside the aggregate, and no dye desorption is observed. The nature of the solid surfaces plays a major role in the adsorption, with the more negative SiO₂ adsorbs more aggregates due to its stronger electrostatic attraction with the surfactant head groups. The sorption behavior enables the aggregate to be used as a potential delivery vehicle for hydrophobic molecules from aqueous solutions onto solid surfaces, such as in coating applications.

The study on the adsorption of the PES aggregates onto SiO₂ nanoparticles is continued in chapter 7 using scattering techniques. While previous work established that the aggregate adsorbs onto flat SiO₂ surface following a two-step mechanism, which is then extended onto the curved surface in chapter 6, the structure of the resulting PES-SiO₂ nanoparticle aggregate is not known. Neither is the effect of the surface curvature, both of which are the focus of this chapter. The semi-flexible PES aggregate has been found to adsorb onto the SiO₂ nanosphere surface to form core-shell sphere aggregate with negligible interaggregate interaction. The thickness of the adsorbed layer is a function of the sphere curvature, with less curved surface adsorbs more rods. Combining with the previously obtained flat surface adsorption data, the trend extends all the way to the flat surface. Furthermore, for the smallest spheres, with high specific surface areas, only the initial step of surfactant adsorption creating hydrophobic anchor takes place. The next step of rod adsorption to these anchor points is suspended, due to either the insufficient number of anchor points per surface area or the bending energy cost that is too high to be overcome.

This thesis aims to show the versatility of the polyelectrolyte-surfactant (PES) aggregate structure, and hence its solution properties, while still retaining its robustness at each individual set of solution conditions. Extending the previous works by Kline,³¹ Gerber,⁴² and Kuntz,⁴³ by changing the solution pH, the aggregate structure is forced to reversibly transform between a semi-flexible rod and a string-of-pearl. They represent a region of the PES aggregate formation (that of hydrophobic polymer and varying electrostatic attraction of opposite

charged moieties) that exhibits distinctive aggregate structural behavior. The interactions of the PES aggregate with other particles are also explored. Its capability to solubilize hydrophobic molecules, together with its ability to adsorb onto oxide nanoparticles, offers exciting opportunities for future applications such as delivery vehicles.

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Chapter 2

General materials and methods

The details of the synthesis of the main materials will be covered in this chapter. Also included are experimental techniques that will be used in many of the works in the thesis, including Small Angle Neutron Scattering (SANS), Static Light Scattering (SLS), Dynamic Light Scattering (DLS) and others. The techniques and materials that are only employed/used in specific chapters will, however, be described in those corresponding chapters.

2.1 Wormlike micelle template polymerization

The polymerization work was done originally by Kline,¹ Gerber,²⁻⁴ and Kuntz,⁵⁻⁸ and is summarized here.

Aggregates are prepared by polymerization of wormlike micelles, although it has been shown that the aggregates are equilibrium structures and can be prepared either by *in situ* polymerization or by mixing of prepared polymer chain and surfactant molecules.⁹ Polymerization of the wormlike micelle system was first performed by Kline.¹ In that work, aggregates of cetyl trimethyl ammonium and poly(4-vinyl benzoate), or pC₁₆TVB, are prepared by free radical polymerization of micelles of the surfactant, cetyl trimethyl ammonium (C₁₆TA⁺), with a reactive counterion, vinyl benzoate (VB⁻) using a water-soluble initiator. The cationic surfactant C₁₆TA⁺ has a hydrocarbon tail group and a positively charged trimethylammonium head group while VB⁻ consists of a vinyl group connected to the para position of negatively charged benzoate ion. The structure of both $C_{16}TA^+$ and pVB are shown in Figure 2.1. The resulting polymer pVB is negatively charged (it is more correctly written as pVBⁿ⁻, but for simplicity the polymer chain in this paper is represented as pVB). It is worth noting that the polymerization approach yields a polyelectrolyte in which *every* monomer has a charge group. The polymer chain is hydrophobic due to the polystyrene-like backbone with multiple aromatic groups and a long hydrocarbon chain, and is not soluble at neutral pH without the aid of surfactants. The polyelectrolyte-surfactant aggregate product is found to be polydisperse in length, with the molecular weight controlled by initiator concentration and reaction temperature in ways consistent with polymer grown by free radical polymerization.³



Cetyltrimethyl Ammonium C₁₆TA

poly 4-vinyl benzoate

Figure 2.1: Chemical structures of the surfactant and the polyelectrolyte.

2.1.1 Surfactant-Monomer Preparation

The surfactant/counterion pair, denoted $C_{16}TVB$, is synthesized from commercially available cetyltrimethylammonium bromide, or $C_{16}TAB$ (98% purity, BDH Limited, Poole, UK) via two counterion exchange steps. The first step is to replace the bromide counterion (Br⁻) of the surfactant with a hydroxide counterion (OH⁻) using DOWEX ion-exchange resin (99% monosphere 550 Å anion exchange resin) obtained from Sigma-Aldrich (St. Louis, MO). In the second step, $C_{16}TAOH$ is neutralized by 4-vinylbenzoic monomer (97%) from Sigma Aldrich (St. Louis, MO), in which OH⁻ counterion is replaced by VB⁻ counterion. $C_{16}TVB$ precipitates in a chilled water bath with high conversion, and the purity of the product has been verified by NMR.¹⁰ The result is a purified complex salt of the cationic surfactant and anionic polymerizable counterion.

2.1.2 Formation of PES aggregates by polymerization

The dried C₁₆TVB is suspended in deionized water in preparation for free radical polymerization. The reaction is performed under N_2 (grade 5.0) to avoid scavenging of the free radicals by dissolved oxygen. The reaction mixture, a viscoelastic, wormlike micellar solution, is allowed to stir at 60°C. It is then initiated using a water soluble initiator 2,2'-azobis[2-2(imidazolin-2-yl) propane] dihydrochloride, or VA-44, (Wako Chemicals USA, Inc., Richmond, VA). The reaction proceeds with stirring for 3 hours to ensure high conversion ($\sim 96\%$), yielding the polymerized product, $pC_{16}TVB$. UV-Vis spectrometry is used to verify near complete conversion; lack of vinyl peaks signifies high conversion. At neutral pH, the product is fully characterized for aggregate dimensions using SLS, which provides a z-average radius of gyration, Rg, and a weight-average molecular weight MW. Some batch to batch variation in the molecular weight and size of the aggregates is seen, but the variation is small, and specific characterization will be indicated in the individual chapters. The $pC_{16}TVB$ product is then freeze-dried and stored dry until use.

2.2 Silica nanoparticle preparation

Sol-gel processes are popular methods used to make small metal oxides particles, one of which is the Stöber process that produces silica at the nanometer/micrometer size. Stöber studied the formation of spherical silica from alcoholic solution of tetraethylorthosilicate (TEOS).¹¹ The choice of catalysts and experimental parameters such as temperature and mixing speed control the average size and size distribution of the silica product. In the original Stöber work, NH₃ is used as a catalyst to generate large size spherical silica, from hundreds of nanometers, to micrometer sizes. Particle size can be reduced to the nanometer range by using L-lysine as a catalyst/stabilizer at room temperature.¹² Silica particles are the preferred spherical particles because the size can be easily varied, the surface is relatively uniform, and the surface charge density is known as a function of the pH.¹³ In all cases, the sizes of the particles are hydrodynamic diameters, measured using dynamic light scattering, the principle of which will be included in Section 2.5.

2.2.1 L-lysine silica

As previously mentioned, the approach using L-lysine at room temperature results in silica particles in the nanometer size range.¹⁴ 1g of l-lysine is mixed with 200ml of distilled water (85% solubility limit of l-lysine) and stirred for 30 minutes to ensure complete dissolution. TEOS is then added, and the mixture is stirred vigorously for 3 days. L-lysine was purchased from Sigma Aldrich (St. Louis, MO) in powder form, while 98% TEOS was purchased from Aldrich.

Upon completion, the final solution of SiO₂/lysine/H₂O/ethanol is used within two weeks. The particles are negatively charged at neutral pH with a zeta potential of - 38mV, while the isoelectric point has been found at approximately pH 2. Particle sizes could be increased to tens of nanometers by performing the synthesis at elevated temperatures.

2.2.2 Ludox silica

Ludox SiO₂ SM-30, HS-40, and TM-40 were kindly donated by Grace (Columbia, MD), the specifications of which are included in Table 2.1. Stock solutions were filtered using 220 nm Millipore membrane filters and diluted to achieve the desired final concentrations, then used immediately. Apart from a low concentration of inorganic salts (mainly sulfates), there is no additional stabilizer in the stock.

	Ludox SM	Ludox HS	Ludox TM
Reported diameter (nm)	8	12	22
Stock concentration (%wt)	30	40	40
рН	9.8	9.8	9.8

Table 2.1: Reported diameters, stock concentrations, and stock solution pH of Ludox.

2.2.3 Stöber silica

The Stöber process is used to synthesize larger size SiO_2 particles. Appropriate amounts of reagent grade ethanol, deionized water, and ammonia (28% volume stock) are prepared with slow stirring. TEOS is then added, and the solutions are stirred for three days until the reaction is completed. Ethanol was purchased from Sigma-Aldrich (St. Louis, MO), and ammonia from Fluka (Milwaukee, WI). The solutions are centrifuged at high speed, the supernatant removed and replaced by DI water. The process is repeated three times to wash off any unreacted TEOS, and to substitute ethanol solvent with deionized water. This process also increases the SiO₂ concentration several-fold. The final solution is then stored until use.

2.3 Small angle neutron scattering (SANS)

Small angle neutron scattering (SANS) measurements are performed at the NIST Center for Neutron Research in Gaithersburg, MD, using the NG3 and NG7 30m SANS instrument with three sample-to-detector distances of 1.3, 3.5, and 13.3m to provide an overall q-range from 0.0035 to 0.45Å⁻¹. As shown in Figure 2.2, leaving the reactor, the neutrons pass through a neutron velocity selector that selects the neutron beam wavelength, and the neutron guides that collimated the beam. A 1.2 cm diameter collimated beam of neutrons with a wavelength of 6 Å and a wavelength spread of $\Delta\lambda/\lambda = 0.143$ impinges on samples held between quartz plates with a 2mm path length. The scattered neutrons are collected by a 2D detector, and the magnitude of the scattering vector, **q**, is used to describe the trajectory of the scattered beam:

$$q = \frac{4\pi}{\lambda} \sin\!\left(\frac{\theta}{2}\right) \qquad [2.1]$$

with λ being the wavelength of the incident neutron beam. Higher q values provide information correspond to smaller length scales.



Figure 2.2: SANS instrument diagrams. (top) diagram of the NG7 30 m SANS instrument at the National Institute for Standards and Technology (NIST, Gaithersburg, MD). (bottom) simplified experimental diagram. Both diagrams are available on the NIST website (www.ncnr.nist.gov/programs/sans/).

Scattered intensity is corrected for background and empty cell scattering and circularly averaged to I(q) using software provided by NIST (NIST SANS

Reduction version 5.1 on IGOR).¹⁵ The relationship between I(q) and q is generally expressed as:

$$I(q) = \phi V(\Delta \rho)^2 P(q)S(q) + I_o \qquad [2.2]$$

with Φ being the volume fraction of the scatterers in solution, V the volume of a scatterer. $\Delta \rho$ is the contrast of the scatterer, defined as the difference between the scattering length densities of the scatterer and the solvent. All three are scaling factors, independent of q. P(q) is the geometric form factor, which has the shape information. S(q) is the structure factor and takes care of the deviation of the actual scattering curve from the form factor, usually caused by particle interactions within the system. S(q) is assumed to be unity for a dilute solution of isotropic particles with negligible interactions. I_o is the scattering intensity from the background and the incoherent scattering of the components of the solution (mainly the solvent).

The radial dimension of the aggregates is determined by an analysis of SANS data at high-q (q>0.04 Å⁻¹) using the Guinier approximation^{16,17} of

$$qI(q) = K_{BR} \exp\left(\frac{-q^2 R_{g,cs}^2}{2}\right) \qquad [2.3]$$

where $R_{g,cs}$ is the radius of gyration of the micellar cross-section, and K_{BR} is the bending rod constant. Both K_{BR} and $R_{G,CS}$ can be obtained from a linear fit of the plot of qI(q) versus q². For a cylinder, the radius r is given by $r = 2^{1/2}R_{g,cs}$. At dilute concentrations where interparticle effects are negligible, the full qdependence of neutron scattering is related to the form factor, P(q). The form factor of a rigid cylinder is given by

$$P(q) = \int_{0}^{\pi/2} f^{2}(q, a) \sin a.da ,$$

where $f(q, a) = 2V \frac{\sin\left(\frac{qL}{2}\cos a\right)}{\frac{qL}{2}\cos a} \frac{J_{1}(qr\sin a)}{(qr\sin a)},$ [2.4]

where L is the rod length, J_1 is the first order Bessel function, and $V=\pi R^2 L$. The form factor in equation 2.4 gives $I(q) \sim q^{-1}$ in the intermediate q range (~0.08>q>0.04 Å), which appears as a flat region on a Holtzer, or bending rod, plot of q I(q) versus q.¹⁷ In previous work, the longest polymer-surfactant aggregates at neutral pH are observed to have some flexibility, seen as a low-q upturn in a Holtzer plot. Those samples are modeled using the form factor for a semi-flexible chain.^{9,17} In that model, the ratio of contour length over the persistence length, L/L_p, is adjusted to best capture the experimental data while keeping other structural parameters the same.

Beside the cylinder, the other basic particle shape that will be used in this work is the sphere. The form factor of a monodisperse sphere is given as:¹⁸

$$P(q) = \left(\frac{\left[\sin\left(\frac{qD_s}{2}\right) - \left(\frac{qD_s}{2}\right)\cos\left(\frac{qD_s}{2}\right)\right]}{\left(\frac{qD_s}{2}\right)^3}\right)^2 \qquad [2.5]$$

To take into account the polydispersity, the normalized Schulz distribution¹⁹ is chosen to describe the distribution in diameter,
$$f(D_s) = (z+1)^{z+1} \left(\frac{D_s}{D_{s,ave}}\right) \frac{\exp\left[-(z+1)\left(\frac{D_s}{D_{s,ave}}\right)\right]}{\frac{D_{s,ave}}{2}\Gamma(z+1)}$$
[2.6]

with $z = (p)^{-2} - 1 = \left(\frac{2\sigma}{D_{S,ave}}\right)^{-2} - 1$. In this expression, σ^2 is the variance of the

distribution and $D_{S,avg}$ is the average diameter of the sphere. The form factor for polydisperse spheres becomes:

$$P_{poly}(q) = (\Delta \rho)^2 \int_{0}^{\infty} f(D_s) D_s^{-6} P(qD_s) dD_s \quad [2.7]$$

where N_0 is the total number of particles per unit volume.²⁰

The resulting curves from the data reduction procedure are fitted with these form factors using NIST SANS Analysis software version 4.0 on IGOR to extract fit parameters.²¹ The non-linear least-square fitting uses the Levenberg-Marquardt algorithm,^{22,23} with the quality of fit reported as the χ parameter where

$$\chi = \sqrt{\frac{\chi^{(2)}}{N - f - 1}}$$
, with N being the number of data points and f the number of

degrees of freedom in the fit. Instrumental smearing, in this case pin hole smearing, is approximated as a Gaussian function²⁴ and handled automatically by the software.

2.4 Static light scattering (SLS)

Since the incident photon in Static Light Scattering (SLS) has a much longer wavelength than the neutron used in SANS does, SLS is used to probe larger length scales (> 100 nm) that SANS cannot probe. SLS experiments are performed using a BI-200SM (Brookhaven Instruments, Holtsville, NY) goniometer. The instrument laser provides vertically polarized light of wavelength 532 nm, while the scattering angles are between 70° and 130°. Samples are placed in borosilicate scintillation vials (sample path length = 2.5 cm, Fisher Scientific, Pittsburgh, PA) for measurements and were referenced against scattering from a toluene standard. The instrument bath is filled with decahydronaphthalene (cis+trans mixture, Sigma-Aldrich, St. Louis, MO) and measurements are made at 25° C.



Figure 2.3: Simplified SLS instrument diagram

The Zimm analysis²⁵ is performed to obtain R_g , M_w , and B_2 for the aggregates, using the following equation:

$$\frac{K.c}{R_{\theta}} = \left(\frac{1}{M_{W}} + 2B_{2}c\right) \left(1 + \frac{16\pi^{2}R_{g}}{3\lambda^{2}}\sin^{2}\left(\frac{\theta}{2}\right)\right) \quad [2.8]$$

with the optical constant
$$K = \frac{4\pi^2 n_o^2 (dn/dc)^2}{N_A \lambda^4}$$
 [2.9]

and Rayleigh ratio
$$R_{\theta} = R_{ref} \left(\frac{I_{solu}(\theta) - I_{solv}(\theta)}{I_{ref}(\theta)} \right)$$
 [2.10]

where c, M_w , Rg, and B_2 are the mass concentration, weight-averaged molecular weight, z-averaged radius of gyration, and second virial coefficient of the aggregates, respectively; λ is the laser wavelength, θ is the scattering angle, n_0 is the solvent H₂O refractive index, N_A is the Avogadro number, dn/dc is the refractive index increment of solutions of pC₁₆TVB in H₂O solvent; R_{ref} is the Rayleigh ratio of the reference material toluene ($3.5 \cdot 10^{-5} \text{ cm}^{-1}$),²⁶ I_{solu}(θ), I_{solv}(θ), and I_{ref}(θ) are the measured SLS intensities at angle θ for the solution, solvent, and reference material, respectively.

2.4.1 Differential refractometry

Differential index of refraction, dn/dc, is the solution property that represents the dependence of the refractive index of the solution on the concentration of the solute, and is required for the analysis of SLS data. A Brice-Phoenix differential refractometer²⁷ (Model BP-2000-V, Phoenix precision instrument company, Philadelphia, PA) has been used to measure the dn/dc of the solutions of $pC_{16}TVB$. Ambience temperature is used, since the temperature coefficient of the difference in refractive indices between a solution and its solvent is much smaller than that of the refractive index of solution or solvent alone. A mercury lamp with a green filter (546nm) is used as the light source. The

sample cell is fabricated as sinter-fused optical glass square, and a thin diagonal glass partition inside which divides the cell into two equal compartments, one for the solvent and one for the solution. The cell holder can be rotated about a vertical axis through 180° by mean of a handle projecting from the fixed housing. The light beam, emerging from the cell, has been deviated through an angle which is proportional to the refractive index difference between the media. A projector lens projects the image of the split onto the focal plane of the objective of a microscope fitted with a micrometer eyepiece having a 10mm fixed scale.

Both halves of the cell are first filled with the solvent. Reading of the location of the split is done with the handle of the cell holder toward the lamp (d_1') , and then 180° away from the lamp (d_2') . Then, one half of the cell is refilled with the solution at a certain concentration, and the reading is repeated $(d_1 and d_2)$. Δn can be calculated as $\Delta n = k * [(d_2 - d_1) - (d_2' - d_1')]$, with k being the calibration constant for the selected wavelength. The experiment is repeated with different solution concentration. Finally, Δn is plotted as a function of concentration c, the slope of which provides dn/dc.



Figure 2.4: Schematic for the Brice-Phoenix BP-2000-V, including both (top) overall setup and (bottom) cell. Images are obtained from instrument manual.

As an example, experiments are performed for solutions of $pC_{16}TVB$ aggregates at neutral pH, and the results are shown in Figure 2.5. The linearity of

the Δn versus the concentration of pC₁₆TVB aggregate data allows the slope, which is dn/dc, to be extracted at 1.89*10⁻⁴ L/g.



Figure 2.5: Difference in refractive indices of solutions of $pC_{16}TVB$ at neutral pH as a function of its concentrations. The line is the linear fit of the data, with the slope being $1.89*10^{-4}$ L/g.

2.5 Dynamic light scattering

In dynamic light scattering (DLS) experiments, visible light shone through the sample solution is scattered on interaction with particles. Density fluctuation due to Brownian random motion over time translates to the fluctuation in intensity. Intensity of light scattered and its fluctuation with time can be analyzed to determine the fluctuations provides relaxation time scales, and then the diffusion coefficients.

In particular, keeping the scattering angle θ fixed, the light scattering intensity is measured as a function of time, for a given time t_n , in time step Δt . I(θ ,t) is the current intensity, while I(θ) is the average value over the time period. The fluctuation is expressed in the autocorrelation function:

$$C(q,\tau) = \lim_{m \to \infty} \frac{1}{n} \int_{0}^{m} I(q,t) \cdot I(q,t+\tau) \cdot dt$$
[2.11]

where τ is the delay time. If I(q,t) is non-periodic, the Seigert relation is expressed as:²⁸

$$\frac{C(q,\tau)}{[I(q)]^2} = g^{(2)}(q,\tau) = 1 + \xi |g^{(1)}(q,\tau)|^2$$
[2.12]

The digital correlator builds the autocorrelation function from the intensity data fed by the PMT. If the scatterers are assumed as monodisperse hard spheres, $g^{(1)}$ is expressed as:

$$g^{(1)}(q,\tau) = \exp(-\Gamma(q).\tau)$$
 [2.13]

In a dilute solution, assuming diffusion is purely translational while the rotational component is negligible, the relaxation frequency can be related to the translational diffusion D_t via:

$$\Gamma(q) = D_t \cdot q^2 \cdot n^2 \qquad [2.14]$$

with n as the refractive index of the solvent. For polydispersed samples, algorithm like CONTIN^{29,30} can be used to extract Γ , the decay rate. The results can be

presented as diffusion coefficients, or if the scatterers are hard spheres, as hydrodynamic diameters d_H using the Stokes-Einstein equation:

$$d_{H} = \frac{k_{B}T}{3\pi\eta D_{T}}$$
 [2.15]

where k_B is the Boltzmann constant, T is temperature (K), and η is the viscosity of the solvent. Conversion of d_H to a aggregate dimension, such as contour length and diameter, requires detailed knowledge of the aggregate structure. Since this requires extra information that must be obtained using other techniques, d_H is considered as the characteristic size and its interpretation is discussed.

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Chapter 3

Structural characterization of a surfactant-polyelectrolyte aggregate through neutron contrast matching

Previously, the equilibrium structure in aqueous solution of a polyelectrolyte-surfactant aggregate, $pC_{16}TVB$, has been proposed to be a semiflexible rod. In this work, small angle neutron scattering and static light scattering have been performed on pC₁₆TVB to provide more direct evidence for the distribution of the components within its structure. With the surfactant $C_{16}TA^+$ being deuterated, its scattering length density is separated from that of the polymer chain, which enables the contrast matching technique to be employed. The aggregate has been confirmed to have a core-shell cylinder structure, with the shell consisting of the surfactant head group, while the surfactant tail group and the polymer chain remain in the core. In a 100% D₂O solvent, the aggregate scattering is dominated by the polymer chain, which has been used to determine its conformation. Of the common structural models for polymer chains, the wormlike chain model is the most consistent with the experimental data. As more surfactants are added, there are signs of a drop in chain flexibility, although the experimental evidence is inconclusive.

3.1 Introduction

For surfactant-polyelectrolyte systems in which attractive interactions lead to the formation of stable aggregates, many possible aggregate structures are envisioned ^{1,2} and the aggregate structure often determines the bulk properties of the solution. Beside the commonly encountered "string-of-pearl", or "necklace" structure, an alternate structure observed in polyelectrolyte-surfactant aggregates, or PES aggregates, is that of a cylindrical aggregate with the polyelectrolyte chain trapped in the interior of a cylindrical micelle. Under appropriate conditions, the polyelectrolyte will contribute to the structure in two ways; hindering dissociation of surfactant and maintaining structure, and also acting as a counterion to control local curvature of the surfactant interface.

A specific system of polyelectrolyte and cationic surfactant, namely aqueous solutions of the surfactant, alkane trimethyl ammonium, $(C_nTA^+$ where n denotes the number of carbons in the alkane tail group), and the polyelectrolyte poly(4-vinylbenzoate), (pVB), shows this structure at neutral pH conditions. Here, experimental work has been done to provide direct evidence of the aggregate structure when n is equal to 16. In particular, as illustrated in Figure 3.1:, using the neutron contrast matching technique, the solvent composition is varied to match out one component so that the scattering of the other component can be studied independently. In the case where $100\%D_2O$ solvent is used and the surfactant is essentially matched out, the data will be matched with simulated data from structural models to determine the conformation of the polyelectrolyte chain. The composition of the aggregate is also varied to extract the effect of each component on the conformation of the other component.



Figure 3.1: Illustration for the neutron contrast matching scheme: one component is matched out to facilitate the study of the conformation of the other component by varying the solvent composition. The polymer chain conformation drawn here is only for illustration purpose, and might not represent the exact conformation in the aggregate.

3.2 Background

3.2.1 Polymer chain conformation

In D_2O solvent, the scattering off the polymer chain contains the information about its conformation, resulting in the need to look at different models of chain conformation reported in the literature. They vary depending on the charge state of the chain and the solvent quality. Three of the most common models will be considered below, including the random coil, the necklace, and the wormlike chain, all of which are illustrated in Figure 3.2.



Figure 3.2: Polymer chain conformation models, from top to bottom: random coil, necklace, and wormlike chain.

The simplest model, the *random coil*, is an ideal freely-jointed chain with N subunits, each with a unit length, and no part of the chain excludes another from any location. The model is used to describe polymer coils in θ -solvent or in the melt state.³ These are typically neutral and flexible polymer chains. Polystyrene, which constitutes the backbone of the pVB chain, together with the slightly sulfonated derivatives, have this conformation in the toluene solvent.⁴ The form factor of a random coil is calculated as a double sum of exponentials, then

re-written in terms of the mean-square radius of gyration of the chain $\langle Rg^2 \rangle$, called the Debye function⁵

$$P(q) = \frac{2}{(q^2 < Rg^2 >)^2} [\exp(-q^2 < Rg^2 >) - 1 + q^2 < Rg^2 >]$$
[3.1]

with P(q) being the form factor of the chain, **q** the scattering vector, and R_g the radius of gyration. At low values of q, it can be reduced to the first approximation by the Zimm function:⁶

$$P(q) = [1 + (qR_g)^2/3]^{-1}$$
 [3.2]

While at high values of q:

$$P(q) = [1 + (qR_g)^2/2]^{-1}$$
 [3.3]

The full equation 3.1 is used to produce the $P(q).q^2$ versus q plot, or the Kratky plot,⁷ which tends to be flat for the SANS-applicable q range. The data is included in Figure 3.3, where R_g is set at 65nm. The downturn at very low value of q signifies the length of the random coil, in this case controlled by R_g .



Figure 3.3: Kratky plot of a random coil using equation 3.1. R_g is set at 65nm.

