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Assembly of Nanostructures at Solid-Liquid and Liquid-Air Interfaces

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ASSEMBLY OF NANOSTRUCTURES AT SOLID-LIQUID AND LIQUID-AIR INTERFACES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by

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Vita
Abstract

Molecular and nanoscale colloids such as surfactant, fatty acid and metallic nanoparticles are widely used in numerous applications such as detergents, biomedicine, and catalyst. The assemblies of these colloids show different morphological behavior in aqueous solution due to the wide range of intermolecular interactions such as hydrogen bonding, van der Waals, and electrostatics. The morphology of these assemblies can be changed by environmental factors including temperature, ionic strength, and salinity. However, the guidance to direct assembled state of colloidal assemblies at heterogenous interfaces under various external stimuli remains poorly understand. In this Ph.D. dissertation, we show the adsorption and reconfiguration of nanostructures on liquid-solid and liquid-vapor interfaces using adsorption isotherms, spectrophotometry, and small angle neutron scattering techniques.

The adsorption and self-assembly at solid-liquid interface are investigated using nonionic, ionic amphiphiles, and metallic nanoparticles as model materials. We show that the binding and reorganization of these assemblies on silica-based adsorbents are impacted by temperature, presence of counterions, and dispersion salinity. The effect of temperature on morphological change of nonionic surfactant (“soft matter”) in silica pore is first studied, and this change is attributed to the change in hydration state of the headgroups of the surfactant. We further investigate the assembled state of “hard matter” i.e. gold nanoparticle in propylamine modified silica porous materials, and we demonstrate the spatial distribution and catalysis activity of gold nanoparticles in different pore size silica porous materials in dispersion of increasing salinity. Moreover, the effect of counterion on the surface organization of fatty acid adsorbed on silica nanoparticle is uncovered. We find that the phase behavior of fatty acid on silica surface is governed by their ionization state, and we report that the interfacial activities of fatty acid-based
materials regulate the stability of liquid-vapor interface i.e. foam in aqueous solution. We extend this concept to a long-term thermostimulable foam in high alcohol solvents (> 75 vol%) formed by the natural fatty acid crystals. My Ph.D. works provide fundamental science to surface chemistry of molecular and nanoscale colloids, which is crucial in the development of new multiresponsive materials, personal care products, cosmetics and sensors.
Chapter 1. Introduction

1.1 Research objective

Colloid science was introduced to the scientific community in 1861 by Thomas Graham, who was one of the founders of colloidal chemistry and famous for his work in gas diffusion and dialysis. Colloids are mixtures in which the dispersed phase is suspended in the continuous phase, and the size of the dispersed substance is approximately from nanometers to a few micrometers. Colloidal materials play a vital role in many applied chemical engineering fields including pharmaceutical, paints, ink, and food industries.

Molecular and nanoscale colloids such as amphiphiles and metallic nanoparticles (NPs) show complex phase behaviors and catalytic activities in aqueous solution. Assembled state and morphology of these colloids in aqueous solution are governed by the intermolecular and intramolecular interactions such as van der Waals, electrostatic, steric and depletion forces. These interactions are crucial to direct the physical and chemical properties e.g. shape, size, wettability and stability of the materials. Although the phase behavior of molecular and nanoscale colloids in bulk are well-established, the adsorption and morphology of these materials vicinity to heterogenous interfaces remains poorly understood. This is challenging due to the complicated interactions between assemblies and interfaces, the obstruction of the adsorbents and the lack of facile characterization experimental tools. In this dissertation, we use adsorption isotherm and small angle neutron scattering (SANS) to overcome these limitations, and characterize the assembled state of molecular and nanoscale colloids at the heterogenous interfaces.

We focus on various interactions to direct the adsorption and morphology of assemblies such as surfactant, fatty acid and metallic NPs on the heterogenous interface, including liquid-vapor
interface and solid-liquid interface in this Ph.D. dissertation. The self-assembled state of colloids on the liquid-solid interfaces is dependent on the interactions between: i) the molecules adsorbed on the solid-liquid interface, ii) molecules on the solid-liquid interface and free molecules in bulk solution, and iii) free molecules in bulk solution. For example, the adsorption amount and self-assembled state of surfactants in mesoporous silica materials are governed by hydrogen bond, van der Waals and electrostatic interactions. The adsorption and configuration of surfactants are altered in the silica pores by varying the environments such as surface modification, salt addition, and temperature. The adsorption and morphology of self-assembled molecules on air-liquid interface i.e. aqueous foam impact the stability of the bubbles. The strategies to direct the foam properties by manipulating the structural and phase behavior of self-assembled molecules on liquid-air interface presents the landscape for ultra-stable and stimuli-responsive foams, which provides a fundamental basis for improved materials for sensors, oil recovery, personal and home care products.

1.2 Adsorption at solid-liquid interface and liquid-air interface

Adsorption is an interfacial phenomenon where adsorbate transfer from a liquid or gas phase to a fluid-fluid or solid-fluid interface. The adsorption exists at the boundaries between two phases in chemical, physical and biological systems, and it is widely used in pharmaceutical process, industrial applications, and catalysts. The adsorption is classified into two categories: (1) Physisorption: the adsorption in which the molecular interactions between the adsorbate molecules or colloids and the adsorbent are governed by physical forces like van der Waals forces, and (2) Chemisorption: the adsorption involves the chemical interaction such as covalent bonding and electrostatic attraction between the adsorbate and adsorbent. The adsorbed number of molecules on the adsorbent under equilibrium state can be represented using adsorption isotherm, which is
stemmed from its reliance on the temperature, and over fifteen isotherm models has been
developed such as Langmuir, Frenundlich, Brunauer–Emmett–Teller (BET) and Gu-Zhu model.\textsuperscript{28}

Amphiphiles such as surfactant and fatty acid are molecules consisting of a polar hydrophobic
region and a non-polar hydrophilic region, which self-assembles into different structures such as
micelles, bilayers, and cylindrical shape in aqueous solution.\textsuperscript{29} The self-assembled structures are
changed when the amphiphile molecules are introduced into solid-liquid interface.\textsuperscript{30} Though the
structures and phase behavior of amphiphile molecules in aqueous solution have been well
investigated and characterized, there are only few experimental studies that uncover the adsorption
process and self-assembled state of amphiphile molecules on solid-liquid interface. This
knowledge gap is due to the intricacy of the morphological behavior of amphiphile molecules on
the solid-liquid interface, which is related to the surface properties and curvature of solid substrate,
the chemical nature of amphiphiles and the dispersion medium.\textsuperscript{31–33} In addition to the basic
physical properties of adsorbate and adsorbent, the interactions between the amphiphiles and solid
surface, and the external stimuli such as temperature, pressure, light, field and salinity play
important roles in governing the adsorption process and morphological behavior of amphiphiles
on the solid-liquid interface.\textsuperscript{34}

Metallic nanoparticles (NPs) are the nanoscale materials composed of pure metals such as gold,
platinum, and silver, and they are widely used in biomedical and industrial applications.\textsuperscript{35–39}
However, the metallic NPs favor to aggregate in the aqueous media due to their high surface
energy.\textsuperscript{40} The strategies to stabilize the metallic NPs in aqueous solution is to graft capping agents
by rendering the energy barrier against aggregation.\textsuperscript{41} Surfactant, long-chain amine, organic thiol
compounds and polymers such as polyacrylate, polyethylenimine, and polyacrylonitrile are widely
utilized as capping agents, which plays governing roles to control the stability, solubility, structure
and size of metallic NPs in aqueous solution. Covalent bonding is the most widely used method for NPs immobilization, however, it is unfeasible to scale up due to the complicated preparative procedures. Besides, the structural features of metallic NPs under confinement remains unknown because of the lack of a facile experimental tool that allows in-situ structural characterization of NPs within the confined pore-space. As a part of this Ph.D. project, we experimentally investigate the effect of temperature, pore size, salt and counterions on the adsorption and structure of assemblies formed by surfactant, fatty acid and metallic NPs on silica materials using adsorption isotherms and SANS technique, and present the change of assembled state of nanostructure on the solid-liquid interface in various environment.

Fatty acid is an important component in living creature, and it consists of carboxylic acid polar head group and an aliphatic hydrocarbon chain. The fatty acids are widely used in various fields such as cosmetics, personal care, material recovery processes and drug delivery. However, the high Krafft temperature of long chain fatty acid leads to the low solubility of fatty acid in aqueous solution at room temperature, which limits their utilization in many applications. In order to overcome this disadvantage, the counterions are introduced to interact with fatty acids to decrease their Krafft temperature and thus increase the solubility in aqueous solution. It has been reported that the fatty acids show different morphologies in aqueous solution such as spherical micelles, wormlike micelles, vesicles and bilayers in the presence of counterions. These rich assembled states directly affect the interfacial activities of fatty acid in aqueous solution, which governs the properties of emulsion and aqueous foam.
Aqueous foams are formed by introducing air in liquid phase, which contributes to a liquid-air interface in the solution. Foams are utilized in diverse applications including oil recovery, food industry, cosmetic products and detergent due to their unusual properties, and the structure of foams is governed by the liquid portion, bubble size, and the physicochemical properties in the media. Foams are thermodynamically unstable and collapse with time by (A) Coarsening (Oswald ripening): the air diffuses from small bubbles to large bubbles due to the difference of Laplace pressure and resulting into the breakdown of small bubbles, (B) Coalescence: fusion of two or more air bubbles because of the unstable liquid film, and (C) Drainage: outflow of the liquid from foams driven by the gravity and capillarity. These three mechanisms are synergistic and contribution to each other in the destabilization process of the aqueous foam.

Foam stabilizers such as surfactant, polymers, nanoparticles and fatty acids are used to stabilize the aqueous foam and avoid the destabilization of the air bubbles. The adsorption of stabilizers on air-liquid interface increases the foam stability via enhancing the interfacial viscoelasticity, forming thick layers on liquid-air interface, and avoiding drainage and coarsening by jamming or aggregation on bubble films and in liquid channels. The foam stabilizers play an important role in forming foams in high alcohol content solvent, which is potentially used in personal care and home care products. However, generation of long-term stable foam in high alcohol content solvent remains a challenge due to the lacking of repulsive force i.e. disjointing pressure between the bubbles. As a part of this Ph.D. project, we demonstrate that the foam stability can be controlled by altering interfacial activity of fatty acid-silica complex on liquid-air interface. Moreover, we generated the ultra-stable foam in high alcohol content solvent using the natural fatty acid crystalline particles.
We demonstrate the fatty acid platelet crystals on liquid-air interface protecting the bubbles against coarsening and coalescence, and propose the thermostimulable foam by running heating-and-cooling cycles.

1.3 Overview of the dissertation

For this Ph.D. project, we investigated the adsorption and assembly of various nanostructures at heterogeneous interfaces. We first used the porous silica materials and silica nanospheres as model materials to study the adsorption and assembled state of nano-assemblies at solid-liquid interface. The effect of pore diameter, temperature, and dispersion salinity on the adsorption and morphological change of model chemicals including the nonionic ethoxylate surfactant triethyleneglycol monohexyl ether (C₆E₃) and gold nanoparticles (AuNPs) under porous silica materials is investigated. Besides, we studied the impact of counterions on surface structure of fatty acid on silica nanoparticle and corresponding interfacial activity of silica-fatty acid complex in the mixture. On the other hand, the thermos-responsive foams with long-term stability are formed using fatty acid crystals in high alcohol content solvents.
1.4 Outline of the dissertation

This dissertation contains nine chapters and the contents and details of each chapter are given as follows:

After the introduction to the studied fields and model systems in this dissertation, the main synthesis and characterization methods including mesoporous silica materials synthesis, functionalization of silica material surfaces, nitrogen adsorption isotherms, zeta potential, surface tension measurement, small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), and Ultraviolet-visible (UV-vis) spectroscopy are provided in Chapter 2.

In Chapter 3, we present the analysis methods of the SANS data including the model of self-assemblies decorated in silica porous material and the raspberry-like bead model. Besides, this chapter explains the Sang-Vinu-Coppens (SVC) model to calculate the maximum pore-filling
fraction, and investigate the interactions between particle-particle and between particle-surface using Derjaguin–Landau–Vervey–Overbeek (DLVO) theory.

In Chapter 4, we show the effect of temperature on the adsorption and morphological change of C₆E₃ under silica nonporous materials. We find that the C₆E₃ shows an increase in situ aggregation behavior in silica pores upon increasing the temperature above the lower critical solution temperature (LCST). We present that the C₆E₃ surfactant is able to reversibly uptake and release secondary molecules from silica pore by altering the temperature.

In Chapter 5 and 6, we investigate the adsorption, assembled state and catalytic activity of AuNPs in various pores size of silica materials under different dispersion salinity. We extend the SANS analysis method to provide the adsorption state of nanoparticles in the cylindrical pores of silica nanomaterials. We demonstrate the impact of pore diameter and salinity on the assembled state and spatial distribution of AuNPs within silica porous materials, and obtain a comprehensive view of the packing and catalytic activity of these NPs.

In Chapter 7, we present the morphology of decanoic acid adsorbed on aminopropyl-modified silica nanoparticles in the presence of counterion. We show that the self-assembly of fatty acid transfers from discrete patches to a continuous bilayer on silica surface, and this structural change governs the stability of the foam generated by the fatty acid-silica mixture. Chapter 8 provides a strategy to obtain the ultra-stable foam in high alcohol content using fatty acid crystals. We highlight that the fatty acid crystals are adsorbed at the liquid-air interface preventing the bubbles from coalescence.

In Chapter 9, we summarize the work which provides the insight into the assembled state of nanostructures on silica materials, and we present a better understanding of the generation of long-
term stable foam in high alcohol solvent. Besides, we propose the prospect of the studies and the corresponding potential applications of our projects.
Chapter 2. Experimental Methods

2.1 Materials used in the synthesis

Following are the details of the chemicals used in the synthesis. The list provides the supplier of the chemicals and their purity: tetraethyl orthosilicate (TEOS, Sigma-Aldrich, ≥ 99%), HCl (5N, VWR), ammonium fluoride (NH₄F, Alfa Aesar, ≥98%), decane (Sigma-Aldrich, ≥ 99%), hexane (Sigma-Aldrich, ≥ 99%), hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich, ≥ 99%), gold chloride trihydrate (HAuCl₄·3H₂O, Sigma-Aldrich, ≥ 99.9%), sodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O, Sigma-Aldrich, ≥ 99%), sodium borohydride (NaBH₄, Sigma-Aldrich, ≥ 98%), (3-Aminopropyl)triethoxysilane (APTES, Sigma-Aldrich, ≥ 98%), and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (Pluronic P123, Sigma-Aldrich, ≥ 98%)

2.2 Synthesis of mesoporous silica materials

The model mesoporous silica materials MCM-41 and SBA-15 with pore diameters (d_pore) of 4.1, 4.8, 8.4, 12.0 and 15.6 nm were synthesized using previously reported methods. These silica materials had cylindrical nanopores arranged in two-dimensional (2D) hexagonal closed packed (hcp) lattice. Details of the synthesis methods used in our work are provided below.

Synthesis of MCM-41 silica material

The mesoporous silica was synthesized using CTAB as the structure directing template in the presence of silica precursor TEOS under alkaline conditions. Here, 1.0 g of CTAB was mixed with 480 mL deionized water, and 1.4 mL of 5 M NaOH was added into the solution. The mixture was kept at 80 ºC for 2 hours under constant stirring and reflux. The product was filtered, washed with deionized water, and dried at 70 ºC in the oven. Then the organic template was removed from the silica materials by calcination at 550 ºC for 4 h.
Synthesis of SBA-15 silica material

Santa Barbara Amorphous (SBA) with 2D hexagonal pore structure was first synthesized in 1998 by Stucky and groups. The synthesis of such mesoporous material is based on the self-assembly of cationic or anionic surfactant (template) under either acidic or basic conditions. SBA-15 materials with different pore diameters were synthesized following the established method. For \( d_{\text{pore}} = 4.8 \) nm pore diameter, SBA-15 is synthesized by dissolving 2.84 g of P123 in 90 g deionized water and 48 g of 5 M HCl solution. The mixture is equilibrated at 35 °C for 2 hours, and then 8.0 g TEOS added dropwise and reacted for 20 h at 35 °C. Stirring was maintained throughout. For \( d_{\text{pore}} = 8.4 \) nm, TEOS, \( \text{H}_2\text{SO}_4 \), \( \text{H}_2\text{O} \) and P123, were dissolved into deionized water in the molar ratio of \( 1 \text{TEOS} / 5.9\text{H}_2\text{SO}_4 / 323\text{H}_2\text{O} / 0.017\text{P123} \), kept at 40 °C for 5h, and then aged at 105 °C for 20 hours in an autoclave. In the case of \( d_{\text{pore}} = 12.0 \) nm pore diameter, 2.4 g P123 was dissolved in 84 mL HCl aqueous solution (1.3 N) at 25 °C for 6 hours. Then 0.027g of \( \text{NH}_4\text{F} \) was added to the mixture, kept for 20 minutes. At this stage, 14.3 g decane and 5.5 mL TEOS were premixed and then dropwise added into the mixture, kept at 30 °C for 20 hours, and then transferred into a convection oven for further reaction (no stirring) at 100 °C for 48 hours. The SBA-15 with \( d_{\text{pore}} = 15.6 \) nm pore size was synthesized using a similar method as 12.0 nm SBA-15, but with premixed 8.45 g hexane with 5.5 mL TEOS added to the mixture of P123, HCl and \( \text{NH}_4\text{F} \). The mixture was kept at 15 °C for 20 hours. The four silica material products were filtered, washed with deionized water, dried at 100 °C, and calcined at 550 °C for 5 hours to remove the surfactant template.

2.3 Synthesis of gold nanoparticles

The AuNPs were synthesized by reducing \( \text{HAuCl}_4 \cdot 3\text{H}_2\text{O} \) using \( \text{NaBH}_4 \) in the presence of sodium citrate solution. In a typical synthesis, 0.01 g \( \text{HAuCl}_4 \) and 0.0075 g sodium citrate was
mixed with 100 mL deionized water, and then 3 mL of 0.1 M freshly prepared NaBH₄ solution was added to the mixture under constant stirring at 20 °C. The mixture transformed to pink immediately after adding NaBH₄ solution, indicating the formation of AuNPs. During the synthesis, sodium citrate was used as a capping agent which induced a negative charge (zeta potential = -41.4 mV at pH 6) on the particles and provided kinetic stability to the AuNPs in low salinity aqueous solutions via electrostatic double layer repulsion.

2.4 Propylamine functionalization of silica materials

The propylamine-functionalized silica nanoparticles were synthesized by controlled surface modification of commercially available Ludox-TMA colloidal silica (Sigma-Aldrich). The silica nanoparticle dispersion was dialyzed for 7 days using ultrapure water with a resistivity of 18.2 MΩ-cm, changing water every day to remove any undesired foreign molecules in the dispersion. The propylamine-functionalized silica materials (mSiO₂) play a crucial role for covalent binding of molecules to the silica surface. Generally, the silica surface is functionalized using 3-aminopropyl)triethoxysilane (APTES) by grafting method, which allows organosilane species bonding to silanol groups on silica surface.

![Figure 2.1. Schematic representation of the synthesis of amine-functionalized silica materials using APTES under acidic condition.](image-url)
In a typical synthesis, 22.2 g of 27 wt % Ludox-TMA dispersion was mixed with 12 mL of acetic acid and 3.8 mL of deionized water (Figure 2.1.). The mixture was transferred into a round-bottom flask, fitted with a reflux condenser, and heated to 80 °C. After 30 min of equilibration, 0.7 mL of APTES was added to the flask containing the mixture with constant stirring. The mixture was reacted for 16 h at 80 °C under reflux. The dispersion containing modified silica nanoparticles was removed from the flask and dialyzed for 24 h using deionized water at pH 4. The larger aggregates from the dialyzed $m$SiO$_2$ were removed by filtering it through a syringe filter with a pore size of 220 nm. The pH of the filtered nanoparticle solution was adjusted to 4, and the $m$SiO$_2$ dispersion was stored at 4°C. We further chemically modified the pore walls of the silica materials with propylamine groups.\textsuperscript{17} The propylamine functionalization of the mesoporous silica was achieved by reacting with APTES in acidic solution. In a typical synthesis, 1.0 g prepared silica material was mixed with 4.0 mL acetic acid and 6.0 mL deionized water. The mixture was equilibrated at 80 °C for 30 minutes under reflux, and then 0.12 mL APTES was added. This mixture continued to react for 16 hours under reflux, and the product was filtered, washed five times with 100 mL deionized water, then dried at 60 °C for 24 hours.

2.5 Nitrogen adsorption

![Figure 2.2. Schematic of BET theory interpreting the multilayer adsorption model](image)
Specific surface area (\(S_A\)) of the silica materials was measured using nitrogen gas adsorption at \(-195.15^\circ C\). The adsorption isotherm is represented by the BET theory, which extended the monolayer adsorption model (Langmuir model) to multilayer adsorption model (Figure 2.2.). The BET model is given by

\[
\frac{P}{P_0} \frac{V}{[1-(P/P_0)]} = \frac{c}{V_m c} \left( \frac{P}{P_0} \right) + \frac{1}{V_m c}
\]

where \(P/P_0\) is the relative pressure of the adsorbed gas, which is the ratio of equilibrium pressure to the saturation vapor pressure, \(V\) is the number of adsorbates, \(V_m\) is the amount of monolayer adsorbates, and \(c\) is the BET constant,

\[
c = \exp \left( \frac{\Delta E}{RT} \right)
\]

where \(\Delta E\) is the heat change from the adsorption of first layer to the higher layer. The BET plot is obtained by representing the first term in equation 2-1, \(\frac{P_0/P}{V[1-(P_0/P)]}\), as a function of \(P_0/P\), and the plot shows the linear relation at \(0.05 < P_0/P < 0.3\). Then, the specific surface area can be calculated based on \(V_m\) by the following equation

\[
S_A = \frac{a V_m N_A}{m v}
\]

where \(a\) and \(v\) are the area of cross section and molar volume, respectively, of the adsorbed gas molecules (for nitrogen, \(a = 0.162 \text{ nm}^2\)), \(N_A\) is Avogadro constant, and \(m\) is the mass of given sample.

2.6 Zeta potential

Zeta potential is the electrical potential difference between the bulk dispersion medium and the stationary layer of fluid adhere on the surface of particles (Figure 2.3.). The zeta potential plays an important role in governing the stability of colloidal dispersion. Basically, the dispersions with lower zeta potential are commonly unstable state leading to flocculation, coagulation, and
aggregation because the electrostatic repulsive force loses to the attractive van der Waals force. On the contrary, the dispersions with high zeta potential remain physical stability due to the high electrostatic repulsion between particles in the dispersion.

![Figure 2.3. Schematic representing the distribution of the ions around negatively charged colloidal particle in bulk medium.](image)

In a typical measurement, the colloidal dispersion is filled in the cuvette which is designed for zeta potential measurement, and the voltage is applied to the dispersion. The colloidal particles move towards the oppositely charged electrodes under electrical field, and the velocity is proportional to their zeta potential. This electrophoretic mobility ($\mu_E$) of particles in electrical field is monitored using a laser light, and the mobility is quantified by the shifting of scattered laser frequency. Combining the electrophoretic mobility and Henry’s law, zeta potential is given as\(^{71}\)

$$\zeta = \frac{3\eta \mu_E}{2\varepsilon f(\kappa c)} \quad (2-4)$$

where $\zeta$ is zeta potential, $\eta$ is viscosity, $\varepsilon$ is the dielectric constant of the dispersion medium, and $f(\kappa c)$ is Henry’s function.
2.7 Optical tensiometer

Optical tensiometer is widely utilized to measure the value of contact angle, surface tension, and interfacial tension. The static contact angle is measured using sessile drop method. To measure the static contact angle, a droplet is positioned on the solid or crystalline surface, and the drop profile is recorded by high speed camera. Then, Young-Laplace fitting method was applied to describe the shape of the drop, and the contact angle is determined by the tangent at contact points.

The surface tension of a liquid drop also can be decided using the tensiometry with pendent drop method. In a typical measurement, a droplet was pushed out from a syringe and suspended on the needle tip, and the surface tension was obtained by shape analysis combining with Young-Laplace equation. Here, the surface tension of the droplet is given by\(^{72}\)

\[
\gamma = \frac{R^2 \Delta \rho g}{\beta} \tag{2-5}
\]

where \(\gamma\) is surface tension, \(R\) is radius of drop curvature at apex, \(\Delta \rho\) is density difference between the pendent drop and air, \(g\) is gravitational constant, and \(\beta\) is a shape factor. Here, the \(\beta\) term is extracted using Young-Laplace equation,
\[
\frac{dx}{db} = \cos \alpha \\
\frac{da}{db} = \sin \alpha \\
\frac{d\alpha}{db} = 2 - \frac{(\sin \alpha)}{x} + \beta a
\]  

where \(a\) is the vertical distance from droplet apex, \(b\) is the arc length of the drop surface, \(x\) is horizontal distance from apex to surface of the droplet, and \(\alpha\) is the angle between the surface tangent and horizontal axis. The analysis software provides support, such as capturing the image of the hanging droplet, locating the slope, and performing the Young-Laplace fitting to accurately obtain the value of surface tension.

2.8 Small Angle Scattering

The small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) techniques are applied in the field of colloidal science to characterize the morphological properties of hard and soft materials in aqueous solutions.\textsuperscript{73,74} In both measurements, the small angle scattering results from the elastic-coherent scattering of the incident beam. The scheme of the setup for the small angle scattering is shown in Figure 2.5. The incident beam \((k_0)\) is scattered by the sample at angle \(\theta\), and the scattered beam \((k_f)\) is received by the 2D detector. For this small angle scattering, the scattering vector \(q\) is given as

\[
q = |\vec{q}| = |\vec{k}_f - \vec{k}_0| = \sqrt{k_f^2 - k_0^2 - 2k_fk_0\cos \theta} = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}
\]

where \(\vec{k}_f = \vec{k}_0\) and \(\lambda\) is the wavelength of incident beam.
These two instruments share the same basis but different radiation source. In a SAXS measurement, X-rays are scattered by the electron clouds and provide the clues about the electrons number in the various part of the materials. While the type of radiation for SANS is neutrons which interact with atomic nuclei of the materials. Since the energy of neutrons is significantly lower than X-rays at the same wavelength, the SANS instrument is widely used to investigate the biological samples. Besides, neutrons are much more efficiency to pass through the samples than X-ray because they are neutral and only scattered by the atomic nuclei. Therefore, the SANS instrument can be applied to probe the samples under complex experimental gears, such as temperature controller, press chambers, and shearing apparatus. In a typical measurement, we uncover the assembled state of adsorbates on silica-based absorbents by SANS, and the total scattering intensity ($I_q$) is given

$$I_q = \varphi \Delta \rho^2 V F(q) S(q)$$  \hspace{1cm} (2-10)

where $\varphi$ is the volume fraction of scattering object, $\Delta \rho$ is the scattering length density (SLD) contrast between self-assemblies and absorbents, $V$ is the volume of a single scattering object, $F(q)$ and $S(q)$ are the form factor and structure factor of scattering object, respectively. The total
scattering intensity of a multicomponent sample originates from the sum of scattering contrast of each material in the mixture, which results into a complex scattering profile. In order to simplify the analysis model, we perform the measurement under absorbents (in our work silica materials) contrast matched condition, where $\Delta \rho$ between silica and liquid medium is zero. The neutron and X-ray SLD of silica materials, C$_6$E$_3$, AuNPs, and decanoic acid are listed in Table 2.1. The contrast matched condition for one of the materials in the mixture can be achieved in SANS measurement by changing the volume ratio of H$_2$O to D$_2$O in the dispersion because the SLD of H$_2$O is negative and D$_2$O is positive. However, this contrast matched sample is not feasible in SAXS by using H$_2$O/D$_2$O mixture and the total scattering profile come from all materials in the sample.

Table 2.1. Scattering length density of different materials used in SANS and SAXS experiments

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O</th>
<th>D$_2$O</th>
<th>Silica</th>
<th>C$_6$E$_3$</th>
<th>AuNPs</th>
<th>Decanoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray SLD</td>
<td>9.45</td>
<td>9.35</td>
<td>18.80</td>
<td>8.81</td>
<td>120.20</td>
<td>8.46</td>
</tr>
<tr>
<td>($\times 10^{-4}$nm$^2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron SLD</td>
<td>-0.56</td>
<td>6.43</td>
<td>3.54</td>
<td>0.14</td>
<td>4.50</td>
<td>0.10</td>
</tr>
<tr>
<td>($\times 10^{-4}$nm$^2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.9 Ultraviolet-visible Spectrophotometry

The Ultraviolet-visible spectroscopy (UV-vis) is commonly used in analytical chemistry for quantifying the dispersed sample such as metallic nanoparticles, biomolecules, and part of organic chemicals. UV-Vis spectroscopy is a class of absorption spectrum that applies light in the visible and UV ranges of the electromagnetic spectrum (Figure 2.6.). The photons in the chemicals absorbed energy from the incident beam of spectrophotometer and moved to a higher energy state. Four typical transitions including $\sigma - \sigma^*$, $n - \sigma^*$, $\pi - \pi^*$, and $n - \pi^*$ can be observed using UV-Vis spectroscopy, and the transition order follows: $n - \pi^* < \pi - \pi^* < n - \sigma^* < \sigma - \sigma^*$. The
energy absorption of electrons contributes to the formation of the absorbance spectra, which is related to the concentration and molecules number in the dispersion. The absorption of radiation for a compound results into a specific spectrum, which can be used as marker or probe for the compound. In a typical measurement, the droplet was pipette to the pedestal, and the concentration of the sample can be obtained using the Beer-Lambert law:

\[ \text{Abs} = \varepsilon cl \]  

(2-10)

where \( \text{Abs} \) is the absorbance value, \( \varepsilon \) is the extinction coefficient of the compound and \( l \) is the path length of the solvent which remains constant. It should be noted that the Beer-Lambert law is only feasible to the dilute dispersion.

![Figure 2.6. Scheme of sample measurement using UV-Vis spectroscopy instrument](image-url)
Chapter 3. Modeling and Theory

3.1 Model of self-assemblies adsorbed in 2D hexagonal porous silica material

The total scattering intensity \( I_T \) of self-assemblies adsorbed in SBA-15 under silica contrast matching is a sum of two independent contributions: Bragg scattering from the pore lattice decorated by surfactants \( I_B \), and diffuse scattering from surfactant aggregates in the pores \( I_D \):

\[
I_T = I_B + I_D
\]  

(3-1)

The Bragg scattering contribution \( I_B \) is given as:

\[
I_B = \varphi \Delta \rho ^2 V |F(q)| ^2 S(q)
\]  

(3-2)

where \( \varphi \) is the volume fraction of scattering object, \( \Delta \rho \) is the scattering length density contrast between self-assemblies and medium, \( V \) is the volume of assemblies formed, \( |F(q)| ^2 \) is the form factor of self-assemblies in the pore, and \( S(q) \) is the structure factor of a 2D hexagonal pore lattice given as:

\[
S(q) = q^{-2} \sum_{hk} m_{hk} S_{hk}(q), \quad \text{where } m_{hk} \text{ is the multiplicity factor of a reflection with Miller indices } hk.
\]

The Bragg peaks are modeled by Gaussian functions:

\[
S_{hk}(q) = \alpha_{hk} \exp \left[-w(q - q_{hk})^2\right] \text{ located at positions } q_{hk} = \frac{4\pi}{a} \sqrt{\frac{h^2 + k^2 + hk}{3}}, \text{ where } a \text{ is the lattice parameter of the mesoporous silica}^{75-77}, \alpha_{hk} \text{ is the amplitude of peak } (hk), \text{ and } w \text{ is the width of Gaussian peaks, which is be kept constant in data fitting routine.}
\]

The diffused scattering contribution \( I_D \) is modelled using Teubner-Strey function:

\[
I_D(q) = \frac{I_0}{\left(1 - \frac{I_0}{I_m}\right) \left(\frac{q^2}{q_m^2} - 1\right)^2 + \frac{I_0}{I_m}}
\]  

(3-3)

where \( I_m \) and \( q_m \) are the coordinates of the maxima of the correlation peak, and \( I_0 \) is the forward scattering intensity at \( q = 0 \). Here we estimate two characteristics of the self-assembled aggregates, namely quasiperiodic distance between self-assembled domains \( d \), and a decay length...
(ξ) of this quasiperiodic order. These characteristic lengths are estimated experimentally by the diffused scattering parameters \( I_m, q_m, \) and \( I_0 \) from equation 3-3 as:

\[
d = 2\pi \frac{\sqrt{2}}{q_m} \left[ \frac{1}{s^{1/2} + 1} \right]^{-1/2}, \quad \xi = \frac{\sqrt{2}}{q_m} \left[ \frac{1}{s^{1/2} - 1} \right]^{-1/2}
\]  

(3-4)

where \( s = I_0/I_m \). The quantity \( \xi / d \) is the measure of the polydispersity of the domain size.

![Figure 3.1](image)

Figure 3.1. The schematic representation of the assemblies adsorbed on silica porous material under contrast matched condition.

### 3.2 Raspberry model under core contrast-matched conditions

The total scattering intensity of raspberry-like structure with core particle contrast-matched with the continuous medium can be represented as:

\[
I_{RB} = I_{ls} + I_s
\]

(3-5)

where the \( I_{ls} \) is the scattering intensity of core-particle complex, and \( I_s \) is the free particles in solution. In our case, the experiments were performed at 0.5 maximum surface excess, where there are no free particles in the solution. Then the equation (3-5) is given

\[
I_{RB} = I_{ls} = (\Phi_s^T \Phi_s^a N (\Delta \rho)^2 V_s) P_{ls}
\]

(3-6)

where \( \Phi_s^T \) is volume fraction of small particles, \( \Phi_s^a \) is the fraction of the total small particles that are adsorbed on the core. \( N \) is the number of small particles of volume \( V_s \), and scattering contrast \( \Delta \rho \) adsorbed onto the core particle. \( P_{ls} \) is the form factor of the core-particle complex, which is obtained by
\[ P_{ls} = \frac{1}{M^2} \left[ N(\Delta \rho)^2 V_s^2 \Psi_s^2 + N(N - 1)(\Delta \rho)^2 V_s^2 S_{pp} \right] \]  \hspace{1cm} (3-7)

\[ M = N \Delta \rho V_s \]  \hspace{1cm} (3-8)

\[ S_{pp} = \Psi_s^2 \left[ \frac{\sin(q(r_s + r_l))}{q(r_s + r_l)} \right]^2 \]  \hspace{1cm} (3-9)

where \( S_{pp} \) is the particle-particle correlation term and \( \Psi_s \) is the integration and normalization function of form factor of small particles. Besides, the \( \Phi_s^T \Phi_s^a \) is related to the covered fraction of the core surface (\( \chi \)), which is

\[ \Phi_s^T \Phi_s^a = \frac{\chi \Phi l \Phi s}{4(r_s + r_l)} \]  \hspace{1cm} (3-10)

where \( \Phi_l \) is the volume fraction of the core particle of radius \( r_l \), and \( r_s \) is the radius of small particles. Further, the \( \chi \) can be represented by \( N \)

\[ \chi = \frac{N(r_s + r_l) V_s}{4r_s V_l} \]  \hspace{1cm} (3-11)

where \( V_l \) is the volume of core particle. Then, we plug equation (3-7) - (3-11) into equation (3-6) and obtain

\[ I_{RB}(q) = \frac{N \Phi l \Phi s V_s^2 \Delta \rho^2 \Psi_s^2}{16 V_l} \left[ 1 + (N - 1) \left[ \frac{\sin(q(r_l + r_s))}{q(r_l + r_s)} \right]^2 \right] \]  \hspace{1cm} (3-12)

where

\[ \Psi_s = \frac{3[\sin(qr_s) - qr_s \cos(r_s)]}{(qr_s)^2} \]  \hspace{1cm} (3-13)
3.3 Derivation of pore filling fraction using SVC model

The maximum amount of AuNPs can be arranged in pores with cross-section area

\[ A_{\text{pore}} = \frac{\pi}{4} d_{\text{pore}}^2 \]

is given\(^80,81\)

\[ n_{\text{max}} = \frac{N}{N_A A_{\text{pore}} \sigma} V_{\text{pore}} \]  \hspace{1cm} (3-14)

where \(N\) is the number of molecules that can be accommodated side-by-side in a cross-section of the pore, \(N_A\) is the Avogadro constant, \(\sigma\) is the diameter of AuNPs, and \(V_{\text{pore}}\) is the specific pore volume of the \(m\)SiO\(_2\). Here, a 2D model of AuNPs packing is applied without consideration of packing effects in the direction of the pore axis in equation (3-14). The volume fraction of AuNPs is represented by

\[ f = \frac{NV_{\text{AuNPs}}}{(\pi/4)d_{\text{pore}}^2 \sigma} \]  \hspace{1cm} (3-15)

where \(V_{\text{AuNPs}}\) is the volume of an AuNP, and \(V_{\text{AuNPs}} = \pi \sigma^3 / 6\). Plugging this into equation (3-15) and combing with equation (3-14) gives

\[ n_{\text{max}} = \frac{6}{N_A \pi \sigma^3} f V_{\text{pore}} \]  \hspace{1cm} (3-16)
By introducing the pore size distribution function $M(d_{pore}) = (dV_{pore}/d(d_{pore}))d_{pore}$, given

$$n_{max} = \frac{6}{N_A \pi \sigma^3} \int f(d_{pore}) M(d_{pore}) d(d_{pore})$$

(3-17)

with

$$f = \frac{2N}{3(d_{pore}/\sigma)^2}$$

(3-18)

where the integral extends over the relevant pore size. Depending on ratio of $d_{pore}/\sigma$, the $N$ value is obtained by

$$N(d_{pore}/\sigma) = \begin{cases} 0 & d_{pore}/\sigma < 1 \\ 1 & 1 < d_{pore}/\sigma < 2 \\ N_1 & 2 < d_{pore}/\sigma < 3 \\ N_1 + 1 & 3 < d_{pore}/\sigma < 4 \end{cases}$$

(3-19)

with

$$N_1 = \pi \left( \arcsin \frac{\sigma}{d_{pore}-\sigma} \right)^{-1}$$

(3-20)

### 3.4 DLVO theory

According to DLVO theory, the net interaction energy between colloidal particles ($U^{DLVO}$) dispersed in an aqueous medium is the sum of electrostatic ($U^{Elec}$) and van der Waals ($U^{vdw}$) interactions given as

$$U^{DLVO} = U^{Elec} + U^{vdw}$$

(3-21)

For a pair of spherical AuNPs of radius $R$, the electrostatic and van der Waals interaction energy is estimated using following equations

$$U^{Elec}_{\text{AuNP-AuNP}} = 32\pi \varepsilon_0 \varepsilon_r \left( \frac{k_B T}{e} \right)^2 R \tanh^2 \left( \frac{e \phi_0}{4k_B T} \right) \exp (-\kappa h)$$

(3-22)

and
\[ U_{\text{vdw}}^{\text{AuNP-AuNP}} = -\frac{AR}{12h} \]  

(3-23)

where \( U_{\text{Elec}}^{\text{AuNP-AuNP}} \) and \( U_{\text{vdw}}^{\text{AuNP-AuNP}} \) are respectively the electrostatic and van der Waals interactions, \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) is the dielectric constant of the medium, \( k_B \) is Boltzmann constant, \( T \) is the temperature, \( e \) is the electric charge, \( \phi_0 \) is the surface potential of the interacting particles, \( \kappa \) is the inverse of Debye length, \( h \) is the distance between the colloidal particles, and \( A \) is the Hamaker constant of the colloidal particles. In our case for simplicity reasons, we assume the surface potential \( \phi_0 \) to be equal to the zeta potential of sodium citrate-capped AuNPs in dispersion. For calculating the interaction between the AuNPs and tubular silica pore, we approximate the pore-wall as a flat surface and the DLVO interaction energy between a particle and a plane is estimated as\(^{1,82}\)

\[ U_{\text{Elec}}^{\text{mSiO}_2-\text{AuNP}} = \pi \varepsilon_0 \varepsilon_r R \left[ 2 \phi_0 \phi_1 \ln \left( \frac{1 + \exp (-\kappa h)}{1 - \exp (-\kappa h)} \right) + (\phi_0^2 + \phi_1^2) \ln \left( 1 - \exp (-2\kappa h) \right) \right] \]  

(3-24)

and

\[ U_{\text{vdw}}^{\text{mSiO}_2-\text{AuNP}} = -\frac{AR}{6h} \]  

(3-25)

where \( U_{\text{Elec}}^{\text{mSiO}_2-\text{AuNP}} \) and \( U_{\text{vdw}}^{\text{mSiO}_2-\text{AuNP}} \) are respectively the electrostatic and van der Waals interactions between an AuNP and \( m\text{SiO}_2 \) flat surface, and \( \phi_1 \) is the surface potential of \( m\text{SiO}_2 \). Here we assume that the surface potential of \( m\text{SiO}_2 \) is equal to the zeta potential of propylamine-modified nanoparticles.
Chapter 4. Pore Uptake and Demixing of Surfactant Solutions in Silica Porous Materials

4.1 Introduction

Adsorption and self-assembly of molecules in spatially confined pores play a critical role in oil and natural gas recovery, water purification and targeted drug delivery\textsuperscript{33,83–86}. The uptake and release of molecules from porous materials is governed by the chemical design of the pore-wall and molecules, local pore-curvature, and environmental stimuli such as salinity, temperature, and pressure\textsuperscript{6–8,33,87,88}. Understanding the principles governing the self-assembly and stimuli induced reconfiguration of soft matter in porous confinement is the key to develop advanced materials with programmable molecular uptake and release properties. The phase behaviour of the soft matter in micro- and meso- confinements of hard matter have been explored primarily using theoretical and simulation approaches\textsuperscript{11–14}. Previously, classical thermodynamics\textsuperscript{89} and mean-field lattice theory\textsuperscript{90} have shown that the self-assembled structure of molecules such as diblock copolymers depends on the confinement geometry and degree of confinement i.e. relative size of pore space and assembling molecules\textsuperscript{91,92}. Mesoscale dissipative particle dynamics simulations have been used to study the state behaviour of adsorbed aggregates of model amphiphiles on hydrophilic/hydrophobic mesopores\textsuperscript{93–96}. While these theoretical studies have predicted a rich phase behaviour of soft matter in hard material confinement, there are only a few experimental studies that explore such self-assembly process\textsuperscript{15–18}. Recent experimental studies using SANS as primary characterization tool have been used to unravel the effect of pore-confinement on the self-

\begin{footnotesize}
\end{footnotesize}
assembly of non-ionic surfactants on hydrophilic surfaces. It was shown that $n$-dodecyl-penta(ethylene glycol) (C$_{12}$E$_5$) surfactant$^{75,77,97}$ forms discrete surface patches on hydrophilic tubular pore wall of silica SBA-15 materials. These self-assembled patches can be altered by programming the pore wall-surfactant interactions using additive molecules$^{75}$. Instead of introducing a co-adsorbing molecule, the pore wall-surfactant and surfactant-surfactant interactions can also be altered by external stimuli such as temperature.