The often encountered *necklace* model, also called the *string-of-pearl* or the *blob model*, includes a series of polymer blobs alternated by more linear polymer segments. Weakly to moderately charged polyelectrolytes belong in this category. In dilute solution, the form factor can be expressed as: ⁸

$$P_{intra}(q) = \frac{1}{N^2} \langle \sum_{i,j} exp(i\boldsymbol{q}.\boldsymbol{rij}) \rangle = \frac{1}{N^2} \langle \sum_{i,j} \frac{\sin(qr_{ij})}{qr_{ij}} \rangle$$
[3.4]

where r_{ij} is the vector between the ith and jth monomers on the chain. Liao *et al.*⁸ used the above equation to simulate the data for a short polymer chain, which showed local maxima in a Holtzer plot. As blob size increases, the location of the maxima moves to higher q, and the intensity decreases.

The last model, the *Kratky-Porod worm-like chain*, is similar to the freely joined chain, but the discrete segments are replaced by a continuous elastic medium. It is often used to describe semi-flexible chains such as moderately charged polyelectrolytes. The best approaches reported for fitting the scattering of worm-like chains are the Monte-Carlo simulations by Potschke *et al.*⁹ and Perdersen and Schurtenberger *et al.*¹⁰ Of the analytical approaches, including ones by Hermans and Hermans *et al.*,¹¹ Koyama *et al.*,¹² Norisuye *et al.*,¹³ Kholodenko *et al.*,¹⁴ and Sharp and Bloomfield *et al.*,¹⁵ Kholodenko has been shown to provide the closest description, while Sharp and Bloomfield (SB), a relatively simple model, is appropriate when a rough estimate is needed. SB describes the polyelectrolyte chain as wormlike with a finite length L and a persistence length L_p. The SB form factor is given by:

$$P(q) = \frac{2[\exp(-x)+x-1]}{x^2} + \left[\frac{4}{15} + \frac{7}{15} - \left(\frac{11}{15} + \frac{7}{15x}\right)\exp(-x)\right]\frac{2l_P}{L}$$
[3.5]
with $x = \frac{Lq^2l_P}{3}$.

The form factor of the Kholodenko model requires one numerical integration, but is valid at all values of q. Let b be the Kuhn length (which is half of the persistence length L_p), L be the contour length:

$$P\left(\frac{L}{b}, qb\right) = \frac{2}{x} \left[I_{(1)}(x) - \frac{1}{x} I_{(2)}(x) \right] \quad [3.6]$$

where

x = 3L/b

$$I_{(n)}(x) = \int_0^x f(z) z^{n-1} dz$$

$$f(z) = \frac{1}{E} \frac{\sinh(Ez)}{\sinh(z)}, q \le \frac{3}{b} \qquad \qquad f(z) = \frac{1}{E} \frac{\sin(\hat{E}z)}{\sinh(z)}, q > \frac{3}{b}$$
$$E = \left[1 - \left(\frac{1}{3}bq\right)^2\right]^{1/2} \qquad \qquad \hat{E} = \left[\left(\frac{1}{3}bq\right)^2 - 1\right]^{1/2}.$$

To calculate the scattering form factor, both L and L/b are needed, which are related by R_g . Since the rod is confined inside the aggregate, its conformation is determined by the aggregate. Assuming the polymer chain has the same R_g value with the aggregate, R_g measured from SLS experiments (Table 3.4) can be used. Taking into account the effect of excluded volume, R_g can be expressed as:¹⁶

$$\langle Rg^2 \rangle = \alpha \left(\frac{L}{b}\right)^2 * \langle Rg^2 \rangle_o$$
 [3.7]
with $\alpha(x)^2 = \left[1 + \left(\frac{x}{3.12}\right)^2 + \left(\frac{x}{8.67}\right)^3\right]^{\frac{\varepsilon}{3}}$

and $\varepsilon = 0.170$ for a semi-flexible chain.

The ensemble average of the square of the radius of gyration for a semiflexible chain is:¹⁷

$$< Rg^{2}>_{o} = \frac{L^{2}}{6\left(\frac{L}{b}\right)} \left[1 - \frac{3}{\frac{2L}{b}} + \frac{3}{2\left(\frac{L}{b}\right)^{2}} - \frac{3}{4\left(\frac{L}{b}\right)^{4}} \left[1 - \exp(-2\left(\frac{L}{b}\right)) \right] \right]$$
 [3.8]

First, an R_g value is chosen from Table 3.4. A value of L/b is picked based on our best knowledge of the flexibility of the chain. Both of them are plugged in Equation 3.6 to find the value of $\langle Rg^2 \rangle_0$, which is then plugged in to Equation 3.7 to find the corresponding value of L. Both L and L/b become the input of Equation 3.5, and the plot of P(q) versus q is compared with the experimental data at the same R_g . If they deviate, the value of L/b is adjusted, and the loop is repeated until a good fit is found.

3.2.2 Polymer chain conformation under biaxial compression: Chain in a tube

In forcing the polymer chain inside a tube, the diameter of tube D defines the blob size. With the exclusion volume being taken into account, D can be approximated as $b.g^{3/5}$, with g and b being the number of monomers in a blob and the monomer size, respectively. L, the length of the tube occupied by a polymer chain, is the size of one blob D times the number of these blobs N/g: ³

$$L \approx D\left(\frac{N}{g}\right) \approx \left(\frac{b}{D}\right)^{2/3} Nb$$
, [3.9]

with N being the total number of monomers in the chain. The tube length increases linearly with the number of monomers, while it increases as the tube gets smaller.

3.2.3 Contrast matching technique

Scattering techniques are popular in colloids and polymer science due to the ability to non-invasively probe the structure of complex systems.¹⁸ Unfortunately, most systems have multiple components with different responses to neutrons, and it is not straightforward to model composite scattering curves. There are clever scattering schemes employed to simplify the analysis by

selectively blocking out the scattering of one component, while studying the other.^{19,20} These techniques are known as contrast matching in Small Angle Neutron Scattering (SANS) and Small Angle Xray Scattering (SAXS), and refractive index matching in Static Light Scattering (SLS). SANS contrast matching for aqueous solutions has a major advantage due to the large difference between coherent neutron scattering densities of the otherwise chemically similar H₂O and D₂O.²¹ This allows for a wide variation of the scattering length density (SLD) of the solvent to match the SLD of common particles by adjusting the relative content of deuterated and protonated water.^{22,23} Some of the early SANS contrast matching experiments were performed by Stuhrmann^{24,25} in a biological system, in which the solvent composition was varied to match the contrast of one component, effectively rendered it invisible under the neutron beam. Contrast matching has been used in numerous systems including surfactant micelles with rhodopsin,^{26,27} liposome with pneumolysine,²⁸ DNA with histone,²⁹, silica in Pluronic block copolymer,³⁰ among others. Core-shell systems have also been studied.31,32

3.3 Materials and methods

3.3.1 Formation of PES complexes by polymerization

Traditionally, the complex is synthesized *in situ*, with the polymerization of the wormlike micelles being described in Section 2.1. The micellar template has equal number of surfactant and monomer molecules. In this work, it is necessary to vary the surfactant to monomer ratio in the aggregate. Setting the

micellar template composition prior to the polymerization is problematic, since that would also change the shape of the template itself and the nature of the resulting polymer chain. Dialyzing the final aggregate to completely strip off the surfactants, then re-adding an appropriate amount of them is the better approach. However, since $C_{16}TA^+$ interacts strongly with pVB, it is not possible to perform the dialysis within a reasonable timeframe. As a result, the pVB is synthesized separately.

The dried 4-vinylbenzoic monomer (97%, Sigma Aldrich, St. Louis, MO) is suspended in deionized water in preparation for free radical polymerization. The VB-H concentration is kept at 100mg/ml, while NaOH (98.5%, Acros Organics, Pittsburgh, PA) is added to convert the neutral VB-H to VB⁻. The concentration of NaOH is 1M. The reaction is performed under N₂ (grade 5.0) to avoid scavenging of the free radicals by dissolved oxygen. The reaction mixture, a viscoelastic solution, is allowed to stir at 60°C until homogeneous. It is then initiated using the water soluble initiator VA-44. The reaction proceeds with stirring for 5 hours to ensure good conversion, yielding the polymerized product, pVB.

The final solution, now containing pVB, unreacted VB⁻, 1M NaOH, and H₂O solvent, is transferred to Spectra/Por dialysis tubing (Spectrum Laboratories, Rancho Dominguez, CA). The dialysis is first done with 1M NaOH as the outer solution to remove unreacted VB⁻. then with pure deionized water to bring the pH back down to neutral. The outer solution is replaced by fresh one twice a week, while the total dialysis time is two months. The pVB product is then freeze-dried

and stored until use. Samples are prepared by re-suspending pVB in aqueous solution, while hexadecyltrimethylammonium-d42 bromide (d-C₁₆TAB, 98% deuterated, CDN Isotopes, Pointe-Claire, Quebec, Canada) is added at the desirable molar ratio of VB⁻:C₁₆TA⁺. Note that in the surfactant molecule, all available hydrogen atoms, including the ones in the tail and the head groups, are replaced by deuterium atoms. The solutions are made fresh, gently mixed in a circular rotator for two hours then equilibrated for 24 hours before use.

3.3.2 Characterization of aggregates

Small angle neutron scattering (SANS) measurements are performed at the NIST Center for Neutron Research in Gaithersburg, MD, using the NG3 30m SANS instrument with three sample-to-detector distances of 1.3, 3.5, and 13.3m to provide an overall q-range from 0.0035 to 0.45Å⁻¹. SANS principles and data treatment are explained in Section 2.3, including the expression for the angle-averaged form factor of a rigid cylinder at dilute concentrations, where interparticle effects are negligible. For a core-shell cylinder, the form factor is given by^{32,33}

$$P(q) = \frac{scale}{V_{shell}} \int_{0}^{\pi/2} f^{2}(q,\alpha) \sin \alpha d\alpha,$$

$$f(q,\alpha) = 2(\rho_{core} - \rho_{shell})V_{core}J_o(q\frac{L}{2}\cos\alpha)\frac{J_1(qr\sin\alpha)}{(qr\sin\alpha)}$$

$$+ 2(\rho_{shell} - \rho_{solvent})V_{shell}J_o\left[q(\frac{L}{2} + t_{shell})\cos\alpha\right]\frac{J_1[q(r+t_{shell})\sin\alpha]}{[q(r+t_{shell})\sin\alpha]}$$
[3.10]

where J_o is the zeroth order Bessel function $J_o(x) = \frac{\sin(x)/x}{x}$, $J_1(x)$ is the first order Bessel function $J_1(x) = \frac{(\sin x - x \cos x)}{x^2}$, r is the radius of the core, while t_{shell} is the thickness of the shell, $V_{core} = \pi r^2 L$, and $V_{shell} = \pi (r + t_{shell})^2 (L + 2t_{shell})$, ρ_{core} and ρ_{shell} are scattering length densities of the core and the shell, respectively. α is defined as the angle between the cylinder axis and the scattering vector, **q**.

The resulting curves from the data reduction procedure are fitted with these form factors using NIST SANS Analysis software version 4.0 on IGOR to extract fit parameters.³⁴ In this work, χ is referred to as the fit quality parameter, accompanied by values of N and f used in the fits.

Static Light Scattering (SLS) is also used to probe larger length scale (> 100 nm) than what SANS can provide. SLS experiments are performed using a BI-200SM (Brookhaven Instruments, Holtsville, NY) goniometer. SANS principles and data treatment are explained in Section 2.4. The instrument laser provided vertically polarized light of wavelength 532 nm, while the scattering angles are between 70° and 130°. The refractive index increment, dn/dc, required for some of the SLS data analysis, is obtained using a Brice-Phoenix differential refractometer³⁵ (Model BP-2000-V, Phoenix precision instrument, Philadelphia, PA).

The $pC_{16}TVB$ aggregate is suspected to have a core-shell structure, with the core and the shell having their own distinct values of SLD^{20} . Finding the

chemical composition of each, which determines the SLD, is the focus of the early part of this work. Table 3.1 includes the SLD values of all major chemical species and a few of the combinations that will be used.

Component	SLD (x10 ⁻⁶ Å ⁻²)
surfactant	
$d-C_{16}TA^+$	7.5
$d-C_{16}TA^+$ head group	7.2
$d-C_{16}TA^+$ tail group	7.6
polyelectrolyte	
pVB	1.9
PES combination (1:1 molar ratio)	
$d-C_{16}TA^+$ head group + pVB	3.7
$d-C_{16}TA^+$ tail group + pVB	5.5
$d-C_{16}TA^+ + pVB$	5.5
solvents	
$100\%D_2O:0\%H_2O$	6.3
$95\% D_2O: 5\%H_2O$	6.0
$90\% D_2O: 10\% H_2O$	5.7
$77.4\% D_2O: 22.6\% H_2O$	4.8
$51\% D_2O: 49\% H_2O$	3.0

Table 3.1: Calculated SLD for pC₁₆TVB aggregate components and solvents

There are two main ways that the three species, including the surfactant head group, the surfactant tail group and the polyelectrolyte chain, can be distributed into a core-shell cylinder. In all cases, as a requirement for the micellar formation, the surfactant head group must reside at the micelle-water interface, or in the shell, while the surfactant tail group is shielded away from the aqueous solvent and remains in the core. The polyelectrolyte chain has been shown to be near the interface due to electrostatic attraction with the surfactant head group, but stays on the inside due to its highly hydrophobic polystyrene backbone. The exact location of the pVB chain is the determining factor, whether it is i) in the shell, or ii) in the core. With regard to the neutron contrast matching technique, other minor points will also be discussed, including whether the whole cylinder could be considered a homogeneous instead of core-shell cylinder, and whether the pVB chain is well dispersed with whichever species it resides with. The term *homogeneous* here implies that the whole cylinder could be considered as having a single uniform SLD value.

To differentiate these scenarios, experiments are designed with two main sets of sample solutions: one set with the composition of the solute kept constant and the solvent composition varied between 100%D₂O and 51%D₂O; and another set with the solvent composition kept constant and the solute composition varied from the molar ratio of VB⁻:C₁₆TA⁺ of 0.8:1 (surfactant rich) up to 9:1 (polymer rich). For the sake of simplicity, from here on, when VB⁻:C₁₆TA⁺ is used, it stands for the molar ratio of VB⁻:C₁₆TA⁺. Two experimental techniques are used, SANS and SLS. Their data will be mainly represented by the scattering plots (I versus q), although the Holtzer plots (I*q versus q) or the Kratky plots (I*q² versus q) could also be used. Fittings will be then done to confirm the distribution of components in the aggregates, and the conformation of the polymer chain.

3.4 Results

Figure 3.4 shows the scattering intensities as a function of the scattering vector q for the first set of $pC_{16}TVB$ samples, where solute composition is fixed so the SLD of the shell and the core remain unchanged, no matter how they are composed. At the same time, the solvent composition is varied to change the contrast of the shell/core, which is the difference between the SLD of the core/shell and the solvent. This is the traditional method to determine the experimental match points.



Figure 3.4: Scattering intensities of solutions of $pC_{16}TVB$ with VB⁻: $C_{16}TA^+$ of 1:1 and various solvent compositions. The concentration of $pC_{16}TVB$ is kept fixed at 5mg/ml, while the solution pH is neutral. The background scattering intensities are subtracted. For the top right inset, square root of the scattered intensities of the same samples as a function of the mole fraction of D₂O in the D₂O/H₂O solvent mixture, sampled at low (solid circles), intermediate (empty circles), and high q (solid triangles), respectively.

After subtracting the background scattering, consisting mainly of the incoherent scattering from the solvent and the hydrogenated polymer chain, it is clear that the solution with 100% D_2O solvent scatters the weakest. In fact, the top right inset indicates that as the fraction of D_2O in the solvent decreases, or the SLD of the solvent decreases, the scattering intensities increase at all q. At the same time, the shape of the curves evolves with the change in the solvent. At the solvent composition of 51% D_2O , the curve exhibits all the signs of a rigid rod, with a cross section at low q representing a diameter, and a negative one slope at intermediate/high q, characteristics consistent with a rigid rod. As the fraction of D_2O increases, so does the solvent SLD, and the slope at high q starts to drop, while the slope at intermediate q remains essentially the same. At the solvent composition of 100% D_2O , there is virtually no difference in slope between the high and intermediate q region. Features in the low q region also change; an upturn is becoming more prominent as the solvent becomes richer in D_2O .

These features point to the same conclusion that in the D_2O -poor solvent, the scatterer is a cylinder with a clearly defined diameter and a rather rigid conformation. As the D_2O fraction increases, the drop in high q slope does not mean the diameter physically shrinks, but more likely some part of the cylinder being matched out while the rest is not, and whatever left has a negligible cross section, for example, one of a polymer chain. The upturn at low q indicates a much longer and/or more flexible structure compared to the previous cylinder. At the solvent composition of 100% D_2O , the scattering resembles a long flexible/semi-flexible polymer chain, or at least one that is dominated by it. This also means that the scattering from the surfactant is mostly matched to the solvent, agreeing with the fact that at 100%D₂O solvent condition, the contrast for the polymer chain is $4.4 \times 10^{-6} \text{\AA}^{-2}$, much higher than $1.4 \times 10^{-6} \text{\AA}^{-2}$ for the surfactant.

The scattering intensities as a function of the scattering vector q for the second set of $pC_{16}TVB$ samples are shown in Figure 3.5, where the solvent composition is fixed at 100%D₂O so that the scattering intensities are dominated by those of the polymer chain, and solute composition is varied. The background scattering is subtracted from the measured intensities.



Figure 3.5: Scattering intensities of solutions of $pC_{16}TVB$ at various solute compositions and fixed solvent composition of 100% D₂O. The concentration of $pC_{16}TVB$ is kept fixed at 5mg/ml, while the solution pH is at neutral. In the top right inset, square root of the scattered intensities of the same solutions are sampled at low (solid circles), intermediate (empty circles), and high q (solid triangles), respectively.

The scattering intensities are very low for the VB: $C_{16}TA^+$ of 1.2:1 and 1.3:1 samples, almost to the noise level. They increase only slightly for the VB⁻ $:C_{16}TA^+$ of 1:1 and 0.8:1 samples, while the high polymer composition samples scatter strongly. The top right inset shows scattering intensities increase as the VB⁻ portion becomes higher. In an aggregate of surfactant and polymer chain at $100\%D_2O$, the solvent composition where surfactant scattering is minimized, if the molar total of VB⁻ and $C_{16}TA^+$ is kept constant, the maximum total intensity will occur at the minimum surfactant composition, 9:1 in this case. This agrees with the observation that the surfactant is indeed almost matched out, and the drop in its number barely registers in the overall scattering, which is dominated by the polymer scattering. It is not entirely clear, however, why there is a slight dip in intensity for the VB: $C_{16}TA^+$ of 1.3:1 sample, typically a strong sign of the existence of a match point, which should be 0.8:1 for this case. It is likely due to the other factor in estimating intensity, the total volume fraction. If the packing of the components, or worse, the structure of the aggregate, change as a function of component composition, its volume fraction, hence its total scattering intensity will change.

The shape of the scattering curve sheds more light onto the structure change argument. For all 100%D₂O samples, including the previously discussed sample with VB⁻:CTA⁺ of 1:1, there is neither a significant cross section nor a distinct turnover between the intermediate and high q portions of the curves. In contrast, the sample with the solvent composition of $51\%D_2O$ and VB⁻:CTA⁺ of 1:1 has both. Overall, for samples with 100%D₂O solvent, it seems the scattering

intensities are still predominantly from the polymer chain, and the change in chain structure mentioned above, if occurs, might not be too significant as the curves still have similar shape. At low q, an increase in VB⁻ composition reduces the upturn, which means either less flexibility, short length, or other interactions that come in play.

Alternatively, the data from Figure 3.5 is re-calculated and represented in the form of a Kratky plot in Figure 3.6. Although no distinct trend can be observed from the curves, their general features, or the lack thereof, are used to develop hypotheses about the conformation of the polymer chain in the $pC_{16}TVB$ aggregate. In particular, it is clear that random coil is not a probable conformation for the polymer chain. The Kratky plot of a random coil scattering data, based on equation 3.1, should have a flat profile, which is not observed in this data.



Figure 3.6: Kratky representation of the scattering of solutions of $pC_{16}TVB$ at various solute compositions and a fixed solvent composition of 100% D₂O. The concentration of $pC_{16}TVB$ is kept fixed at 5mg/ml, while the solution pH is at neutral.

Prior to fitting structural models of the aggregate to the I(q), and despite the high polymer-surfactant binding,³⁶ it is impertinent to verify that free spherical surfactant micelles indeed do not form in solution. Kuntz³⁷ had indicated a binding fraction of 0.988 at 1mg/ml. Although the polymer used in that work has a slightly different molecular weight from the polymer used here due to a different synthesis, it is reasonable to expect the binding fraction to be between 0.990 and 0.995 at the operating concentration of 5mg/ml. That corresponds to 0.025-0.050 mg/ml of free surfactant for sample solution at VB⁻:C₁₆TA⁺ of 1:1, well below 0.36mg/ml, the CMC of C₁₆TAB, making it is unlikely there are any free $C_{16}TAB$ spherical micelles in solution. To be sure, for each set of experimental scattering data that needs to be fitted, various amounts of simulated free micelle scattering are subtracted. The sphere scattering is generated using polydisperse (Schulz) sphere model,³⁸⁻⁴⁰ with d-C₁₆TAB micelle size reasonably assumed to be similar to the size of its hydrogenated counterpart, since the same has been shown to be true for an analogous surfactant, TTAB.⁴¹ This has no impact on the quality of the fit for any of the model proposed.

%D ₂ O	100%	95%	90%	77%	51%
Core radius (Å)	10	11	12	15	17
Shell radius (Å)	7	8	7	5	3
Length (Å)	7669	16851	16156	14905	14514
SLD core $(x10^{-6} Å^{-2})$	5.80	5.76	5.79	5.94	5.24
SLD shell $(x10^{-6}\text{\AA}^{-2})$	7.19	7.16	7.22	7.10	7.28
SLD solvent (x10 ⁻⁶ Å ⁻²)	6.33	5.99	5.65	4.79	2.79
Incoherent background (cm ⁻¹)	0.0002	0.0007	0.0008	0.0004	0.0008
X	1.39	1.66	1.34	2.14	4.26

Table 3.2: Fitting parameters for the scattering of $pC_{16}TVB$ solutions at VB⁻: $C_{16}TA^+$ of 1:1 and various solvent compositions

VB : $C_{16}TA^+$	1:1	1.2:1	1.3:1	5:1
Core radius (Å)	10	9	10	21
Shell radius (Å)	7	9	7	2
Length (Å)	7669	7461	27486	6747
SLD core $(x10^{-6}\text{\AA}^{-2})$	5.80	7.59	7.18	5.48
SLD shell (x10 ⁻⁶ Å ⁻²)	7.19	5.61	5.49	6.68
SLD solvent (x10 ⁻⁶ Å ⁻²)	6.33	6.33	6.33	6.33
Incoherent background (cm ⁻¹)	0.0002	0.0001	0.0003	0.0007
χ	1.39	1.26	1.07	1.27

Table 3.3: Fitting parameters for the scattering of $pC_{16}TVB$ solutions at a solvent composition of 100%D₂O and various solute compositions

Considering the aggregate being a core-shell cylinder with the shell consisting of head groups of the surfactant, the fitting parameters for the solvent series and the solute series are provided in Table 3.2 and Table 3.3, respectively. Of the solvent series, the 90% D₂O scattering curve has the best quality, with the core/shell SLD being close to the expected values and low $\chi^2/N.$ The only problem is that the shell seems too thick, while the total radius of the cylinder is only 18.2Å. This is smaller than the expected 22Å, which has been determined previously to be the radius of the aggregate consisting of pVB and hydrogenated $C_{16}TA^{+}$ at a molar composition of 1:1 and in 100% D₂O solvent. In Table 3.2, less D_2O in the solvent corresponds to bigger core and thinner shell, while the total increases slightly. Of the scattering data from the solute series, the fit of the VB⁻ $:C_{16}TA^+$ of 5:1 data provides the best results, with all expected values for the parameters. The quality of the VB⁻: $C_{16}TA^+$ of 0.8:1 scattering data is too noisy to fit. The shape of the VB⁻: $C_{16}TA^+$ of 9:1 curve does not match one of a core-shell cylinder well. Although a forced fit is still successful, the rest of the data (for 1.2:1 and 1.3:1 samples) are also noisy, with unexpectedly exchanged SLD values for the core and the shell.

To extend the reach of the scattering data lower q values where details about the overall lengths could likely be obtained, SLS experiments have been performed on the hydrogenated systems with VB⁻: $C_{16}TA^+$ of 9:1, 5:1, 1:1, and 0.8:1, all with a solvent composition of 0% D₂O, and all at the pC₁₆TVB concentration of 2mg/ml. It should be noted that this is not a matching experiment, and the solvent composition is not varied. In this particular solvent composition, the aggregate as a whole, not the polymer chain, is probed. Since the polymer chain conformation is controlled by the surfactant structure, it can be assumed that behavior of the length and flexibility of the chain is analogous to one of the aggregate itself.



Figure 3.7: Static light scattering intensities of solutions of hydrogenated- $pC_{16}TVB$ at various solute compositions and the solvent composition of 0% D₂O. The concentration of $pC_{16}TVB$ is kept fixed at 2mg/ml to minimize multiple scattering effect, while the solution pH is at neutral.

Even if the solvent composition was to be varied, however, unlike their SLD, the refractive indices of D_2O and H_2O , the relevant variables for light scattering, are practically the same, rendering their ability to vary the solvent refractive indices. Similarly, the close refractive indices of the hydrogenated and deuterated versions of $C_{16}TAB$ enable the use of the earlier one in this particular

part of the experiment due to its more abundant availability. The absolute values of the slopes of the SLS segments drop with the pVB proportion. As more surfactant is added, the slope approaches negative one, the slope of a rigid rod, and then passes it. This means two possibilities. If flexibility is the main cause, more adsorbed surfactant molecules will lead to more rigid structures. However, if the length of the aggregate is the main cause, additional adsorbed surfactant molecules will result in shorter, or more compact, aggregates.

To extract the molecular weight and second virial coefficient of the aggregate from SLS data, correct dn/dc values of the samples, not readily available in the literature, must first be obtained using a differential refractometer. For the samples with high proportion of pVB, the measured dn/dc values are negative, with light scattering being cited previously as a possible explanation.^{42,43} Therefore, dn/dc is instead calculated based on the weighted-average of dn/dc values of C₁₆TAB (0.151 cm³/g)^{44,45} and pVB. There is no reported dn/dc for pVB in aqueous solution due to its insolubility in the medium, so it will be calculated instead from the refractive index, reported to be 1.58.⁴⁷ Assuming a mass density of 1.0g/cm³, a common value for polymer with a hydrocarbon backbone, dn/dc can be estimated to be (1.58-1.33)/1 = 0.25cm³/g. Using the mass fraction data from Table 3.5, new dn/dc values have been calculated and shown in Table 3.4.