A characteristic feature for surfactants of $n$-alkyl poly(oxyethylene) ether family (abbreviated as C$_n$E$_m$) is their ability to reversibly hydrate and dehydrate in response to the change in solution temperature$^{98-100}$. In bulk aqueous solution, C$_n$E$_m$ surfactants show a concentration and temperature dependent phase behaviour with a characteristic lower critical solution temperature (LCST). At temperatures well above the LCST, the critical micellar concentration (cmc) line of these surfactants nearly coincides with the phase boundary curve of liquid-liquid coexistence. Therefore, the state of the phase-separated surfactants can be viewed as co-existence of dilute and concentrated micellar solutions$^{101}$. This co-existence of multiple phases drives a complex phenomenon where the adsorption of such non-ionic surfactants on solid surfaces increases with increasing temperature, referred to the anomalous temperature dependence of C$_n$E$_m$ surfactant adsorption$^{92,101-103}$. The increase in adsorbed amount with temperature is in contrast to the decreased adsorption of simple molecules such as gases and other hydrocarbons. A theoretical model accounting for this unusual phenomenon of non-ionic surfactants was developed by Bock and Gubbins, showing that this inverse temperature effects arise from the change in H-bonding between water, surfactant and adsorbing surface.$^{103}$ Recently, the anomalous adsorption of Triethyleneglycol monohexyl ether (C$_6$E$_3$) surfactant on CPG silica porous material with increasing temperature was experimentally studied$^{101,102}$. While it was demonstrated that the
amount of surfactant adsorbed increases with temperature, the local structure and assembled state of the surfactant molecules remains unknown.

In this chapter, we combine Small Angle Neutron Scattering (SANS) experiments with adsorption isotherms to investigate the effect of temperature-induced demixing, as well as the morphology of self-assembled aggregates formed by C₆E₃ surfactant in strongly confined tubular pores of silica SBA-15. We find that C₆E₃ surfactant in pores of SBA-15 material show a temperature-dependent state behaviour, evidenced by the existence of anchored surfactant head groups and the condensation of non-anchored molecules. The morphology of the aggregates on pore surface is highly dependent on the pore loading and temperature. We find that an increase in temperature above the LCST of C₆E₃ drives an increase in the thickness of surface aggregates formed by the surfactant molecules. Further we demonstrate that the surfactant micelles with model molecules (here dye) solubilized in their micellar-core can be reversibly transferred between the pore-space and bulk solution upon increasing-decreasing temperature cycles. The study provides a fundamental understanding of the re-assembly of surfactant molecules in response to change in temperature, and provides the basis of designing new porous materials with stimuli-responsive molecular uptake and release properties.
4.2 Characterization of SBA-15 silica

Figure 4.1. (a) Transmission electron microscope (TEM) image and (c) schematic showing tubular nanopores of SBA-15 silica material forming 2D hexagonal lattice. (b) SAXS profile of SBA-15 silica showing the presence of Bragg peaks corresponding to the 2d hexagonal lattice of the tubular pores as shown in a and c. (d) Nitrogen gas adsorption isotherm for SBA-15 silica showing a characteristic adsorption-desorption hysteresis. The pore diameter was estimated using the relative pressure at the capillary condensation step.

The synthesized SBA-15 materials were characterized using Transmission Electron Microscopy (TEM), Small Angle X-ray Scattering (SAXS), and nitrogen gas adsorption. The TEM micrograph of the SBA-15 silica material was performed on JOEL JEM 2011 and shown in Figure 4.1a. The TEM micrograph shows the presence of 8-9 nm diameter cylindrical pores in silica grains of typical size ~ 100 nm. The bulk characterization of the porous material was performed using Small Angle X-ray Scattering (SAXS). The SAXS measurements were performed on Xenocs Xeuss instrument fitted with a Pilatus3 1M detector. The SAXS profile for SBA-15 silica material is shown in Figure 4.1b, where I(q) is scattering intensity and q is the scattering vector related to x-ray wavelength (λ) and scattering angle (θ) as $q = \left(\frac{4\pi}{\lambda}\right) \sin\left(\frac{\theta}{2}\right)$. Because of the 2D hexagonal pore
lattice of the SBA-15 material, the scattering profile show characteristic diffraction peaks at \( q = 0.61, 1.06, 1.23 \text{ nm}^{-1} \). These three dominant Bragg peaks correspond to (10), (11) and (20) miller indices of the 2D hexagonal ordered pore lattice (Figure 4.1b, and 4.1c). The location of the Bragg peaks is used to determine the lattice parameter, \( a \), for the mesoporous silica as \( a = \frac{4\pi}{q_{10}}\sqrt{3} \), where \( q_{10} \) is the scattering vector for the peak maximum with miller index (10). From our SAXS experiments we estimate \( a = 11.8 \text{ nm} \) for synthesized SBA-15 silica material. The average pore diameter (\( D_{\text{pore}} \)) of the SBA-15 material was calculated using nitrogen gas adsorption (Micromeritics, ASAP 2020). \( D_{\text{pore}} \) is calculated to be \( 8.6 \text{ nm} \) from the relative pressure at the capillary condensation step of the isotherm shown in Figure 4.1d, indicating that the pore wall thickness between the cylindrical pores is \( 2.2 \text{ nm} \) (Figure 4.1c).

### 4.3 Adsorption of C₆E₃ in porous silica

The binding of non-ionic surfactants in tubular pores of silica is quantified by measuring adsorption isotherms using solvent depletion method. In a typical adsorption isotherm measurement, increasing amounts of Triethyleneglycol monohexyl ether (C₆E₃, purity ≥ 99%, Anatrace) surfactant was added to 0.1 g of SBA-15 silica powder dispersed in water. The mixtures of SBA-15 and C₆E₃ were equilibrated for 24 hours at a fixed temperature. The mixture was then centrifuged at 11,000 rpm for 1 hour to remove SBA-15 with adsorbed surfactant. The supernatant was carefully removed, and the equilibrium concentration of C₆E₃ \( (c_0) \) in the supernatant was determined using surface tension calibration curve that is, Gibbs isotherm for the surfactant adsorption as shown in Figure 4.2. The surface tension was determined by pendant drop tensiometry (Theta Biolin Scientific), and drop-shape analysis was performed using Young-Lapalce equation. Further experimental details on measuring adsorption isotherms can be found elsewhere. The amount of surfactant adsorbed (\( \Gamma \)) in the pores of SBA-15 silica was
given as $\Gamma = (c - c_0)V/m$, where $c$ is the initial concentration of surfactant in the silica-surfactant mixture such that $(c-c_0)$ is the concentration of C$_6$E$_3$ adsorbed, $V$ is the volume of aqueous solution, and $m$ ($= 0.1$ g) is the mass of SBA-15 silica added to the solution.

![Surface tension calibration curve of C6E3 solution](image)

Figure 4.2. Surface tension calibration curve of C6E3 solution. The black circles are the experimental data, and the red lines are guides to the eye. The equation of the straight line representing the surface tension decrease in the range Cs < cmc is given in the plot. The experiments show that cmc of the C6E3 surfactant is ~ 94 mM.

Here we experimentally determine adsorption isotherms for C$_6$E$_3$ into the pores of SBA-15 material at three distinct temperatures, namely 20°C (< LCST), 38°C (~ LCST), and 45°C (> LCST). The equilibrium amounts of C$_6$E$_3$ adsorbed in SBA-15 at three temperatures are shown in Figure 4.3a. The adsorption isotherms show a sigmoidal shape, which is a characteristic of the cooperative adsorption behaviour well-known for binding of non-ionic surfactants onto hydrophilic surfaces$^{24,92,100}$. This cooperative adsorption of non-ionic surfactants onto hydrophilic SBA-15 silica is represented by Gu-Zhu adsorption model$^{15}$

$$\Gamma = \frac{\Gamma_{\text{max}}K_{\text{ads}}c_0^n}{1 + K_{\text{ads}}c_0^n}$$

(4-1)
where, $\Gamma$ is the amount of surfactant adsorbed, $\Gamma_{\text{max}}$ is the maximum surface excess, $c_0$ is the equilibrium concentration of surfactant in bulk, $K_{\text{ads}}$ is the equilibrium constant of adsorption which is proportional to the binding affinity of surfactant, and $n$ is the cooperativity factor. The maximum surface excess ($\Gamma_{\text{max}}$) for C$_6$E$_3$ in SBA-15 increases from 3.4 µmol/g to 7.3 µmol/g upon increasing the temperature from 20°C to 45°C. We find that the binding constant ($K_{\text{ads}}$) increases and cooperativity factor ($n$) decreases with increasing temperature (Figure 2b). The increase in $\Gamma_{\text{max}}$ and $K_{\text{ads}}$, and decrease in $n$ highlight the modifications in the local interactions driven by the change in hydration state of the surfactant and the pore-wall. At 20°C (< LCST), the C$_6$E$_3$ surfactant molecules adsorbed on silica surfaces by hydrogen bonding. Upon increasing the temperature, the surfactant molecules as well as silica pore-wall lose weakly bound water of hydration. This change in the hydration state of surfactant head groups and the silica pore-wall drives a change in the adsorption mechanism of surfactant, where at lower temperature strong H-bonding dominates, at higher temperature only van-der Waals interactions drive the adsorption. This change in interactions drives an increase in the value of adsorption constant and maximum surface excess. Furthermore, the change in the local hydration environment drives a phase separation of C$_6$E$_3$ molecules in the pore space. The phase separated surfactant phase is akin to the highly concentrated surfactant micelle phase, where the strong attraction between the dehydrated surfactant molecules drive the increase in pore-uptake. We believe that this change in interaction is responsible for the observed decrease in the value of cooperativity factor $n$. 
Figure 4.3. (a) Adsorption isotherms for C₆E₃ surfactant in nanopores of SBA-15 silica material at 20°C (> LCST), 38°C (~ LCST) and 45°C (> LCST). The discrete points are the measured experimental values, and solid lines are fits using GuZhu model as given by equation 4.1. (b) The increase in the maximum surface excess, $\Gamma_{max}$ of C₆E₃ in SBA-15 silica; (c) cooperativity factor, $n$; and (d) binding constant, $K_{ads}$ for C₆E₃ with increasing temperature. The values of $\Gamma_{max}$, $n$, and $K_{ads}$ are determined by model fitting of the experimental adsorption isotherms. The changes in $\Gamma_{max}$, $K_{ads}$ and $n$ values highlight the change in the surfactant-surfactant and surfactant pore-wall interactions with increasing temperature.

4.4 Structural changes in the surfactant assemblies

The increase in temperature drives an increase in the pore-uptake of C₆E₃ and reconfiguration of the surfactant assemblies in the pore space. Here we use SANS to extract quantitative information on the state of surfactant self-assemblies in the tubular pores of SBA-15 silica. The SANS experiments were performed in H₂O/D₂O mixtures matching the scattering length density of silica ($3.54 \times 10^{-4}$ nm⁻²). In a typical SANS experiment, a fixed surfactant amount is added to the SBA-15 slurry in H₂O/D₂O. The slurry is packed into the quartz cuvettes, and the temperature is precisely controlled using a thermostat. The SANS experiments were performed at ORNL-HIFR GP-SANS instrument using pin-hole collimation at neutron wavelength of 6 Å. Further details on the SANS experiments can be found in previous publications.\(^{75,77}\)
Figure 4.4. SANS profiles for C₆E₃ adsorbed in the cylindrical pores of SBA-15 in silica contrast-matching H₂O/D₂O mixture. The profiles are measured at three concentrations of C₆E₃ on silica and three distinct temperatures namely 20°C (<LCST), 38°C (~LCST) and 45°C (>LCST). The circles are the measured experimental data points, and the red lines are the model fits (I_Total) of the data using equations 2-4. The green filled regions are Bragg scattering contributions (I_Bragg), and blue lines represent the diffused scattering contribution (I_Diff) to the total scattering. (a-c) The SANS profile of SBA-15 with 0.16 M C₆E₃ which is equivalent to 60% of maximum surface excess (0.6Γₘ) at 20°C. The inset in (a) is the zoomed-in plot of the scattering profile and corresponding fit. (d-f) and (g-i) SANS profiles and fits to the experimental data for SBA-15 with 0.31 M and 0.41 M concentration of C₆E₃. The effective pore filling fraction f_eff reduces upon increasing temperature due to increase in maximum surface excess of the surfactant in SBA-15 pore space (Fig. 4.3). The value of f_eff for the SANS measurement at a given temperature is provided in each plot and summarized in Table 4.1. The numbers shown in the parenthesis in each plot represent the miller indices of the Bragg reflection peaks namely (10), (11) and (20). The relative intensity of the (10) peak and overall Bragg scattering contribution to the total scattering increases upon increasing temperature from 20°C to 45°C.

It has been shown that at lower surfactant loading the diffused scattering arises from the spatial correlation among small surface micelles formed in pore space, while at higher surfactant loadings
diffuse scattering is the result of patches of bilayer adsorbed at the pore wall. This knowledge can be applied to characterize the temperature induced reconfiguration of the self-assembled state of C₆E₃ in SBA-15 pores.

Table 4.1. Total concentration and effective pore loading of C₆E₃ surfactant in SBA-15. Here Γₘ is maximum surface excess of the surfactants determined by independent adsorption measurements as shown in section 4.3.

<table>
<thead>
<tr>
<th>Set</th>
<th>Total conc. of C₆E₃ (M)</th>
<th>Temperature (°C)</th>
<th>Maximum surface excess, Γₘ μmol/g</th>
<th>Effective pore filling (fₑff)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Set 1</td>
<td>0.16</td>
<td>20</td>
<td>3.4</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38</td>
<td>6.5</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>7.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Set 2</td>
<td>0.31</td>
<td>20</td>
<td>3.4</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38</td>
<td>6.5</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>7.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Set 3</td>
<td>0.41</td>
<td>20</td>
<td>3.4</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38</td>
<td>6.5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>7.4</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The maximum amount of surfactant that can be adsorbed in the pore-space increases with increasing temperature. Therefore, excess amount of surfactant in the bulk solvent unadsorbed at lower temperature can be spontaneous adsorbed upon increasing the temperature. To capture the spontaneous redistribution of the surfactant molecules in pore space and bulk solvent, we define an effective pore filling fraction as \( f_{eff}(T) = \Gamma(T)/\Gamma_m(T) \). The \( f_{eff} \) is the measure of fraction of pore occupied by the surfactant at a fixed temperature. Here \( f_{eff} < 1 \) highlights that all added surfactant is adsorbed within the pores, and \( f_{eff} > 1 \) indicates that the surfactant is partitioned between the pore-space and bulk solvent. It should be noted that \( f_{eff} \) is not the fraction of pore-volume occupied by the surfactant but the fraction of adsorbed surfactant with respect to the maximum possible amount of adsorption at a defined temperature. At a given surfactant concentration, \( f_{eff} \) decreases upon increasing the temperature (Table 4.1), highlighting the increased uptake of C₆E₃ molecules in the SBA-15 pores. Here we perform SANS experiments.
with fixed concentrations of C₆E₃ in the solution and increasing the temperature as summarized in Table 4.1.

The SANS profiles for SBA-15 with adsorbed C₆E₃ under silica contrast matched conditions are shown in Figure 4.4. The SANS experiments are performed with three surfactant concentrations at 20°C, 38°C and 45°C (Table 4.1). The experimental SANS profiles are fitted using the model presented in chapter 3 (eq. 3-3 and eq. 3-4). We find that the model effectively represents the experimental scattering profile for C₆E₃ in the ordered pore lattice of SBA-15. The SANS profiles show a decrease in the (10) peak intensity with respect to (11) and (20) peaks upon increasing surfactant concentration (Figure 4.4a, d, f). This relative decreased in (10) peak is a result of surfactant patches formed at the silica pore wall. The volume-averaged configuration of the discrete surfactant patches is a layer of adsorbed surfactant molecules on the pore wall, which can be represented by the form factor of a hollow cylinder. Previously we showed that the first minimum of the form factor of the hollow cylinder is situated at a q value near the (10) Bragg reflection. The location of form factor minimum drives the observed decrease in the relative intensity of (10) peak in SANS profile (not discussed here).

The SANS profile at a given surfactant loading changes significantly upon increasing the temperature (Figure 4.4a-c, d-f, g-i). This change in scattering profile is the signature of the change in local self-assembled configuration of the adsorbed surfactant in the pore space. We find that for 0.16 M concentration of C₆E₃, the scattering intensity in the range 0.4 nm⁻¹ < q < 1 nm⁻¹ increases upon increasing the temperature from 20°C to 45°C (Figure 4.4a-c). We quantify the increase in Bragg scattering in terms of integrated Bragg scattering intensity \( \dot{I}_{\text{Bragg}} = \int q^2 I_{\text{Bragg}}(q) dq \). The change in \( \dot{I}_{\text{Bragg}} \) with increasing temperatures at three surfactant concentrations is shown in Figure 4.4a. We find that for all surfactant concentrations \( \dot{I}_{\text{Bragg}} \) increases with increasing
temperature. This increase can be attributed to two factors: (a) Increase in the pore uptake of C₆E₃; and (b) Increase in the volume of individual assembly formed by the surfactant (eq. 3-3). It should be noted that for lowest surfactant concentration of 0.16 M, the $f_{\text{eff}} < 1$ at all investigated temperatures (Table 4-1), i.e. the surfactant remains completely adsorbed in the pore space regardless of the solution temperature. Therefore, the factor (a) does not play any role at the lowest C₆E₃ concentration, and the observed differences in scattering profile with increasing temperature is solely due to change in local self-assemblies of the molecules in the pore space. However, for higher surfactant concentrations of 0.31 M and 0.41 M at 20°C, the $f_{\text{eff}} > 1$, and a small fraction of the surfactants remain in bulk and contribute to the total scattering. Increasing the temperature for the higher C₆E₃ concentration leads to the pore uptake of the unadsorbed surfactant and contributes to observed increase in the $I_{\text{Bragg}}$. It should be noted that the scattering originating from any unadsorbed surfactant will not contribute to the Bragg scattering, but will only impact the diffused scattering contribution.