$VB^-:C_{16}TA^+$	$dn/dc (cm^3/g)$	MW ($x10^6$ g/mol)	R _g (nm)	$B_2(x10^{-4})$
9:1	0.232	0.51±0.04	104±7	-0.2±0.5
5:1	0.221	$0.40{\pm}0.02$	60±7	1.7±0.5
1:1	0.183	2.10±0.13	69±2	1.2 ± 0.1
0.8:1	0.179	1.39±0.09	63±4	1.0±0.2

Table 3.4: Calculated values of dn/dc for $pC_{16}TVB$ samples, together with extracted SLS parameters.

The radius of gyration of the aggregate, R_g , provides insight into the conformation of the polymer chain. R_g remains relatively constant as the fraction of VB⁻ increases, until it reaches 9:1 where it nearly doubles. This is likely due to minimal change in conformation of the polymer chain (except for the flexibility) until the surfactant is depleted in the 9:1 sample. The change observed at the highest pVB proportion is probably a result of the polymer chain being altered significantly. Also, B₂ becomes very small and switches sign from positive to negative at 9:1. Being a measure of the relative strength of the molecule-solvent interaction compared to the molecule-molecule interactions are much more attractive at 9:1. This is consistent with our understanding of the system at 9:1, in which less surfactant is available to interact with the chain/monomer and bring them apart. Caution should be taken in using this particular observation, however, as the error for this particular value of B₂ is rather high.
$VB^-: C_{16}TA^+$	$VB^-: C_{16}TA^+$	MW of aggregate	MW of pVB
molar ratio	mass ratio	(10^6 g/mol)	(10 ⁶ g/mol)
9:1	0.82:018	0.51±0.04	0.42±0.03
5:1	0.71:0.29	0.40±0.02	0.29±0.02
1:1	0.33:0.67	2.10±0.13	0.69±0.04
0.8:1	0.28:0.72	1.39±0.09	0.39±0.03

Table 3.5: Molecular weights of pVB in an aggregate

The molar ratio of VB: $C_{16}TA^+$ has been converted to mass ratio. Assuming uniform distribution of polymer chains within the sample solution, the molecular weight of the polymer in a single aggregate is calculated in Table 3.5. Attempts to perform SLS on pVB-only solution to directly obtain the molecular weight of the polymer chain have not been successful due to its insolubility in common solvents, including water, benzene, toluene, hexane, cyclohexane, and various trifluoroacetic acid/water mixtures. The presence of the carboxylate groups prevents its solubilization in benzene, while its polystyrene backbone does not let it to solubilize in aqueous solvent. Of the polymer solubilized by surfactant molecules, the molecular weights of the polymer in each corresponding aggregates are not too different, indicating similar number of chain(s) per aggregate.

Lastly, polymer-dominated scattering data in Figure 3.5 is compared with the data generated by a couple of worm-like chain models. Attempts to fit the polymer chain conformation to the Sharp and Bloomfield model for worm-like chain (Matlab program based on equation 3.5) works well for 9:1 data in Figure 3.8, but the fit quality gets progressively worse as more $C_{16}TAB$ is added, probably a sign of evolving chain structure. It should be noted that this model assumes short chains and uses L_p as the only fitting parameter. To account for the long chain lengths, which the curves in Figure 3.5 imply, a more complete model is needed, such as the Kholodenko model.



Figure 3.8: Fit of Sharp and Bloomfield model to the scattering of $pC_{16}TVB$ with VB⁻:C₁₆TA⁺ of 9:1 and a solvent composition of 100%D₂O. The contour length L is 43nm and persistence length L_p is 4nm.

Next, the experimental data are plotted together with the Kholodenko simulation data for worm-like chains to i) verify their resemblance, if any, and ii) extract the flexibility L/b of the chains as a function of surfactant concentration. The results are shown in Figure 3.9, using the average values of R_g in Table 3.4.

The simulations have also been done for other values of R_g within the small standard deviation (not shown), but the difference is not significant.



Figure 3.9: Holtzer plots of Kholodenko worm-like chain model simulations with different pairs of R_g and L/b. The sub-figures are denoted, clockwise, A, B, C, and D, with R_g of 63nm, 69nm, 60nm, and 104nm, respectively. With each R_g , several values of L/b are used. Also included are the experimental scattering profiles of the pC₁₆TVB in 100% D₂O solvent and VB⁻:C₁₆TA⁺ of 0.8:1, 1:1, 5:1, and 9:1 for A, B, C, and D, respectively.

Attempt to match the simulated data with the VB⁻:C₁₆TA⁺ of 0.8:1 and 1:1 data has not been made due to the high level of fluctuation. For the VB⁻:C₁₆TA⁺ of 5:1 data, the slope of the low q upturn looks like the one of L/b of 100. For the VB⁻:C₁₆TA⁺ of 9:1 data, it is even higher, probably L/b of 400. The q dependence of the scattered intensity is not inconsistent with the worm-like chain scattering,

and there is indeed some level of flexibility within the chain. For the solvent composition of 51% D₂O (and a VB⁻: $C_{16}TA^+$ of 1:1) sample, which is far from the matched point for the surfactant, the scattering is once again of the whole rod rather than of only the polymer chain. A comparison of this with the worm-like chain model is shown below.



Figure 3.10: Holtzer plots of Kholodenko worm-like chain model simulations with R_g of 63nm and various L/b, represented by curves. Also included is the SANS scattering of pC₁₆TVB with the VB⁻:C₁₆TA⁺ of 1:1 and the solvent composition of 50% D₂O in open circles, and the SLS data of hydrogenated-pC₁₆TVB with the VB⁻:C₁₆TA⁺ of 1:1 and a solvent composition of 0% D₂O in open triangles.

It is clear that the worm-like chain simulated data is not a good match for the SANS experimental data for the system with $VB^-:C_{16}TA^+$ of 1:1 and a solvent composition of 51% D₂O. The system, after all, most likely resembles the scattering of the full $pC_{16}TVB$ aggregate, itself a semi-flexible rod. Interestingly, when an appropriate vertical shift is applied to the SLS data, which has arbitrary unit to begin with, the slope of the data matches quite well with the low q slope of the SANS data. Since the SLS data describes a full rod, this might confirm the previous suggestion that the aggregate at VB⁻:C₁₆TA⁺ of 1:1 and a solvent composition of 51% D₂O is itself a full rod. The downturn on the data at low q could be due to the concentration effect, which has been observed previously in SANS data of hydrogenated pC₁₆TVB system (Figure 3.11).



Figure 3.11: Holtzer plots of hydrogenated- $pC_{16}TVB$ with VB: $C_{16}TA^+$ of 1:1 and a solvent composition of 100% D₂O. The data for the 6.0mg/ml and 0.5mg/ml solutions are represented by closed circles and open circles, respectively.

3.5 Discussion

3.5.1 Polymer-dominated scattering

There are two scattering components within the system, the surfactant and the polymer chain, and the scattering intensities depend on their volume fractions and contrasts. On its own, the volume fraction of the polymer chain is much less than that of the surfactant molecules. With everything else equal, the surfactant scattering would dictate one the scattering from the entire aggregate. However, once contrast is considered, theoretically the surfactant scattering could be completely eliminated by making its contrast zero, or in other word, setting the solvent SLD the same with the surfactant SLD. Since $d-C_{16}TAB$ SLD is higher than pure D_2O SLD (Table 3.1), it is not possible to completely match the surfactant scattering. 100% D₂O solvent is the closest it can get to the matched point. This is true regardless of whether the surfactant molecule is considered as a whole, or as separate head and tail groups, since both SLD are very close. At the same time, with the polymer chain having a lower SLD than that of any solvent composition used in this work, its contrast increases with the D₂O fraction in the solvent, while the surfactant contrast drops. At near surfactant match point, the polymer chain scattering becomes dominant, compounded by the fact that the contrast term is being squared in the scattering intensity calculation. In 100% D₂O solvent, the scattering is effectively one of the polymer chain. Keeping the solvent composition fixed at this point while replacing more and more VB⁻ with $C_{16}TA^+$, the overall scattering drops. This means the surfactant is indeed almost matched

out, and the increase in its number barely registers in the polymer-dominated overall scattering.

3.5.2 Surfactant – polymer distribution in the aggregate

With varying solvent compositions, a homogeneous rod scattering curve would only change its intensity, due to the altered contrast, not its shape. On the contrary, for an inhomogeneous rod, the different responses of different components would change the curve shape. As seen in Figure 3.4, when the solvent composition approaches 100% D₂O, the slope at low q starts to creep up. As a result, the rod is not homogeneous, but it is instead a core-shell cylinder. The positive slope change at low q itself can be assigned to the increasingly dominant scattering of the polymer chain, which should be more than 1 micron in contour length. For the core-shell cylindrical structure, a look at Table 3.1 shows the effect the polymer chain has in lowering the overall SLD of the component it resides in, due to its low SLD. Attempts to fit the experimental scattering data to a core-shell cylinder model, where the shell consists of the polymer chain and the head groups of the surfactant, have not been successful.

The only scenario left is the one where the shell consists of the head groups of the surfactant. The fitting parameters in Table 3.2 and Table 3.3 suggest that, i) the general structure of the aggregate is indeed surfactant head shell – surfactant tail/polymer chain core, but ii) the core composition might has been oversimplified, as the quality of the fit is still lacking. The possibility of a core in which the surfactant tail groups and the polymer chain cannot be considered

homogeneous (to be represented by a single SLD) is rather high. The low-q upturn in Figure 3.4 is a good indication that the surfactant part is gradually being matched out as the deuterated solvent composition increases, leaving the polymer chain itself being scattered. This prompts the need to match the characteristics of the 100% D_2O scattering intensities with the popular models for polymer chain scattering in the literature.

3.5.3 Polymer chain conformation in the core

In 100% D₂O solvent, the scattering has been shown to be primarily of the polymer chain alone. There are a few commonly employed models for polymer chain conformations in the literature, including random coil, necklace, and worm-like chain. Data from Figure 3.6 eliminate the random coil as a possible structure for pVB in $pC_{16}TVB$ rod due to the lack of a flat region. Physically, this makes sense since the random coil model is usually reserved for completely neutral chain, which has no monomer-monomer electrostatic repulsion. In this case, the solution pH will need to be drastically reduced for that to happen. Even then, other attractive forces could come in place. Both the necklace and the worm-like chain models are promising conformations for the polymer chain. However, the peak typically observed in chains that have the necklace model, sometimes called the polymer peak, is not seen in the scattering data, making it highly unlikely that the polymer chain assumes a necklace conformation.

The last model to consider is the worm-like chain. Sharp & Bloomfield model (Figure 3.8) is not the perfect model to use in this case, but at least it helps

show the consistent signs of the chain being worm-like. The Kholodenko model is a more refined worm-like chain model by, among other things, taking into account the long contour length of the chain. It seems to better resemble the experimental data (Figure 3.9), although more work will need to be done. There is some flexibility within the chain, and the flexibility L/b increases from the VB⁻ : $C_{16}TA^+$ of 5:1 data to the VB⁻: $C_{16}TA^+$ of 9:1 data, supporting the argument that as more surfactant is added, the chains get more flexible. Unfortunately, there is no definite trend for the higher surfactant ratio data.

3.6 Conclusions

Previous work has proposed the equilibrium structure in aqueous solution of a particular polyelectrolyte-surfactant aggregate, $pC_{16}TVB$, to be of a semiflexible rod, with the surfactant head groups at the water interface, the surfactant tails pointing toward the core, while the polymer chain stays in the core, but near the core-shell boundary. Here, small angle neutron scattering and static light scattering have been performed on $pC_{16}TVB$ in an attempt to provide more direct evidence for the distribution of the components within its structure. With the surfactant $C_{16}TA^+$ being deuterated, its scattering length density is separated from one of the polymer chain, which enables contrast matching technique to be employed. It is confirmed that the aggregate has a core-shell cylinder structure, with the shell consisting of the surfactant head group, while the surfactant tail group and the polymer chain remain in the core. In a 100% D₂O solvent, the aggregate scattering is dominated by the polymer chain, which has been used to derive its conformation. Of all the common structural models for polymer chains, the worm-like chain model is the most consistent with the experimental data. As more surfactants are added, there are signs of a drop in chain flexibility, although the experimental evidence is inconclusive.

3.7 References

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Chapter 4

Local effects of solution pH on the PES aggregate

4.1 Introduction

In chapter 3, one structure of the PES aggregate was studied, the cylindrical aggregate with the polyelectrolyte chain trapped in the interior of a cylindrical micelle. We also mentioned another group of PES that has a far more common structure: polymers and surfactants that form "string-of-pearl", or "necklace" structures in aqueous solution, where spherical surfactant micelles formed along the backbone are connected by the polymer chain. This structure has been proposed for many systems including a majority of ionic surfactants mixed with nonionic polymers systems, the most common examples being PEO-SDS¹⁻⁹ and PVP-SDS.¹⁰⁻¹² This type of structure was first successfully demonstrated by Cabane,² while the name itself was coined by Shirahama.¹ This string-of-pearl structure is common in polymer-surfactant aggregation, with the local details of the structure depending on chain solubility, curvature of the micelle surface and, in the case of charged systems, specific interactions between the surfactant and polymer.

A dramatic change in structure of the $pC_{16}TVB$ aggregate in aqueous solution has been observed on decreasing the pH. Here, we present the experimental work done to probe the structural change and efforts to elucidate the structure at low pH, or acidic, conditions. We propose that this system has been transformed from the rod-like structure at neutral pH conditions to the "string-ofpearl" structure at very low pH conditions as depicted in Figure 4.1b.



Figure 4.1: The aggregate system studied. (a) Chemical structure of the surfactant and polyelectrolyte. (b) The proposed structural transition observed with pH from a cylindrical structure of surfactant constraining a loosely coiled polyelectrolyte to a string-of-pearl structure.

4.2 Background

4.2.1 Aggregate structure and interactions

The structure of pC_nTVB at conditions of neutral pH has been established in Chapter 2, and especially Chapter 3. Hydrophobic and electrostatic interactions between the polyelectrolyte and the surfactants define the resulting aggregate structure.¹³ Therefore, it is reasonable to speculate that once the number of charged groups of the pVB backbone is reduced, the structure will change. In fact, we argue that the structure of the aggregates at neutral pH is somewhat uncommon, that of a tube of surfactant with a trapped polyelectrolyte chain, and changes to the more common string-of-pearl structure at lower pH. Since carboxylic acid is a relatively weak acid, the number of charged groups on the pVB chain is lowered by driving the pH of the solution below the pKa of pVB. In particular, a strong acid (HCl) is used to protonate carboxylate groups into carboxylic groups, leading to significant change in the observed solution behaviors. The structure for the low-pH aggregate is proposed to be a string-ofpearl. In other words, the drop of pH converts the aggregate from having a semiflexible rod-like structure, which is not typical for similar polyelectrolytesurfactant systems, to having a more common structure of string-of-pearl (see Figure 4.1b).

4.2.2 Counterion binding

For surfactant micelles, a variety of aggregate structures can form such as spherical or rodlike micelles, vesicles or lamellar phases.¹⁴ The factors governing the micellar shape have been discussed extensively.¹⁵⁻¹⁷ In his seminal work, Israelachvili¹⁷ has proposed that the shape is determined by a balance between the tendency of the alkyl chains to minimize their water contact, which tends to minimize the area-to-volume ratio, and the electrostatic repulsion between the charged head groups, which tends to maximize the area to volume ratio. Since the ratio is larger for a sphere than for a cylinder, any effect that decreases the electrostatic repulsion between head groups, such as an increased counterion

binding, will promote the formation of rod-shaped micelles. For a given system, the degree of counterion binding increases with increasing surfactant concentration.

Counterions can be divided into two groups based on their types of interactions: Coulombic and specific. Coulombic counterions are strongly hydrated,¹⁸ and they behave as if they are large. Specific counterions are polarizable with low charge density and interact strongly with micellar surface.¹⁹ The distinction between Coulombic and specific counterions is based on the major character exhibited by an ion; a Coulombic interaction depends on the state of charge of the counterion and is a purely electrostatic interaction. On the other hand, a specific interaction depends mainly on other characteristics of the ion such as polarizability, hydrophobicity, etc. Because of their nature, the specific counterions are likely to be located in an inner region while the Coulombic ones locate further away from the surface. The location of the solubilized counterion further increases the hydrocarbon volume, making the area to volume ratio even smaller. The Hoffmeister series²⁰⁻²⁸ provides a rough estimate of the order of interaction strength, or the penetration of the counterions on the Stern layer of surfactants: $CO_3^- < SO_4^{2-} < S_2O_3^{2-} < H_2PO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < F^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < S^- < S^-$ SCN⁻.

Bulkier counterions usually have stronger affinity to the surfactant head group. Salicylate, or Sal⁻, a widely used counterion with $C_{16}TA^+$ to create rod-like micelles, has a reported CMC of 0.15mM,^{29,30} much smaller than $C_{16}TAB$ or $C_{16}TACl$. The comparison is done at the same 1:1 ratio of $C_{16}TA^+$ surfactant to

counterions. The aromatic part of the counterion is solubilized in the micelle. Thus, there is indeed a chemical component that increases the degree of binding of the salicylate ion as compared to the bromine ion, explaining the observation of rod-shaped micelles³⁰⁻³³ at a much lower concentration in the C₁₆TASal system than in the C₁₆TAB system. The binding preference also means that it is possible to displace a weaker binding counterion with the addition of a stronger binding one. For C₁₆TA⁺ surfactant micelles, it has been shown that Br⁻ or Cl⁻, being very weak binding counterions, are displaced by aromatic counterions, NO₃⁻, N₃⁻, HCO₂⁻, OH⁻. F⁻.³⁴

4.3. Materials and methods

4.3.1 pH measurement

The pH of the solutions is measured using an Accumet pH probe and an Accumet AR50 benchtop meter (Fisher Scientific, Pittsburgh, PA). The probe, a liquid-filled, glass body single-junction combination Ag/AgCl electrode that measures concentration of protons in solution, is first calibrated using standard buffer solutions of pH 4.0, 7.0, and 10.0 (Fisher ChemAlert series, Fisher Scientific, Pittsburgh, PA). Buffer solutions of pH 2.0 and 1.0 are also available to check the probe accuracy in highly acidic solutions.

4.3.2 Nuclear Magnetic Resonance (NMR)

A radio-frequency pulse (1-500Mhz) is used to excite the molecules to high energy levels, which re-emit radio-frequency waves when falling back to the ground state. The separation between the resonance frequency and an arbitrary frequency is called the chemical shift. The more shielded the atoms, with higher induced field generated by the electrons, are under lower effective magnetic field, hence having lower (up field) chemical shift. The spin-spin relaxation time T_2 characterizes how long it takes to return the net magnetization M_{xy} perpendicular to the field back to equilibrium value after perturbation. T_2 and the half-width of the peak are inversely proportional. More mobile atoms have longer T_2 , which leads to immobilized atoms having short T_2 and broad peaks:

$$\frac{1}{T_2} = \pi . \Delta v_{1/2} \quad [4.1]$$

T2 also varies inversely with τ_m , the global tumbling constant,³⁵ which is itself directly proportional to viscosity (derived with the help of rotational diffusion):

$$\tau_M = \frac{1}{6D_{ROT}} = \frac{\mu^* V_h}{kT} \quad [4.2]$$

with V_h as the hydrodynamic volume. A combination of equations 4.1 and 4.2 leads to the inverse relationship between T_2 and viscosity.

Proton Nuclear Magnetic Resonance (¹H NMR) is used to determine the mobility of the species and their positions within the aggregate structure. All ¹H NMR measurements are performed using the Bruker Avance 500 (500 MHz, 11.7 T). Samples are freeze-dried and re-suspended in D₂O with appropriate amounts of DCl, obtained from Cambridge Isotopes Laboratory (Andover, MA).

Diffusion-ordered spectroscopy (DOSY) seeks to separate the NMR signals of different species according to their diffusion coefficient. A series of spin echo spectra is measured with different pulsed field gradient strengths, and

the signal decays are analyzed to extract a set of diffusion coefficients with which to synthesize the diffusion domain of a DOSY spectrum.

4.3.3 Potentiometry basics

Potentiometry uses species-sensitive electrodes to detect the concentration level of specific ions in the solution.³⁶ In this work, a $C_{16}TA^+$ selective electrode is used in combination with a reference electrode to detect the concentration of free $C_{16}TA^+$ in a solution of p $C_{16}TVB$ at low pH. There are two main potentials involved in this process: the phase-boundary potential between the liquid – membrane interface, and the potential attributed to the diffusion of ion through the membrane. Their combination can be ideally expressed using Nernst equation (assuming there is a single selective cation):

$$E = E_o - \frac{RT.\ln 10}{nF} \log a \qquad [4.3]$$

where E and E_0 are measured and standard potentials, respectively. R is the universal gas constant, T is the temperature (K), F is the Faraday constant, n is the charge of cation, a is the activity of the cation in solution.

A simple relationship is used to relate activity to concentration: $a = c * \gamma$, where c is the concentration and γ is the activity coefficient. At very low ionic strength, the solution is ideal, γ is assumed to be unity, and hence activity is simply equal to concentration. The slope of E-E_o versus logc is simply $\frac{RT.\ln 10}{nF}$, which turns out to be -58mV for n=1. This assumption is valid for most solutions where the ionic strength is not too high. Once the high ionic strength becomes too high, however, γ is less than one, and the actual relationship between a and c must be evaluated. At this particular ionic strength:

$$E = E_o - \frac{RT \cdot \ln 10}{nF} \log a = E_o - \frac{RT \cdot \ln 10}{nF} \log c^{\alpha} = E_o - \frac{\alpha RT \ln 10}{nF} \log c \qquad [4.4]$$

with α represents the deviation from ideality of the solution. The value of α should be less than unity, which means the slope of the curve will be less than -58mV.

4.3.4 Surfactant sensitive electrode preparation

Following the steps described by Xu *et al.*,³⁷ a silver wire is electrochemically coated with a layer of AgCl to create the approriate conducting wire. About 3 inches of the wire tip is then dipped in PVC/THF solution for 5 seconds. This is repeated 30 times, with 5 minutes in between to let the solvent evaporate. This step deposites PVC on the wire to insulate. About an inch of PVC is then stripped away, the exposed tip is then dipped 30 times in activated-PVC/C₁₆TA⁺/THF solution to generate the electro-sensitive layer. The structure of activated PVC is shown in Figure 4.2. Finally, the tip of the electrode is "conditioned" by soaking it in 2xCMC C₁₆TAB solution for a week.



Figure 4.2: Chemical structures of PVC and activated PVC.

To create the room temperature $C_{16}TAB$ calibration curve, $C_{16}TA^+$ selective electrode is used in combination with a reference Ag/AgCl electrode to measure the respond to solutions of pure $C_{16}TAB$ surfactant, with concentration range between 10^{-8} and $10^{-3}M$. The calibration curve for $C_{16}TAB$ is then recreated at pH 1 and 0.1mM NaCl. At the same time, a dilution series of p $C_{16}TVB$ at pH 1 is also performed. The aggregate concentration varies from 2mg/ml to $5x10^{-4}$ mg/ml, or the equivalent $C_{16}TAB$ concentration from 4.6mM to 10^{-3} mM. Temperature is again at room condition. A re-circulating bath connected to the stirrer/heater is used. Concentration range is the same as before.

4.3.5 Zeta potential measurement

The potential at the surface of shear between the aggregate and its surrounding medium is known as the zeta potential, which is related to the charge at the surface of the aggregate itself. Several phenomena can be exploited as a basis for measuring zeta potential, involving the movement of the charged particle relative to the surrounding fluid, induced by, or causing an electric field. Depending on which is the case, it is either electrophoresis, or electroosmosis.

In this work, electrophoresis is used to measure the zeta potential of the aggregate. Under an electric field, when an equilibrium is established between the force caused by the field and the viscous force opposed to it, the aggregate moves

with a constant velocity. The velocity per unit electric field is called electrophoretic mobility μ_E , which is related to the zeta potential ζ by the Henry equation:

$$\mu_E = \frac{2\varepsilon\zeta}{3\eta} f(Ka) \qquad [4.5]$$

where ε is the dielectric constant, η is the viscosity of the medium. In aqueous solution and moderate ionic strength, f(Ka) is 1.5 (Smoluchowski approximation), while it is 1.0 for small particles in low dielectric media (Hückel approximation).

The electrophoretic mobility is measured first, then converted to zeta potential. All measurements were made using a Zetasizer 3000 HSA instrument (Malvern Instruments, Worcestershire, UK). The laser wavelength is 633nm, while the voltage is kept at 120V. The sample cell is a quartz capillary with 50mm separation between the electrodes. Between sample loadings, the sample cell was flushed with ethanol and water several times to avoid cross contamination. All data was collected at 25°C.

4.4 Results

The working range of a typical pH probe excludes extremely acidic and extremely basic regimes. To verify, the probe has been used to measure the pH of aqueous solutions of HCl at various concentrations, the values of which are then compared with the calculated pH using the relationship $pH = -log[H^+]$.



Figure 4.3: Solution pH measured using pH probe in comparison with the calculated values of pH.

Figure 4.3 shows that indeed, as $[H^+]$ increases above 0.01M, the probe starts to overestimate the solution pH. For the sake of consistency, the calculated values will be used in reporting the solution pH. For example, a stated pH 1 solution means the concentration of proton is 0.1M. It has been observed that when the pH of the solution of pC₁₆TVB is varied between neutral and very acidic, the solution properties change significantly. The focus of this work will mainly be on characterizing the solutions at the two extreme pH values, neutral and 1.0, where the difference is the most drastic.



Figure 4.4: Proton nuclear magnetic resonance (¹H NMR) spectrum for $pC_{16}TVB$ solutions. The concentration and temperature are kept constant at 6mg/ml and 25°C, respectively. Insets magnify peaks between 5 and 9 ppm. The top Figure 4.4(A) is for a neutral pH solution, while the bottom (B) is for a pH 1 solution.

To better understand the internal structure of the aggregate at the two pH conditions, ¹H NMR was performed on the solutions. Figure 4.4 shows the ¹H NMR spectra of $pC_{16}TVB$ solutions at neutral (pH = 7.2) and acidic (pH = 1.0) conditions. In each case, the inset magnifies peaks between 5 and 10 ppm, those of the benzoate group. The standard peak of H₂O is near 4.70ppm, which is also the highest peak. The upfield peaks of hydrogen atoms on hydrocarbon chains do show a measureable change on lowering the pH. This shift is probably due to the ring current effect³⁸ observed when the distance between the alkyl chains of the surfactant is forced into close proximity to the benzene rings of the polyelectrolyte. At the same time, shifts are also seen in most of the downfield peaks, corresponding to para, ortho, meta hydrogens on the benzoate group.

Figure 4.4A shows the spectrum for the neutral pH solution, with ortho hydrogen peak at 7.80 ppm and meta hydrogen peak at 7.27 ppm. The next three peaks are likely from unreacted monomer molecules. Figure 4.4B shows the spectrum of the pH 1 solution, with ortho and meta peaks at 7.91ppm and 7.41 ppm, respectively. Therefore, as pH drops, the peaks from the benzene ring shift downfield (by 0.11ppm and 0.14ppm for the ortho and meta groups, respectively). The observed difference cannot be explained simply by the difference in electronegativity of carboxylate/carboxylic groups. Literature³⁹ and simulation^{40,41} both predict upfield shifts for the ortho peak when the carboxylate groups of the polymer chain are protonated into carboxylic groups which is contrary to the observation. There must be other factors in effect, such as the hydrophilicity of the environment of these groups. For the chemical shifts of ortho hydrogen to

increase, the benzene ring must be exposed to a more polar (aqueous) environment at acidic pH than at neutral pH.⁴¹ Since the difference in chemical shifts is relatively small, only a fraction of the benzoic groups of the polymer chain are exposed.

The NMR data show both the similarities and the differences between the aggregates at two different pH. In both cases, there is a level of penetration of the benzene rings of pVB into the surfactant micelle. However, at pH 1.0, a few of the rings, hence the segments of the chain that they connect to, shift outward and become exposed to the surrounding water solvent. This is the sign that either the polymer chain or the surfactant micelle, or most likely both, has changed its conformation.

DOSY is used on $pC_{16}TVB$ solutions at acidic (pH 1) and neutral (pH 7) conditions to separate NMR signals of different species according to their diffusion coefficients. The data is shown in Figure 4.5.



Figure 4.5: ¹H NMR spectrum (bottom and top axis) and the logarithm base 10 of diffusion coefficients (right axis) of $pC_{16}TVB$ at neutral pH (orange) and pH 1 (brown), concentration at 6mg/ml.

Each cluster corresponds to a specific peak. Both clusters for $pC_{16}TVB$ at pH 1 have the same diffusivity, approximately $9*10^{-12}$ m²/s. All three clusters for $pC_{16}TVB$ at pH 7 have the diffusivity of $2*10^{-11}$ m²/s. The bottom left peak is for water, which is the same for both case, and is a reference. Diffusivities can be converted to hydrodynamic diameters using the Stokes-Einstein relationship. The hydrodynamic diameter of the aggregate at pH 1 is found to be 1.9 times larger than the one at pH 7. This is in close agreement with what was obtained from dynamic light scattering experiment, showing that the aggregate gets bigger as pH drops.

Figure 4.6 shows the result of the most commonly used method to test the accuracy of a surfactant sensitive electrode. An aqueous solution of $C_{16}TAB$ is prepared, with the concentration varies as needed. The response of the $C_{16}TA^+$ sensitive electrode, in term of the EMF values, to the change in $C_{16}TA^+$ concentration is examined.



Figure 4.6: EMF as a function of total $C_{16}TA^+$ concentration in aqueous solution of $C_{16}TAB$. The $C_{16}TAB$ calibration curve is obtained at room temperature and neutral pH. The line is the fit of experimental data in the linear region.

The lower detection limit of this electrode is a little less than 10^{-7} M. The curve starts to flatten out at about 0.95mM, where additional C₁₆TAB would generate surfactant micelles in solution instead of increasing the monomer concentration. The electrode only detects free surfactant in solution. The reported value of CMC of C₁₆TAB at room temperature is about 0.92mM, close to what is

obtained here. The slope is 53 ± 1 mV/decade of $C_{16}TA^+$ concentration (mV/M). In comparison, the theoretical prediction of this slope can be readily obtained from the Nernst equation to be 57.2mV/M. Although the measured slope is slightly lower than the expected value, or the response of the electrode is slightly sub-Nernstian, it can be used to approximate the concentration of $C_{16}TA^+$ in solution. With its quality verified, the electrode is then used in the solutions of $pC_{16}TVB$ and $C_{16}TAB$, both at pH 1, to detect the concentration of free $C_{16}TA^+$ surfactants. The data are included in Figure 4.7.



Figure 4.7: EMF as a function of total $C_{16}TA^+$ concentration in aqueous solutions of p $C_{16}TVB$ (open squares) and $C_{16}TAB$ (open circles). $C_{16}TAB$ and p $C_{16}TVB$ curves are obtained at room temperature and pH 1. The lines are the fits of experimental data in the linear region.

Judging from the CTA⁺ concentration where the curve flattens off, the effective CMC of $C_{16}TAB$ at pH 1 is 0.08mM, one order of magnitude lower than the CMC measured at neutral pH. This drop is expected, since the high ionic strength induces an electrostatic screening effect that reduces the electrostatic barrier of ionic surfactant micellization, resulting in a much lower CMC. The slope of the linear region for the $C_{16}TAB$ solution at pH 1 is 43.4±1mV/M, significantly depressed from the value measured at neutral pH. The reduced value of the slope is expected due to the ionic strength, but the existence of the linear region still allows the data to be used to correlate between the emf values and the concentration of free surfactant at this specific solution pH.

For the pC₁₆TVB solution at pH 1, it is known that the electrode only responds to free C₁₆TA⁺. Since the equivalent C₁₆TA⁺ concentration in pC₁₆TVB solution represents the total C₁₆TAB available, the fact that it takes less C₁₆TA⁺ in pure surfactant solution to achieve the same potential signal means that only a part of the surfactant remains free in the solution, while the rest binds to the aggregate. Using the correlation between the emf response and the C₁₆TA⁺ concentration obtained previously for the C₁₆TAB solution at pH 1, the emf response for the pC₁₆TVB solution at pH 1 can be converted to show the concentration of free (dissociated) C₁₆TA⁺ surfactants that exist in that solution.

In analyzing the curves in Figure 4.7, we extract a measure of the concentration of $C_{16}TA^+$ bound to the aggregate. The total $C_{16}TA^+$ concentration is defined as C_T , while the free $C_{16}TA^+$ concentration is defined as C_F , so the binding fraction of $C_{16}TA^+$ can be calculated simply as:

%bound =
$$\frac{C_T - C_F}{C_T} * 100\%$$
 [4.6]

This calculation is repeated for every potential value to derive the binding curve, shown in Figure 4.8.



Figure 4.8: Fraction of surfactant molecules $C_{16}TA^+$ that bind to pVB chain to form pC₁₆TVB aggregate, from data potentiometry measurements. Solid circles represent the neutral pH data, while open circles the pH 1 data. The temperature is kept constant at 25°C. The overall ratio between the monomer unit VB of polymer chain pVB and the total surfactant in the solution is kept at 1:1 at all cases.

Figure 4.8 shows the fraction of $C_{16}TA^+$ that binds to the p $C_{16}TVB$ aggregate versus the total surfactant concentration at two different pH conditions. For the p $C_{16}TVB$ solution at neutral pH, the binding curve starts at about 87% bound, which corresponds to a dilute solution of 2 μ M. The bound fraction increases with concentration, and flattens out at concentration just above 1.2 mM

total surfactant. The aggregates at pH 1 behave similarly; the first data point collected is at 12% (10μ M); and the bound fraction rapidly reaches 87% (0.3mM). The point where the curve reaches a plateau shifts to slightly higher total surfactant concentrations, from 1.2 mM at neutral pH to about 1.75 mM at pH 1. At the same concentration, the binding fraction of $C_{16}TA^+$ in p $C_{16}TVB$ solution at neutral pH is always higher than that at pH 1. With the attraction between $C_{16}TA^+$ and pVB being strongly electrostatic, $C_{16}TA^+$ partitions to the aggregates, hence the higher binding fraction at relatively low $C_{16}TA^+$ concentration. For a $pC_{16}TVB$ solution, it is more thermodynamically favorable for $C_{16}TA^+$ to reside in free solution only at low concentration.⁴² It is evident from Figure 4.8, however, that at very low concentrations, more surfactants dissociate from the aggregate as pH drops. A large portion of the -COO⁻ groups are protonated to uncharged -COOH groups, reducing the electrostatic attraction that drives the surfactant to the aggregate. The partitioning of surfactants to the bulk due to decrease in pH and subsequent neutralization of charged groups on the polyelectrolyte is only 2% at 1.2mM and 0.8% at 3.9 mM. Therefore, within the concentration range of interest, there is very little surfactant dissociation from the aggregate at either pH.

The partial-neutralization of the polymer chain at low pH and the dissociation of surfactant from the aggregate, however little they are, both affect the surface charge of the aggregate, reflected in its zeta potential. Figure 4.9 shows the zeta potential of the aggregate $pC_{16}TVB$ measured in aqueous solution as HCl is used to change the pH from neutral to acidic.



Figure 4.9: Zeta potential of $pC_{16}TVB$ as a function of aqueous solution pH. HCl is used to acidify the solution from neutral pH.

At neutral conditions, the aggregate is almost neutral with a -1mV zeta potential. This is consistent with the charge neutral stoichiometry of the species in the system. Furthermore, previous work using surfactant-sensitive electrode has also shown that at neutral pH, a very small amount of positively charged surfactants dissociate, leaving the aggregate slightly negatively charged (see Figure 4.8). As pH drops, there are three opposing processes that affect the aggregate charge. The protonation of pVB chain increases the aggregate charge as a whole, while the association of the newly-introduced Cl⁻ counterion to the adsorbed head group of the surfactant and the additional surfactant dissociation at lower pH both lead to lower charge. The fact that the observed zeta potential

drops with pH indicates that i) pVB chain is protonated, ii) the protonation is more effective than the dissociation of $C_{16}TA^+$ from pVB, and iii) despite the counterion Cl⁻ swarms the free solution, its binding to $C_{16}TA^+$ of the aggregate is too weak, if at all, to change the aggregate charge.

From the two binding curves in Figure 4.8, it can be seen that not all $C_{16}TA^+$ binds to pVB, even at neutral pH. There is still a small fraction that remains in the free solution due to thermodynamics. It is known that the binding fraction drops as pC₁₆TVB concentration decreases.⁴³ Binding fraction is also lowered by lowering the pH. If, at pH 1, the number of $C_{16}TA^+$ dissociated was equal to the number of H⁺ associated with the polymer chain, a binding site on the polymer could only be either protonated or bound to $C_{16}TA^+$, and there would be no un-protonated-AND-unbound state. After all, the proton concentration of 0.1M is much higher than the total concentration of binding sites, it is not likely that the negatively charged site stays unbound. Unfortunately, this would also mean that the overall charge of the aggregate remains unchanged, which zeta potential data in Figure 4.9 have proven to be untrue. Since the overall charge increases, the protonation rate of the polymer backbone must be higher than the dissociation rate of $C_{16}TA^+$, which is the difference between the two binding curves in Figure 4.8. If, hypothetically, the protonation rate of the polymer backbone was to be exactly equal to the dissociation rate of $C_{16}TA^+$, the result is plotted in Figure 4.10.



Figure 4.10: degree of protonation of pVB in the aqueous solution of $pC_{16}TVB$ as a function of $C_{16}TA^+$ concentration

Note that the maximum value hovers at around 50-60%, which means the actual maximum has to be higher than 50-60%, which makes sense in several ways. Firstly, this number, obtained at pH 1, is slight higher than 50% protonation which was used to define the pKa of pVB, on its own is expected to be in between 1 and 2. Secondly, the trend is logical. As $pC_{16}TVB$ concentration decreases, it is thermodynamically favorable for some $C_{16}TA^+$ to dissociate, the number of $C_{16}TA^+$ that competes with H⁺ for the binding sites is less, H⁺ binding increases, or degree of protonation increases.

The nature of the binding of $C_{16}TA^+$ and pVB at pH 1 can also be analyzed using the potentiometry data. The ratio of the amount of $C_{16}TA^+$ that
binds to pVB and one that remains free in solution plotted against the amount of bound one, the standard Scatchard plot, is shown in Figure 4.11. As the bound amount increases, the ratio drops, a classic indication of uncooperative binding. With the interaction being mainly electrostatic, more $C_{16}TA^+$ binding means more sites being neutralized, or less driving force for the next molecule to come in. At very low total $C_{16}TA^+$ concentration, the number of binding sites on pVB overwhelms the available $C_{16}TA^+$, hence the driving force is very high. At high $C_{16}TA^+$ concentration, that driving force drops, the binding is neither uncooperative nor cooperative, and the curve flats out.



Figure 4.11: Scatchard plot of the bound/free surfactant ratio as a function of the bound surfactant

4.5 Discussion

4.5.1 Counterion effect

At neutral pH, although it is not well known which shape the counterion VB⁻ will induce on the $C_{16}TA^+$ surfactant micelle, there is evidence that suggests the structure is cylindrical. The VB⁻ counterion binds more strongly than the Sal⁻ counterion, and $C_{16}TASal$ itself has a rodlike structure. The chemical structure of the counterion provides an explanation, with Sal⁻ having an additional OH group on the ortho-carbon. That additional group makes Sal- slightly more hydrophilic, reducing the binding driving force. At the same time, the intra-structure hydrogen bond between the H of that OH group and the O of the nearby C=O group draws away parts of the negative charge, further reducing the electrostatic attraction for binding. Furthermore, the viscosity of $C_{16}TVB$ solution is observed to be higher compared to one of the $C_{16}TASal$ solution at the same concentration, another sign of wormy micelles.

Without the VB⁻ counterion, Coppola *et al.* reported the structure diagram of $C_{16}TA^+$ in aqueous solution with Br⁻ as the counterion.⁴⁴ The surfactants exist as monomers up to 0.92mM, the CMC. At 0.92mM, spherical micelles start to form, and coexist with monomers up to 340mM. At this point, the spherical micelles transform to cylindrical micelles. Since Cl⁻ counterion binds slightly more weakly than Br⁻ counterion, supported by the higher CMC (1.3mM) of $C_{16}TACl$, it is safe to assume that up to at least 340mM, the CTACl micelle is spherical. However, with VB⁻ counterion, cylindrical micelles start to form at low $C_{16}TA^+$ concentration (<0.01mM). When VB⁻ counterion is removed by protonation and replaced by Cl⁻ counterion, it is only logical to expect the structure to return to what it should be, spherical. The range of concentration used in this work is up to 10mg/ml of pC₁₆TVB, or 22.8mM of C₁₆TA⁺. At this concentration of C₁₆TACl, which is far above the CMC of 1.3mM, but below the sphere-cylinder transition concentration of 340mM, the micelle shape is almost certainly spherical.

The location of the pVB chain, which at low pH consists of a mixture of protonated VB and un-protonated VB⁻, can also be revealed by analyzing the behavior of the counterions. It is known that Sal⁻ counterion penetrates the micellar interface.⁴⁵⁻⁴⁷ The VB⁻ counterion is an even stronger binding counterion than Sal⁻, hence should be deeper inside the micelle. Shikata *et al.*⁴⁸ showed that the protonated version of Sal⁻, the salicylic acid, exists at a much deeper position inside the $C_{16}TA^+$ micelle than Sal⁻ itself. Similarly, the protonated version of VB⁻, vinyl benzoic acid, should penetrate deeper than VB⁻. This indicates that with the addition of HCl, once a critical pH is reached, the VB/VB- counterions, and ultimately the pVB chain, recede into the core of the aggregate, especially when the electrostatic attraction of the counterions and the surfactant head groups is significantly reduced.

4.5.2 Free CTACl micelles in solution

A concern with the potentiometric data analysis process is that at high aggregate concentration, the free surfactant concentration is high enough that free micelles could form, and the amount of bound surfactants cannot be accurately assigned solely as those that bind to the aggregates. Note that the main argument for structural transformation at low pH is the drop in binding fraction of $C_{16}TA^+$ at low pH. The amount bound is calculated by subtracting the amount free in the solution from the total added. However, this binding not only is polymersurfactant binding, but might also be surfactant-surfactant binding in free micelles. Fortunately, a look at Figure 4.7 indicates EMF still increases even at very high overall $C_{16}TA^+$ concentration. If free micelles were to form, the EMF curve should have been flat. The curve still has a positive slope, so free micelle has not yet formed.

The drop in pH of the solution has altered the balance that holds the aggregate together. The protonation of a fraction of carboxylate groups significantly reduces the level of electrostatic attraction between surfactant and monomer units of the chain, while generating carboxylic groups with the ability to form hydrogen bonds, The partial neutralization of the chain, together with the ability of the weak-binding Cl⁻ counterion to promote spherical micelles with $C_{16}TA^+$ suggests a different aggregate structure at pH 1.

The product of the transformation is proposed to be a "string-of-pearl", or necklace, structure, a series of smaller spherical micelles that are connected by the polymer chain. The gap between two adjacent spheres is determined by the balance between electrostatic repulsion between the two charged spheres and the hydrophilicity/hydrophobicity of the exposed polymer chain. The chain is likely to be neutralized inhomogeneously along the backbone. Deprotonated segments are charged and retain their conformation in the micelle core due to their electrostatic attraction with the surfactant head groups. At the same time, the protonated segments, capable of forming hydrogen bonds with surrounding water molecules and also among themselves, are likely coiled up. The chain can be considered as a random copolymer of protonated pVB(-H) and deprotonated pVB segments so the structure will be between the two structures proposed in Figure 4.1B; this may explain the dynamic nature of the structure near the proposed pKa. The transition between the two structures should be completely reversible via the control of solution pH.

4.6 Conclusions

The drop in pH of the solution has altered the balance that holds the $pC_{16}TVB$ aggregate together. The protonation of a fraction of carboxylate groups significantly reduces the level of electrostatic attraction between surfactant and monomer units of the chain, while generating carboxylic groups with the ability to form hydrogen bonds. This partial neutralization of the chain, together with the ability of the weakly-binding Cl⁻ counterion to promote spherical micelles with $C_{16}TA^+$ suggests a different aggregate structure at pH 1. The product of the transformation is proposed to be a "string-of-pearl", or necklace, structure, a series of spherical micelles that are connected by the polymer chain, with gaps between adjacent spheres. The chain can be considered as a random copolymer of protonated pVB(-H) and deprotonated pVB segments.

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Chapter 5

Macroscopic effects of solution pH on the PES aggregate structure

5.1 Introduction

Work on the water-soluble $pC_{16}TVB$ aggregate has been performed at neutral pH conditions,¹⁻⁶ but a dramatic change in structure has been observed on decreasing the pH. Previously, the local effect of dropping the solution pH on $pC_{16}TVB$ was analyzed. The addition of HCl altered the balance that held the $pC_{16}TVB$ aggregate together. The protonation of a fraction of carboxylate groups on the polyelectrolyte significantly reduces the level of electrostatic attraction between surfactant and monomer units of the chain, while generating carboxylic groups with the ability to form hydrogen bonds. This partial neutralization of the chain, together with the ability of the weakly-binding Cl⁻ counterion to promote spherical micelles with $C_{16}TA^+$ suggests a different aggregate structure at pH 1. The product of the transformation is proposed to be a "string-of-pearl", or necklace, structure, a series of smaller spherical micelles that form along the backbone and are connected by the polymer chain, with gaps (expected to be small) between adjacent spheres (Figure 4.1B). The chain is considered a random copolymer of protonated pVB(-H) and deprotonated pVB segments.

In this chapter, the macroscopic solution properties and structural properties are quantified to further elucidate the proposed "string-of-spheres" structure at low pH, or acidic, conditions.

5.2 Background

The hydrogen bond, or H-bond, is often the result of the interaction between a proton-donating bond X-H and a proton acceptor Y, where X and Y designate electronegative atoms such as O, N, or Cl.⁷ In some cases, π -electrons or carbon atoms may act as H-bond acceptors,⁸ but the bond strength is relatively weak (0.5 – 4 kcal/mol). Strong H-bond can be 15 – 60 kcal/mol, such as F-H…:F, which is still less than the typical covalent bond, 100 – 200 kcal/mol. The typical H-bond length is a few angstroms, with the bond length inversely proportional to the bond strength. Overall, H-bond is very similar to ionic bond, but weaker, and the electrostatic force is inversely proportional to the square of the distance. Thermal energy provided by simply heating up the solution might be enough to disrupt the network of H-bonds.

5.3 Materials and methods

Preparation of both neutral and acidic $pC_{16}TVB$ solutions is similar to those described in the Sections 2.1 and 4.3.

5.3.1 Turbidimetry

Turbidity measurements are performed using a Laboratory Turbidimeter Model 2100A (Hach Chemical Company, Ames, Iowa). The turbidimeter operates on the principle that light, passing through a substance, is scattered by particulate matter suspended in the substance. In this instrument, a strong beam of white light is sent upward through a cell containing the sample. An amount of light (proportional to turbidity) is scattered at a 90° angle to the beam and is received by a photomultiplier tube. This light energy is, in turn, converted to an electrical signal which is measured by the instrument. The unit of measure used is the Nephelometric Turbidity Unit (NTU), with higher NTU corresponding to more turbid sample. The instrument is calibrated with the provided stabilized Formazin turbidity standards.

5.3.2 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) measurements are performed using the Malvern NanoSizer ZS (Malvern Instruments, Malvern, UK), with a laser wavelength of 633nm. Each sample is run 10 times at angle of 173° , and the average result and standard deviation reported. Temperature equilibration time inside the instrument is set at 10 minutes. Disposable optical cuvettes with path length of 1cm are used. The principles of DLS are presented in Section 2.5. In all measurements, a single decay of the correlation function is observed while a slow mode is not. Conversion of the hydrodynamic diameter, d_H, to an aggregate dimension requires knowledge of the aggregate structure. Since this requires other techniques, we report d_H and discuss interpretation.

5.3.3 Small Angle Neutron Scattering (SANS)

Small angle neutron scattering (SANS) measurements are performed at the NIST Center for Neutron Research in Gaithersburg, MD, using the NG3 30m SANS instrument with three sample-to-detector distances of 1.3, 3.5, and 13.3m to provide an overall q-range from 0.0035 to 0.45Å^{-1} . The principles of SANS are presented in Section 2.3. Solutions of 0.5mg/ml pC₁₆TVB in D₂O solvent at pH

1.0 and pH 7.0 are prepared, and two sets of experiments are performed. For the first set, scattering intensities for both solutions are collected at the solution temperature of 25° C. For the second set, scattering intensities for the pH 1 solution are collected at various temperatures including 5°C, 25°C, and 40°C. For all cases, the data are presented as Holtzer plots, qI(q) versus q.⁹

5.3.4 Rheology

The Gemini 200 Advanced Rheometer (Malvern Instruments, UK) is used to measure the rheological properties of aqueous solutions of $pC_{16}TVB$. A cone and plate geometry is employed, with a cone angle of 4° and a cone diameter of 40mm (CP4/40). A shear stress sweep from 0.3 to 100 Pa has been done at the angular frequency ω of 1 rad/s. Results are used to find a linear region and choose the stress for frequency sweeps. The frequency sweep from 50 to 0.005 rad/s is then performed on all samples. The elastic modulus G' and the viscous modulus G" are defined as: $G'(\omega) = \frac{\sigma_0}{\gamma_0} .\cos \delta$ and $G''(\omega) = \frac{\sigma_0}{\gamma_0} .\sin \delta$, with σ , γ , and δ being the shear stress, shear strain, and phase angle, respectively. The complex modulus can be obtained as $G^* = \sqrt{G'^2 + G''^2}$, and the complex dynamic viscosity $\eta^* = G^*/_{\omega}$. The zero frequency viscosity, η^*_{o} , is the low frequency plateau in viscosity. The moduli, G' and G", are plotted as functions of the frequency. The intersection of the two curves provides the crossover frequency ω_{xo} and the crossover modulus G_{xo} . Relaxation time τ is defined as $1/\omega_{xo}$.

5.4 Results

Figure 5.1 shows the most marked manifestation of solution properties on pH. For a semi-dilute solution of 10mg/ml, solutions of pC₁₆TVB at neutral pH are low viscosity, optically clear, liquids (the inverted vial on the left in Figure 5.1), consistent with a weakly charged, rod-like particle structure. The properties of these solutions are not strong functions of temperature, ionic strength, or solution concentration.^{1-3,5,6,10} On lowering the pH to values near 1.0, the viscosity increases drastically, and the solution appears to gel and becomes slightly turbid (shown in the inverted vial on the right in Figure 5.1). This phenomenon is reversible and the solution reverts to a low viscosity liquid on increasing the pH. To elucidate the conformational change that causes this phenomenon, we characterize dilute solutions and investigate the impact of pH on individual aggregates.



Figure 5.1: pH-induced gelation of $pC_{16}TVB$ aggregate solution. Both vials have the same (moderate) concentration of 10mg/ml at 25°C. The solution on the left is at neutral pH, which flows to the bottom upon inverting. The solution on the right, contains the same solution but at pH 1, a gel.

Even at much lower concentrations, the solutions are observed to be slight turbid at low solution pH. Figure 5.2 shows the turbidity of a 1mg/ml pC₁₆TVB solution as the solution pH is varied from neutral to very acidic. Unlike the previous gelation observation where the solution is at 10mg/ml, or semidilute, here the solution is in the dilute regime. This is much closer to the condition where all scattering experiments (DLS, SLS, and SANS) are performed, where no gelation is observed, and the overall turbidities are rather low. However, the trend is still observed, as pH drops, the solution becomes more turbid. The transition starts at pH values around 1-2. At such a low concentration, this must mean that something significant has been altered either in the aggregate structure or in the aggregate-aggregate interaction.



Figure 5.2: Turbidities of aqueous solutions of 1mg/ml pC₁₆TVB as a function of solution pH.

Small-angle neutron scattering (SANS) is then used to characterize the local structure (dimensions less than 100 nm) of the aggregate to determine if it is maintained through this drastic macroscopic change. The form factor, shown in Figure 5.3, is measured for dilute solutions at both neutral and acidic pH. The data are presented as Holtzer plots to emphasize the rod-like structure.



Figure 5.3: Holtzer plot, qI(q) versus q, for 0.5 mg/mL pC₁₆TVB in D₂O solutions at two different values of pH. Solid circles represent neutral pH and open squares represent acidic conditions (pH=1). The rigid rod from factor (r = 2.0nm, L > 100nm) and form factor for a semi-flexible rod model (r = 2.0nm, $L/L_p = 7.3$) are represented as lines.