Diffused scattering is the major contributor to the total scattering originating from the surfactant adsorbed in the contrast matched silica matrix. This diffused scattering originates from the quasiperiodic order of the surfactant patches in the pore and micelles in bulk solvent. We find that the integrated diffused scattering intensity ($I_{\text{Diff}}$) increases with increasing concentration of C₆E₃ at 20°C. This change is attributed to the net increase in the number of surfactant assemblies present upon increasing the surfactant concentration. However, upon increasing the temperature $I_{\text{Diff}}$ increases for 0.16 M C₆E₃, and decreases for 0.31 M C₆E₃ concentration. This redistribution of $I_{\text{Diff}}$ with increasing temperature is due to the change in form factor and correlation distance between the surfactant assemblies formed in the pore space. Here the quasiperiodic distance ($d$) and a decay length ($\xi$) are estimated using equation (3-4) in chapter 3. The change in the
quasiperiodic distance and decay length for C₆E₃ with increasing surfactant concentration and temperature is shown in Figure 4.5c-d. At 20°C (< LCST), the value of $d$ increases from 4.2 to 5.2 nm and $\xi$ decreases from 1.45 to 1.25 nm with increasing bulk concentration of C₆E₃. This observation for C₆E₃ is in contrast to the previously reported $d$ and $\xi$ trends for C₁₂E₅, where $d$ decreases with the increasing surface loading in SBA-15 while $\xi$ increases. The observed difference in surface aggregation of C₆E₃ from C₁₂E₅ is the result of the difference in chemical design of the two surfactants. A weaker cooperativity among C₆E₃ in comparison to C₁₂E₅ drives the adsorption of the C₆E₃ molecules on silica pore-wall in the form of individual molecules and small surface patches. Due to the formation of smaller surface aggregates for C₆E₃, the quasiperiodic distance ($d$) will be smaller for comparable molar concentration with C₁₂E₅.

The SANS profiles show a complex redistribution of total scattering intensity upon increasing the temperature. However, the presence of Bragg peaks in SANS profiles at all tested temperatures reconfirm that C₆E₃ remains adsorbed in the pores, which otherwise would lead to disappearance of the Bragg peaks. In addition, the absence of any secondary Bragg peak(s) at high-$q$ regions upon increasing temperature highlights that the demixed surfactants in the pore exists as a liquid-like disordered phase and not an ordered crystal phase. Based on our analysis of the SANS profiles, we find that at all surfactant concentrations, the quasiperiodic distance $d$ between surfactant aggregates increases with increasing temperature. The increase in value of $d$ at fixed surfactant concentration highlights the formation of larger surface aggregates upon increasing temperature of bulk solution. The model analysis shows that the correlation decay length decreases with increasing the temperature, indicating that the surfactant assemblies become less polydisperse i.e. more uniformly sized upon increasing temperature. We believe that upon increasing temperature from 20°C to 45°C, the surfactant phase separates into surfactant-rich and depleted
phases within the pore-space. The surface bound patches at lower temperature are expected to coalesce into larger aggregates upon increasing the temperature, similar to the mechanism of destabilization of emulsion droplets in bulk solvents. The release of bound water from individual surfactant molecules upon increasing temperature above LCST makes the surfactant aggregates hydrophobic i.e. “oil-like”. We believe that a combination of hydrophobic and van der Waals interactions between the silica pore wall and dehydrated C₆E₃ aggregates drives the observed reconfiguration of surfactant self-assemblies.

Figure 4.5. (a-b) Integrated Bragg and diffused scattering intensities obtained by analysis of the experimental SANS data for C₆E₃ in SBA-15 as shown in Figure 4.4. The \( I_{\text{Bragg}} \) increases with increasing temperature and \( I_{\text{Diff}} \) shows a concentration dependent increase/decrease with the temperature. (c-d) Increase in the quasiperiodic distance (\( d \)) between the surfactant assemblies and the corresponding change in the decay length (\( \xi \)) of the quasiperiodic order. The values of \( d \) and \( \xi \) are estimated by the diffused scattering contribution using equation 3-4.
4.5 Directed uptake and release of molecules from pore space

Figure 4.6. (a) UV/vis spectra of the dye (Sudan I) absorption to evaluate the selective adsorption capability of surfactant C₆E₃. (b) Schematic representation of self-assembled structures of surfactant-dye complex in mesoporous SBA-15 silica material. (c) Change of dye concentration in supernatant as a function of heating/cooling cycles, demonstrating a reversible process of dye uptake and release. The surfactant-dye complex self-assemblies change from patch bilayers to discrete clusters at pore wall upon heating up, i.e. the dye does not change the response of surfactants to temperature. (d) Photographs of the mixture of C₆E₃, SBA-15 and Sudan I. The supernatant solution becomes clear after increasing the temperature, as the surfactant-dye complex are adsorbed in the pore.

The temperature driven increase in the adsorbed amount of C₆E₃ in SBA-15 silica pores is completely reversed upon decreasing the temperature. This reversibility and spontaneity in the partitioning of excess surfactant in the pore space and solvent bulk allows for the developing new materials with on-demand uptake and release of model molecules. To demonstrate such ability of SBA-15 loaded with C₆E₃ surfactant we used 1-(phenyldiazenyl)naphthalen-2-ol (Sudan-I, purity > 93%, Tokyo Chemical Industry) as a model hydrophobic dye. The Sudan-I is insoluble in water
but only dissolves in hydrophobic cores of micelles formed by nonionic surfactants\textsuperscript{111–113}. In a typical experiment we prepare a 1:10 molar mixture of C\textsubscript{6}E\textsubscript{3}: Sudan I. The dye is selectively solubilized in the hydrophobic cores of the micelles, which induces an orange color to the mixture. Here we add SBA-15 silica powder to the above C\textsubscript{6}E\textsubscript{3}/dye mixture, and allow the dye-surfactant-SBA-15 ternary mixture to equilibrate at a given temperature for 24 hours. We determine the equilibrium concentration of the dye ($c_{dye}$) in the supernatant using UV/vis spectrophotometry (NanoDrop, ThermoFisher Inc.). A typical spectrophotometry absorbance curve for the supernatant at 20°C and 45°C is shown in Figure 4.6a. The absorbance spectra at 20°C shows a peak at wavelength 480 nm, which is characteristic of the orange color of the Sudan-I dye\textsuperscript{111}. The absorbance value (Abs) at the characteristic wavelength (here 480 nm) is related to the equilibrium concentration of the dye ($c_{dye}$) by Beer-Lambert law i.e. $\text{Abs} = \varepsilon l c_{dye}$, where $\varepsilon$ is the extinction coefficient of the dye and $l$ is the path length of the solvent which remains constant. We find that the absorbance value for the supernatant decreases from 2.0 to 0.4 upon increasing the temperature from 20°C to 45°C. The decrease in the absorbance value of the supernatant shows a decrease in equilibrium concentration of the dye in the bulk solvent. This decrease in dye concentration with increasing temperature is attributed to the pore-uptake of the micelle-dye complex by the SBA-15 silica material (Fig. 4.6b). We find that upon lowering the temperature back to 20°C i.e. cooling the solution, the characteristic orange color of the supernatant and corresponding absorbance spectra can be reobtained. We investigated the reversibility of the temperature driven pore-uptake and release of the micelle-dye composite by cycling the temperature multiple times between 20°C and 45°C and monitoring the corresponding change in the $c_{dye}$ in each cycle (Fig. 4.6c, d). We find that for the tested 20 cycles, the dye concentration in the supernatant was reversibly changed from 0.7 to 3.0 mM upon changing the temperature from 20°C to 45°C and back. This controlled the
release and uptake of the dye molecules highlight the potential applicability of the silica porous materials loaded with surfactant to be used as thermoresponsive molecular delivery vehicles. The on-demand release and uptake of model dye can be extended to biological active molecules such as proteins, lipids and nucleic acids. Further work on such porous materials and their mixtures with benign surfactants may enable designing new materials for targeted delivery and uptake of molecules widely used in biomedical detection, sensing and imaging.

4.6 Conclusions

In this chapter, the effect of confinement on temperature-induced demixing of non-ionic surfactant C₆E₃ is investigated by a combination of SANS experiments and adsorption isotherms. It is found that at low surfactant concentration, C₆E₃ adsorbs as individual molecules on the tubular pore walls of SBA-15 silica material. This morphology transforms into discrete patches upon increasing the amount of surfactant in the solution. Interestingly, we find that the maximum amount of surfactant that can be loaded in the pore space increases with increasing temperature. This increase in the pore loading upon increasing temperature is driven by the combination of hydrophobic and van der Waals interactions between the pore wall and demixed surfactant-rich phase. We find that upon increasing the temperature the discrete surface patches formed by the surfactant at lower temperature to form large-globule-like disordered liquid phase adhered to the pore wall. This change in morphology is attributed to change in the hydrated state of the surfactant head groups and silica pore wall. We show that the increased adsorption of C₆E₃ in porous silica materials above its LCST enables reversible partitioning of molecules between the pore space and bulk solvent. We show that a model hydrophobic dye (here Sudan – I) selectively solubilized in the surfactant micelle cores can be reversible uptaken and released from the pore by heating-and-cooling cycles. This comprehensive study presents an experimental-simulation approach to
understand the complex effect of confinement on the adsorption and phase separation of molecules in hard matter confinement. Furthermore, it lays a foundation for developing advanced porous materials with programmable temperature induced uptake and release abilities.
Chapter 5. Characterization of Nano-assemblies inside Mesopores using Neutron Scattering

5.1 Introduction

Adsorption of dissolved matter and nanoparticles in porous materials controls various important processes including contaminant transport in subsurface water systems, water treatment, and drug delivery.114–119 Synthetic porous materials provide a platform to isolate, and stabilize metastable states of the adsorbates and harvest their unusual physical and chemical properties.33,120,121 The affinity and amount of adsorbate immobilized in a porous material is experimentally quantified by adsorption isotherms. Several studies have been reported on the binding of molecules/nanoparticles (NPs) from aqueous solution to the pores of hard material.122–125 These studies demonstrate that the adsorption of molecules/NPs in porous materials is primarily governed by the pore wall-NP/molecule interactions, interparticle/intermolecular interactions and the degree of the pore confinement. While numerous measurements are reported on the amount of adsorbate in porous materials, only a few studies investigate the nanoscale structures of adsorbates formed in porous materials.126,127 This lack of knowledge exists due to the inherent complexity with the morphological characterization of the matter immobilized in the nanopores using conventional techniques such as infrared spectroscopy, and electron microscopy.128 In these techniques, the porous matrix interferes with the measurements, and limits information on the assemblies formed by adsorbate molecules/nanoparticles in pores. Such limitations can be readily overcome by Small Angle Neutron Scattering (SANS) performed in conditions where the solvent matches the

scattering length density of the porous matrix.\textsuperscript{73,129} The primary challenges in such SANS studies are in the details of analysis of the data and relating the obtained scattering profiles to the structures of nano-assemblies formed in the pores.

In recent years, Findenegg and co-workers developed a methodology for characterizing surfactant self-assemblies formed in ordered cylindrical nanopores of silica SBA-15 materials.\textsuperscript{76} This methodology uses a combination of Bragg scattering and diffuse scattering contributions to analyze and predict the self-assembled structures formed by surfactant molecules in mesoporous silica materials. The SBA-15 silica used in the experiments has cylindrical pores arranged in two-dimensional (2D) hexagonal closed packing (hcp) with a characteristic lattice parameter.\textsuperscript{16,75,77} The approach used Gaussian distribution functions to represent individual Bragg peaks, and the information on the interparticle arrangement leading to the appearance of such peaks is lost. In this chapter, we extend the previous SANS analysis approach developed by Findenegg and co-workers and present a model for investigating the assembly and spatial distribution of metallic nanoparticles and surfactant molecules in the mesoporous silica materials.

Here we develop a new approach of systematically analyzing the adsorption and assembly of discrete species in the cylindrical pores of silica materials. We show that the assembled state of discrete species is dependent on the pore structure and pore filling fraction, evidenced by our numerical simulations of SANS profile. We further apply this new approach to study the adsorption of triethyleneglycol monohexyl ether (C\textsubscript{6}E\textsubscript{3}) and gold (Au) NPs adsorbed in silica SBA-15 material, and the structural details of these two materials are identified using the Bragg and diffuse scattering contributions to the experimental SANS profiles. Inclusion of the diffuse scattering is important since it provides correlations information, such as charge density variations that is important for determining small scale interparticle structure. It can be thought as the
scattering contribution arising from the “disorder” in the structures. Significant differences between scattering profiles of C₆E₃ micelles and Au NPs in SBA-15 pores are found and attributed to differences in internal structure of these species and their spatial distribution. The study reveals the assembled state of nano-objects in pores in response to the change in pore radius and concentration of adsorbate, and provides a new analysis method to probe the nanostuctured assemblies under confinement.

5.2 Model for analysis of SANS profiles

Neutrons scatter from heterogeneous dispersions due to the difference in the scattering length density (SLD) between the dispersed phase and the continuous medium. For amorphous silica, the neutron SLD is 3.47×10⁻⁴ nm⁻², which can be matched by an aqueous solvent containing 59 wt-% D₂O and wt-41% H₂O.¹³⁰ In the absence of an additional phase, the SANS experiments performed under such solvent matched conditions show no scattering signal, i.e. the dispersion shows a constant, angle independent scattering similar to a homogenous medium. Such contrast matching enables the use of SANS for selectively probing the structure formed by adsorbates such as surfactants, polymers and NPs within the confined pore space of silica nanomaterials.⁷³,⁷⁶,¹³¹

Previously, Findenegg et al. used SANS to investigate the self-assembly of non-ionic ethoxylated surfactants in cylindrical pores of SBA-15 silica material.⁷⁵,⁷⁷,¹³² According to the previously developed method, the total scattering intensity \([I_{total}(q)]\) originating from the molecular self-assemblies of surfactants formed in the pores of SBA-15 silica (under contrast match) is given as⁷⁵

\[
I_{total}(q) = I_{Bragg}(q) + I_{Diff}(q)
\]  

where \(q = \frac{4\pi}{\lambda}\sin \frac{\theta}{2}\) is the scattering vector, \(\lambda\) is the wavelength of incident neutrons, \(\theta\) is the scattering angle, \(I_{Bragg}(q)\) is the Bragg scattering contribution from the pore lattice with pores
containing adsorbate, and $I_{Diff}(q)$ is the diffuse scattering attributed to the inhomogeneous
distribution of the scattering objects within the cylindrical pores but also outside the pores if
unadsorbed objects exist. This diffuse scattering contribution is approximated using the Teubner-
Strey function$^{78}$

$$I_{Diff}(q) = \frac{I_0}{(1-\frac{I_0}{I_m})\left(\frac{q^2}{q_m^2}-1\right)^2 + \frac{I_0}{I_m}^2}$$

(5-2)

where $I_m$ and $q_m$ represent the coordinates of the maximum in the correlation peak, and $I_0$ is the
forward scattering intensity. The Bragg scattering contribution $[I_{Bragg}(q)]$ is given as$^{133}$

$$I_{Bragg}(q) = \varphi V_{Part} (\Delta \rho^2) P(q) S(q)$$

(5-3)

where $\varphi$ is the volume fraction of the scattering object, $V_{Part}$ is the volume of the single scattering
object/particle, $\Delta \rho$ is the SLD contrast between the scattering object and the solvent, $S(q)$ is the
structure factor, and $P(q)$ is the form factor of the scattering object.

In the analysis method presented by Findenegg et al., $I_{Bragg}(q)$ was represented by
individual Gaussians representing the respective Bragg peaks.$^{76}$ Our approach for extending this
method is to replace the Gaussian peaks and instead generate Bragg scattering contributions by
indirect Fourier transformation of the stochastic configurations of scattering objects adsorbed on
the cylindrical pore walls. The first step for such approach is to rearrange equation (5-3) for a
mesoporous material where each cylindrical pore contains $n$ scattering objects:

$$I_{Bragg}(q) = \frac{n N_{pore}}{V} V_{part}^2 (\Delta \rho^2) P(q) S(q)$$

(5-4)

$N_{pore}$ is the total number of cylindrical pores in the scattering volume $V = \frac{3\sqrt{3}}{2} H^2 L$ with $L$ being
the length of the pore, and $H = 2ma + (m - 1)(d - 2a)$, where $m$ is the order number of the 2D
$hcp$ porous matrix, $a$ the pore radius, and $d$ is the lattice parameter (Figure 5.1a and discussed
below). Note that the pore matrix must be contrast matched and the Bragg scattering contribution
is only from scattering objects adsorbed on the pore walls. Assuming that each scattering object is a sphere of fixed radius $R$ and uniform SLD, the form factor, $P(q)$, can be written as:

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

(5-5)

In our model, the structure factor, $S(q)$ is estimated in two steps. Step 1: A Monte-Carlo type approach is used to generate stochastic configurations of the scattering object bound to the pore walls of porous matrix. Step 2: Calculation of an averaged radial distribution function and corresponding indirect Fourier transformation of the state, which provides an average structure factor of the scattering object distribution within the porous matrix. Here we only focus on the cylindrical pores arranged in 2D hcp matrix, mimicking silica SBA and MCM materials. We use Scilab software package to generate the porous matrix using centered hexagon number method. In this method, $N_{\text{pore}}$ is given as

$$N_{\text{pore}} = 3m^2 - 3m + 1$$

(5-6)

where $m$ is the order number of the 2D hexagonal pattern. The order number was kept constant at $m = 5$, i.e. $N_{\text{pore}} = 61$. The lattice parameter, $d$, of the porous matrix was input in the model and the x-y coordinates (position vectors) of center of pores were generated as

$$x = \frac{-(2m-k-2) \times d}{2} + o \times d; \quad y = \frac{+\sqrt{3}}{2} \times k \times d$$

(5-7)

where $k$ and $o$ are integers such that $0 < k \leq m, 0 < o \leq m$ and $o < (2m - k - 1)$. After obtaining the coordinates of the centers of the pores, the scattering objects were randomly distributed within the pores of fixed length $L = 20$ nm (Figure 5.1a). The position vectors of the $n$ spherical scattering objects of radius $R$ within each pore are obtained by use of the random point generator function in Scilab. Hard-sphere interactions between the scattering objects were accounted for by rejecting position vectors of the scattering objects with interparticle distance less
than $2R$. Note that the model does not incorporate any other interparticle interaction. The random point generation method described above is repeated for multiple iterations for improving the statistics. The orthographic views of one such iteration with $n = 6$ scattering objects (here with $R = 1.75$ nm) within the cylindrical pores of radius $a = 4.3$ nm and $d = 11.9$ nm are shown in Figure 5.1b-d. The snapshot shows a random distribution of spheres adsorbed on the walls of the cylindrical pores. Using this configuration, an average structure factor is obtained by indirect Fourier transformation as

$$S(q) = 1 + \frac{1}{nN_{pore}} \sum_{i \neq j}^{nN_{pore}} \sin\left(q(r_i - r_j)\right)$$

where $r_i - r_j$ is the center-to-center distance between the spheres $i$ and $j$ in the pore-space. The total scattering profiles are obtained using equations 1-8 and represent the scattering originating from the discrete objects adsorbed in the confined pores. Note, this method is purely stochastic, and no minimization of the ensemble energy is performed, which is the case with conventional Monte-Carlo simulations. Despite the lack of energy minimization, we believe that our method captures the time and spatially averaged characteristics of SANS data obtained for nanoscale assemblies formed in the porous materials. In the following sections, we first investigate the effect of pore diameter, lattice parameter and adsorbate concentration on the scattering profile, and then test the applicability of our approach on model experiments performed on the adsorption of surfactant and metal NPs in the cylindrical pores of SBA-15 silica.

5.3 Model predictions for the effect of pore system structure on SANS profile
Figure 5.1. (a) The schematic representation of SBA-15 silica materials with 2D hexagonal lattice. (b-d) Snapshot of a random configuration of spheres adsorbed in cylindrical pores as generated using equation (5-7). For this calculation $R = 1.75$ nm, $a = 4.3$ nm and $d = 11.9$ nm.