At neutral pH, the scattering is typical of a rigid cylinder with a sharp drop at higher q due to the finite cross section. This has been reported and is consistent with the scattering of the form factor of a rigid cylinder.¹ The radius of the cylindrical cross-section is found to be 2nm, close to the length of a $C_{16}TA^+$ surfactant.³ The overall length cannot be extracted from the SANS data as the Holtzer plot reaches a plateau at low q. As shown from the fitted form factor, the length is greater than 100 nm, but an upper limit cannot be determined from SANS alone. Assuming that the structure is truly rod-like, then the radius of gyration R_g obtained via static light scattering provides a measure of the length; for rigid rods, $L^2 = 12 \cdot R_g^2$ which provides an estimated rod length of 185nm (given an $R_g = 53.6$ nm). As pH is dropped to acidic values of pH~1.0, the scattering at high q remains essentially the same, indicating that the cylindrical cross section is maintained. The intermediate region is still relatively flat, indicating rod-like regions within the new structure. At low q, there is an upturn in the scattering intensity which is due to either increased level of flexibility or structure factor effects due to interactions between aggregates.

Given the low concentration, the low q upturn is assumed to be due to flexibility, and a semi-flexible rod model¹¹ is used to compare to the low pH data. The radius is 2nm, while a persistence length L_P has been introduced to account for flexibility. The lack of observable plateau in the curve at low q means L cannot be extracted using the model. Therefore, the ratio of L to L_P is varied to account for the upturn near q=0.1 nm⁻¹. As shown in Figure 5.3, with $L/L_p = 7.3$, the model compares well to the experimental data. This simple analysis is consistent with a flexible aggregate.

However, for an aqueous solution of aggregates with known hydrogen bonding capability, the inter-aggregate interaction might still contribute a small part in the upturn. The protonation of COO- groups of the backbone pVB to COOH groups introduces a hydrogen bonding capability to the system. Experiments on the system at pH 1.0 and various solution temperatures are performed to verify that. Figure 5.4 shows the scattering intensities of the solution of $pC_{16}TVB$ at 0.5mg/ml concentration and pH 1.0, but at temperatures varying between 5 and 40^oC. Indeed, as the temperature drops, the upshift at low q values increases, a sign of hydrogen bonding. As the temperature of the solution increases, the H-bond, being a relatively weak bond, is disrupted by the additional thermal energy. The fact that the curves follow the expected trend for hydrogen bonding is a clear evidence of the small contribution of inter-aggregate interaction to the low q upturn.



Figure 5.4: Holtzer plot, qI(q) versus q, for 0.5 mg/mL pC₁₆TVB in D₂O solutions at pH 1.0, but at various solution temperatures. Empty triangles, circles, and squares represent 5°C, 25° C, and 40° C data, respectively.

To probe the system at a larger length scale than what SANS can do, DLS is employed. Figure 5.5 shows the multi-angle DLS data of $pC_{16}TVB$ in acidic solutions, at pH values of 2.6 and 1.1.



Figure 5.5: Multi-angle DLS of $pC_{16}TVB$ at two different solution pH, 2.6 (circles) and 1.1 (triangles). The solid lines are linear fits of respective data sets, with R^2 being 0.98 for pH 2.6 data, and 0.97 for pH 1.1 data.

The observed R² values indicate good linear fits. The decay rates, extracted from the reduced autocorrelation functions using CONTIN, are functions of the diffusivities and q. A crucial assumption to extract the translational diffusivity from the decay rate is that it is the dominant mode of diffusion within the system. Once that is the case, the decay rate can be approximated as $\Gamma = D_T \cdot q^2$, or in other words, the plot of decay rate versus q² would be linear. Concentrated solutions, very large particles, or anisotropic particles violate this crucial assumption. Other modes of diffusion, notably rotational diffusion, might not be negligible, and the analysis of DLS data becomes much more complicated. Fortunately, the linearity of the data is an indication that the assumption of translational-only diffusion of the aggregate in acidic solutions being the dominant form of diffusion is valid. This enables the conversion of the results of DLS to aggregate sizes.

Once the assumption is verified, DLS is used to investigate the impact of pH on the overall size of the aggregate at dilute concentrations. Figure 5.6 shows effective hydrodynamic diameter, $d_{\rm H}$, measured for a 0.83 mg/ml solution of pC₁₆TVB at different values of pH, which is controlled by adding HCl.



Figure 5.6: Hydrodynamic diameter d_H of pC₁₆TVB measured in solutions ranging from very acidic to neutral. Concentration and temperature are kept constant at 0.83mg/ml and 25°C. The two dotted lines represent pH 1.0 and pH 7.0 for reference purposes.

For values of solution pH between neutral and pH~2.0, there is little change in the aggregate size, which is shown to be $d_{\rm H} \sim 60$ nm. The aggregate size increases drastically as pH drops below pH~2, and reaches values close to 100nm at the lowest pH values. The transition point resembles the one observe in the turbidimetry data, and is very close to the pKa of the pVB polyacid chain. Defined as the pH at which 50% of carboxylate groups are protonated, the pKa is predicted to be $\sim 1.2^{12}$ This suggests the importance of protonation states of such groups on the overall structure. Larger error bars on the data at low pH indicate a more dynamic structure as there are greater variations in the measured hydrodynamic diameter. The samples are stable with time, similar results are seen on samples stored for months, but these low-pH samples do appear more sensitive than at higher pH. The increase in d_H at pH 1.0 compared to the one at neutral pH is significant, and cannot be accounted for by the increased viscosity of HCl solutions.¹³ The increase in d_H is due to the change in overall structure of the aggregate.

The dependence of d_H on the solution pH, together with the evidence from NMR (the benzene rings experience a more polar surrounding) and SANS (aggregate has some rigid rod-like regions but with higher overall level of flexibility and/or inter-aggregate interaction), prompts the need for the reevaluation of properties such as the dependence of size on temperature and concentration at pH near the pKa. In Figure 5.7, DLS is used to measure d_H at two different values of pH as a function of temperature between 5 and 40°C. At each temperature in 5°C intervals, two hours of equilibration is allowed prior to measurement. Not shown here is the reverse direction from 40° C cooling back down to 5°C, which shows no hysteresis.



Figure 5.7: Hydrodynamic diameter of two different pH solutions of $pC_{16}TVB$ measured at temperatures between 5°C to 40°C. The concentration is kept constant at 0.83mg/ml.

At neutral pH, the d_H of approximately 55-60nm is not a function of temperature. In marked contrast, at pH ~1.0, the aggregate is clearly affected by temperature change, with d_H decreasing as temperature increases. This is consistent to a structure dominated by hydrogen bonding rather than electrostatics. Hydrogen bonds between COOH groups and the surrounding water molecules, being much weaker than the Coulombic forces,¹⁴ are disrupted at higher temperature. The impact of hydrogen bonding between the COOH groups

and water is the reason why the PES aggregate has a temperature-sensitive conformation in water.



Figure 5.8: Hydrodynamic diameter of $pC_{16}TVB$ aggregate measured over a range of concentrations from 0.3mg/ml to 2.0mg/ml and two pH values of 1.0 (open circles) and neutral (solid circles). Temperature is kept constant at 25°C.

In Figure 5.8, the hydrodynamic diameter of $pC_{16}TVB$ aggregates is measured at different concentrations and two values of pH. At neutral pH, the d_H is independent of concentration, indicating that these concentrations are in the dilute limit and there are limited interactions between aggregates. At acidic pH, dilute solutions behave similarly, while above 0.9mg/ml, d_H appears to increase with concentration. It appears that the limit for interactions between aggregates has moved to a lower concentration, indicating that the aggregates are larger and, more likely, subjected to increased inter-aggregate interactions. The decrease in critical concentration does not infer that SANS results presented earlier are due to structure factor effects as those data were measured at a concentration of 0.5 mg/mL where interactions are observed but weak.

The reversibility of the structural change is verified with DLS. In Figure 5.9, the $d_{\rm H}$ of pC₁₆TVB aggregates are measured at various values of pH. Initially, the solution pH is dropped from neutral to a value of 1.0 using concentrated HCl. During this phase, COO⁻ groups are protonated into COOH groups, and at the same time Cl⁻ concentration increases, reaching a concentration of 0.1M at pH 1.0. As previously described in Figure 5.6, the d_H increases as pH drops. At pH 1.0, concentrated NaOH is added to the solution to bring the pH back to neutral. The concentration of Cl⁻ remains at 0.1M during this phase; while Na⁺ is introduced and reaches concentrations of 0.1M.



Figure 5.9: Hydrodynamic diameter of $pC_{16}TVB$ measured at various pH values. The concentration and temperature are kept constant at 1mg/ml and 25°C, respectively. Solid circles are measured as HCl is used to lower pH, while open circles represent data measured as NaOH is used to increase pH. The inset depicts the corresponding change in salt concentration (Cl⁻ and Na⁺) during these two stages.

The value of d_H at neutral pH at both the beginning and the end of the cycle is the same. The reproducibility of the hydrodynamic diameter of the aggregate after one complete cycle of HCl/NaOH addition is an indication of the reversibility of the pH-induced transition. The hysteresis in size at intermediate values of pH is due to the resulting salt concentration of the acid-base reaction. The additional NaOH increases the pH of the solution by neutralizing a portion of pre-existing HCl, and at the same time increases the concentration of NaCl. Unlike the aggregate at neutral pH, where the surfactants and polymers are bound by very strong electrostatic attraction, and whose structure is practically immune to ionic strength up to 0.3M of salt,² the reduced attraction in the intermediate pH

region renders the aggregate susceptible to change in ionic strength. Significantly higher ionic strength then screens electrostatic repulsion between surfactant head groups, leading to higher aggregation number, or larger aggregate size. Upon recovering neutral pH, that effect is minimized, and d_H goes back to the expected value. The reversibility also indicates that the $C_{16}TA^+$ surfactant is robust at low pH, and its hydrolysis does not occur. The effect of ionic strength on d_H in the intermediate pH region has been independently verified by adding NaCl into a mid-pH-range solution and using DLS to check for the variation in d_H .



Figure 5.10: Hydrodynamic diameter of $pC_{16}TVB$ measured at pH value of 2.1 and various NaCl concentration. The concentration and temperature are kept constant at 1mg/ml and 25°C, respectively.

Figure 5.10 shows the effect of ionic strength on the hydrodynamic diameter of $pC_{16}TVB$ at pH 2.1. As more NaCl is added, the measured

hydrodynamic diameter increases from 33nm to 112nm. Notice that pH 2.1 is the intermediate pH with the hysteresis as described in Figure 5.9. In order to drop the pH from 2.1 to 0.9, about 120mM of HCl needs to be added. Similarly, to bring the pH back up to 2.1, that much NaOH is needed. The result of the neutralization is 120mM of NaCl in the solution of pH 2.1 pC₁₆TVB aggregate. That corresponds to d_H of about 89nm based on the extrapolation of data in Figure 5.10, which is not too far from the value in Figure 5.9. This is the conclusive evidence that the hysteresis observed in Figure 5.9 is caused by the salt generated from the neutralization of HCl by NaOH.

The effect of Cl⁻ on the structural change is further analyzed. In Figure 5.11, the d_H of pC₁₆TVB aggregates is measured at various Cl⁻ concentrations, using either HCl, or NaCl. As it has been shown previously, the use of HCl has two consequences: protonation of VB⁻ and the introduction of Cl⁻. The effect is the increase in measured hydrodynamic diameters. Instead of HCl, the use of NaCl to introduce the equivalent concentration of Cl⁻ does not generate the same effect, with the aggregate dimensions remain essentially unchanged. This shows the importance of the protonation on the size change and eliminates the role of Cl⁻ when it is not in combination with H⁺.



Figure 5.11: Hydrodynamic diameter of $pC_{16}TVB$ measured at various Cl⁻ counterion concentrations. The concentration and temperature are kept constant at 1mg/ml and 25°C, respectively. Solid circles are measured as HCl is used to introduce Cl⁻ into the system, while open triangles represent data measured as NaCl is used instead.

Figure 5.12 shows rheological data for the acidic $pC_{16}TVB$ solution at a representative concentration, pH, temperature, and temperature equilibration time. The cross-over of G' and G'' provides the values for (ω_{xo} , G_{xo}) and the starting point to catalog the rest of the parameters. The solution is clearly a viscoelastic solution, not really a gel as initially suggested. This rheology is reminiscent of worm-like micelle solutions or self-associating polymer solutions.^{15,16} At neutral pH, the solution is essentially a dispersion of hard rods, thus the rheology at these concentrations is Newtonian or possibly shear thinning. Viscoelasticity like that seen in Figure 5.12 requires a new timescale in the solution, something more

common in interacting macromolecular solution. The linkages are most likely intra-aggregate hydrogen bonds caused by protonated –COOH groups at low pH.



Figure 5.12: Rheological data of the solution of $pC_{16}TVB$ at 19.3mg/ml and 0.20M concentration of HCl. The temperature is kept at 25°C.

Table 5.1, 5.2, and 5.3 tabulate the crossover behavior of the $pC_{16}TVB$ solution to the change in solution temperature, pH, and $pC_{16}TVB$ concentration. The trends further support the fact that the viscoelasticity is caused by some sort of effective network linkage. For each solution, a pre-determined sequence of temperatures is imposed, with returns to $25^{0}C$ in between to check for structural integrity. As the temperatures increases, the viscosity drops and vice versa. This is an indication of hydrogen bonding, where an increase in temperature provides the necessary thermal energy to break up some of the weak bonds, disrupting the

network structure and decreasing the solution viscosity. In Table 5.1, the attention is paid to the rheological properties as a function of $pC_{16}TVB$ concentration. Cross-over frequency ω_{xo} drops as concentration increases from 12.5 to 19.3 mg/ml, consistent with an increase number of sticking points in the network.

pC ₁₆ TVB concentration	Т	ω _{xo}	G _{x0}	G*	τ	η*
(mg/ml)	(K)	(rad/s)	(Pa)	(Pa)	(s)	(Pa.s)
12.5	298	1.93	0.95	1.34	0.52	0.69
12.5	303	5.73	1.00	1.41	0.17	0.25
12.5	298	0.88	1.48	2.09	1.14	2.38
12.5	293	0.21	2.05	2.90	4.78	13.86
12.5	298	0.98	1.69	2.39	1.02	2.44
12.5	288	0.04	3.06	4.33	23.53	101.92
12.5	298	1.22	1.88	2.65	0.82	2.17
19.3	298	0.87	2.72	3.85	1.15	4.42
19.3	303	3.84	2.56	3.62	0.26	0.94
19.3	298	0.63	3.96	5.61	1.59	8.89
19.3	293	0.15	5.23	7.39	6.84	50.57
19.3	298	0.65	4.53	6.40	1.54	9.85
19.3	288	0.03	7.10	10.04	31.40	315.41
19.3	298	0.71	4.71	6.65	1.41	9.40

Table 5.1: Rheological data of solutions of $pC_{16}TVB$ at two concentrations, 12.5 and 19.3mg/ml. The solution pH is kept at 0.96, which corresponds to a HCl concentration of 0.11M. The data of each sample is collected in that heating-cooling order: 298K - 303K - 298K - 298K - 298K - 298K - 298K, with a 30 minutes equilibration time in between.

Similarly, as seen in Table 5.2 when the HCl concentration increases from 0.11 to 0.20 M, ω_{xo} drops while G_{xo} increases. More HCl induces more protonation of the backbone, creates more hydrogen bonds, and hence increases the number of sticking points, leading to lower ω_{xo} and higher G_{xo} .

T (K)	ω _{xo} (rad/s)	G _{xo} (Pa)	G* (Pa)	τ (s)	η* (Pa.s)
298	0.21	10.93	15.45	4.74	73.28
303	0.79	10.42	14.73	1.27	18.70
298	0.21	14.28	20.20	4.67	94.34
293	0.09	14.23	20.12	10.71	215.41
298	0.45	59.52	84.18	2.23	187.55
288	0.04	19.47	27.53	25.15	692.50
298	0.34	90.73	128.31	2.90	371.96

Table 5.2: Rheological data of solutions of $pC_{16}TVB$ at a concentration of 19.3mg/ml. The solution pH is kept at 0.70, which corresponds to a HCl concentration of 0.20M. The data of each sample is collected in that heating-cooling order: 298K - 303K - 298K - 293K - 298K - 298K - 298K, with a 30 minutes equilibration time in between.

The temperature equilibration time is also an important factor in this experiment, especially with the heating mechanism of the setup being from the bottom plate. The experiment is repeated at the same aggregate concentration (12.5mg/ml) and HCl concentration (0.11M), but with only half the temperature equilibration time (15 minutes). The data are shown in Table 5.3, which indicates that the system has not had enough time to come to equilibrium. As a result, the data that corresponds to longer equilibration time (30 minutes) has been used instead.

T (K)	ω _{xo} (rad/s)	G _{xo} (Pa)	G* (Pa)	τ (s)	η* (Pa.s)
298	1.18	1.02	1.44	0.85	1.23
303	8.18	1.05	1.48	0.12	0.18
298	0.79	1.60	2.26	1.27	2.87
293	0.18	2.33	3.29	5.56	18.27
298	0.92	1.89	2.67	1.09	2.91
288	0.04	3.42	4.83	25.00	120.84
298	0.63	2.46	3.48	1.60	5.58

Table 5.3: Rheological data of solutions of $pC_{16}TVB$ at a concentration of 12.5mg/ml. The solution pH is kept at 0.96, which corresponds to a HCl concentration of 0.11M. The data of each sample is collected in that heating-cooling order: 298K - 303K - 298K - 298K - 298K - 298K - 298K, with a 15 minutes equilibration time.

5.5 Discussion

One complication in interpreting the DLS data is the effect of multiple scattering, which typically becomes a problem when the solution is not dilute. The assumption of the DLS measurement being performed in dilute concentration has been verified experimentally. The dilution data in Figure 5.8 shows that the concentration has no effect on the hydrodynamic diameter when it is lower than 1.0mg/ml for the solution of $pC_{16}TVB$ at pH of 1.0. The number becomes 2.0mg/ml or higher at pH of 7.0. Both of them will be correlated with the overlap concentration C*, which typically marks the transition between dilute and semi-

dilute regime. It can be calculated as¹⁷ $C^* = \left(\frac{1}{Rg^3}\right) \left(\frac{M}{N_A}\right)$.

For the pH 7 aggregate, with R_g measured using SLS, C* turns out to be 14.5mg/ml, well above the highest concentration used in this work, 2.0mg/ml. Unfortunately, it is not entirely clear what the R_g value should be for the low pH

aggregate. The use of SLS requires the knowledge of dn/dc at this new solution pH, which could not be obtained. Unlike the data for solutions of aggregates at neutral pH (Figure 2.5), where Δn versus concentration is linear, the data for acidic solutions of aggregates are not. There are two different problems at the two concentration regimes: excessive light scattering for moderately concentrated solutions, and low signal to noise ratios for dilute solutions. However, a rough estimate of R_g can be done using d_H, which at pH 1 doubles over that of the neutral value. If R_g is also doubled, which is admittedly a big assumption, C* will be 1.8mg/ml, not too far from the experimentally obtained value of 1.0mg/ml. As a result, it is safe to assume that the DLS measurements for the aggregate at both pH values are performed in dilute solution.

The experimental data show the difference of $pC_{16}TVB$ aggregates at neutral and acidic pH. The polyelectrolyte chain is protonated with the addition of HCl. The surfactant binding curve measured via potentiometry assures that although there are surfactants dissociating from the aggregate due to the drop in pH, the relative change is small, so the aggregates are not destroyed. However, the aggregate hydrodynamic size almost doubles at pH 1 compared to neutral pH, while at the same time it becomes susceptible to variation in temperature and concentration. SANS shows a further change of slope at low q, indicative either of flexibility or inter-aggregate interaction although no significant change in the local cross section of the aggregates. ¹H NMR (see section 4.4) supports a structure in which the carboxylate/carboxylic groups are more exposed to the surrounding water than at neutral pH. All of these structural changes are completely reversible with some hysteresis in the intermediate pH region due to high ionic strength effect.

The drop in pH of the solution has altered the balance that holds the aggregate together. The protonation of a fraction of carboxylate groups significantly reduces the level of electrostatic attraction between surfactant and monomer units of the chain, while generating carboxylic groups with the ability to form hydrogen bonds. Evidence of this bonding is visible by the gel at pH 1 and 10 mg/ml (Figure 5.1), by the behavior of low-q SANS temperature data (Figure 5.4), by the strong dependency of hydrodynamic size on temperature (Figure 5.7), and by the behavior of rheological properties (ω_{xo} and G_{xo}) with change in temperature (Table 5.1). Internally, the balance is no longer being dominated by electrostatic attraction. There are three indirect consequences of this change in balance of forces. Firstly, the flexibility of the chain has increased since it is no longer locked in near the interface by the electrostatic attraction with $C_{16}TA^+$ molecules. Secondly, the surface of the aggregate now becomes positively charged due to the loss of negative charge of some of the now neutralized VB-H, resulting in inter-aggregate repulsion. Both of these are possible causes for the observed negative slope in the low q region of the $pC_{16}TVB$ Holtzer plot (Figure 5.3). Thirdly, segments of the chain, equipped with hydrogen bonding capability, can afford to be exposed to the aqueous environment instead of in the hydrophobic core. This partial neutralization of the chain, together with the ability of the weak-binding Cl⁻ counterion to promote spherical micelles with C₁₆TA⁺ suggests a different aggregate structure at pH 1. The product of the transformation

is proposed to be a "string-of-pearl", or necklace, structure, and has been described in the previous chapter.

Overall, the model is consistent with experimental observations at various length scales. Locally, the cross-section remains the same (SANS) as pH drops from neutral to acidic, which is consistent since both the rod-like and the stringof-pearl structure have the same cross-section dictated by the surfactant dimension. The overall shape of the aggregate in both regions of pH still has rodlike regions (SANS). The published form factor predicted for a string of closely is consistent with this picture.¹⁸ Considering the overall packed spheres hydrodynamic size of the aggregates, $d_{\rm H}$ doubles during the transition. Transforming a packed structure (cylinder) to a less packed one (sphere) would naturally result in an increase in size. The number of surfactant molecules per aggregate is not expected to change drastically (as shown in Figure 5.10), by the surface area per surfactant for a cylindrical interface (when the VB⁻ acts as counterion) is expected to be smaller than the surface area per surfactant for a spherical interface (when Cl⁻ acts as the counterion). Macroscopically, solution behavior is also consistent with the proposed model. The aggregates can be considered as elongated "sticky" objects, capable of network formation at moderate to high concentration, which is supported by rheological data. Gelation and viscoelastic behavior are common in attractive hydrophilic polymer systems, for example, hydrophobically-modified water-soluble polymers form transient networks; networks that exhibit gel-like behavior.¹⁹⁻²¹ Although the domination of hydrophobic interaction and the reduction of electrostatic interaction is the main

cause for the possible structure shift of the system, it is likely that the increasing strength of the H-bond is what supports the new structure and defines the properties of the new system.

5.6 Conclusions

At neutral pH, aggregates of $C_{16}TA^+$ and pVB⁻ form a stable, rod-like structure that is insensitive to most changes in solution conditions. Lowering pH allows the structure to be altered from cylinder to a structure more consistent with a string-of-pearl (spherical micelles connected by the partially solubilized polyelectrolyte chain). This change is driven by a reversible protonation of the pVB⁻ chain that stabilizes the aggregate. The hydrodynamic diameter of the aggregate is doubled, in agreement with the expected drop in micellar packing factor during a cylinder-to-sphere transition. Aggregate cross-section remains the same between cylindrical and spherical micelles. The exposed segments of pVB chain to the surrounding aqueous environment have also been detected by ¹H NMR. Hydrogen bonding, a by-product of the protonation, causes the dependence of hydrodynamic diameter on temperature, and formation of network structure in the viscoelastic aggregate solution at low pH. At low enough pH (1.0) and high enough $pC_{16}TVB$ concentration (10 mg/ml), gelation is observed. Interactions between adjacent aggregates at pH 1.0 have also been observed in the low q region of the Holtzer plot, and in the dependence of hydrodynamic diameter on concentration at above 0.9 mg/ml. The addition of NaOH, a strong base, returns the structure a rod-like cylinder.
5.7 References

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Chapter 6

Dye solubilization and polyelectrolyte-surfactant aggregate adsorption onto oxide nanoparticle surfaces

Work has been done on a unique rod-like polyelectrolyte-surfactant aggregate, poly-cetyltrimethylvinylbenzoate, denoted $pC_{16}TVB$, that is capable of solubilizing various hydrophobic dyes such as pyrene and Nile red. The dye solubilization starts at low aggregate concentrations. Dropping the solution pH from neutral to acidic increases the solubilizing power by a factor of ten. Using the dyes as tracking molecules, the adsorption of the dye-saturated aggregate onto the surfaces of Silicon Dioxide (SiO₂) and Titanium Dioxide (TiO₂) nanoparticles has been studied. The adsorption has no effect on the location of the pre-absorbed dye molecules within the aggregate, and no dye desorption is observed. $pC_{16}TVB$ adsorption onto TiO₂ surfaces is stronger than onto SiO₂ surfaces, reflecting the slightly less negative charge of the TiO₂ surfaces. Applications for the aggregate include the solubilization of hydrophobic molecules in aqueous solvent, and the use of the aggregate as a delivery vehicle for hydrophobic molecules from solution to the solid surface, like in the case of coating.

6.1 Introduction and background

There are many uses of polymer-surfactant aggregates in aqueous solution in industrial applications, including as solubilizing agents.¹⁻⁶ The binding of polymers on the surfactant micelles lowers the critical aggregation concentration of the surfactant aggregates and changes the solubilizing power. We have developed a material, $pC_{16}TVB$, in our laboratory which can solubilize hydrophobic molecules in aqueous solution even at low concentrations, and acts as a delivery vehicle for those molecules onto solid surface, which enables the investigation of interactions at the solid-liquid interface. Using pyrene and Nile red dyes as tracking molecules, UV-visible and fluorescence spectroscopies are used to monitor changes in aggregate adsorption onto two different oxide surfaces, SiO₂ and TiO₂, at different aggregate concentrations. The structures of the dyes are shown in Figure 6.1. The wide variety of the dimensions of both the aggregate and the nanoparticles makes the study of the curvature effect on the adsorption possible.

The adsorption of this aggregate onto flat SiO₂ surfaces was studied previously,⁷⁻⁹ using atomic force microscopy (AFM) and quartz crystal microbalance with dissipation monitoring (QCM-D). The adsorbed rodlike micelle aggregates are seen to form a close-packed monolayer with a high degree of order over micrometer length scales, while maintaining the cylindrical structure of the aggregate with little or no flattening. The adsorption isotherm data, recorded by QCM-D, indicates a two-stage mechanism: an adsorbed film of free $C_{16}TA^+$ ions is initially adsorbed to create the hydrophobic anchor points. The weakly negatively charged aggregates adsorb irreversibly onto the charge-reversed surface, with the adsorbed mass being increased dramatically. For this chapter, we would like to extend this knowledge to adsorption of the rod-like PES aggregates onto a curved surface of similar materials, specifically onto SiO₂ and TiO₂ nanoparticles.



Figure 6.1: Chemical structure of the hydrophobic dyes, pyrene and Nile red.