The SANS profile from the adsorbate in the porous matrix under contrast matched conditions is dependent on the characteristics of both the pore and the adsorbate. To understand the contributions of these two factors on the scattering profile, we simulate $I_{Bragg}$ for spherical NPs adsorbed in the cylindrical pores of a silica material with increasing lattice parameter, $d$. The simulations are performed using the method described in section 5.2 with increasing $d$, here with values of 5, 10 and 15 nm. The radius of the pore, $a$, was kept fixed at 2 nm, $n = 5$ particles per pore, and $N_{pore} = 61$. The averaged $I_{Bragg}$ is obtained by performing the calculations for 7 iterations, i.e. $7 \times 61 \times 5 = 2135$ particles, and is shown in Figure 5.1. The scattering profile shows the characteristic diffraction peaks due to the 2D hexagonal symmetry of the pore lattice. These diffraction peaks correspond to the (10), (11) and (20) Miller indices of the 2D $hcp$ lattice, which shift to smaller momentum transfers with increasing $d$ (Fig. 5.1). We find that the (10) peak intensity is highest, followed by (11) and (20) peaks, which is in agreement with the characteristic scattering originating from the adsorbate bound to the porous matrix.
We find that the absolute peak intensities are strongly dependent on the pore diameter, i.e., the peak intensities decrease with increasing \( a \) (Fig. 5.2). This decrease is attributed to the decrease of pore filling fraction \( (f) \) and increase in correlation distance between the scattering objects adsorbed in the pore spaces.\(^{76}\) The pore filling fraction is defined as \( f = nV_{\text{part}}/V_{\text{pore}} \), where \( n \times V_{\text{part}} \) is the total volume of the adsorbate in the pore, and \( V_{\text{pore}} \) is the pore volume. Note that \( f \neq \phi \) in equation 3 because \( f \) excludes the volume occupied by the material forming the porous matrix. In our calculations, we find that as the pore radius decreases, the increase in \( f \) leads to the increase in the scattering intensity of diffraction peaks. The same amount of adsorbate, if packed into a smaller pore, leads to shorter interparticle distances and higher pore occupation which yields a higher scattering intensity of the diffraction peaks in smaller pores.\(^{76}\) In our case, the value of \( \int I(q)q^2dq \) in the limits of \( q = 0.01 \) to \( 10 \text{ nm}^{-1} \) remains nearly constant, highlighting that the total scattering and invariant originating from the particles do not depend on pore structure, and the redistributions of intensity are the result of changes in local assemblies of particles within the pore spaces.
Figure 5.2. The Bragg scattering profiles from spherical particles \((R = 1.75 \text{ nm})\) adsorbed in cylindrical pores of increasing (a) lattice parameter \(d = 5, 10, 15 \text{ nm}\) at fixed pore radius \((a = 3.2 \text{ nm})\); and (b) pore radius at \(a = 2, 4 \text{ and } 6 \text{ nm}\) at fixed lattice parameter \((d = 15 \text{ nm})\). The diffraction peaks correspond to (10), (11) and (20) miller indices of the 2D hcp pore lattice, which respectively shift to smaller scattering vectors with decreasing \(d\), and the scattering intensity of Bragg peaks decreases with increasing \(a\).

The Bragg scattering of the particles adsorbed in the porous matrix is strongly dependent on the particle concentration (equation 5-3). Now, we perform calculations with \(a = 4.2 \text{ nm}, d = 12.6 \text{ nm}\) and \(R = 1.75 \text{ nm}\) while increasing \(f\) from 0.01 to 0.03. The obtained dependences of \(I_{\text{Bragg}}\) on the number of particles in the pores are shown in Figure 5.3. The scattering intensity of the (10) diffraction peak increases as \(f\) increases. The increase in particle concentration in the pores leads to a lower correlation distance among the particles, which results into increases in the Bragg scattering intensity.\(^{97}\) The increase of scattering intensity with increasing \(f\) is in general agreement with the previously observed experimental scattering profiles.\(^{77}\) Our model calculations indicate that the \(I_{\text{Bragg}}\) is strongly dependent on the pore volume occupied by the adsorbate.
particles. Based on the obtained results of the $I_{Bragg}$, we believe that our random point generation method can be applied to characterize the structural features of diverse categories of soft materials adsorbed within the cylindrical pores arranged in a 2D hcp lattice including surfactant micelles and nanoparticles.

Figure 5.3. The Bragg scattering for porous materials with adsorbed spherical NPs. Here $a = 4.2$ nm, $d = 12.6$ nm, $R = 1.75$ nm with increasing pore filling fraction (a) $f = 0.01$ (b) $f = 0.02$; and (c) $f = 0.03$. The scattering profiles show that (10) is most dominant Bragg peak and its intensity increases with increasing number of spheres adsorbed in the pore space. The schematic inserts in (a-c) are the side and top view of the simulated porous matrix with adsorbed spheres.

5.4 Model application to experimental SANS data

In this section, we test the applicability of the proposed model in representing the experimental SANS profiles. Here, we investigate the adsorption and structure formation by model adsorbates in the pores of SBA-15 silica material. We study solutions of nonionic surfactant $C_6E_3$ and Au NPs, which are model adsorbates with well-understood adsorption characteristics. All experiments were performed at pH 6. For SANS measurements using Au NPs, the pore walls of SBA-15 were chemically modified with propyl amine groups which have positive charges at pH 6. Binding of
Au NPs in the pores of amine modified SBA-15 is driven by the electrostatic attraction between negatively charged NPs and positively charged pore walls. The SBA-15 used in the case of C6E3 was unmodified and carried negative surface charges. The adsorption of C6E3 on unmodified SBA-15 is driven by the hydrogen bonding between the surface silanol groups on pore walls and ethoxylated head group of the surfactant. Here, we focus on the SANS data analysis and measurements of binding energies from adsorption isotherms of these systems will be reported in a forthcoming study.

5.4.1 Au NPs in SBA-15 silica

The SANS analysis method presented in section 5.2. can provide structural information on the assembly of a wide range of molecules or particles in nanopores if the porous matrix is contrast matched. For this study, Au NPs were synthesized using well-established methods. Based on the surface plasmon resonance, the size of our Au NPs was \( R = 1.75 \) nm. We synthesized SBA-15 silica material with \( a = 4.3 \) nm and \( d = 12.6 \) nm, and modified it with amino propyl surface functionalization following a previously reported method. The SANS was performed at the EQ-SANS (Spallation Neutron Source) and GP-SANS (High Flux Isotope Reactor) instruments at Oak Ridge National Laboratory. SANS experiments were performed at fixed amount of SBA-15 with concentrations of Au NPs (\( c_{Au} \)) increasing from 0.06 mg/mL to 0.17 mg/mL. The measured SANS patterns are shown in Figure 4a-c. Here \( \text{D}_2\text{O/H}_2\text{O} \) at 59:41 weight percent was used as solvent, which matched the SLD of the SBA-15 silica (\( \rho = 3.47 \times 10^{-4} \text{ nm}^2 \)). The neutron scattering originated solely from the Au NPs adsorbed in SBA-15, where the neutron coherent SLD contrast between Au NPs and solvent was \( \Delta \rho = 1.1 \times 10^{-4} \text{ nm}^2 \).

The experimentally measured SANS profiles of the Au NPs in SBA-15 pores with increasing \( f \) and corresponding simulated profiles are shown in Figure 5.4. The SANS profiles
show the presence of diffraction peaks characteristic of the pore lattice of the SBA-15 silica. The presence of the diffraction peaks under silica contrast matched conditions indicates that the Au NPs were absorbed into the pore spaces, making the pore system structure “visible” to the incident neutron beam. We find that the intensity of the (10) peak increases with increasing amounts of Au NPs. We simulate the Bragg scattering profile (dashed lines in Figure 5.4) using fixed values of $a$, $d$, and $R$, and changing $f$. We find that the intensity of (10) peak increases with increasing $f$ which is in agreement with the experimental data. Parameter $f$, the fraction of pore volume occupied by the Au NPs, takes values in the range 0.04-0.12. The small pore volume occupancy can be attributed to the electrostatic double layer repulsions between negatively charged Au NPs. Such electrostatic and electroosmotic effects are known to influence the amount of NP adsorption in confined pores.\textsuperscript{43,139}

We find that $I_{\text{Bragg}}$ obtained from our model correctly represents the Bragg peaks, but is unable to represent the whole scattering profile. This mismatch between $I_{\text{Bragg}}$ and experimentally measured curves indicates that the SANS profiles are affected by additional factors, which are missing from $I_{\text{Bragg}}$. We therefore include additional, diffuse scattering contributions to the total scattering as shown in Equations 1 and 2. Inclusion of the diffuse scattering yields excellent representations of the experimental data. In our experiment, the origin of such diffuse scattering can be attributed to the random distribution of Au NPs in the cylindrical pores.\textsuperscript{140} Additional contributions to diffuse scattering may arise from the sodium citrate molecules which are used as a capping agent for Au NPs. Inhomogeneities of citrate capped Au NPs in the silica pore may result in a diffuse scattering contribution towards the total scattering intensity. The positions of the diffuse scattering peak maxima ($q_m$) shifts to larger momentum transfer and the peak intensity parameters ($I_0/I_m$) increases with increasing concentration of Au NPs. This change in the diffuse
scattering parameters can be used to estimate the quasiperiodic distance \( (D) \) between the Au NPs in the pore using following equation:

\[
D = 2\pi \sqrt{\frac{1}{q_m \left[ (1 - I_0/I_m)^{1/2} + 1 \right]^{1/2}}}
\]  

(9)

We find that the distance \( D \) between the Au NPs decreases from 9.1 nm to 6.6 nm as the amount of pore Au particles increases from \( f = 0.04 \) to 0.12. This finding agrees with the results obtained in section 5.3, where we found that correlation distances decrease with increasing \( f \). We conclude that the model qualitatively represents the assemblies formed by the adsorption of discrete particles and provides the spacing state of these particles in the pore volume. Next, we test the applicability of this approach on SANS profiles from adsorbed amphiphilic molecules in silica porous materials, which tend to form complex self-assemblies in pore space.

Figure 5.4. SANS profiles for Au NPs adsorbed in the pore space of SBA-15 under silica contrast-matching condition. The profiles are shown three concentration of Au NPs: (a) \( f = 0.04 \), (b) \( f = 0.06 \); and (c) \( f = 0.12 \). The circles are the SANS experimental data points, the blue lines are the (caption cont’d)
total scattering intensity calculated using the method presented in section 5.2. The $I_{\text{Bragg}}$ and $I_{\text{diff}}$ obtained from equations 2 and 4 are represented by the red dash lines and the solid green lines, respectively. The total scattering intensity, which is contributed by $I_{\text{Bragg}}$ and $I_{\text{diff}}$, quantitively represents the experimental data and shows an increase of $I_{\text{total}}$ with increasing number of Au NPs adsorbed in pore. The insets in (a-c) are the schematics representing the increase in the number of Au NPs in pore space.

5.5 C₆E₃ surfactant solutions in SBA-15 silica

Previously, we studied the morphological behavior of C₆E₃ surfactant in SBA-15 silica using SANS. The SANS experiments for C₆E₃ surfactant in pore space were performed using H₂O/D₂O mixtures that contrast-match SBA silica at three surfactant loadings of 0.16 M, 0.31 M and 0.41M. The measured scattering profiles are shown in Figure 5.5. Here, we use our model presented in section 5.2 to re-evaluate these SANS data, assuming that C₆E₃ forms spherical micelles on the pores. The concentrations of C₆E₃ in all samples are higher than the critical micellization concentration (CMC) of the surfactant. Based on the known self-assembled structure of the surfactant in solvent bulk, we assume C₆E₃ to form spherical micelles of radius $R_m = 1.85$ nm. The scattering profiles are calculated by varying parameter $f$ while fixing parameters $a$, $d$, $N_{\text{pore}}$, and $\Delta \rho$. The scattering profiles were calculated using eq. (1)-(8), and the obtained fits to the experimental are shown in Figure 5.5.

The presence of Bragg peaks in experimental scattering profiles under silica contrast-matched condition is a result of adsorption of C₆E₃ surfactant into the pores. As in the case of Au NPs, we include diffuse scattering contributions in the total scattering model. We find small differences between model based $I_{\text{total}}$ and experiments in the range $q = (0.58 - 1.15)$ nm⁻¹. Furthermore, the measured Bragg peaks are broader than the peaks predicted by our model. Such broadening of Bragg peaks in experiments is likely the result of a combination of polydispersity in the pore radius of SBA-15, and resolution limitations of the SANS instrument, which were not included in the model. Despite these small deviations, the model accurately represents the changes
in peak intensity distribution, i.e., the (11) peak increases in intensity with increasing pore loadings. Based on the analysis of SANS data, we find that the pore filling fraction for concentrations of C₆E₃ of 0.16 M, 0.31 M and 0.41 M are \( f = 0.3, 0.4 \) and 0.6. Values of \( f \) can be estimated independently from adsorption isotherms, as reported in our previous work.¹⁶ The value of \( f \) from excess adsorption is estimated using the following equation:

\[
f = \frac{16\pi R^3_m \times \Gamma \times N_A}{3a \times N_{agg}}
\]

(10)

where \( N_A \) is the Avogadro constant, \( N_{agg} \) is the aggregation number of C₆E₃ in bulk (\( N_{agg} = 55 \)),¹⁴¹ and \( \Gamma \) is the surface excess amount of C₆E₃ in the pores. We calculate the \( f \) values from this equation for 0.16 M, 0.31 M and 0.41 M as 0.3, 0.5 and 0.7, which is in good agreement with the values obtained from SANS using our model.

The location of diffuse scattering maxima, \( q_m \), shifts to larger \( q \) and \( I_0/I_m \) decreases with increasing concentration of C₆E₃. These changes in \( q_m \) and \( I_0/I_m \) indicate changes in the quasi-periodic arrangement of C₆E₃ micelles in the pores. The value of \( D \) increases from 4.4 nm to 5.1 nm with increasing \( f \) from 0.3 to 0.6, which is in agreement with our previous study.¹⁶ The increase of spacing between C₆E₃ surfactant assemblies with increasing pore concentration is opposite to that of Au NPs in silica (discussed in section 5.4.1). As shown in our previous study,¹⁶ the diffuse scattering contribution in the C₆E₃ system originates from both individual molecules and small surfactant patches adsorbed on the pore wall. These small aggregates coalesce into larger aggregates with increasing C₆E₃ concentration, and the quasiperiodic distance between these larger aggregates increases with increasing surfactant concentration. Note that our model assumes the adsorption of discrete spherical micelles on the pore walls, which is not the case for C₆E₃ in SBA.
pores. Despite using this over-simplified approximation, the model is useful in characterizing the qualitative changes in the SANS profiles.

Figure 5.5. SANS profiles for C$_6$E$_3$ surfactant adsorbed in SBA-15 silica materials in H$_2$O/D$_2$O mixture matching the SLD of silica. The profiles are measured at increasing concentration of C$_6$E$_3$ surfactant (a) $f = 0.3$; (b) $f = 0.4$; and (c) $f = 0.6$. The circles are the SANS experimental results, and the blue lines represent the calculated total scattering intensity using eq. (1)–(8). The red dashes are the $I_{Bragg}$ obtained using eq. (4), and the green lines denote the diffuse scattering profiles determined by eq. (2).

5.6 Relative contributions of Bragg and diffuse scattering

The relative contribution of diffuse and Bragg scattering towards total scattering intensity is significantly different for solutions of Au NPs and C$_6$E$_3$ molecules. These differences can be quantified by integrating the scattering intensities using $\bar{I} = \int q^2 I(q) dq$,

estimating their relative contributions as

$$\bar{I}_B = \frac{I_{Bragg}}{I_{total}} \quad (11)$$

$$\bar{I}_D = \frac{I_{diff}}{I_{total}} \quad (12)$$

60
where $\bar{I}_B$ and $\bar{I}_D$ are the integrated Bragg and diffuse scattering, respectively, and $\bar{I}_{\text{total}}$ is the integrated total scattering intensity. The results of $\bar{I}_B$ and $\bar{I}_D$ for C₆E₃ surfactant and Au NPs in nanopores for three values of $f$ are shown in Figure 5.6. For Au NPs, we find that $\bar{I}_B$ increases from 0.5 to 0.7, and $\bar{I}_D$ decreases from 0.5 to 0.3 with $f$ increasing from $f = 0.04$ to $f = 0.12$. For C₆E₃ surfactant solutions, $\bar{I}_B$ decreases and $\bar{I}_D$ increases with surfactant concentration increasing from $f = 0.3$ to 0.6. This shows that $\bar{I}_{\text{Bragg}}$ contribution increasingly dominates $\bar{I}_{\text{diff}}$ with increasing $f$ for Au NPs. An increase of $\bar{I}_B$ for Au NPs contrasts with a decrease of $\bar{I}_B$ for C₆E₃, and the value of $\bar{I}_B$ for Au NPs is always higher than that of C₆E₃. As mentioned in section 5.2, the $I_{\text{Bragg}}$ is related to the pore volume occupation, thus an increase of $f$ for Au NPs causes an increase of $\bar{I}_B$. The assemblies formed by C₆E₃ are dynamic and coalesce to form larger structures in the pore upon increasing surfactant concentration. This coalescence of the surfactant assemblies results in an increase in distance between the surfactant aggregates, thus decreasing $\bar{I}_B$.¹⁶ Note that our mathematical model does not incorporate this coalescence.

![Figure 5.6](image.png)

Figure 5.6. (a) Relative contribution of (a) Bragg scattering intensity determined using eq. (11), and (b) diffuse scattering intensity obtained by eq. (12) for C₆E₃ surfactant and Au NPs. The Au NPs and C₆E₃ surfactant are denoted using the red squares and green circles, respectively, and $f$ represents the pore filling fraction.
In the case of C₆E₃, the diffuse scattering contribution of C₆E₃ surfactant is the dominating contribution in the total scattering profile, which is not the case for Au NPs. The domination of $I_D$ originates from the internal structure and quasiperiodic order of the C₆E₃ assemblies in the silica matrix. The alkyl chains of C₆E₃ molecules form a “fluid-like” core of the surfactant aggregates in the nanopores. This flexible internal structure of the C₆E₃ assemblies is the major factor for the domination of $I_D$.¹⁴² The C₆E₃ aggregates become larger with increasing $f$, which means additional C₆E₃ molecules are packing into the aggregates, leading to an increase in the number of alkyl chains in the aggregates. This increase results in a more flexible intramural structure of C₆E₃ aggregates, and also leads to an increase of $I_D$.¹⁴² In contrast to the surfactant, the liquid-like structure is absent for the “solid” Au NPs, which results in a lower $I_D$. Since the $I_{diff}$ originates from disorder in the arrangement of NPs in pore, the order of Au NPs in the silica pore structure is an additional factor for the value of $I_D$. In our analysis, the highest $I_D$ values for Au NPs are observed at lower $f$, highlighting the irregular pattern of Au NPs in silica pores. With increasing $f$, the NPs arrange in more ordered patterns at the pore walls, which is seen by diminishing $I_D$ values. The analysis of relative scattering contributions clearly shows the differences in internal structures between Au NPs and C₆E₃ aggregates in silica pores, and provides valuable insights into the origins of the principally different diffuse scattering contributions in the two cases.

5.7 Conclusions

The study presents a model to investigate the structure of adsorbed aggregates and NPs in nanoporous materials. The effect of pore fluid structure on the Bragg scattering intensity is investigated using a mathematical model. Increases of simulated Bragg scattering intensity are attributed to increases of pore filling fractions and shortenings of correlation distances between the
particles in the pore space. We then tested the model for analyzing the SANS profiles of Au NP and C₆E₃ surfactant solutions in SBA-15 pores. The method effectively represents the SANS profiles, and quasiperiodic distance among the NPs and surfactant micelles formed in pore space were extracted. We find that quasiperiodic distances decreased upon increasing the pore occupation of Au NPs, while the distance for C₆E₃ aggregates increased with increasing pore uptake of the surfactant. Relative contributions of Bragg scattering and diffuse scattering of Au NPs and C₆E₃ to the total scattering intensity are described in terms of increasing pore filling fractions of material. The relative contributions of Bragg scattering of Au NPs dominate the total scattering intensity due to their rigid internal structure and the decrease of correlation distance between the particles with increasing concentration. The relative contribution of diffuse scattering for C₆E₃ dominates the total scattering because of the flexible intramural structure. This study develops a novel approach to analyze the SANS profiles and provides new fundamental understanding to the assembled state and structural discrepancy of nano-assemblies in nanopores.
Chapter 6. Adsorption and Catalytic Activity of Gold Nanoparticles in Mesoporous Silica

6.1 Introduction

The stability and spatial distribution of metallic nanoparticles (NPs) in aqueous solution is the key in harvesting their unusual properties in the fields of pharmaceuticals, biosensors, and catalysis.\textsuperscript{143–147} Due to the high surface energy and large surface area-to-volume ratio, the dispersed state of metallic NPs in aqueous solution is thermodynamically unfavorable leading to their spontaneous aggregation.\textsuperscript{148–150} A common strategy to stabilize NPs in aqueous medium is via physical/chemical adsorption of surfactants or ligands onto NPs imparting a kinetic barrier against the aggregation.\textsuperscript{151–153} However, the surfactants or ligands can significantly alter the physical and chemical properties of the NPs, especially their catalytic performance in aqueous media.\textsuperscript{154,155} Recent studies have proposed to overcome such limitation by immobilizing catalytic NPs within an inert porous matrix.\textsuperscript{43,156,157} Here the NPs are either synthesized within the confined pore space or the pre-synthesized NPs are physically/chemically adsorbed onto the pore walls. The immobilization of NPs in porous material is anticipated to preserve the NP stability in extreme environments such as high salinity media while retaining the catalytic activity, albeit reduced due to mass transport limitations (discussed later). However, there is a lack of understanding of the impacts of pore diameter, particle concentration and solvent conditions on the assembled state of nanoparticles within the porous material. This limitation exists due to the lack of our ability to effectively characterize nanoparticle assemblies in-situ using traditional spectroscopic techniques.

where the inert matrix interferes. In this study we overcome these challenges by combining nanoparticle adsorption isotherm studies with small angle neutron scattering (SANS), which enables the identification of the in-situ state of NPs. We investigate the binding of model gold (Au) NPs within the mesopores of inert silica matrix (SBA-15 and MCM-41) and quantify the structure and catalytic performance of the NPs in high salinity aqueous medium.