6.2 Materials and Methods

6.2.1 Materials preparation

The preparation of the worm-like template and its polymerization has been discussed in detail in Section 2.1, while the procedure to prepare silica nanoparticles can be found in Section 2.2. The surface of the silica is negatively charged, with the zeta potential ranging between -40 and -45mV at pH 7-7.5, the operating pH range in this work. After synthesis, the silica is used within a month, although the solution itself is stable for several months. The hydrodynamic diameters of silica used in this study include 220nm, 400nm, and 700nm.

TiO₂ used in this work is the commercial Aeroxide TiO₂ P25 powder stock, obtained from Evonik Degussa Corp. (Theodore, AL). It contains both anatase and rutile phases at 3:1 ratio. Before use, the sample is dissolved in DI water, then ultra-sonicated for 45 minutes. Its isoelectric point is measured to be about pH of 6.0. At the working pH condition of about 7.5, the TiO₂ surface is negatively charged, with the surface zeta potential measured at -24.1mV. TEM indicates rather polydisperse sizes and shapes, with the reported surface area is $50-55m^2/g$ on average.^{10,11} Dynamic light scattering provides a hydrodynamic diameter of 48nm, with a distribution between 20 and 70 nm.

To probe the solubilization power of the aggregates, hydrophobic dyes such as pyrene (Sigma-Alrich, St. Louis, MO) and Nile red (MP Biomedicals, Solon, Ohio) are added to aqueous solutions of $pC_{16}TVB$ at different concentrations and values of solution pH. Both pyrene and Nile red are in solid form, varying in crystal size from powder to milimeter chunks. The mixtures are then put in a rotating mixer for a period of time, and centrifuged. The excess solid dye is removed, while the supernatants undergo UV-Visible spectroscopy and fluorescence spectroscopy measurements. The order of these steps, the mixing time, the centrifugation time and speed, the $pC_{16}TVB$ concentration and solution pH values, among other things, vary between experiments, and will be specified accordingly in the result section. All experiments are performed at room temperature.

To probe the adsorption of dye-saturated $pC_{16}TVB$ aggregate onto solid surfaces of oxide nanoparticles, including SiO₂ and TiO₂, a similar procedure is performed on systems with four instead of three components: dye, $pC_{16}TVB$ aggregate, nanoparticles, and solvent water. They are mixed, allowed to equilibrate and at the end, the nanoparticles and adsorbed aggregates, together with the excess solid pyrene are separated out by centrifugation. As before, the experimental parameters vary, and will be specified together with the results. In aqueous solutions, pyrene adsorbs onto both TiO_2 and SiO_2 surfaces to some extent. However, the association is also known to be relatively weak, evident from the ability of benzene solvent to completely wash it off the oxide surfaces.¹²⁻¹⁵ Since benzene, with its ring electrons, is even less hydrophobic of an environment than the micelle core formed by the hydrocarbon tails of the surfactants, it is unlikely that any pyrene molecule remains adsorbed on the oxide surfaces with the presence of pC₁₆TVB. Even in the case when the aggregate itself is saturated and theoretically some pyrene can adsorb onto the oxide surfaces, experimental data for SiO₂ shows that the adsorption of pyrene onto SiO₂ surfaces is negligible. Due to the chemical similarities between the surfaces of SiO₂ and TiO₂, and between the structures of pyrene and Nile Red, we expect similar behavior in the adsorption of Nile Red onto TiO₂.

6.2.2 UV-visible spectroscopy

Using a Varian Cary 300 UV-visible spectrophotometer (Varian, Palo Alto, CA), a spectral scan from 200-800 nm is done using a 1 cm quartz cell. The sampling rate is 10nm per second. All absorbance values used are at least an order of magnitude higher than the instrument resolution. The pyrene peak at 338nm was chosen for analysis. In appropriate situations, the recorded absorbance can be converted into dye concentration using the Beer-Lambert law,¹⁶

$$\log(I_a/I) = A = \varepsilon lC$$
 [6.1]

where I_o and I are the intensity of monochromatic light entering and leaving the sample, respectively, A is the absorbance, ε is the molar extinction coefficient

(mol⁻¹cm⁻¹), which depends on the system (37510 M⁻¹cm⁻¹ for pyrene in water,¹⁷ 56200 M⁻¹cm⁻¹ for pyrene in petroleum)¹⁸, and I is the path length.

6.2.3 Fluorescence spectroscopy

Fluorescence spectroscopy is performed using the Molecular Devices Spectromax M2 Plate Reader. The samples are pipetted into individual clearbottom wells of a 96-well plastic plate. A spectral scan in 2nm increments from 270-600 nm at an excitation wavelength of 240nm was performed. Pyrene peaked at approximately 373nm, 382nm, and 390nm.

6.3 Results

Since pyrene dye is used as a tracking molecule for the $pC_{16}TVB$ aggregates, it is important to confirm its solubility in the aggregates. Using a fluorescence spectrophotometer, a spectral scan in 2nm increments from 270-600 nm at an excitation wavelength of 240nm is performed, the data of which are included in Figure 6.2. The ratio of I₁/I₃, in this case approximately 1.12, provides details about the micro-environment of pyrene. When compared to literature values, we found that this number is very close environments similar to SDS in PEG.¹⁹ This demonstrates that the pyrene is indeed buried in the hydrophobic core of the aggregates and thus, an effective tracking molecule.



Figure 6.2: Fluorescence spectra of aqueous solutions of pyrene-saturated $pC_{16}TVB$. The samples are placed in a 10mm quartz cell. $pC_{16}TVB$ concentration ranges from 0.01 to 1.00mg/ml. The excitation wavelength is 240nm, while pyrene emission peaks at 373nm and 382nm are labeled I₁ and I₃ respectively. As the aggregate concentration increases, both I₁ and I₃ increase.

After confirming that pyrene molecules indeed solubilize into the $pC_{16}TVB$ aggregates, it is necessary to establish a correlation between the absorbance and $pC_{16}TVB$ concentration. Figure 6.3 shows the UV-Vis absorption spectra of the pyrene-saturated aqueous solutions of $pC_{16}TVB$ aggregates. The absorbance peak at 338nm, among other peaks, is characteristic of pyrene. Assuming the absorbed pyrene molecules are distributed evenly among the aggregates, the concentration of pyrene can be used to derive the aggregate concentration in the solutions. The choices of dye and absorbance wavelength must be such that the data i) exhibit a correlation between absorbance and

concentration, ii) do not exceed instrument saturation limit (10.000) within the concentration range, and iii) have absorbance significantly higher than the noise level. Pyrene at 338nm, and later on, Nile red at 552nm, satisfies the requirements.



Figure 6.3: UV-Vis spectra of aqueous solutions of pyrene-saturated $pC_{16}TVB$. A low volume quartz cell with path length of 2mm is used. $pC_{16}TVB$ concentration ranges from 0.01 to 1.00mg/ml. The scan is performed from 200 to 800nm, but there is only meaningful absorbance in the UV region. The zoom-in part of the spectrum between 300 and 370nm is included in the top right inset. As the aggregate concentration increases, the absorbance increases accordingly.

Figure 6.4 plots absorbance at 338nm, extracted from Figure 6.3, as a function of $pC_{16}TVB$ concentration. Noting that in this case, aqueous solutions of $pC_{16}TVB$ and pyrene are prepared at the appropriate aggregate concentrations, allowed to equilibrate for 24 hours, centrifuged to remove excess solid pyrene, then measured for absorbance immediately. It is clear that although the data

below 0.7-0.8mg/ml are relatively linear and hence follow the Beer-Lambert law, the data at higher concentrations do not. As a result, the Beer-Lambert law will not be applied here to derive $pC_{16}TVB$ concentration from absorbance. Instead, extrapolation of the nearest two absorbance data points will be done.

To study the possibility of pyrene desorption from the $pC_{16}TVB$ aggregate after sample preparation, instead of obtaining the absorbance immediately after centrifugation, we let the samples rest for 1, 3, or 5 days, and then measure the absorbance. As a standard data treatment for this and all further experiments, the background absorbance, including the absorbance caused by an insignificant amount of pyrene solubilization in the DI water solvent, and the absorbance of the cell, is subtracted from the results. The data are also included in Figure 6.4, with no observable drops in absorbance, or in other words, no desorption occurs for at least 5 days. The system is already at a stable equilibrium.



Figure 6.4: Absorbance at 338nm of pyrene-saturated $pC_{16}TVB$ in aqueous solution. The sample cell path length is 2mm. $pC_{16}TVB$ concentration ranges from 0.01 to 1.00mg/ml.

A 1 mg/mL pC₁₆TVB stock solution is made and pre-saturated with pyrene. Excess pyrene is removed by centrifugation at 3500rpm for 35min. The supernatant is then diluted by pyrene-saturated DI water to generate solutions with pC₁₆TVB concentrations ranging from 0.01 mg/mL to 1.00 mg/mL, the absorbance of which is then measured, yielding the results shown in Figure 6.5. Note that this is different from the previous experiment, where the aggregates were allowed to solubilize as much pyrene as possible at the corresponding concentration before excess solid pyrene was removed. Here, pyrene is equilibrated with a solution of pC₁₆TVB at the 1.00mg/ml before the dilution step to archive the appropriate aggregate concentration. Knowing that the solubilization capacity of the aggregate is different at different concentrations, and pyrene desorption might occur to bring the system to the new equilibrium at the new concentration, absorbance measurement is done as soon as the final solutions are prepared.



Figure 6.5: Absorbance at 338nm of pyrene-saturated $pC_{16}TVB$ in aqueous solution. The sample cell path lengths are 10mm and 2mm for the closed circles and the open circles data, respectively. The lines are linear fits of experimental data, with the slopes for the 10mm and 2mm cases being 1.69±0.02 and 0.36±0.00 ml/mg, respectively. pC₁₆TVB concentration ranges from 0.01 to 1.00mg/ml.

Two different path lengths are used to check for the possibility of scattering at high concentration and long path length, the presence of which artificially increases the absorbance and renders spectroscopic analysis inaccurate. The ε value for the 10mm path length is 0.17 L/mg.m, almost exactly the same as that for the 2mm path length, 0.18 L/mg.m, confirming the lack of scattering.

Either the 2mm or 10mm cell is appropriate for these experiments and a value of ϵ =0.175±0.005 will be used for all conversions of absorbance to concentration.

The ability of aggregates to solubilize a hydrophobic moiety, namely pyrene, as a function of solution pH is shown in Figure 6.6. It shows the concentration of solubilized pyrene molecules versus the total concentration of $pC_{16}TVB$ for two different solutions. As usual, the background absorbance has been subtracted from the measured absorbance of the sample solutions. The contribution from the pyrene solubilized in the aqueous solvent, considered a part of the background absorbance, is negligible, and hardly changes with solution pH. The Beer-Lambert law is then used to convert the corrected absorbance to concentration value of solubilized pyrene. Since it has been shown in Chapters 4 and 5 that at pH 1.0, the micro-environment the pyrene molecules reside in is still the hydrophobic core the $pC_{16}TVB$ aggregate, the extinction coefficient likely remains close to the value at neutral pH. As a result, the same extinction coefficient has been used for both solutions. For comparison purpose, the value for pyrene in water is used, as the value for pyrene in micellar environment is not available. The aggregate at neutral pH solubilizes less pyrene than the acidified aggregate, indicating a fundamental difference between aggregates at different values of pH. Compared to the rod-like structure at neutral pH, the aggregates at low pH have more nonpolar internal space capable of taking up hydrophobic moieties such as pyrene²⁰. By dropping the solution pH from neutral to 1.0, the pyrene solubilizing power of the aggregate increases by a factor of ten.



Figure 6.6: Concentration of pyrene solubilized in $pC_{16}TVB$ solutions of neutral pH (closed circles) and acidic pH (open circles), as calculated from pyrene solubilization data obtained using UV-Vis measurements. Concentration is kept at or below 0.20 mg/ml to minimize scattering. A quartz cell with 10mm path length is used.

The adsorption of the aggregate onto solid surfaces, in this case SiO₂, is studied. A batch of pC₁₆TVB (1.24mg/ml) is mixed with pyrene solid powder for 24 hours and centrifuged at 3500rpm for 35 minutes. The pyrene-saturated liquid is then divided evenly into four samples, all of which are diluted by the same volume of aqueous solutions to a concentration of pC₁₆TVB of 1.0mg/ml. Solutions of SiO₂ 100nm are added to the first three samples to introduce a SiO₂ final concentration of 0.3%vol, while the last solution is diluted by an equivalent amount of H₂O as a control. All four are put in the rotating mixer. After 29 hours, one with-SiO₂ tube, and the no-SiO₂ tube, are taken off, centrifuged at 6500rpm for 1.5 hours, and the supernatant absorbance is measured. After 53 hours and 72 hours, the process is repeated with the second and third SiO₂ tubes, respectively. The results are presented in Figure 6.7.



Figure 6.7: Absorbance at 338nm of pyrene-saturated $pC_{16}TVB$ in aqueous solutions. The sample cell path length is 2mm. The $pC_{16}TVB$ concentration for the pyrene-saturated stock solution is 1.24mg/ml, while the concentration after the addition (of both H₂O and SiO₂) is 1.00mg/ml. The black columns are data for solutions diluted by H₂O, while the white columns are data for solutions after being treated with the same volume of aqueous solution of SiO₂, as functions of mixing time. In the top right inset, the points are the difference between the two.

For solutions of pyrene-saturated aggregates, the absorbance of the diluted solutions, either with or without SiO_2 , goes down as the mixing time increases. It is likely that some pyrene molecules desorb from the aggregate to reach a new equilibrium at the lower aggregate concentration. Assuming that this is a slower

process and that the excess pyrene molecules adsorb onto the tube wall or otherwise fall out of solution and hence are not counted toward the measured absorbance, over time we get closer and closer to the equilibrium point. On the other hand, samples treated with SiO₂ solutions have lower absorbance, or lower $pC_{16}TVB/pyrene$ concentration, than ones treated with only water. The lost aggregates adsorb irreversibly onto the SiO₂ surface and are removed with it. The drop increases as the mixing time increases, a sign that the aggregate adsorption still takes place at 53 hours and gradually reaches equilibrium at 72 hours.

The mass of adsorbed aggregate per silica surface area, the surface coverage Γ , can be estimated, an example calculation of which is shown below. First, the absorbance is converted to aggregate concentration using data from Figure 6.4. After 29 hours of mixing and then centrifugation, they turn out to be 0.38 and 0.48mg/ml of $pC_{16}TVB$ for the solutions with and without added SiO₂, respectively. The difference of 0.10mg/ml of aggregate is then divided by the silica total surface area. The total surface area of SiO₂ is estimated by assuming a monodisperse size distribution of 100nm in diameter. The total surface area for 0.3vol% of SiO₂ is calculated to be $0.037m^2/ml$ of solution. The mass per area is then found to be 1.22mg/m^2 . Similar calculations for 53 and 72 hours of mixing provide Γ values of 0.83 and 0.78mg/m², respectively. The standard deviation is about 7.5% of the absorbance readings (3 repeats each), which translates to a 15.0% standard deviation in Γ . All three Γ values are less than 4mg/m², obtained previously for the single layer flat SiO₂ surface adsorption.⁹ From these three readings we found an average Γ of 1.55±0.32mg/m².

Next, the solubilization of pyrene onto $pC_{16}TVB$ aggregate as a function of the aggregate concentration is studied. Pyrene, $pC_{16}TVB$ aggregate, and 220 nm SiO₂ are mixed for 24 hours at various aggregate concentrations and then centrifuged at 6500rpm for 1.5 hours. The absorbance of the supernatant solutions are measured and included in Figure 6.8A. The calibration data from Figure 6.4 are used to convert the absorbance to the concentration of aggregates remaining in solution, which is clearly lowered after the SiO₂ treatment. The difference between the remaining concentration and the concentration of aggregate originally in the solution is plotted in Figure 6.8B. This is the amount of $pC_{16}TVB$ that adsorbs onto SiO₂ surface and gets centrifuged down with it. The drops seem to flatten out at high concentration, an indication that the SiO₂ has become saturated with $pC_{16}TVB$, and further introducing more aggregates into the solution only increases the concentration of free aggregates.



Figure 6.8: (A) Absorbance at 338nm of pyrene-saturated $pC_{16}TVB$ in aqueous solution after treatment with 220nm SiO₂ particles. The sample cell path length is 2mm. $pC_{16}TVB$ concentration ranges from 0.01 to 1.00mg/ml. (B) Converted concentration of $pC_{16}TVB$ that adsorbed onto 220nm SiO₂ surface.

There are two components that make the aggregate, the surfactant $C_{16}TA^+$ and the polymer pVB. To illustrate the effect of pVB on the surfactant micelle capacity to solubilize pyrene, $C_{16}TAB$ solutions saturated with pyrene are prepared and treated with 400 nm SiO₂. $C_{16}TAB$ concentration range is equivalent to the one existed in the pC₁₆TVB concentration range examined in this study. The results are shown in Figure 6.9. The absorbance remains negligible until about 0.35-0.43 mg/mL of $C_{16}TAB$ (equivalent to 0.41-0.50 mg/mL of pC₁₆TVB), close to the reported CMC of the $C_{16}TAB$ surfactant at 0.36mg/ml. Before micelle formation, the pyrene molecules do not have hydrophobic hosts to reside in, leading to negligible solubilization and absorbance. Once the micelles are formed, pyrene starts solubilizing, and the absorbance reading starts to rise. This profile is completely different from what we observed in the case of pC₁₆TVB, which starts solubilizing pyrene at a very low concentration due to its extremely low critical aggregation concentration (see Figure 6.4).



Figure 6.9: Absorbance at 338nm of aqueous solution of pyrene-saturated $C_{16}TAB$. The closed and open circles are data for before and after treatment of solutions with 400nm SiO₂ particles, respectively. The sample cell path length is 10mm. $C_{16}TAB$ concentration range is the same as the one that exists in p $C_{16}TVB$ when p $C_{16}TVB$ concentration ranges from 0.01 to 1.00mg/ml.

In Figure 6.8, the fact that the dye remains in the aggregate after the aggregate adsorption onto SiO₂ surfaces has been implied, since the absorbance readings of the supernatant solutions are quite significant. Fluorescent spectroscopy is then used to obtain the precise micro-environment that the pyrene resides in. Figure 6.10 shows I_1/I_3 ratio of solutions before and after treatment with SiO₂ of three different sizes. With variation in SiO₂ sizes and original pC₁₆TVB concentrations, there is no significant difference in the values of I_1/I_3 . The values remain within the 1.0 - 1.2 range, pointing to an overall hydrophobic surrounding. For pyrene residing in aqueous micro-environment, which is polar,

 I_1/I_3 is 1.50 and above.²¹ The ratio drops to 1.00 - 1.40 in a more hydrophobic micellar micro-environment, and finally to 0.60 in a pure hydrocarbon solvent.²¹ The actual values on this range depend on the type of surfactants that form the micelles, how hydrophobic the tails are, and the efficiency of the micelle packing.



Figure 6.10: I_1/I_3 ratios obtained from fluorescence spectroscopy measurements on pyrene-saturated pC₁₆TVB supernatants before (open symbols) and after (closed symbols) treatments with SiO₂ of 220nm (circles), 400nm (triangles), and 700nm (squares) in diameters.

The effect of the addition of SiO_2 on the pyrene location can be understood via its effect on the chemical composition of the aggregate. Due to the negatively charged SiO_2 surface, the positively charged surfactant component, $C_{16}TA^+$, is expected to adsorb more favorable than the negatively charged polymer chain pVB⁻. The presence of SiO_2 could potentially create the driving force to strip some of the $C_{16}TA^+$ off the aggregate, which increases the level of water penetration into the aggregate core. If it was true, the higher polarity of the micro-environment the pyrene molecules experience would lead to higher I1/I3. A first look at the data seems to indicate an increase in I_1/I_3 with SiO₂ treatment, or that the pyrene molecules are experiencing a more polar environment.¹⁹ Unfortunately, assuming error bars for I1 and I3 being the smallest measurable signals at the two respectively wavelengths, the largest standard deviation for the ratio throughout the data set is 0.06, which means that the ratios remain the same before and after treatment with SiO₂, about 1.10 ± 0.06 . Either there is no change in the aggregate composition, or it is too small for the technique to distinguish. At the same time, the insignificant change in aggregate composition means it is highly unlikely that the impact of the adsorption of $pC_{16}TVB$ onto SiO₂ surfaces causes any desorption of pyrene from the aggregate. Furthermore, with the ratio in aqueous solution being much higher than in micellar micro-environment, only a few desorbed pyrene molecules are needed to raise the ratio, which is not observed from the data.



Figure 6.11: I_1/I_3 value for fluorescence spectroscopy data for both before (open symbols) and after (closed symbols) the addition of 700nm SiO₂. The circles are when SiO₂ concentration of 0.1vol% is used, while it is twice that, 0.2%vol, for the triangles.

Figure 6.11 indicates no difference in the ratio when the SiO₂ concentration is doubled, meaning additional SiO₂ has no noticeable effect on the hydrophobic environment that pyrene molecules experience inside the core of the aggregate. This offers more evidence to support the previous argument that no pyrene desorbs from the aggregate as the aggregate adsorbs onto SiO₂ surface. Higher SiO₂ concentration would have increased the pC₁₆TVB adsorption onto SiO₂ surface, and magnified the amounts of pyrene desorbed, if there was any. Figure 6.11 shows no sign of that.

The adsorption work on SiO_2 is extended to TiO_2 , since their surface chemistries are similar. Figure 6.12 shows the UV spectra of the background (cell and water), of the pyrene-saturated aggregate solution, and of the pyrene-saturated aggregate solution after treatment with TiO_2 . Ultra-centrifugation (10000 rpm for one hour) is used to remove TiO_2 and excess solid pyrene.



Figure 6.12: UV-Vis spectra of aqueous solutions of pyrene-saturated $pC_{16}TVB$ with and without TiO₂ treatment. Low volume quartz cell is used, with path length of 2mm. $pC_{16}TVB$ and pre-centrifuged TiO₂ concentrations are 1mg/ml and 0.025%vol, respectively. The scan is performed from 200 to 800nm, but there is only meaningful absorbance in the UV region. The zoom-in part of the spectrum between 300 and 400nm is included in the top right inset.

Unfortunately, after treatment with TiO_2 , the peaks are replaced by a smooth curve that could not be readily analyzed. The complication could be due to the fact that TiO_2 absorbs light extremely strongly in the UV region, and even a small amount of its presence is enough to increase the absorbance. The two main

phases of TiO₂, anatase and rutile, which in typical commercial products size about 50nm or smaller and 200nm, respectively, have absorbance wavelengths of 385nm and 410nm, respectively.²² Anatase comprises 75% of P25 TiO₂, plus the fact that it is considered to be the more photochemically active of the two, leading to a strong absorbance in the high UV range. This range is broad, and could be extended somewhat to lower wavelengths since the particles are polydisperse, which could put it in the absorbance range of pyrene, ~ 338nm. At the same time, the number of adsorbed aggregates onto the same amounts of TiO₂ is not significant enough to change adsorption analysis itself, especially since whatever TiO₂ left in solution after ultra-centrifugation is very small in size and concentration. As a result, a different dye that is also solubilized by pC₁₆TVB but has absorbance peak well into the visible region, where TiO₂ absorbance is negligible, is needed. Nile red, with absorbance peak at 552nm, satisfies the requirements.

Figure 6.13 shows the UV-Vis spectra of the background (cell and water), of the Nile red saturated $pC_{16}TVB$ solutions with and without TiO₂ treatment. In all cases, all components are added in aqueous solutions at the appropriate concentrations, mixed for 24 hours using a rotating mixer, centrifuged at 15000 rpm for 1 hour, then UV-vis spectra are obtained. After treatment with TiO₂, the Nile red peak at 552 nm is partially suppressed although still visible. The aggregate in fact adsorbs onto the TiO₂ surface, and is brought down with it during centrifugation. How low the absorbance at 552 nm becomes depends on the amounts of substrate used to treat the pC₁₆TVB solution with.



Figure 6.13: UV-Vis spectra of solutions which include de-ionized water only, $pC_{16}TVB$ in aqueous solution saturated with Nile red (excess solid Nile red is removed by centrifugation), and $pC_{16}TVB$ in aqueous solution saturated with Nile red and treated with 0.0525vol% and 0.0225vol% of 167nm TiO₂ (solid TiO₂ and excess solid Nile red are removed by centrifugation), respectively. In all cases, the concentration of $pC_{16}TVB$ is 0.1vol%. The inset provides the spectra between 400 and 650nm.

A calibration curve is needed to convert the absorbance data in Figure 6.13 into aggregate concentration. Figure 6.14 shows UV-vis absorbance of the Nile red-saturated pC₁₆TVB aggregate solutions after the background absorbance (water and cell) is subtracted out. In all cases, all components are added in aqueous solutions at the appropriate concentrations, mixed for 24 hours, centrifuged at 15000 rpm for 60 minutes, and then UV-vis spectra are obtained. Noting that this sample preparation procedure is comparable to the one used to produce Figure 6.4, but not to the one employed in Figure 6.5.



Figure 6.14: Absorbance at 552nm of Nile red-saturated $pC_{16}TVB$ in aqueous solutions. The sample cell path length is 10mm. The line is a fit of experimental data, with a slope of 0.24 ± 0.01 ml/mg, respectively. $pC_{16}TVB$ concentration ranges from 0.00 to 1.00mg/ml.

The spectra show Nile red absorbance peaks at 552 nm,²³ directly verify Nile red solubilization into the aggregate. The linearity of the data indicates it follows the Beer-Lambert law. Using Beer-Lambert law on the data from Figure 6.14, the absorbance in Figure 6.13 are converted into the concentrations of pC₁₆TVB remaining in the solution after the treatment with TiO₂, showed in Table 6.1.

TiO ₂ concentration	Absorbance at 552nm	pC ₁₆ TVB concentration	
(%vol)	(background subtracted)	remain (mg/ml)	
0.0523	0.1386	0.578	
0.0225	0.1866	0.778	

Table 6.1: Conversion of Nile red absorbance at 552nm into $pC_{16}TVB$ concentration. Original $pC_{16}TVB$ concentration in both cases is 1.00mg/ml.

The amount of $pC_{16}TVB$ adsorbed onto TiO_2 is calculated as the difference between before and after TiO_2 treatment. It is then divided by the total TiO_2 surface area available to find the surface coverage Γ . SiO_2 data from Figure 6.8 and TiO_2 data from Table 6.1 have been processed using the above mentioned procedure, and the results are included in Table 6.2. From the sizes and densities of the silica and titania nanoparticles, the surface areas are estimated to be 12.40 and 31.25 m²/g, respectively. Multiplying that with the mass concentrations (converted from the volume concentrations), we arrive at the total surface area of nanoparticles per ml of solution.