The AuNPs are often utilized in confined environments such as tissue matrix, porous catalytic supports, and nanotubes. In order to optimize the efficiencies of the nanomaterials, it is critical to uncover and understand the adsorbed state of AuNPs in the confined spaces and the impacts of environmental parameters such as pH and salinity on their properties. Previously, it has been reported that the confinement of porous materials can break the structural symmetry of the adsorbing nanomaterial, and drive the formation of unusual structures such as zigzag, helices, and nanoparticle multilayers. Additionally, such pore-confined nanoparticles can provide control over the selectivity in the product of the catalyzed reaction. Despite the unusual properties of metallic NPs in pores, the surface interactions governing the formation of complex nano-assemblies in confined spaces are poorly understood.

AuNPs are widely used in biomedicine, environmental and industrial applications, primarily because of their unusual optoelectronic and catalytic properties. One of the major challenges faced in using the AuNPs in real environments is stabilization of these particles in extreme pH and salinity conditions. Recently, the partial coating of gold nanorods with silica has been proposed as an alternative which improves the colloidal stability of the core-shell structure and enables the chemical reduction of phenol to non-toxic products. However, the synthesis of such Au-silica core-shell structure requires complex steps, and can be anticipated to suffer from limitations similar to that of silica NPs, which are prone to aggregation in high salinity environment. Here we
show that these limitations can be overcome by immobilizing AuNPs in the pores of SBA-15 and MCM-41 mesoporous silica materials. We investigate the effect of pore diameter and presence of electrolyte (NaCl) on the equilibrium amount of NPs adsorbed in the porous materials and on their catalytic activity.

6.2 Characterization of AuNPs and propylamine functionalization mesoporous silica

The AuNPs were characterized for their size using UV-vis spectrophotometry as shown in Figure 6.1a. The peak at wavelength 520 nm is the signature of surface plasmon resonance from ~4 nm AuNPs, which is confirmed by the Transmission Electron Microscopy (TEM) shown in the inset of Figure 6.1a and 6.2. The 2D hcp structure of pores in mSiO$_2$ led to the appearance of characteristic Bragg peaks in small angle X-ray scattering (SAXS) experiments as shown in Figure 1b. The pore diameter, and lattice parameter of the MCM-41 and SBA-15 silica materials used in the study are shown in Table 6.1.

Figure 6.1. (a) UV-vis spectra of AuNPs synthesized by chemical reduction of HAuCl$_4$. The maximum absorbance was observed at wavelength 520 nm, which is the characteristic surface plasmon resonance of AuNPs with 3-5 nm diameter. This result is in agreement with particle sizes obtained by TEM (inset), which shows that the average diameter of AuNPs in bulk solution is ~4 nm. (b) SAXS profiles of mSiO$_2$ with various $d_{pore}$. The curves are shifted by constant factor of 100 for better visualization. The inset schematic shows the 2D hcp pore lattice with lattice parameter and pore diameter. The numbers in the parenthesis represent the miller indices of the corresponding Bragg peak.
Figure 6.2. (a-d) TEM images of AuNPs in DI water, which shows the average diameter of AuNPs in solution is about 4 nm.

Table 6.1. Characterization of $m$SiO$_2$ using nitrogen gas adsorption and SAXS

<table>
<thead>
<tr>
<th>S. No.</th>
<th>$d_{\text{pore}}$ (nm)</th>
<th>Lattice parameter, $l_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.1 ± 0.1</td>
<td>4.4 ± 0.003</td>
</tr>
<tr>
<td>2</td>
<td>4.8 ± 0.1</td>
<td>5.6 ± 0.002</td>
</tr>
<tr>
<td>3</td>
<td>8.4 ± 0.3</td>
<td>10.7 ± 0.002</td>
</tr>
<tr>
<td>4</td>
<td>12.0 ± 0.3</td>
<td>12.9 ± 0.004</td>
</tr>
<tr>
<td>5</td>
<td>15.6 ± 0.2</td>
<td>16.5 ± 0.006</td>
</tr>
</tbody>
</table>

Note that the pore diameter is determined using nitrogen gas adsorption as shown in Figure 6.3.

Here, the average pore diameter is calculated from the relative pressure ($p/p_0$) at the capillary condensation step of the isotherm using modified Kruk–Jaroniec–Sayari (KJS) model, which is given as (expressed in nm)$^{105}$

$$d_{\text{pore}} = \frac{-1.15}{\log \left( \frac{0.875p}{p_0} \right)} + 0.2 \left[ \frac{60.65}{0.03 - \log \left( \frac{p}{p_0} \right)} \right]^{0.397} + 0.27$$
Figure 6.3. Nitrogen gas adsorption isotherm for different pore diameter of $m$SiO$_2$ showing a characteristic adsorption–desorption hysteresis.

6.3 Adsorption of AuNPs in mesoporous $m$SiO$_2$

To understand the effect of $d_{\text{pore}}$ of $m$SiO$_2$ on the adsorption behavior, the amount of AuNPs adsorbed ($\Gamma$) in the pores of $m$SiO$_2$ is measured using the solvent depletion method.$^{16,106}$ Here the aqueous dispersion containing AuNPs at pH 6 is equilibrated with fixed amount of $m$SiO$_2$ for 24 hours. After equilibration, the $m$SiO$_2$ with adsorbed AuNPs are separated from the dispersion using centrifugation for 30 minutes at ~18,000 g. The concentration of the unabsorbed AuNPs in solvent is determined using its characteristic spectrophotometric absorbance value at 520 nm (Fig. 6.4a, and 6.5). The amount of nanoparticles adsorbed per unit surface area is calculated using the equation $\Gamma = (x - x_0)V/mS$, where is $x$ the initial concentration of the AuNPs in the mixture, $(x - x_0)$ is the concentration of AuNPs adsorbed in $m$SiO$_2$, $V$ is the volume of aqueous solution, $S$ is the specific surface area and $m$ is the mass of $m$SiO$_2$ added to the solution. The isotherms for
the adsorption of AuNPs in $m$SiO$_2$ of increasing $d_{\text{pore}}$ are shown in Figure 6.4a. We find that the maximum amount of nanoparticle adsorbed per unit surface area of $m$SiO$_2$ increases with increasing $d_{\text{pore}}$. Here we use Langmuir model for quantitative analysis of the experimentally obtained isotherms. Mathematically, the Langmuir adsorption model is represented as $^{22}$

$$\Gamma = \frac{\Gamma_{\text{max}} K_{\text{ads}} x_o}{1 + K_{\text{ads}} x_o} \quad (6-1)$$

Here, $\Gamma$ is the amount of AuNPs adsorbed into $m$SiO$_2$ pores, $\Gamma_{\text{max}}$ is the maximum surface excess of the AuNPs, $x_o$ is the equilibrium concentration of AuNPs in bulk, and $K_{\text{ads}}$ is the equilibrium adsorption constant which is the measure of binding energy of nanoparticles to the pore walls.

Based on the analysis of our experimental data, we find that the maximum amount of AuNPs adsorbed on $m$SiO$_2$ increases nearly by an order of magnitude upon increasing $d_{\text{pore}}$ from 4.1 to 15.6 nm. Note that the surface excess is normalized to the surface area, and the observed increase in the adsorbed amount of AuNPs with increasing $d_{\text{pore}}$ is due to the reduced geometric barrier for AuNPs penetrating the $m$SiO$_2$ matrix.$^{169,170}$ At $d_{\text{pore}}$ comparable to the diameter of the AuNPs, adsorption observed is significantly lowered due to the physical barrier for nanoparticles accessing the pore space. The small amount of AuNPs adsorbed at $d_{\text{pore}} = 4.1$ nm is likely due to the binding of the AuNPs on the $m$SiO$_2$ matrix exterior to the pores.
Figure 6.4. (a) Adsorption isotherms for AuNPs binding to the cylindrical nanopores of $m$SiO$_2$ with increasing $d_{\text{pore}} = 4.1, 4.8, 8.4, 12.0$ and 15.6 nm. The scattered points are the experimental data and solid lines represent the best fit to the data using the Langmuir model given by equation 1. (b) Theoretical curves (black line) and experimental data points (circles) of maximum AuNPs packing fraction in $m$SiO$_2$ pores as a function of pore diameter. (c) Schematic representing the change in packing of the AuNPs in silica matrix with increasing $d_{\text{pore}}$ as predicted by the SVC model.

The analysis of the adsorption isotherms gives binding affinity of $K_{\text{ads}} \sim 3.5$ mM$^{-1}$ corresponding to the adsorption free energy $\sim -29.6$ kJ/mol, which is similar to previously reported values for surfactant adsorption onto silica surfaces.$^{171,172}$ Note that the binding affinity values of AuNPs remain independent of the $d_{\text{pore}}$, highlighting that the nature of the chemical species controlling the adsorption remains unchanged i.e. $-\text{NH}_3^+$ (from propylamine) of $m$SiO$_2$ and $-\text{COO}^-$ (from citrate) of AuNPs.
Figure 6.5. The spectrophotometric absorbance calibration curve of AuNPs in bulk solution. The symbols are the experimentally measured absorbance values of a given concentration of AuNPs, and the lines are the linear fits to the experimental data. The equation of line representing the value of absorbance increases as increasing concentration of AuNPs, where x and y are the concentration of AuNPs in bulk and corresponding absorbance value, respectively.

The changes in maximum amount of AuNPs loaded in the pore-space with increasing \( d_{pore} \) can be compared quantitatively as using the maximum packing fraction \( f \). The value of \( f \) can be determined as \( f = nV_{part}/V_{pore} \), where \( n \) is the total number of AuNPs adsorbed, \( V_{part} \) is the volume of a AuNPs which is \((4/3)\pi R^3\), where \( R \) is the mean radius of AuNPs, and \( V_{pore} \) is the total volume of pores. The value of \( n \) is determined experimentally using \( \Gamma_{max} \) as \( n = mS\Gamma_{max}N_A \), and \( V_{pore} = \left( \frac{mS}{\pi d_{pore}} \right) \times \frac{\pi d_{pore}^3}{4} = mSd_{pore}/4 \), where \( l \) is the length of pores. Therefore, the value of \( f \) can be obtained from experimental adsorption isotherms as \( f = \frac{16\pi R^3\Gamma_{max}N_A}{3d_{pore}} \). Assuming
AuNPs as hard spheres, the value of $f$ can be calculated theoretically using a geometrical model proposed by Sang, Vinu, and Coppens (SVC).\textsuperscript{81} The non-linear change in the maximum pore filling fractions with $d_{\text{pore}}$ as estimated using experimental adsorption isotherms (circles) and SVC model (line) are shown in Figure 6.4b. Note that the theoretically predicted value of $f = 0.67$ at $d_{\text{pore}} = 2R$ is due to the assumed spherical shape of the particles adsorbing in tubular pores. This contrasts with the calculations performed by Meissner et al.\textsuperscript{80} where the authors used cylindrical shape to represent the protein molecules adsorbing in the tubular pores and obtained $f = 1$ at $d_{\text{pore}} = 2R$. The experimental value of $f$ shows first a rapid increase followed by a slight decrease with increasing $d_{\text{pore}}$, which agrees with the predictions of the SVC geometric model showing step-changes in the values of $f$ as depicted in Figure 6.4c. The large $f$ values highlight that the AuNPs penetrate the whole pore space, instead of blocking or plugging them at the pore entrance. Such penetration of AuNPs can be achieved by surface diffusion of the particles, as reported previously for flat surfaces.\textsuperscript{173} Note that the electrostatic double layer repulsion between negatively charged AuNPs would contribute to the interparticle separation and corresponding experimental $f$-values.

6.4 Effect of added electrolyte on adsorption

The interparticle repulsions between negatively charged AuNPs can be screened by the addition of electrolyte in the aqueous medium. Here we use NaCl as a model 1:1 electrolyte to screen the electrostatic interactions and investigate the effect of the electrolyte concentration on the colloidal stability and adsorption of AuNPs to $m$SiO$_2$. We measure the adsorption isotherms of AuNPs on $m$SiO$_2$ with $d_{\text{pore}} = 4.1, 4.8, 8.4, 12.0$ and $15.6$ nm in the presence of $10, 25, 50$ and $100$ mM NaCl (Fig 6.6a, 6.6c, 6.7 and 6.8). The adsorption isotherms are measured by adding the electrolyte at two different adsorption stages: (1) Pre-adsorption: NaCl is added prior to the adsorption of AuNPs in $m$SiO$_2$; and (2) Post-adsorption: NaCl is introduced to the dispersion containing $m$SiO$_2$.
with adsorbed AuNPs. In the case where the electrolyte is added to AuNPs dispersion prior to the adsorption, the $\Gamma_{\text{max}}$ is dependent on amount of added salt which decreases with increasing NaCl concentration (Fig. 6.6a and 6.7). The observation can be attributed to the larger size of the aggregates formed by AuNPs at higher NaCl concentration. In stark contrast, the AuNPs remain bound to the pore walls when the electrolyte is added after the completion of the adsorption process (Fig 6.6c).

![Figure 6.6](image)

Figure 6.6. (a) **Pre-adsorption:** Adsorption isotherms of AuNPs in $m$SiO$_2$ with $d_{\text{pore}} = 8.4$ nm upon the addition of NaCl. Here the electrolyte was added prior to the initiation of the adsorption process. (b) Maximum surface excess of AuNPs in $m$SiO$_2$ at pre-adsorption stage with $d_{\text{pore}} = 4.1, 4.8, 8.4, 12.0,$ and $15.6$ nm with increasing concentrations of NaCl. The observed decrease of maximum surface excess with the addition of NaCl is due to the aggregation of AuNPs. (c) **Post-adsorption:** Adsorption isotherms of AuNPs on 8.4 nm $m$SiO$_2$ with increasing concentration of NaCl. The electrolyte is added after loading the AuNPs in $m$SiO$_2$. (d) Maximum surface excess of AuNPs on $m$SiO$_2$ at post-adsorption stage with $d_{\text{pore}} = 4.1, 4.8, 8.4, 12.0,$ and $15.6$ nm upon adding NaCl. The constant maximum surface excess of AuNPs highlights no significant desorption of AuNPs from the pore-wall which results from the strong electrostatic attraction between negatively charged AuNPs and positively charged $m$SiO$_2$. 

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Figure 6.7. Pre-adsorption isotherms of AuNPs on mSiO$_2$ with (a) 4.1 nm, (b) 4.8 nm, (c) 12.0 nm, and (d) 15.6 nm pore diameters in the presence of 0, 10, 25, 50 and 100 mM NaCl. The discrete points are experimental values, and solid lines are fit using Langmuir model.

Figure 6.8. Post-adsorption isotherms of AuNPs in mSiO$_2$ with (a) 4.1 nm, (b) 4.8 nm, (c) 12.0 nm, and (d) 15.6 nm pore diameters with increasing concentration of NaCl. The points are the measured experimental values, and solid lines are represented using Langmuir model.
The electrostatic attraction between the oppositely charged silica pore wall and AuNPs drive the system to a free energy minimum, which is not altered by the addition of salt (Fig. 6.6d). Whereas, in the case of AuNPs dispersed in aqueous medium, the addition of electrolyte screens the electrical double layer repulsions between the nanoparticles leading to the dominance of van der Waals interaction and aggregation. The net interaction energy ($U_{DLVO}$) between a pair of colloidal particles and a particle and a flat substrate can be estimated using Derjaguin-Landau-Vervey-Overbeek (DLVO) theory (See chapter 3 for details). The $U_{DLVO}$ between a pair of AuNPs, and an AuNP and $m$SiO$_2$ surface is shown in Figure 6.9. The interaction energy calculations show that the repulsion between AuNPs is screened upon the addition of NaCl leading to aggregation of the nanoparticles (Fig. 6.9a). However, no significant effect of the addition of salt on interaction energy is observed for oppositely charged AuNPs and $m$SiO$_2$ (Fig. 6.9b). Note that the electronegativity of protonated aminopropyl functional group (-C$_3$H$_6$NH$_3^+$) is lower than that of Na$^+$, i.e. the ion-pair association strength of Na$^+$ is weaker, which restricts the desorption of the AuNPs from the pore wall upon the addition of NaCl.\cite{174} It can be inferred that the adsorption free energy between the $m$SiO$_2$ and AuNPs overwhelms the attraction energy between AuNPs in 100 mM NaCl aqueous solution, and contributes to the stable state of AuNPs on silica pore wall under high salinity conditions.
Figure 6.9. (a) DLVO interaction energy between (a) a pair of AuNPs, and (b) an AuNP and $m$SiO$_2$ surface in the presence of 10, 25, 50, and 100 mM NaCl. The repulsion between AuNPs is reduced with increasing concentration of NaCl, and results in aggregation of the nanoparticles. The attraction between the oppositely charged AuNPs and $m$SiO$_2$ is not significantly impacted upon addition of NaCl. The inserts are schematics of the interaction of AuNP-AuNP and $m$SiO$_2$-AuNP respectively.

6.5 Characterization of AuNPs in $m$SiO$_2$ using SANS and TEM

The adsorption isotherms and corresponding analysis provided an in-depth characterization of the amount of AuNPs loaded in $m$SiO$_2$, but no information was obtained on the assembled state of AuNPs in the pores and corresponding impact of the addition of the electrolyte. We use SANS experiments to uncover the assembled state of AuNPs in $m$SiO$_2$. The SANS experiments were performed using $m$SiO$_2$ with $d_{pore} = 8.4$ nm in D$_2$O and 40:60 mixture of H$_2$O:D$_2$O matching the scattering length density ($3.54 \times 10^{-4}$ nm$^{-2}$) of the silica matrix.$^{16}$ The SANS for $m$SiO$_2$ in D$_2$O shows Bragg peaks characteristic of the 2D hcp pore lattice of the silica matrix. The Bragg peaks disappear when the experiment is performed in H$_2$O:D$_2$O mixture (Fig. 6.10a). We perform SANS on contrast matched $m$SiO$_2$ containing AuNPs at concentration equivalent to $0.9 \Gamma_{max}$ in the presence of 0 and 100 mM NaCl (Fig. 6.10b-c). We find that upon the addition of AuNPs to contrast matched $m$SiO$_2$, the Bragg peaks re-appear which are the signature of the presence of the
nanoparticles within the pore lattice (Fig. 6.10a-c). Previously, it has been shown that the total scattering intensity \( I_{\text{Total}} \) from mesoporous SBA-15/MCM-41 materials with adsorbed molecules/particles under silica contrast matched conditions can be represented as\(^{75}\)

\[
I_{\text{Total}}(q) = I_{\text{Bragg}}(q) + I_{\text{Diff}}(q)
\]

(6-2)

where \( q \) is the scattering vector given as \( q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \), \( \lambda \) is the wavelength and \( \theta \) is the scattering angle; \( I_{\text{Bragg}} \) and \( I_{\text{Diff}} \) respectively are the Bragg and diffused scattering contributions to the total scattering. The Bragg scattering intensity is obtained by a Monte-Carlo simulation approach, where nanoparticles are randomly distributed in the \( m\text{SiO}_2 \) matrix, and \( I_{\text{Diff}} \) is obtained by the Teubner-Strey model. Further details on the model and SANS data analysis are provided in supporting information and our previous publication.\(^{175}\) We find that the theoretical model (lines in Fig. 6.10b and 6.10c) effectively represents the experimental SANS data (circles in Fig. 6.9b and 6.10c).

The presence of Bragg peaks for \( m\text{SiO}_2 \) with adsorbed AuNPs despite being in H\( _2 \)O:D\( _2 \)O mixture matching the scattering length density of silica confirms the presence of AuNPs adsorbed on the pore walls. Since the SANS experiments are performed at 0.9\( \Gamma_{\text{max}} \), all added AuNPs are adsorbed in silica matrix. Based on our analysis of the diffused scattering contribution, we estimate a quasiperiodic distance of 6.9 nm between the AuNPs in the pore space (See Chapter 3). We find that the quasiperiodic distance between AuNPs remains unchanged upon increasing the concentration of NaCl from 0 mM to 100 mM, indicating that the immobilized AuNPs retain their adsorbed spatially separated state in the high salinity aqueous solution. The retention of AuNPs within the pore upon the addition of NaCl highlights that the electrostatic attraction between the pore wall and AuNPs are not significantly screened, as shown in Figure 6.9b. The result is in
agreement with the TEM images (Fig. 6.10e and f), where AuNPs can be observed to be spatially separated and bound to the silica matrix instead of aggregating in the presence of NaCl. Note that the TEM is performed on the dried suspension and SANS profiles are obtained in the presence of solvent, highlighting that the AuNPs retain their adsorbed state upon drying the suspension.

![Image](image.png)

Figure 6.10. (a) SANS profiles for $m$SiO$_2$ in D$_2$O and H$_2$O:D$_2$O mixture matching the scattering length density of $m$SiO$_2$ (b-c) SANS profiles (circles) and corresponding model fits (red lines) for AuNPs adsorbed on 8.4 nm pore diameter of $m$SiO$_2$ under contrast matched condition in the presence of 0 mM and 100 mM NaCl solution. The increase in scattering intensity at $q < 0.6 \text{ nm}^{-1}$ in (b) and (c) can be attributed to the Porod’s scattering from the nanoparticle adsorbed on the exterior surface of SBA-15 beads. (d-f) TEM images of $m$SiO$_2$, $m$SiO$_2$-AuNPs in DI water and $m$SiO$_2$-AuNPs in 100 mM NaCl aqueous solution, respectively. The insert in (f) shows the aggregates of AuNPs in bulk solvent in the presence of 100 mM NaCl.

6.6 Catalytic activity of AuNPs

The spatial confinement imposed by the nanoparticle adsorption in mesopores and the colloidal stability of AuNPs in aqueous media are critical factors governing their catalytic activity.\textsuperscript{176,177} We use the reduction of 4-nitrophenol (yellow) to 4-aminophenol (colorless) by sodium borohydride (NaBH$_4$) in the presence of AuNPs as a model reaction (Fig. 6.11a) to investigate the changes in the catalytic performance of the nanoparticles when immobilized in the pore space. We perform the reduction of 0.5 mM of 4-nitrophenol by 50 mM NaBH$_4$ at 20 °C using AuNPs as catalyst in
following states: (A) Dispersed in aqueous media, and (B) Immobilized in $m$SiO$_2$ with $d_{pore} = 4.1$, 4.8, 8.4, 12.0 and 15.6 nm (Fig. 6.1b). The amount of AuNPs used in the measurements was equivalent to $\Gamma = 0.7\Gamma_{\text{max}} = 0.002$ $\mu$mol/m$^2$ of $m$SiO$_2$ with $d_{pore} = 4.1$ nm (Fig. 6.4) i.e. identical number of AuNPs present in all tested $m$SiO$_2$ and all added NPs were solely present in their adsorbed state onto $m$SiO$_2$. The spectrophotometric profiles obtained at various time steps during the reaction in the presence of AuNPs in the dispersed state and immobilized in 8.4 nm pore diameter $m$SiO$_2$ are shown in Figure 6c-d. The spectrophotometric profiles show a peak at wavelength 400 nm, which is characteristic of the 4-nitrophenolate anion. The peak intensity gradually decreases with time indicating the decrease in the concentration of 4-nitrophenolate anion (Fig. 6.11c-d). The observed decrease in the peak intensity at 400 nm wavelength is accompanied by an increase of absorbance peak intensity at 300 nm which is indicative of the gradual formation 4-aminophenol. The observed changes in spectrophotometric profiles confirm the reduction of 4-nitrophenol to 4-aminophenol in the presence of AuNPs.

Since the concentration of NaBH$_4$ overwhelmingly exceeds that of 4-nitrophenol, the reduction reaction can be represented using a pseudo-first-order reaction kinetics with respect to 4-nitrophenol. The rate equation for a first order reaction is given as, $kt = -\ln(C_t/C_0)$, where $k$ is the reaction rate constant, $C_0$ is the initial concentration of 4-nitrophenol and $C_t$ is the concentration after time $t$. Note that the absorbance values at wavelength 400 nm are converted to concentrations of 4-nitrophenol using a calibration curve as shown in Figure 6.12. The changes in the values of $-\ln(C_t/C_0)$ with time for an identical number of AuNPs adsorbed in $m$SiO$_2$ with $d_{pore} = 4.1$, 4.8, 8.4, 12.0 and 15.6 nm, for NPs suspended in solvent (DI water), and for only $m$SiO$_2$ are shown in Figure 6e. The value of $-\ln(C_t/C_0)$ shows no change in the absence of AuNPs, but it increases linearly in all other cases. The rate constant is determined by the slope of each curve,
which increases with increasing pore diameter (Fig. 6.11f). The observed decrease in rate constant for particles immobilized in the $m$SiO$_2$ pores can be attributed to two major factors (1) Blocking of the active sites on AuNPs due to their adsorption onto the pore wall, which is confirmed by performing the reduction reaction for AuNPs immobilized on a flat surface showing a slightly lower rate constant than AuNPs in their suspended form (Fig. 6.11e-f); and (2) Limitations in the transport of reactants and products in- and out- of the spatially confined pore space. The reactions in the $m$SiO$_2$ pores are clearly diffusion limited, and factor (1) would be the nearly same for all the porous catalysts except for the one with 4.1 nm pores (as explained below). Configurational transport theory can predict the magnitude of the decrease in the observed $k$’s.
Figure 6.1. (a) The chemical equation of 4-nitrophenol reduction reaction using AuNPs as catalyst. (b) Photographs of the color change every 20 mins for 4-nitrophenol aqueous solution in the presence of $mSiO_2$ ($d_{\text{pore}} = 8.4$ nm) with adsorbed AuNPs. (c-d) UV-vis spectra and reaction constant of 4-nitrophenol reduction with both AuNPs and $mSiO_2$-AuNPs catalyst in DI water. Inserts are the zoom-in plots of absorbance intensity at 250-350 nm wavelength. (e) The relationship between reaction time and $-\ln (C_t/C_0)$ is shown for various pore sizes of $mSiO_2$ containing AuNPs, only $mSiO_2$ matrix, AuNPs in dispersion and AuNPs on a flat silica substrate. (f) The change in reaction rate constant $k$ for 4-nitrophenol reduction as a function of $d_{\text{pore}}$, AuNPs on substrate and dispersed in bulk. (g) Reaction rate constants normalized to the $k$ of the 4.1 nm catalyst.
Figure 6.12. The absorbance calibration curve of 4-nitrophenol in deionized water. The black circles are the absorbance values of known concentrations of 4-nitrophenol, and the black line is the linear representative to the experimental values. The equation of the trendline shows an increase absorbance value as increasing concentration of 4-nitrophenol, where $y$ and $x$ represent the absorbance value and the concentration of 4-nitrophenol in deionized water, respectively.

Assuming our experimental system consists of cylindrical pores of a constant pore tortuosity containing uniform spherical AuNPs of diameter 4 nm. For a pore transport-limited reaction the observed $k$ should be related to the number of reaction sites ($\Gamma'$) times the effective pore diffusivity ($D_e$),\textsuperscript{180} which is in turn proportional to other factors, as shown below:

$$k = \alpha \left( \Gamma' D_e \right)^{1/2} = \alpha \left( \Gamma' D C_f \varepsilon \right)^{1/2}$$ \hspace{1cm} (6-3)

where $D$ is the bulk diffusivity of liquid p-nitrophenol, $C_f$ is the configurational factor for small pores where the molecular size (0.66×0.43 nm elliptical cross section for p-nitrophenol)\textsuperscript{181} approaches that of the pore diameter, $\varepsilon$ is the porosity and $\Gamma'$ is the total number of active site which could be obtained by multiplying $\Gamma$ by the average number of sites per AuNP. The porosity can be calculated as follows:
\[ \varepsilon = \left[1 + \frac{4}{(\rho_s S d_{pore})}\right]^{-1} \left[1 - (f)\left(\frac{\Gamma}{\Gamma_{max}}\right)\right] \] (6-4)

where \( \rho_s \) is the skeletal density of the silica (used the value for quartz), and the other symbols have their previous meanings. The second bracketed term represents the fraction of pore volume occupied by the NPs themselves. The bulk diffusivity for p-nitrophenol in water\(^{182}\) and a \( C_f \) specifically developed for mesoporous silica in this size range\(^{183}\) were taken from the literature, and the normalized \( k \)'s computed as shown in Figure 6.11g. Note that the number of AuNPs per pore (\( \psi \)) can also be calculated:

\[ \psi = \frac{\Gamma}{\Gamma_{max}} \int \frac{\pi}{4} \frac{l d_{pore}^2}{v_{part}} \] (6-5)

For 4.1 nm pores, \( \psi \approx 2 \), and \( \Gamma \) in eq. 6-3 was divided by 4 here, because for 4.1 nm pores a molecule of p-nitrophenol cannot pass the first AuNP; for one-way diffusion both the second NP and the half the first would be inaccessible. For all other pore sizes passage is possible.

The agreement between the normalized (to \( k \) for the 4.1 nm pores) experimental \( k \)-values and the theory using eq. (6-3) is acceptable considering the level of approximation involved. Complicating factors include the possibilities of slightly different NP shapes and sizes in the \( mSiO_2 \), differing tortuosities, and effects of the AuNPs on the \( C_f \) function.

Immobilizing AuNPs in \( mSiO_2 \) maintains their spatially separated state in an extreme environment such as high salinity, allowing retention of catalytic activity. We monitor the change in the kinetics of the reaction upon the addition of NaCl to the aqueous solvent. The change \( -\ln (C_t/C_0) \) with time for AuNPs dispersed in the solvent and immobilized in \( mSiO_2 \) with \( d_{pore} = 8.4 \text{ nm} \) in the presence and absence of 100 mM NaCl is shown in Figure 6.13a-c. Here we represent the rate constants as: \( k_{AuNPS} \) and \( k_{mSiO_2-AuNPS} \) respectively for dispersed and adsorbed (into \( mSiO_2 \)) AuNPs in DI water; and \( k_{AuNPS+NaCl} \) and \( k_{mSiO_2-AuNPS+NaCl} \) respectively for dispersed...
and adsorbed AuNPs in water containing 100 mM NaCl. We find that the rate constant $k$ follows the order: 

$$k_{\text{AuNPs}_\text{+NaCl}} < k_{\text{mSiO}_2-\text{AuNPs}} \approx k_{\text{mSiO}_2-\text{AuNPs}_\text{+NaCl}} < k_{\text{AuNPs}}.$$  

Because the number of AuNPs in all tested samples is identical, the catalytic activities are primarily dependent on the assembled state of AuNPs in different conditions. As discussed earlier, the screening of repulsions between the AuNPs upon the addition of electrolyte results in their aggregation. It is well known that the number of active sites on AuNPs governs the reaction rate.\(^{184}\) The aggregation of AuNPs leads to a sharp decrease in the total surface area and corresponding catalytically active sites exposed to the solvent, which leads to the observed decrease in the reaction rate. We find that 

$$k_{\text{mSiO}_2-\text{AuNPs}} \approx k_{\text{mSiO}_2-\text{AuNPs}_\text{+NaCl}},$$  

indicating that the adsorbed and spatially separated state of the AuNPs in nanopores is maintained upon the addition of 100 mM NaCl, which is also shown in the TEM and SANS studies (Fig. 6.10). The spatially separated state of AuNPs in the pores is preserved up to 1 M NaCl, beyond which the rate constant shows a slight decrease (Fig. 6.13d). At NaCl concentrations above 2 M, a small fraction of AuNPs likely desorb from the surface, leading to the observed slight decrease in their catalytic activity. Further studies are necessary to uncover the effect of such high concentrations of salt on the stability and reactivity of AuNPs in nanopores. Despite the minor decrease in reaction rate, the experiments demonstrate that immobilizing the NPs in silica pores with a positive charge is a viable route to retain the catalytic activity of the AuNPs.
6.7 Conclusion

This study presented the effect of nanoconfinement on the adsorption and assembled state of AuNPs on amine-functionalized porous silica materials. We showed that the maximum amount of AuNPs that can be adsorbed on a silica matrix depends on the ratio of particle-to-pore diameters. This increase results from the increase in the pore volume accessible to the AuNPs. The AuNP catalyst adsorbed in propylamine-modified mesoporous silica shows pore diameter-dependent
reaction kinetics for the reduction of 4-nitrophenol to 4-aminophenol. Decreasing the pore diameter reduces the rate constant, due to transport limitations of reactants and products in and out of the pore space. We also demonstrated that the AuNPs retain their spatially distributed adsorbed state within the pores upon the addition of electrolyte, which leads to the preservation of their catalytic performance. The article helps in addressing a dichotomy on the pore size of inert supports to be used for catalysis. On the one hand, the decrease in pore diameter reduces the reaction rate; on the other hand, increasing the pore diameter results in a decrease in the specific surface area making the flat substrates impractical. For example, an $\sim 50 \, \text{m}^2$ silica wafer is required to drive the same reaction which can be performed with 1 g of mSiO2 with $d_{\text{pore}} = 8.4 \, \text{nm}$ in a vial. This article provides the principle of finding an appropriate pore diameter of inert supports where the nanocatalyst can resist aggregation under extreme salinity environments while retaining a high catalytic activity and the corresponding reaction rates.
Chapter 7. Adsorption of Fatty Acid Molecules on Amine-Functionalized Silica Nanoparticles

7.1 Introduction

The aggregative adsorption of amphiphilic molecules on colloids governs the optical properties, interfacial activity and stability of the particles in the dispersion\(^{185-190}\). The self-assembled state of amphiphilic molecules on colloidal particles is dependent on interaction energy between: (1) Particle surface and unadsorbed amphiphile molecules; (2) Amphiphilic molecules adsorbed on the surface and unadsorbed molecules in bulk solution; and (3) Among the molecules adsorbed on the surface\(^9,14,191\). These interactions determine the morphology of surface-adsorbed aggregates of amphiphilic molecules, and govern the interfacial activity of the colloidal particles with adsorbed amphiphiles. The adsorption mechanism and morphology of the surface aggregates formed by synthetic amphiphiles, such as non-ionic surfactants, onto hydrophilic nanoparticles are well-known and characterized\(^{100,192,193}\). However, the equilibrium morphology of natural amphiphiles, such as fatty acids, adsorbed onto nanoparticles and their impact on the interfacial activity of nanoparticles are poorly understood. This lack in understanding is due to the complexity of the phase behavior of fatty acid molecules, which is highly dependent on the concentration of counterions in the dispersion medium\(^{194,195}\).

Fatty acids are a class of naturally occurring amphiphiles consisting of an aliphatic hydrocarbon chain and carboxylic acid polar head group\(^{196}\). The carboxylic acid head group can exist in either protonated or deprotonated state, which is primarily governed by the presence of

counterion molecules in solution. The concentration of counterion in the solution also governs the morphology of the self-assembled state of the fatty acid molecules and their Kraft temperature. Previously, it has been shown that increasing the fatty acid-to-counterion molar ratio in aqueous solution drives morphological transitions in the self-assembled state of the fatty acids from disc-like micelles, to multilamellar tubules, to discrete spherical micelles. Despite the rich phase behavior of the fatty acid molecules in bulk, the effects of ionization state of the fatty acid molecules on their adsorption onto hydrophilic nanoparticles remains unknown. The self-assembled state and phase behavior of fatty acid in nanoparticle aqueous solution are impacted by the chemical design of the fatty acid molecules, size of the nanoparticles, and environmental parameters such as temperature, salinity, and presence of counterions. Understanding the interactions governing the self-assembly and stimuli induced phase behavior of fatty acids adsorbed at the surfaces of nanoparticles is critical to the development of multifunctional materials with tunable interfacial and bulk properties, such as foam stability and viscoelasticity. In this study, we systematically investigate the effect of counterion on the adsorption, self-assembled state of fatty acid molecules adsorbed at the surface of hydrophilic nanoparticles, and its corresponding impact on the interfacial activity of fatty acid-nanoparticle complex.

We use adsorption isotherms and small angle neutron scattering (SANS) simulations to understand the effect of increasing concentration of counterion on the change of adsorbed amount, and the morphology of the fatty acid molecules formed at amine functionalized hydrophilic nanoparticles. We use decanoic acid (C9H19COOH) and ethanolamine (HOCH2CH2NH2) as model fatty acid molecules and counterion, respectively, and propyl amine (-C3H6NH2) functionalized spherical silica (mSiO2) as model hydrophilic nanoparticles. We find that increasing the counterion-to-fatty acid molar ratio not only determines the amount of fatty acid adsorbed on the
silica nanoparticles, but also governs the morphology of the fatty acid assemblies formed at the $m\text{SiO}_2$ surface. Furthermore, we demonstrate that the morphological change of fatty acid at $m\text{SiO}_2$ impacts the interfacial activity of the composite structure, thus altering the stability of foam formed by the dispersion. This study outlines the relationship of counterion-tuned structure of fatty acid assembly on silica nanoparticle to the interfacial activity of the composite structure, thus providing fundamental insights into the principles of designing nanomaterials with tunable foaming properties.

7.2 Nanoparticle synthesis and characterization

The propylamine functionalized silica nanoparticles (Figure 7.1a) were synthesized by controlled surface modification of commercially available Ludox-TMA colloidal silica (details are shown in Chapter 2). The $m\text{SiO}_2$ nanoparticles were characterized for their size and surface charge by small angle X-ray scattering (SAXS), scanning electron microscope (SEM) and zeta potential measurements. The bulk size characterization of $m\text{SiO}_2$ was performed using SAXS (Xenocs Xeuss 2.0). The SAXS profiles for 0.1 % by weight of $m\text{SiO}_2$ at pH 7 is shown in Figure 1b, where $I(q)$ is the scattering intensity, and $q$ is the scattering momentum transfer related to the X-ray wavelength ($\lambda$) and scattering angle ($\theta$) as $q = \left(\frac{4\pi}{\lambda}\right)\sin\left(\frac{\theta}{2}\right)$. The experimentally measured scattering profile is fitted using a spherical form factor model with log-normal particle size distribution (Figure 7.1b). The form factor model is effective in representing the scattering at $q > 0.2 \text{ nm}^{-1}$, but fails in the region $q < 0.2 \text{ nm}^{-1}$. This disagreement between the experimental data and form factor model is caused by weak aggregation of the nanoparticles at pH 7 (zeta potential $< +15$ mV, Figure 1c), which results in an increase in scattering intensity at $q < 0.2 \text{ nm}^{-1}$. Despite the presence of structure factor, the form factor provides the accurate nanoparticle diameter of $\sim 30 \text{ nm}$, with polydispersity index of 0.1, which agrees with SEM imaging (Figure 7.1b, inset). The
surface charge on the $m$SiO$_2$ is quantified using zeta potential measurement (Litesizer™ 500, Anton Paar GmbH) as a function of pH (Figure 7.1c). The experimental results show that the zeta potential of $m$SiO$_2$ changes from +42.7 mV to -31.1 mV as pH is increased from 2 to 11, and the isoelectric point of $m$SiO$_2$ nanoparticles is pH ~ 8.5. The isoelectric point of the native silica nanoparticles is pH ~ 2, but it changes to pH ~ 8.5 upon surface modification with propylamine surface groups (Figure 7.2). The change in isoelectric point of silica nanoparticles upon surface chemical modification is attributed to the protonation of the aminopropyl functional group at pH < 8. The positive charge on the surface of $m$SiO$_2$ at pH < 8 is the key in directing the adsorption, and corresponding self-assembled state of the fatty acid molecules on the surface of $m$SiO$_2$ nanoparticles.

Figure 7.1. (a) Schematic representation of the synthesis of aminopropyl functionalized silica nanoparticle ($m$SiO$_2$). The aminopropyl groups (-C$_3$H$_6$NH$_2$) were chemically grafted onto commercially available Ludox-TMA silica nanoparticles, and then protonated to -C$_3$H$_6$NH$_3^+$. (b) Experimental SAXS profiles (blue circles) for $m$SiO$_2$ nanoparticles in deionized water at pH 7. (caption cont’d.)
Solid line represents the fit to the experimental data using the form factor of polydisperse spheres. Inset: SEM image showing spherical shape of mSiO$_2$ nanoparticles. The scale bar in the inset is 100 nm. (c) Zeta potential-pH titration curve for the mSiO$_2$ nanoparticles in deionized water. The red line at pH 4.9 represents the $pK_a$ of carboxylic acid group of decanoic acid in water. The black line indicates the isoelectric point of mSiO$_2$ nanoparticles.