	Concentration	Surface area	Adsorbed pC ₁₆ TVB	Γ (mg pC ₁₆ TVB
	(%vol)	(m ² /ml solution)	concentration (mg/ml)	$/m^2$ solid surface)
SiO ₂	0.1000	0.0273	0.296	10.8
TiO ₂	0.0225	0.0281	0.222	7.9
TiO ₂	0.0523	0.0654	0.422	6.5

Table 6.2: Parameters for aqueous mixtures of SiO_2/TiO_2 and $pC_{16}TVB$ aggregate at neutral pH. In all cases, the original $pC_{16}TVB$ concentration is 1.00mg/ml.

There are two observations that can be made. First, as more TiO_2 is added, the actual amount of adsorbed pC₁₆TVB increases, but the TiO_2 surface coverage drops. This makes sense since the driving force for adsorption decreases as the bulk pC₁₆TVB solution drops. Second, the Γ value for SiO₂ is lower than for TiO₂, meaning pC₁₆TVB adsorption onto SiO₂ is weaker than onto TiO₂. It is worth noticing that the total surface area is calculated based on the assumption that both SiO₂ and TiO₂ are non-porous. In reality, a BET (Brunauer – Emmett – Teller) measurement puts TiO₂ surface area at 129.07m²/g, more than 4 times higher. Unfortunately, SiO₂ is not stable in dried form and it is not straightforward to estimate its total surface area in aqueous solution. Furthermore, not all pores are big enough for aggregate adsorption As a result, the non-porous values are used as they are comparable.

6.4 Discussion

The structure of $pC_{16}TVB$ aggregate in aqueous solution at neutral pH conditions has been characterized previously,²⁴⁻²⁸ with the hydrocarbon tails pointing inward, creating a hydrophobic environment to host hydrophobic molecules. The structure is an equilibrium one, dynamic enough to allow the molecules to solubilize into the core, but also permanent enough to keep them in over time. Indeed, experimental data have shown that pyrene (Figure 6.3) and Nile red (Figure 6.13) solubilize into $pC_{16}TVB$ aggregate, and the solubilization is stable over time (for pyrene, Figure 6.4). The solubilizing power can be increased more than 10 times (Figure 6.6), a very significant improvement, by dropping the pH of the solution to 1.0. The structure of the aggregate in this condition has previously been proposed to no longer be rod-like, but instead a string-of-sphere structure, which includes $C_{16}TA^+$ spherical micelles closely connected by the partially neutralized/protonated pVB polymer chain.²⁰ This structure is much less restricted since a spherical micelle is less efficiently packed than cylindrical

micelle, with more internal space in the aggregate core to solubilize more hydrophobic dyes, in this case pyrene.²⁹

The ability of the dye-loaded aggregate to adsorb onto solid substrate, in particular those surfaces of oxide nanoparticles such as SiO_2 (Figure 6.7) and TiO₂ (Figure 6.13), has also been confirmed. No unloading of the dyes is detected during or after the adsorption process. In fact, the location of the dyes before and after the aggregate-substrate adsorption never seems to change (Figure 6.10 and Figure 6.11). As it turns out (Table 6.2), the surface coverage of $pC_{16}TVB$ on TiO_2 is less than on SiO₂. To understand this observation, we need to take a look at the surface chemistry of the substrates, SiO₂ and TiO₂, which are quite similar, with either the X-O⁻ or the X-O-H (X = Ti/Si) exposed depending on the pH of the solution. The main difference is the surface charges expressed via the measured zeta potentials at the working pH, \sim 7.5, where TiO₂ surface is less negative than SiO_2 surface, or in other words, it has a lower density of X-O⁻ groups at the surfaces. It is worth noting that work done on the adsorption of pC₁₆TVB on flat SiO₂ surface⁷⁻⁹ has shown that the first layer of aggregate adsorption is irreversible, an indication of a rather strong binding. Since the aggregate itself is very weakly negatively charged, almost neutral, for the first step of the proposed mechanism of flat surface adsorption, a few cationic surfactant molecules dissociate from the aggregate and adsorb head first onto the SiO₂ negatively charged surface. The aggregate then adsorbs onto these hydrophobic anchor points on the surface. With SiO₂ surface being more negative than TiO₂ surface, the driving force for that initial step might be stronger, but the

stability of the aggregate as a whole on the surface could be less. The higher Γ in the case of SiO₂ compared to TiO₂ proves that the scale is tipped toward the first step as the more important one.

The ability of the $pC_{16}TVB$ aggregate to both solubilize hydrophobic molecules and adsorb onto solid surfaces opens up the possibility of applications for the system. First, due to its solubility in aqueous solvents, the aggregate can be used to solubilize hydrophobic molecules like hydrophobic dyes which would otherwise be insoluble in water. Since the CAC for the aggregate is very low, or in other words, the ability of the aggregate to solubilize hydrophobic molecules already exists at very low aggregate concentration, $pC_{16}TVB$ is the ideal host for solubilizing very small amounts of those molecules. It applies to the cases when the molecules are very expensive, or due to some particular reasons the concentration has to be kept low. If solution conditions permit, the pH can be dropped to increase the solubilizing power of the aggregate, and the difference in the powers of the aggregate at different solution pH could be utilized in an absorbate loading-unloading scenario. Second, the fact that the dye-loaded aggregate remains intact and does not unload any dye molecules upon its adsorption onto solid surfaces indicates that it can be used as a delivery vehicle for hydrophobic molecules, such as in coating applications.

6.5 Conclusions

Work has been done on the solubilization of hydrophobic dyes, pyrene and Nile red, into the $pC_{16}TVB$ rod-like aggregate, and then the adsorption of the dye-

saturated aggregate onto solid surfaces of SiO₂ and TiO₂ nanoparticles. The dye solubilization starts at very low aggregate concentration, and occurs irreversibly. Dropping the pH of the solution from neutral to 1.0 increases the solubilizing power by a factor of more than ten times. The adsorption of the dye-saturated aggregate onto solid surfaces has no effect on the location of the dye molecules within the aggregate, and no dye desorption is observed. Due to the slightly less negative charge of TiO₂ surface, $pC_{16}TVB$ adsorption on it is stronger than on SiO₂ surface. Applications for the system include the solubilization of hydrophobic molecules in aqueous solvent, especially those where only a very small amount is available, and the use of the aggregate as a delivery vehicle for hydrophobic molecules from the solution to a solid surface.

6.6 References

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Chapter 7

Effect of surface curvatures on the adsorption of the polyelectrolytesurfactant aggregates

Previously, the adsorption of a polyelectrolyte-surfactant rod, $pC_{16}TVB$, onto flat silica surfaces has been studied, and a two-step mechanism proposed. In the last chapter, it has been shown that the same aggregate, $pC_{16}TVB$, is capable of absorbing various hydrophobic dyes such as pyrene and Nile red. They are then used as tracers to probe the adsorption of the dye-saturated aggregate onto titania (TiO_2) and silica (SiO_2) nanoparticles, extending the work from flat to curved oxide surfaces. No dye desorption is detected upon the aggregate adsorption. In order to better facilitate the use of the materials in future applications, more information about the curve surfaces adsorption is needed, and thus obtained in this chapter. In particular, the rod-sphere adsorption and the effect of size ratio on the conformation of the resulting rod-sphere aggregate in aqueous solution are explored using small angle neutron scattering and dynamic light scattering. The semi-flexible $pC_{16}TVB$ rods adsorb onto the silica nanosphere surface to form core-shell sphere aggregate with negligible inter-aggregate interaction. The thickness of the adsorbed rod-like layer is a function of the sphere curvature, with less curved surface adsorbing more rods, agreeing with data on silica flat surfaces where one or more layers of adsorbed rods are observed. It is shown that for the smallest spheres, due to the high specific surface area, the mechanism of rod adsorption is suspended after the initial step of surfactant anchoring, and a single layer of surfactant thickness is more likely than a full layer of rod thickness.
7.1 Introduction and background

The semiflexible polymer-surfactant (PES) aggregate in aqueous solution is capable of altering both the bulk solution properties and the interfacial properties, including those of the solid-liquid and liquid-liquid¹⁻⁴ interfaces. The material is developed in the laboratory, $pC_{16}TVB$, can be used to investigate these interactions at the solid-liquid interface, with the silica solid surface curvature being varied, as shown in Figure 7.1. The dimensions L and D_R can be controlled and varied over a wide range. This enables us to use the relation of L and solid curvature as a variable to study the interactions. The flexibility of the rod, characterized as the ratio between contour length and persistence length L/L_p , and relates to depletion forces,⁵⁻⁷ can also be manipulated. The flexibility of the dimensions enables a large set of scenarios for curved surface adsorption. In particular, using these semi-flexible rods and model silica spheres, the equilibrium colloidal structures formation and how they affect solution properties will be studied. For this chapter, the length and flexibility of the rod will be fixed, while the size of the spheres is varied.



Figure 7.1: Schematic of the two colloidal species interacting in solution; silica spheres and rod-like PES aggregates. For the spheres, the diameter is given by D_S , and assumed to be polydisperse. For the rod-like PES aggregates, L is the rod contour length, l_P is the rod local persistence length, and D_R is the rod diameter. The product is a core-shell sphere, with the core being the silica sphere, and the shell made of PES aggregates. Figure dimensions are not to scale.

The structure of pC_nTVB rods in aqueous solution has already been established.⁸⁻¹³ The adsorption of this rod onto flat silica surface was studied previously,¹⁴⁻¹⁶ using atomic force microscopy (AFM) and quartz crystal microbalance with dissipation monitoring (QCM-D). The adsorbed rodlike micelle aggregates are seen to form a close-packed monolayer from AFM images with a high degree of order over micrometer length scales, while keeping their cylindrical structure with little or no flattening. The adsorption isotherm data, recorded by QCM-D, indicate a two-stage mechanism: an adsorbed film of free $C_{16}TA^+$ ions is initially produced at low concentrations to create the hydrophobic anchor points. The weakly anionic aggregates can adsorb irreversibly onto the charge-reversed surface, with the adsorbed mass being increased dramatically. This knowledge is extended to adsorption of the rod-like PES aggregates onto a curved surface of similar material, specifically silica nanoparticles and silica colloidal particles.

Chapter 7 shows that pyrene, a hydrophobic dye, is solubilized into the core of the $pC_{16}TVB$ rod, which is also hydrophobic.¹⁷ Regardless of the original rod-like PES concentrations used, the absorbance of the solutions always drops after the treatment with silica. This indicates that rod-like PES aggregates adsorb and are removed with the silica spheres, bringing the adsorbed pyrene molecules together with them, as expected. The equilibrium coverage determined after waiting for 1-3 days is 0.72 ± 0.14 mg/m², smaller than 4mg/m², which was previously reported for these pC₁₆TVB aggregates adsorbed on flat silica

surfaces.¹⁶ But the value is of similar order and demonstrates that aggregate adsorption onto silica spheres occurs.

7.2 Materials and methods

All pC₁₆TVB used in this chapter were synthesized using the worm-like template polymerization process. pC₁₆TVB and various silica synthesis procedures are described in Sections 2.1 and 2.2, respectively. The silica used includes the Ludox SM, HS, and TM, with the information provided by the manufacturer included in Table 2.1. The Stöber silica and L-lysine silica are used when larger or smaller sized silica particles are needed, respectively. For all cases, the surfaces of the silica are negatively charged, with the zeta potential ranging between -40 and -45mV at pH 7-7.5, the operating pH range in this work.

7.2.1 Samples preparation

Several different sets of solutions are prepared for scattering analysis. Solutions of 0.1vol% silica in D₂O (or 2.2mg/ml) and then 0.1vol% pC₁₆TVB rods in D₂O (or 1mg/ml) are prepared to extract form factors of the individual components. Solutions of silica (Ludox TM) in different ratios of D₂O to H₂O are prepared to determine the scattering length density (SLD) of the silica. A similar series is prepared with 0.1vol% pC₁₆TVB to determine SLD of the rod-like PES aggregates. Finally, two series of samples containing both silica and pC₁₆TVB are prepared; one series to "match" the silica (63.0mol% D₂O and 37.0mol% H₂O) and the second to "match" the PES aggregates (13.6mol% D₂O and 85.4mol% H₂O). In all cases, the solutions are essentially neutral, with pH ranging between 7.0 and 7.6. The slight variation has negligible effect on either inter- or intraparticle interactions.

7.2.2 Dynamic light scattering (DLS)

Dynamic light scattering (DLS) measurements are performed using the Malvern NanoSizer ZS (Malvern Instruments, Malvern, UK), with a laser wavelength of $\lambda = 633$ nm. Each sample is run 10 times at angle of 173°, and the average result and standard deviation reported. Temperature equilibration time inside the instrument is set at 10 minutes. Disposable optical cuvettes with path length of 1cm are used. In all measurements, a single decay of the correlation function is observed. The principles of DLS are included in Section 2.5.

7.2.3 Small angle neutron scattering (SANS)

Small angle neutron scattering (SANS) measurements are performed at the NIST Center for Neutron Research using the NG3 30m SANS instrument. SANS principles, data reduction and fitting procedures are in Section 2.3. Also included are the form factors of a rigid cylinder (to describe the rod-like aggregate) and of a polydispersed sphere with a normalized Schulz size distribution (to describe the silica sphere), both in dilute solutions. The sphere form factor is then expanded to a core-shell sphere:¹⁸

$$P(q) = \frac{scale}{V_{shell}} \left[\frac{3V_{core}(\rho_{core} - \rho_{shell})J_1\left(\frac{qD_s}{2}\right)}{\frac{qD_s}{2}} + \frac{3V_{shell}(\rho_{shell} - \rho_{solvent})J_1\left(\frac{qD_{shell}}{2}\right)}{\frac{qD_{shell}}{2}} \right]^2 [7.1]$$

where $D_{shell} = D_s + 2 * t_{shell}$, t_{shell} is the thickness of the shell, $V_i = \left(\frac{4\pi}{3}\right) \left(\frac{D_i}{2}\right)^3$,

and the Schulz distribution is then included to take into account polydispersity in the core diameter.

A number of other structure models have also been used to fit the data in this work but only these previously-mentioned models describe the experimental data.

7.2.4 3D Dynamic light scattering

Three dimensional dynamic light scattering (3D-DLS) measurements are performed using the 3D cross-correlation instrument^{19,20} at the Adolphe Merkle Institute (Fribourg, Switzerland). A HeNe laser (Spectra Physics) with a wavelength $\lambda = 633$ nm is employed. The original beam is split into two beams, both of which are then focused on the scattering cell by a lens. Disposable optical tubes with path length of 1cm are used as the cell. An identical lens changes the direction of the scattered beams back to parallel, both of which are detected by a photomultiplier tube (PM, H5783P-01, Hamamatsu) via single mode fiber (Dantec DAN 60 x 30). After processing, the signal is fed into a digital correlator (ALV 5000/E, ALV) to generate the cross intensity autocorrelation functions, with measurement duration of 120 seconds. The functions, with multiple scattering surpressed, are analyzed using a second order cumulant analysis²¹ and an inverse Laplace transform algorithm (CONTIN).²² From here, data analysis is similar to the one in normal DLS experiment. Each sample is run at three different angles of 60° , 90° , and 120° , the average d_H and standard deviation are reported. The temperature is held at 25° C and equilibrated for five minutes prior to each measurement.

7.3 Results

The sizes of all silica nanoparticles are determined (and in the cases of Ludox silica, verified) independently using DLS. Ludox silica hydrodynamic diameters are 8, 14, 23nm for SM, HS, TM respectively, close to the reported sizes of 8, 12, and 22nm. The smaller L-Lysine silica is measured at 6nm. Several silica nanoparticles made using Stöber process tend to be bigger, including 50 and 170nm (used in SANS experiments together with the Ludox and L-Lysine silica), and 80nm (used in 3D-DLS together with other Ludox and Stöber silica). In all cases, hydrodynamic diameters are measured immediately before use, and attempts have been made to keep the set of nanoparticles consistent throughout the different experimental sets. One exception, due to the batch size limitation, is the 50nm silica, which is replaced by the 80nm batch in the 3D-DLS experiment.

An accurate knowledge of the match points of both the silica and the aggregate is needed for further experiments, so the minimum intensity measurements are performed. Figure 7.2 shows the SANS scattered intensity of silica particles or the rod-like $pC_{16}TVB$ aggregates as a function of the mole fraction of D₂O in the D₂O/H₂O solvent mixture. The solvent compositions are chosen such that the calculated scattering length density (SLD) value of the

individual components^{23,24} lies in the middle of the SLD range of the solvent mixtures. Each experiment is performed at 13m detector distance to minimize background scattering. The SLD of silica is not expected to be a function of particle size, so only one silica size was chosen for this set of experiments, the Ludox TM. Solvent scattering, mainly incoherent, is subtracted using measured solvent scattering data at the same scattering conditions. Incoherent scattering from the hydrogenated rod is expected to be much more significant than the one from the silica sphere, neither of which has been subtracted. A procedure similar to the one described previously is used,²³ which postulates the minimum scattered intensity is the point where the SLD of the solvent mixture is exactly the same as the SLD of the solute. At that composition, the solute scattering is "matched" by the solvent scattering. For silica, the match point is 63.0mol% D₂O, very close to that reported in the literature.^{23,25-27} For the rod-like PES aggregates, the matched point for pC₁₆TVB is at 13.6mol% D₂O.



Figure 7.2: Square root of the scattered intensity at low q for silica (closed circles) and $pC_{16}TVB$ (open circles) as a function of the mole fraction of D₂O in the D₂O/H₂O solvent mixture. The silica used is Ludox TM at 0.1vol% (2.2 mg/mL). For $pC_{16}TVB$ the concentration is 0.5vol% (5 mg/mL). The incoherent scattering contribution from the solvent have been independently measured and subtracted out from the overall scattering. Incoherent scattering from the hydrogenated rod is expected to be much more significant than the one from the silica sphere, neither of which has been subtracted.

Another preparation step is the determination of accurate shapes, sizes and the size distributions of the silica particles using SANS. The knowledge will be used in the data fitting procedures. Figure 7.3 shows scattered intensities as a function of q for a series of silica spheres of various sizes in D₂O. The silica spheres include both those synthesized using L-lysine and Stöber processes, and the Ludox silica (SM, HS, TM). The background scattering is subtracted from the overall scattered intensities.



Figure 7.3: SANS scattered intensities of silica spheres of different sizes. The sphere concentrations are individually kept at 0.1vol% in 100% D₂O, except for the case of 14nm silica where it is 0.3%vol. The solid lines are fitted form factors (polydisperse sphere form factor) to the experimental data. For clarity purpose, the curves are shifted arbitrarily.

For all cases, there are three recognizable regions. The high q region has the lower signal and high incoherent background. The intermediate q region contains most of the local maxima and minima, which relate to the sizes of the spheres. Figure 7.3 also includes the model fits to the experimental data of sphere form factors. A polydisperse sphere model with a Schulz size distribution is employed. The SLD of silica is fixed at 3.5×10^{-6} (Å⁻²), using the value from the minimum scattered intensity of silica experiments (Figure 7.2). The solvent SLD is constrained between 6.3×10^{-6} (Å⁻²), that of 100mol% D₂O solvent, and 5.7×10^{-6} (Å⁻²), that of 91mol% D₂O solvent, to account for some H₂O solvent in the silica stock solutions. For the case of the 2nm silica, due to the nature of the synthesis, the stock solution is the most dilute and some H₂O dilution in the final solution mixture is unavoidable. That is not a problem for the Ludox stock solutions (~8-23nm), with concentrations more than ten times higher, or the Stöber stock solutions (~50-170nm), which can be made significantly more concentrated by repeated centrifugations and resuspensions. The rest, including mean diameter, volume concentration, and polydispersity, are the fitting parameters and are let run free. The values of χ range between 1.0 and 6.8, indicating good fits. All parameters are included in Table 7.1.

	L-lysine	Ludox SM	Ludox HS	Ludox TM
	(2nm)	(8nm)	(14nm)	(23nm)
SLD sphere ($x10^{-6} \text{ Å}^{-2}$)	3.5	3.5	3.5	3.5
SLD solvent ($x10^{-6} \text{ Å}^{-2}$)	5.8	6.3	6.2	6.3
Volume concentration	0.08%	0.09%	0.27%	0.10%
Mean diameter (nm)	6.4	8.0	15	27
Polydispersity	0.23	0.35	0.19	0.18
χ (N,f)	1.0 (110,3)	2.3 (148,3)	2.7 (145,3)	1.8 (142,3)

	Stöber	Stöber
	(50nm)	(170nm)
SLD sphere ($x10^{-6} \text{ Å}^{-2}$)	3.5	3.5
SLD solvent ($x10^{-6} \text{ Å}^{-2}$)	6.3	6.3
Volume concentration	0.07%	0.14%
Mean diameter (nm)	44	137
Polydispersity	0.21	0.18
χ (N,f)	6.8 (155,3)	3.3 (155,3)

Table 7.1: Parameters extracted from scattering of dilute silica spheres in 100% D_2O . The numbers in parenthesis following silica names are sizes measured using DLS. The fit is characterized by χ . The polydispersity of the spheres, is defined as $2\sigma/D_s$, with σ^2 being the variance of the distribution, and D_s being the mean particle diameter.

Of the fitted parameters, the sizes of the silica spheres are close, but not the same as the values obtained from DLS, with reasonably small polydispersity. The diameter obtained from SANS is diameter of gyration Dg, defined as twice the geometric averaged distance of the scatterers from the center of the object, similar to the ones obtained from SLS. On the contrary, DLS provides hydrodynamic diameter D_H, which is a z-average value corresponding to the size of an effective sphere that moves as a Brownian particle. It includes both the hydration (hydro) and the shape (dynamic) effect, hence tends to be bigger than $D_g.$ Although the $D_g\!/D_H$ ratio of 0.78 is generally used for a solid sphere,^{28} experimental data provided by van Blaaderen et al.²⁹ have shown that it is not necessarily true for silica spheres. Here, only the ratio for the Stöber silica values is close. From this point on, for the sake of consistency, the DLS values will be used to identify the silica sample used. The extracted volume concentration is close to estimated values, a reassuring sign that the stock concentrations are correct. The concentration of silica chosen is low enough to avoid any concentration effects, indicated by the lack of low q upturn in the scattering curves. The fitted values for the solvent SLD provide a measure of the concentration of H₂O remaining in the solution. Since the fitted solvent mixture SLD is essentially that of D_2O for the larger spheres, there is negligible amount of H_2O in the mixtures. The one exception is the smallest silica sphere sample, where the solvent is of 7mol% H₂O. Fortunately, this concentration should not affect the processes of interest.

The effect of added silica spheres on the conformation of the rod-like PES aggregates is shown in Figure 7.4, which includes two sets of scattered data. Notice that the L-Lysine silica is not used, as its mixture with the rod is not as stable as others, and the possible aggregation during scattering would hinder the analysis of the individual unit structure.



Figure 7.4: SANS scattered intensities of mixtures of $pC_{16}TVB$ rods and silica spheres of different sizes. The rod and sphere concentrations are each kept at 0.1%vol. The silica diameter is varied from 8 to 170nm. The solvent is a mixture of 63%mol D₂O and 37%mol H₂O, at which composition the SLD is matched to the silica. The scattered intensity of $pC_{16}TVB$ rods in the same solvent is also included for comparison. The solid lines are fitted form factors to the experimental data: core-shell sphere form factors to mixture scattered data; and semi-flexible cylinder form factor to $pC_{16}TVB$ -only scattered data. For clarity purpose, the curves are shifted arbitrarily.

The first set is the scattered intensity of the $pC_{16}TVB$ rod-like PES aggregates, at a concentration of 0.1vol% (1 mg/mL) and a solvent composition at

63mol% D₂O : 37mol% H₂O. The background scattering (which is the flat background at high q, includes mostly incoherent scattering of the solvents and some of the rod) is subtracted out. The curve has the well-known negative one slope in the intermediate q region, characteristic of rigid regions within the rod. Fitting of the experimental data with the structure model of a semi-flexible rod, also shown, yields an excellent match, with a D_R of 4.4nm. The length of the rod L cannot be determined using this data, since it would need lower q than the range SANS provides. However, knowing that the structure is truly a rod, data from other techniques such as SLS that have been done previously on a similar batch of rods provide an L value of 185nm.^{9,17}

The second set consists of scattered intensities as a function of q for a series of pC₁₆TVB rods and silica spheres. The size of the spheres, D_S, is varied from 8nm to 170nm. Both sphere and rod concentrations are fixed at 0.1vol% each. The D₂O/H₂O solvent composition is set so that scattering from silica spheres is the same as the solvent, or "matched out". The background scattering, which is the flat intensity region at very high *q*, is measured and subtracted from the data. The background is primarily incoherent from hydrogen in the solvent, the PES aggregates, and the silica. For example, for the 8nm silica-rod mixture, the incoherent background is I_{bgd} = 0.46cm⁻¹, which is close to the combination of (independently measured) incoherent scattering of the solvent mixture (I_{bgd} = 0.23cm⁻¹), the rod-like PES aggregates (I_{bgd} = 0.05cm⁻¹), and the silica spheres (I_{bgd} = 0.05cm⁻¹). In all cases, similar features are found: a local maximum at intermediate/high *q*, immediately followed by a local minimum at a slightly

smaller q. The intermediate q features clearly move systematically with the size of the silica particles. In comparison, the pC₁₆TVB rod-like PES aggregate scattering at the same solvent conditions, also included, does not have this feature.

The results above indicate that in silica-matched solvent condition, the scattering curves from $pC_{16}TVB$ -silica mixtures do have different features compared to those of $pC_{16}TVB$ alone. Since silica is matched to the solvent, the scattering would be one of a rod if the PES aggregates were either not adsorbed to the spheres or if the PES aggregates were "coated" with silica spheres. As a result, the presence of silica spheres has induced changes in the $pC_{16}TVB$ rod-like PES aggregate, most likely the rods adsorb at the silica-water curve interface, consistent with previous work that showed the same rods indeed adsorb onto flat silica interface.¹⁴⁻¹⁶

Following the determination that $pC_{16}TVB$ does indeed adsorb onto silica surface, the core-shell sphere structure is the most logical option. Figure 7.4 shows that the model fits to the scattered intensities. A core-shell sphere with a polydisperse core model is used and all parameters are included in Table 7.2. The core diameters are known from the silica form factors (see Figure 7.3). The scattering length density (SLD) of the silica core and the solvent is fixed at $3.5x10^{-6}$ (Å⁻²), using the value from the minimum scattered intensity experiments (Figure 7.2). Similarly, the shell SLD is fixed at $0.37x10^{-6}$ (Å⁻²), the SLD of the rod-like PES aggregates. Ranges are used for the total volume concentration, knowing the amount of $pC_{16}TVB$ and silica that were put into the mixture. As a result, the shell thickness, t_{shell} , and the total volume concentration of the shell are the only two fitting parameters.

The data for the 23nm and 50nm series are re-plotted in Figure 7.5 to emphasize the quality of the fits. The group of minima and maxima at intermediate q provides information about the size of the silica core. Getting the shell thickness t_{shell} , which usually can be obtained from the very high q data, is much trickier. In a silica-match solvent condition, the background scattering is significantly higher than the aggregate scattering at very high q, leading to a low signal-to-noise ratio. As a result, instead of using the high q data, t_{shell} is extracted by simultaneously optimizing overall scattering intensity and the slopes leading to the high q region.



Figure 7.5: SANS scattered intensities of mixtures of $pC_{16}TVB$ rods and silica spheres of different sizes from Figure 7.4. The data of only two sphere diameters are showed, 23nm and 50nm, together with the model fits.

The fits between experimental data and the core-shell sphere form factor are good, with χ values ranging between 1.2 and 3.0. Of all the fits, the mixture of 23nm silica sphere and pC₁₆TVB rod provides the best fit. The quality deteriorates a bit from there, in both larger and smaller silica sphere directions. When the silica core diameter is larger than 23nm, attempts have been made to correct for the scattering of the excess, un-adsorbed rods in the solution. The fits shown in Figure 7.4 of the 50nm and 170nm cases are the results of that effort.

Parameters	8 nm	14 nm	23 nm	50 nm	170 nm
	core	core	core	core	core
Core SLD ($x10^{-6}$ Å ⁻²)	3.5	3.5	3.5	3.5	3.5
Shell SLD ($x10^{-6} \text{ Å}^{-2}$)	0.37	0.37	0.37	0.37	0.37
Solvent SLD (x10 ⁻⁶ Å ⁻²)	3.5	3.5	3.5	3.5	3.5
Core diameter (nm)	8	15.4	26.7	43.9	136.5
Core polydispersity	0.35	0.19	0.18	0.21	0.18
Shell thickness, <i>t</i> _{shell} (nm)	1.6	2.0	2.3	1.5	3.0
Total volume concentration (%)	0.25	0.20	0.23	0.17	0.2
χ (N=155,f=2)	2.0	3.0	1.7	1.4	1.2

Table 7.2: Core-shell sphere parameters for $pC_{16}TVB$ -silica with silica-matched solvent data. Of all the parameters, only t_{shell} and total volume concentrations (of both the cores and the shells) are allowed to run free, while the rest predetermined in standalone experiments, the SLD parameters (core, shell, solvent) from minimum scattered intensities experiments, while the core parameters(diameter, polydispersity) from silica-only experiments.

For all cases, the concentration of both $pC_{16}TVB$ and silica is 0.1vol%. It is easy to show that the ratio of surface area of the spheres to the total mass of rodlike particles is inversely proportional to the radius of the spheres. Therefore, as the core size is increased while the volume ratio of components is kept fixed, the available silica surface area for adsorption drops (total number of spheres drops as D_S^{3} , while individual sphere surface area only increases as D_S^{2}). In other words, the likelihood of excess rods in solution increases with increasing core size. Five different D_S are studied. For the smallest D_S , the number of rods present is not enough to fully cover the sphere surfaces, while there is excess for the three larger core sizes. For all cases, the locations of the maxima and minima match between the data and the fit, meaning the aggregate has the physical dimensions (core diameter, t_{shell}) that correspond to these q values. However, for the two largest D_S (the smaller of which is shown in Figure 7.6), the intensities in a few regions do not match very well. The increasingly large concentration of excess rods would also scatter, contributing to the overall intensity and adding some levels of smearing to the minima/maxima established by the core-shell sphere scattering, hence increasing χ of the fits.

For the 23nm case, the fit provides very low χ value, and the parameters are included in Table 7.2. There are only three fitting parameters, two of which are strongly correlated, t_{shell} and the total volume concentration of sample in the solution. For the 50nm and 170nm cases, χ values increase noticeably, so an additional fitting parameter has been added: the concentration of free pC₁₆TVB rods that scatter in the mixture. The experimental scattering data of pC₁₆TVB are used rather than a rod-like form factor. They are, for the 50nm and 170nm cases, 0.035 and 0.043vol%, respectively. The resulting fit and the effect of the inclusion of excess rod scattering are illustrated in Figure 7.6 for the 50nm case, and the χ value indeed decreases significantly. At the other extreme, the smaller the size becomes, the harder it is to fit the data with a core-shell sphere form factor, assumingly because there is not even a full layer, probably just patches of adsorbed $pC_{16}TVB$, or some surfactant adsorption.



Figure 7.6: Experimental scattering curve of mixture of 0.1%vol pC₁₆TVB and 0.1%vol silica 50nm in D₂O/H₂O solvent (open circles). The solvent composition is 63%mol D₂O, 37%mol H₂O to match the SLD of silica. Also included are the experimental scattering of 0.0345%vol of pC₁₆TVB in the same solvent condition (open squares), the core-shell sphere fit (dash line), and the core-shell sphere fit that takes into account excess non-adsorbed rod scattering (solid line).

In the next set of experiments, the behavior of the other component, the silica spheres, in the presence of pC₁₆TVB rod-like aggregates is explored, and the data are included in Figure 7.7. Scattering intensities of mixtures of pC₁₆TVB rods and silica spheres are shown as open symbols, with the pC₁₆TVB scattering being matched out by adjusting the solvent composition. The scattered intensities of silica only, closed symbols, with the same shift factors as the mixture, are also included. For all three silica sizes (D_s = 8nm, 23nm, and 170nm), the matched

scattering and the sphere-only scattering of the same size are similar, both in features and in overall intensities, except for the very high q region, where the scattering becomes noisy. The noise is the result of subtracting a high level of background scattering created by the high H_2O composition solvent, necessary to create the pC₁₆TVB-matched solvent, from the total scattering. Clearly, the presence of the rod does not affect the form factor of the sphere. The sphere scatters just as it does on its own, no sphere-sphere interactions are observed.



Figure 7.7: SANS scattered intensities of mixtures of $pC_{16}TVB$ rods and silica spheres of different sizes (open symbols). The rod and sphere concentrations are individually kept at 0.1vol%. The silica diameter is varied from 8 to 170nm. The solvent is a mixture of 14mol% D₂O and 86mol% H₂O, at which composition its SLD is matched with the measured pC₁₆TVB SLD. For clarity purpose, the curves are shifted arbitrarily. The scattered intensities of silica spheres of different sizes are also included (closed symbols).

Furthermore, the $pC_{16}TVB$ -matched data provides information about the level of inter-aggregate interaction in the mixture solution. The rod-sphere

interaction is already known to be significant, and results in the core-shell sphere aggregate. The rod-rod interaction, on the other hand, is weak enough compared to the previous interaction to allow for the packing of multiple rods on one sphere surface. Figure 7.7 shows the close resemblance between the $pC_{16}TVB$ -silica scattered intensities at $pC_{16}TVB$ -matched solvent condition and the silica scattering intensities. With the shell being matched out, the scattered curve is expected to be only from the silica. The fact that the scattering is so similar to the simple silica sphere itself is an indication that the silica sphere behaves just like when it is free in the solution. In other words, there is only one silica sphere per aggregate, and there are negligible interactions between the resulting aggregates.

To obtain more information about the layer thickness, another scattering technique is attempted, 3D dynamic light scattering (3D-DLS). This provides another set of thickness data to compare with SANS results.

	8 nm	14 nm	80 nm	170 nm
	core	core	core	core
Silica only D _H (nm)	11.9±1.4	15.5±1.9	62.8±1.3	156.0±10.5
Silica+pC ₁₆ TVB D _H (nm)	13.8±0.7	16.7±1.6	68.1±2.3	165.3±11.2
Shell thickness (nm)	1.0±0.8	0.6±1.3	2.7±1.3	4.7±7.7

Table 7.3: Hydrodynamic diameters of the silica core and $pC_{16}TVB$ shell spheres; and of the silica spheres, measured using 3D DLS. The shell thickness is half the difference between these measured diameters.

Table 7.3 shows D_H values of the silica core on its own, and of the silica core – $pC_{16}TVB$ shell aggregate, obtained using 3D-DLS. The usual assumptions for DLS are applied here, including hard spheres, which is consistent with a silica sphere and somewhat consistent with the core-shell sphere. Shell thickness is half

of the difference between silica D_H and the core-shell D_H . As the core size increases, the average shell thickness increases, but so does the error. Notice that unlike the case of SANS data where the scattering from the excess of rod-like aggregates can be subtracted out, there is no straightforward way to do that for the DLS data. As a result, the data has not been corrected, and the increasing uncertainty at large silica core sizes might be due to this reason.

7.4 Discussion

Table 7.2 and its other representation, Figure 7.8, summarize the mass of rods adsorbed onto the sphere surface, expressed via the adsorbed layer thickness, as a function of the sphere surface curvature. As D_s increases from 8 to 170nm, t_{shell} increases from 1.6 to 3.0nm (SANS data). This could be due to the fact that elastic energy cost the rods have to overcome in order to adsorb onto the curve surface is less with flatter silica surface. At the smaller D_s , the closeness of t_{shell} to the length of a surfactant molecule suggests a single layer of surfactant adsorption. For the flat surface, t_{shell} is close to one layer of rod adsorption, consistent with previous report¹⁴⁻¹⁶ that at this concentration, more than one layer of rods can adsorb, one of which irreversibly.



Figure 7.8: Thicknesses of absorbed PES layers on silica surfaces, extracted from core-shell sphere model fits to experimental data (circles), and from AFM data reported previously for flat silica surface adsorption (squares).

The validity of the single layer of surfactant adsorption argument is supported by the flat surface data reported previously by Biggs *et al.*¹⁶ In that work, adsorption isotherm of pC₁₆TVB onto flat silica surface is represented by the plot of the Sauerbrey (adsorbed) mass density³⁰ as a function of bulk rod concentration. It is shown that the adsorption increases with the bulk rod concentration, starting with a few dissociated surfactant molecules adsorbing onto the silica surface due to electrostatic attraction, with the tail groups pointing away from the surface. The whole pC₁₆TVB rod then adsorbs onto these hydrophobic anchor points. Some of the outer adsorption layers can be rinsed away using deionized water, but the innermost layer is irreversibly adsorbed, corresponding with approximately 4 mg/m² of pC₁₆TVB. During this adsorption process, since the flat surface has a very low specific surface area, which leads to a small number of rods adsorbed, the bulk rod concentration can be treated as constant. This does not apply to curve surfaces of nanoparticles, where specific surface areas are orders of magnitude higher. The much higher level of adsorption significantly depletes the bulk rod concentration. As an example, for the case of 23 nm silica at 0.1vol% and pC₁₆TVB at 1mg/ml concentration, assuming one full layer of rods on the sphere surface, it can be shown that the bulk rod concentration is one decade lower than the total rod concentration, dropping from 1mg/ml to 0.1mg/ml. This corresponds to a much lower adsorbed mass density on the adsorption isotherm, or thinner adsorbed layers, consistent with SANS data. Admittedly, this calculation is not meant to be rigorous, especially since the intrinsic effect of curvature itself on the adsorption via increased bending energy cost has been neglected. It does, however, point to the feasibility of our argument. In fact, it is believed that for the smallest spheres, the bulk rod concentration is so low that after the initial step of surfactant adsorption, there are simply not enough rods to further adsorb on those hydrophobic anchor points. The adsorption mechanism freezes after the first step.

It is, however, important to acknowledge the complexities of the fits for t_{shell} . With the silica core being matched out by the solvent, the scattered intensity is determined by the pC₁₆TVB layer thickness and its volume concentration in solution. Theoretically, change in t_{shell} would also be accompanied by change in

local minima/maxima that corresponds to that physical dimension. However, since t_{shell} is much smaller compared to D_s, in the experimental data, it would be impossible to differentiate the *q* locations associated with t_{shell} that are half a nanometer or less apart. Assumptions have to be made to fix the volume concentration before a t_{shell} could be derived. Since the silica sphere volume is fixed, the only assumption is that the SLD of pC₁₆TVB is the same as the one in the bulk (no rod swelling or compressing due to the adsorption), and the layer thickness, reported in Table 7.2, is derived.

In light of the surfactant adsorption observation, fitting of the corematched core-shell sphere data, shown in Table 7.2, has been re-done. If the SLD of the shell is changed to one of the surfactant and fit for the shell thickness and the total volume concentrations while keeping everything else fixed, the thicknesses remains unchanged statistically. Instead, the parameter that changes is the total volume concentration, which shifts slightly lower. This is consistent with the change in the contrast, and supports the model of the core-shell sphere. With the core scattering being matched out, the overall scattering is dominated by the shell, and is directly proportional with the shell contrast. Since the contrast is increased by replacing the mixed shell SLD with the deuterated surfactant SLD, in order to keep the overall intensity constant, the total volume concentration has to drop. The volume changes are however rather small since the shell volume is a very small part of the core-shell sphere.

Similar effort done with another scattering technique, DLS, represented by data in Table 7.3, offers further support to the argument of a curvature dependent

adsorption. Despite the particle sizes for this batch are slightly different from the one used in the SANS experiment, the same trend is observed: the bigger sphere leads to the thicker adsorbed layer. Unfortunately, the propagated errors become too large. For example, for the 170nm silica core, the standard deviation actually becomes larger than the average value itself. However, this insight is consistent with the prediction.

7.5 Conclusions

There is limited understanding of the structure of colloid dispersions of spherical and rod-like particles. Several structures formed using these particles have been reported, but a fundamental understanding of the adsorption does not exist. Previously, adsorption of a particular rod onto flat oxide surfaces has been studied, and a two-step mechanism proposed. Here, it is extended to the curve surface. In particular, rod-sphere adsorption and the effect of size ratio on the conformation of the resulting rod-sphere aggregate are explored. Small angle neutron scattering and dynamic light scattering have been used to study the behavior of a rod-sphere system in aqueous solution. Some of the semi-flexible rods adsorb onto the silica nanosphere surface to form core-shell sphere aggregate with negligible inter-aggregate interaction. The thickness of the adsorbed rod-like layer is a function of the sphere curvature, with less curved surface adsorbing more rods, agreeing with data on silica flat surfaces where one or more layers of adsorbed rods are observed. For the smallest spheres, due to the high specific surface area, the mechanism of rod adsorption is suspended after the initial step of surfactant anchoring, and a single layer of surfactant thickness is more likely than

a full layer of rod thickness. Future work is needed to probe the other two parameters of this system, the rod flexibility and the charge ratio of the two components, the knowledge of which could be useful in standardizing the prediction of the fundamental structural unit and the properties of the suspensions.

7.6 References

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Chapter 8

Conclusions

This thesis improves the knowledge of the inter- and intra-aggregate interactions of commonly encountered colloidal species, including polyelectrolytes, surfactants and metal oxide nanoparticles. Polyelectrolytesurfactant aggregates (PES), formed by the complexation of the two named components, have diverse sets of properties, which are controlled by a wide range of parameters, both within the aggregates themselves and with the surrounding environment. A particular PES system, denoted $pC_{16}TVB$, which self-assembles in aqueous solution, is the main focus of the thesis. The goals consists of understanding i) the aggregate structures in different solution conditions, which change the integrities of the individual surfactants and polymers components, how they interact among themselves and with the surrounding solvents, ii) its ability to solubilize different hydrophobic dyes, or the interaction of the aggregate with small molecules and iii) its ability to adsorb onto oxide nanoparticles, or the interaction of the aggregate with bigger particles (but still in the sub-micron size region).

8.1 Intra-aggregate interactions

The aggregate structure is the product of the balance between surfactant head groups – polyelectrolyte charge groups electrostatic interactions and surfactant tails – polyelectrolyte backbone hydrophobic interactions. At neutral solution pH, aided by SLS, SANS contrast matching, and the deuteration of the surfactant molecules, the structure is shown to be one of a core-shell cylinder, with the shell consisting of surfactant head groups. The surfactant tail groups point toward the core center, while the polyelectrolyte also resides in the core, but remains close to the core-shell interface for charge neutralization. The polymer chain conformation is that of a worm-like chain.

As the pH drops to highly acidic conditions, the effects of the new solution conditions alter the local balance of interactions, with the hydrophobic interaction being increasingly dominant while the electrostatic interaction reduced. Together with the neutralization of a large fraction of the cylindrical-micelle-promoting VB⁻ counterions, it forces the structure to transform into a more commonly seen necklace, in which the polymer chain connects a series of spherical surfactant micelles, with the adjacent spheres closely spaced, but not touched. The solution properties are impacted accordingly, becoming viscoelastic due to the introduction of hydrogen bonding capacity into the system, while solubilizing a factor of ten times more hydrophobic molecules. The macroscopic effects, illustrated by experimental evidence from SANS, SLS, DLS, NMR, and potentiometry via surfactant sensitive electrode, are consistent with the proposed necklace structure. The cross section remains the same, while the hydrodynamic diameter doubles, in agreement with the expected drop in micellar packing factor and the negligible dissociation of surfactant molecules during the cylinder-sphere transition. The exposed segments of the polymer chain, which reside in the gaps between the spheres, have also been detected. Hydrogen bonding capacity manifests in the dependence of the hydrodynamic diameter on temperature and

aggregate concentration, and the network structure in the viscoelastic solution at low pH. All structural transformations can be reversed with the addition of a strong base to return the solution pH to neutral.

8.2 Aggregate interactions with other particles

Treating the $pC_{16}TVB$ aggregate as a whole, its interactions with other particles become the focus, from small ones like dye molecules, to bigger ones like silica and titania nanoparticles, and all the way to flat surfaces. Making use of the highly hydrophobic core as an ideal host for hydrophobic molecules, the solubilization of hydrophobic dyes such as pyrene and Nile Red into $pC_{16}TVB$ aggregates starts at very low aggregate concentration, while the solubilizing power, which is already high at neutral pH, could be improved by a factor of ten at acidic conditions, a major advantage for the potential application as a solubilizing agent.

Using the solubilized dyes as tracking molecules, the adsorption of $pC_{16}TVB$ onto TiO_2 and SiO_2 nanoparticles are analyzed, extending the previous flat surface adsorption work This moves the study to a larger size than the previous dye molecules, but still much smaller than the flat surface, while the surface curvature is introduced. The adsorption has no effect on the location of the solubilized dye molecules inside the aggregate, and no dye desorption is observed. The nature of the solid surfaces plays a major role in the adsorption, with the more negative SiO₂ adsorbs more $pC_{16}TVB$ due to its stronger electrostatic attraction with the surfactant head groups. Using small angle neutron

scattering technique, semi-flexible $pC_{16}TVB$ rods have been found to adsorb onto the SiO₂ nanosphere surface to form core-shell sphere aggregate with negligible inter-aggregate interactions. The thickness of the adsorbed layer is a function of the sphere curvature, with less curved surface adsorbed more rods. Combining with the previously obtained flat surface adsorption data, this trend extends all the way to the flat surface. However, unlike the flat surface cases, in which the adsorption mechanism had been shown to consist of two main steps, with some dissociated surfactant molecules adsorbing head first via electrostatic attraction with the surface to create hydrophobic anchor points for subsequent aggregate adsorption, the high bending energy cost and the insufficient number of anchor points (distributed over a very high total sphere surface area) suspend the adsorption after the initial surfactant adsorption step.

The thesis shows the versatility of the polyelectrolyte-surfactant (PES) aggregate structure, and hence its solution properties, while still retaining its robustness at each individual set of solution conditions. Extending the previous works by Kline,¹ Gerber,² and Kuntz,³ by changing the solution pH, the aggregate structure is forced to reversibly transform between a semi-flexible rod and a string-of-pearl. They represent a region of the PES aggregate formation (that of hydrophobic polymer and varying electrostatic attraction of opposite charged moieties) that exhibits distinctive aggregate structural behavior. The interactions of the PES aggregate with other particles are also explored. Its capability to solubilize hydrophobic molecules, together with its ability to adsorb onto oxide

nanoparticles, offers exciting opportunities for future applications such as delivery vehicles.

8.3 Future directions

8.3.1 Cross-linked PES aggregate with divinylbenzene (DVB)

Since the monomer VB⁻ has only one polymerizable vinyl group, the polymer product is a linear chain, with its length depending on the reaction condition. This has multiple impacts on how the aggregate properties and structure respond to changes both internally and from the surrounding environment. As solution pH varies, it has been shown in chapter 4 and 5 that the structure of the aggregate transforms from a semiflexible rod into a series of spherical surfactant micelles connected by the polymer chain. At the same time, the polymer chain itself extended significantly, from a non-protonated worm-like chain (chapter 3) to one with alternating protonated-nonprotonated segments.

One obvious direction to explore is to restrict the freedom of the polymer chain to change its conformation, and observe the change in both solution properties and aggregate structure once external parameters are altered. That could be done by the addition of a cross-linker into the polymerization mixture. Divinylbenzene (DVB, Sigma Aldrich), with the structure shown in Figure 8.1, is a good candidate, with two vinyl groups enabling it to react to two different VB⁻ monomer units within the chain. It is also miscible in the reactant mixture, and the reaction conditions are similar to those of VB⁻. Kline *et al.* (pending patent) has shown that the solution of cross-linked aggregates at moderate concentration and neutral pH forms a hydrogel, which persists well after the removal of excess water solvent.

The structure of the cross-linked aggregate and its solution properties at low solution pH should be explored, at both dilute and moderate concentrations. With the orientation of the monomer units being restricted by cross-linking, it is unlikely that the polymer chain would be able to extend to the same level when the solution pH drops. Its effect on the chain conformation, and hence the aggregate structure, remains to be seen, but the one on solution properties, especially at intermediate-to-high concentrations, is known. A good understanding of the change in aggregate structure due to crosslinking will explain its ability to form the hydrogel network. How far it differs from the noncrosslinked solution depends on the level of cross-linking, which can be controlled straightforwardly by adjusting the amount of DVB used. At the same time, even at neutral pH, the short length of the crosslinker DVB molecule means that the uniformity of the aggregate structure will not be as high as the noncrosslinked one, depending on the distance between the monomer units that DVB happens to connect.



Figure 8.1: Chemical structure of divinylbenzene

8.3.2 The use of different acids and surfactant tail lengths

In chapter 4 and 5, it has been shown that the use of HCl to drop the solution pH has the primary effect of protonating the polymer chain pVB, substituting the VB⁻ counterion with the much weaker binding Cl⁻ counterion that promotes spherical micelles. The result is the structural transformation to one of a necklace. It means that if other counterions are to be used instead of Cl⁻, the structure could have been different.

HNO₃ has been used to acidify solution of $pC_{16}TVB$, at the same concentrations and temperature as the HCl experiment. The hydrodynamic diameters measured using DLS show similar trend, with the size increases as the values of the solution pH drops. The data is shown in Figure 8.2. There are a number of differences between this result and the result in Figure 5.6, which is obtained at neutral pH conditions. Firstly, the transition point occurs at about pH 2.5, a whole pH unit higher than in the case of HCl. Secondly, all solutions with pH values lower than 1.7 exhibit precipitation/phase separations, which prevents d_H from being obtained. This does not happen until solution pH lower than 0.5 when HCl is used instead. Lastly, for those d_H at the lowest pH point that could still be obtained for the HNO₃ case, the values are similar to the ones for HCl case, despite the whole unit of pH difference.



Figure 8.2: Hydrodynamic diameter d_H of pC₁₆TVB measured at pH ranging from 1.9 to neutral. Concentration and temperature are kept constant at 0.83mg/ml and 25°C. HNO₃ acid is used.

The overall effect that HNO₃ has on the solution properties is clear. However, the role of the NO₃⁻ counterion in pushing the gelation point to a higher pH is not. The gelation itself was thought to depend primarily on the protonated VB groups of the polymer chain, which had hydrogen bonding capability, while the Cl⁻ counterion had little role beside shaping the surfactant micelles. At the same time, it is also unclear what the shape of the resulting aggregate is. NO₃⁻ counterions are known to bind stronger than Cl⁻ counterions, and tend to promote wormlike micelles, or cylindrical structure.⁴ However, compared to VB⁻, its binding is much weaker, and hence requires a much higher $C_{16}TA^+$ concentration for wormlike micelle to be formed. If the cylindrical structure is indeed what selfassembles in the system, then we are looking at one that has characteristics closer
to a rod than a string-of-pearl. SANS experiment should be performed on this system to provide a more definite answer. Other counterions that promote different micellar shapes could be used, and the resulting structures could further validate the role of the counterions and provide a means to reversibly access a solution with diverse properties.

An interesting approach would be to combine this with the idea from section 8.1, meaning substituting the counterion of the cross-linked system. As acids are added, both the polymer chain and the surfactant micelle change their conformations. The two processes can be de-coupled by cross-linking the polymer chain, which significantly reduces its response to that addition. By observing what happens to the solution once acids are added, direct evidence of whether the polymer chain or the surfactant micelle has the dictating role in both aggregate structure and solution properties can be obtained.

Similarly, instead of changing the counterions, other surfactants could be used. $C_{14}TA^+$ and $C_{18}TA^+$ have the same head group as $C_{16}TA^+$, so their interactions with the counterions are unlikely to be altered. The difference in tail length could change the nature of the surfactant micelle: its cross section, the available space for the polymer chain to reside in and possibly its hydrophobicity.

8.3.3 The use of different solid surfaces and hydrophobic dyes

While SiO₂ nanoparticles are widely used, the usefulness of the aggregate could be extended by the investigation of its adsorption onto other solid surfaces. Preliminary works on Pt and Fe₃O₄ nanoparticles have been done using SANS that showed signs of aggregate adsorption. The data are included in Figure 8.3. The scattering intensities of the mixtures are clearly not the sum of the individual component scatterings. The intermediate-q slopes are no longer negative one, which is characteristic of rod-like segments, but increase slightly. Additionally, for the solution of $Fe_3O_4/pC_{16}TVB$, another turnover is observed at a q value of about 0.01 (Å⁻¹). The high q scattering seems to remain unchanged, however.



Figure 8.3: Scattering intensities of dilute solutions of Fe₃O₄ only, Fe₃O₄ with pC₁₆TVB, Pt only, Pt with pC₁₆TVB, and pC₁₆TVB only as a function of the scattering vector. The solvent is 100%D₂O, no contrast matching is employed. The hydrodynamic diameters of F₃O₄ and Pt are about 250nm and 25nm, respectively. The concentration of pC₁₆TVB is kept fixed 1mg/ml. Background scatterings have been subtracted.

On the other hand, so far, only Nile Red and pyrene have been used in solubilization experiments. More dyes need to be studied, especially those with direct industrial applications, like the ruthenium family of dyes that is used in Dye Sensitized Solar Cell. These are much less hydrophobic than the molecules used so far, and it would be interesting to find out more about the solubilization efficiency for these types of molecules.

8.4 References

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