Figure 7.2 (a) SAXS profile for SiO$_2$ nanoparticles in deionized water at pH 7. Experimental profile is shown by squares, and the dashed line represents the fit to the experimental data using the form factor of polydisperse spheres (Particle diameter = 30 nm, polydispersity index 0.1). (b) Zeta potential titration curve for unmodified, native SiO$_2$ nanoparticles.

7.3 Adsorption of fatty acid on mSiO$_2$

In this study, we use decanoic acid as model fatty acid and control its protonation state using ethanolamine as counterion. We define the counterion-to-fatty acid molar ratio ($R$) as the ratio of the total number of ethanolamine to the fatty acid molecules in the solution. The value of $R$ is equivalent to the fraction of the fatty acid molecules with dissociated carboxylate ion i.e. $R \equiv \frac{n_{\text{COO}^-}}{n_{\text{total}}}$, where $n_{\text{COO}^-}$ is the number of deprotonated fatty acid molecules and $n_{\text{total}}$ is the total number of fatty acid molecules in the solution. To understand the effect of protonation state of fatty acid on its interaction with mSiO$_2$, we experimentally measure the adsorption isotherms of the decanoic acid onto mSiO$_2$ nanoparticles with $R$ increasing from 0.05 to 1.0. The adsorption isotherms were measured at pH 6, where the net charge on mSiO$_2$ is positive, and an electrostatic
attraction exists between the deprotonated carboxylate group of the fatty acid and propyl ammonium group on the surface of $m$SiO$_2$ nanoparticles.

The adsorption isotherms were measured using solvent depletion method.$^{106}$ In a typical adsorption experiment, increasing amounts of fatty acid at fixed $R$ were added to 1 wt. % $m$SiO$_2$ aqueous dispersion. The pH was adjusted to 6 by adding small amounts of 5 N aqueous HCl or NaOH solution. The mixture was equilibrated at 20 °C for 24 h, and then the $m$SiO$_2$ with adsorbed fatty acid molecules was removed by centrifuging the dispersions at 18000 rcf for 2 hours. Electrostatic attraction between the oppositely charged fatty acid molecules and silica surfaces further drives fatty acid mediated aggregation of $m$SiO$_2$ nanoparticles, thus destabilizing the dispersion. The aspect of aggregation of $m$SiO$_2$ nanoparticles into fractal superstructures, while interesting, is beyond the scope of this study, which is focused on understanding the self-assembly of fatty acid molecules on nanoparticles.

Based on visual inspection of the sample and known adsorption mechanism of amphiphile molecules$^{16}$, fatty acid molecules in their mixture with counterion and $m$SiO$_2$ are present in three distinct forms, namely, (a) undissolved fatty acid gel ($c_u$, unprotonated form), (b) unadsorbed fatty acid in bulk solution ($c_o$, protonated form), and (c) adsorbed fatty acid onto $m$SiO$_2$ ($c_{ads}$, protonated form) as shown in Figure 2a. The fractions of total fatty acid concentration ($c_t$) existing in these three forms were determined by systematically separating the mixture using centrifugation. The mass density of the native protonated fatty acid is $\sim$ 0.893 g/cm$^3$$^{206}$ therefore the concentration of fatty acid in undissolved gel form ($c_u$) was determined by physically collecting the pallets floating on the liquid-air interface in the vial after centrifugation. The concentration of undissolved fatty acids decreases with increasing $R$, as shown in Figure 7.3.
Figure 7.3. Concentration of undissolved fatty acid in bulk solution at different counterion-to-fatty acid molar ratio, $R$. The concentration of undissolved fatty acid decreases as $R$ is increased in bulk solution. Here acronym FA refers to fatty acid.

The concentration of fatty acid dissolved in aqueous solution but unadsorbed onto $m$SiO$_2$ was determined by first carefully removing the aqueous supernatant from the centrifuged sample, and then measuring the concentration of the fatty acid in supernatant using surface tension. The surface tension of the supernatant was measured using an optical tensiometer (Attension Theta, Biolin Scientific), where the shape of the pendant droplet is analyzed using Young-Laplace equation$^{16,107,108}$. The relationship between surface tension and concentration of the fatty acid in the supernatant was determined for different calibration solutions with known concentrations, yielding a calibration curve, as shown in Figure 7.4.
Figure 7.4. Surface tension calibration curve of fatty acid solution at $R = 1.0$. The black circles are the experimentally measured surface tension values of a given fatty acid solution, and the red lines are the linear fits to the experimental data. The equation of line representing the surface tension decrease in the range $c_t < \text{cmc}$ is given in the plot, where $\sigma$ and $C_s$ are the surface tension and concentration of the supernatant, respectively. The experiments show that the $\text{cmc}$ of FA is about 0.5 mM. Here acronym FA refers to fatty acid.

When the unknown concentration of deprotonated fatty acid in the supernatant was higher than critical micellization concentration (CMC) of the molecules, the unknown concentration was determined by systematic dilutions until the measured surface tension is below its characteristic value at CMC. The net unknown concentration of the supernatant was calculated by multiplying the concentration estimated for the diluted sample (from surface tension calibration curve) and the dilution factor. It should be noted that fatty acid molecules only in the deprotonated state ($-\text{COO}^-$) are surface-active and reduce the surface tension, as shown in Figures 7.4 and 7.5. Therefore, the surface tension measurements enable selective determination of concentration of fatty acid molecules in the dissolved (deprotonated) state.
Figure 7.5. Surface tension for fatty acid in deionized water at $R = 0$ at room temperature. The surface tension values remain constant (as water ~72 mN/m) upon increasing fatty acids concentration, indicating that the fatty acid in protonated state are interfacially inactive, and does not contribute in decreasing the surface tension.

The amount of fatty acid molecules adsorbed onto $m$SiO$_2$ nanoparticles ($\Gamma$) is obtained from the equation $\Gamma = c_{ads} V / m_z$, where $V$ is the volume of the aqueous solution, $m_z$ is the mass of $m$SiO$_2$ in bulk solution, $c_{ads} = c_t - (c_o + c_u)$ is the concentration of fatty acid molecules adsorbed onto $m$SiO$_2$, $c_t$ is the total concentration of fatty acid, $c_o$ is the concentration of dissolved but unadsorbed fatty acid in the solution, and $c_u$ is the concentration of undissolved fatty acid molecules (Figure 7.6a). It should be noted that for $R = 1$, the value of $c_u = 0$ i.e. all fatty acid exists either in dissolved or adsorbed state (protonated forms), and for $R = 0$, $c_u = c_t$ i.e. the fatty acid molecules exist only as undissolved gel state (deprotonated form). The adsorption isotherms of fatty acid molecules bound to $m$SiO$_2$ nanoparticles at five $R$ values are shown in Figure 7.6b. At all tested counterion concentrations, the amount of fatty acid adsorbed on $m$SiO$_2$ shows an initial increase followed by a plateau, which is characteristic of the molecular adsorption
on a surface with fixed number of binding sites\textsuperscript{16}. This experimentally measured adsorption isotherms can be represented by a Langmuir adsorption model given as\textsuperscript{22}

\begin{equation}
\Gamma = \frac{\Gamma_{\text{max}}K_{ads}c_o}{1 + K_{ads}c_o}
\end{equation}

Here, \( \Gamma \) is the amount of fatty acid adsorbed onto \( m\text{SiO}_2 \), \( \Gamma_{\text{max}} \) is the maximum surface excess of the fatty acid, \( c_o \) is the equilibrium concentration of dissolved but unadsorbed fatty acid in bulk, \( K_{ads} \) is the equilibrium adsorption constant, which is proportional to the binding affinity of the fatty acid molecules to \( m\text{SiO}_2 \) nanoparticles. The Langmuir model is the simplest two-parameter model that allows representing the maximum amount of fatty acid adsorbed and its binding affinity for \( m\text{SiO}_2 \) in terms of \( \Gamma_{\text{max}} \) and \( K_{ads} \).

The experimental adsorption isotherms data are fitted using Langmuir model given in equation 7-1 (Figure 7.6a) keeping \( \Gamma_{\text{max}} \) and \( K_{ads} \) as free fit parameters. The values of \( \Gamma_{\text{max}} \) and \( K_{ads} \) as obtained by the least squares fitting of experimental data with increasing \( R \) are shown in Figure 7.6b and 7.6c. We find that \( \Gamma_{\text{max}} \) increases (nearly) linearly with increasing \( R \). The values of \( \Gamma_{\text{max}} \) increases from 1.0 μmol/m\textsuperscript{2} to 16.0 μmol/m\textsuperscript{2} (Figure 7.6c) as \( R \) increased from 0.05 to 1.0, i.e., the number of fatty acid molecules adsorbed onto \( m\text{SiO}_2 \) increases with increasing \( R \). The observed linear increase in the maximum surface excess of fatty acid molecules can be attributed to the linear increase in the concentration of deprotonated (negatively charged carboxylate) fatty acid molecules with increasing \( R \)\textsuperscript{194}.
Figure 7.6. (a) Schematic of the solvent depletion method used for experimentally measuring the adsorption isotherm of fatty acid molecules onto $m$SiO$_2$ nanoparticles. (b) Adsorption isotherm for fatty acid on $m$SiO$_2$ at increasing counterion-to-fatty acid molar ratio ($R$). The discrete points are experimental values, and solid lines are fits using Langmuir adsorption model given by equation (1). (c) Maximum surface excess $\Gamma_{\text{max}}$, and (d) adsorption isotherm constant $K_{\text{ads}}$ of fatty acid on $m$SiO$_2$ with increasing $R$, as obtained by fitting the experimental data using Langmuir model.

We find that the $K_{\text{ads}}$ also shows only a slight increase from 0.4 mM$^{-1}$ to 1.4 mM$^{-1}$ with increasing $R$ from 0.05 to 1.0. This slight increase in $K_{\text{ads}}$ with $R$ is an indicative of the small increase in adsorption free energy of the fatty acid molecules onto $m$SiO$_2$ surface. It should be noted that because pH of the aqueous solution was kept fixed (at pH 6) the surface charge of $m$SiO$_2$ can be approximated as constant for all $R$. Assuming that the charging of the silica and fatty acid molecules involves monovalent ions only, and that the surface charge density of $m$SiO$_2$ at pH 6 is low, the free energy of adsorption can be calculated from $K_{\text{ads}}$ as $\Delta G_{\text{ads}}^0 = -N_A k_B T \ln (55.5 \times \ldots}$
\[ \Delta G_{ads}^0 \] , where \( N_A \) is the Avogadro number, \( k_B \) is Boltzmann constant, and \( T \) is the temperature\textsuperscript{171,172}. We find that \( \Delta G_{ads}^0 \) increases from \(-24.2\) to \(-27.4\) kJ/mol upon increasing \( R \) from \( 0.05 \) to \( 1 \). Two key conclusions drawn from these values are: Firstly, the value of \( \Delta G_{ads}^0 \) is lower than the adsorption free energy of cationic surfactants on silica surface. This lowering of adsorption free energy in our case can be attributed to the smaller surface charge density on the synthesized \( m\text{SiO}_2 \) nanoparticles\textsuperscript{207}. Secondly, only a small increase in the \( \Delta G_{ads}^0 \) highlights that the chemical nature of the functional group binding to \( m\text{SiO}_2 \) at low and high \( R \) values is similar, which is carboxylate group of the decanoic acid. The adsorption isotherms show that the amount of fatty acid bound onto \( m\text{SiO}_2 \) increases, but do not provide any insight into the self-assembled state and morphology of the surface adsorbed molecules. To uncover the self-assembled state of the fatty acid on \( m\text{SiO}_2 \) nanoparticles, we perform small angle neutron scattering analysis for dispersions of \( m\text{SiO}_2 \) with adsorbed fatty acid, as discussed in the next section.

### 7.4 Small Angle Neutron Scattering experiments

The increase in counterion-to-fatty acid molar ratio leads to an increase in the amount of fatty acid molecules adsorbed on \( m\text{SiO}_2 \) nanoparticles. This increase in surface adsorption of fatty acid molecules will drive a morphological change in the fatty acid assemblies formed on the surface of \( m\text{SiO}_2 \) nanoparticles. Here we characterize the morphology of the fatty acid molecules on \( m\text{SiO}_2 \) using SANS. The experiments were carried out at silica contrast matched condition, where 62.5 wt. \% deuterium oxide (D\textsubscript{2}O) and 37.5 wt. \% H\textsubscript{2}O was used as the solvent\textsuperscript{100,193}. Therefore, the neutron scattering originated solely from the fatty acid molecules and their assemblies in the solution. The SANS experiments were performed at ORNL’s HFIR facility using the GP-SANS instrument with pinhole collimation at neutron wavelength of 6 Å. Further details about the SANS experiments can be found in previous publications\textsuperscript{75,77}. 

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The SANS experiments were performed at constant total concentration of fatty acid and $m$SiO$_2$, with increasing counterion-to-fatty acid molar ratio from $R = 0.05$ to 1.0. Here the fatty acid concentration was 0.03 M, which was equivalent to the 0.5 $C_{max}$ at $R = 1.0$ (Figure 7.6b). Therefore, for SANS at $R < 1.0$ the fatty acid existed in three states as discussed in the previous section (Figure 7.6a). The SANS profiles for $m$SiO$_2$ with adsorbed fatty acid under silica contrast-matched conditions with increasing $R$, at pH 6 and 20 °C are shown in Figure 7.8a. The curves show an increase in the low-$q$ ($< 0.15$ nm$^{-1}$) scattering with $I(q) \propto q^{-2}$. This proportional increase in the scattering intensity is likely a combination of the scattering due to the fatty acid mediated aggregation of $m$SiO$_2$ nanoparticles, and the presence of large fatty acid gel phase clusters in the solution. The SANS profiles also show enhancement of the primary form factor oscillation at $q \sim 0.15$ nm$^{-1}$ with increasing $R$. Additionally, the primary minima show a slight shift to higher $q$ values upon increasing $R$ (Figure 7.8a), indicating a decrease in the size of fatty acid assemblies on $m$SiO$_2$ nanoparticles. Detailed characteristics of self-assemblies formed by molecules on nanoparticles can be obtained by fitting the experimental SANS data to theoretical form factor models. In our case, such model dependent analysis is not feasible because of too many unknown and unconstrained fit parameters. Therefore, we first perform model independent analysis of the SANS data using Porod’s law and determine the change in the surface-to-volume ratio of the fatty acid assemblies with increasing $R$. According to Porod’s law, the scattering intensity at large $q$ ($\to \infty$) is represented as $I(q) = \frac{2\pi(\Delta\rho)^2}{q^4} \frac{S}{V}$ where $\Delta\rho$ is the scattering length density contrast between the scattering object and surrounding medium, and $\frac{S}{V}$ is the surface area-to-volume ratio of the scattering object. Analyses of our SANS data (Figure 7.7) show approximately 10 times increase in the SV upon increasing $R$ from 0.05 to 1.0. This increase in surface-to-volume ratio indicates a significant decrease in the size of self-assembled structures formed by fatty acid, highlighting a
phase transition of fatty acid from the bulk gel phase to surface-adsorbed layer upon increasing counterion concentration. Note that since scattering intensity is in arbitrary units, the observed increase in the values of $\frac{S}{V}$ with increasing $R$ only represents qualitative changes.

Figure 7.7. (a) SANS profiles and fitting curve in Porod's region for fatty acid molecules adsorbed on $m$SiO$_2$ nanoparticles in H$_2$O/D$_2$O mixture matching the scattering contrast of silica. The profiles were measured at increasing $R$ from 0.05 to 1. The curves are shifted by a constant factor of 10 for better visualization. (b) Surface area-to-volume ratio of fatty acid adsorbed on $m$SiO$_2$ nanoparticles at different counterion-to-fatty acid molar ratio, $R$.

A complete SANS data analysis is limited due to the fatty acid induced aggregation of $m$SiO$_2$ nanoparticles and corresponding emergence of structure factor in the scattering profile which requires additional parameters. Therefore, instead of direct fitting the experimental data we systematically simulate the SANS profiles, which provide a qualitative information on the morphology of the assemblies formed by fatty acid molecules on $m$SiO$_2$ nanoparticles.

Previous studies have shown that amphiphilic molecules can adsorb onto nanoparticles in two morphological states, namely continuous layers or discrete patches$.^{100}$ To understand which of the two morphologies is formed by fatty acid molecules on $m$SiO$_2$, we test the applicability of
spherical shell and raspberry-like form factor models in representing the experimental SANS profiles. The spherical shell model represents the formation of a continuous layer of fatty acid on $m$SiO$_2$ nanoparticles$^{186}$. Here we simulate the SANS profiles for using a shell model with fixed core radius of 15 nm with 0.1 polydispersity index (Figure 7.1b) and increasing the shell thickness from 0.6 nm to 3.0 nm (Figure 7.8c). These thickness values are used because of the characteristic length of decanoic acid molecule, which is 1.2 nm$^{47}$, therefore, 1.2 nm and 2.4 nm correspond to continuous homogeneous monolayer and bilayer structures, respectively. We find that the primary oscillation at $q \sim 0.25$ nm$^{-1}$, characteristic of the shell thickness, is present in all simulated cases, which is in qualitative disagreement with the experimental SANS profiles (Figure 7.8a, b) for $R < 0.5$. The experiments show the presence of a smeared oscillation at $R < 0.5$. This qualitative mismatch between the experimental and simulated SANS profiles suggests that the self-assembled state of the fatty acid on $m$SiO$_2$ is more complex than a continuous shell of fatty acid molecules formed on nanoparticles.
Figure 7.8. (a) SANS profiles for fatty acid molecules adsorbed on $m$SiO$_2$ nanoparticles in H$_2$O/D$_2$O mixture matching the scattering contrast of silica. The profiles were measured at increasing $R$ from 0.05 to 1. The curves are shifted by a constant factor of 10 for better visualization. (b) Zoomed-in plot of the scattering intensity from $q = 0.07$ to 1 nm$^{-1}$. The primary minima of SANS profile shift to higher $q$ values upon increasing $R$, indicating a decrease in the characteristic size of the self-assemblies formed by fatty acid molecules on $m$SiO$_2$ upon increasing counterion concentration. (c and d) Simulated SANS profiles using spherical shell and raspberry-like form factor models, respectively. The spherical shell form factor model provides poor representation of the experimental data (shown in a) both qualitatively and quantitatively. The primary oscillation of raspberry-like form factor model qualitatively represents the experimental SANS data, and captures the change in the morphology of adsorbed fatty acid. The inserts in (c) and (d) are the respective conceptual schematics of the used form factor models.

The second possible morphological state of fatty acid on $m$SiO$_2$ nanoparticles is discrete patches. Here we test the presence of such configuration of fatty acid on the nanoparticles by simulating the scattering profile using a raspberry-like form factor. The model represents the form factor of a large sphere with small spheres randomly adsorbed on its surface. The total scattering intensity of such raspberry-like structure with core particle contrast-matched with the continuous medium is given as$^{79}$
\[ I_{RB}(q) = \frac{N\phi_l V_l^2 \Delta \rho^2 \psi_s^2}{16 V_l} \left[ 1 + (N - 1) \left[ \frac{\sin(q(r_l+r_s))}{q(r_l+r_s)} \right]^2 \right] \] (7-3)

\[ \psi_s = 3\frac{[\sin(qr_s) - qr_s \cos(r_s)]}{(qr_s)^2} \] (7-4)

where \( N \) is the number of small particles of radius \( r_s \), volume \( V_s \) and scattering contrast \( \Delta \rho \) adsorbed onto the core particle, \( \phi_l \) is the volume fraction of the core particle of radius \( r_l \), volume \( V_l \), and \( q \) is the scattering vector (see Chapter 3.2 for detailed derivation). The raspberry-like form factor model accounts for all the self-correlation and cross-correlation for small spheres randomly adsorbed onto a larger spheres\(^79\). The simulated SANS profiles for a contrast-matched sphere with increasing number of surface adsorbed smaller spheres are shown in Figure 7.8d. The profiles are simulated for core particle radius \( r_l = 15 \) nm, \( r_s = 4 \) nm with increasing \( N \) from 12 to 200. The simulated curves using raspberry-like form factor show an oscillation in the range \( 0.15 < q < 0.3 \) nm\(^{-1}\). This oscillation is the signature of the characteristic correlation distance between the surface adsorbed small spheres. The oscillation gets pronounced upon increasing \( N \) because of the increasing correlation in spatial distribution of the surface adsorbed particles (fatty acid in our case) which is the characteristic diameter of the core particle (Figure 7.8d). The observed behaviour of smearing of the primary oscillation at low \( N \) is characteristic of the patchy nature of the surface adsorbed structures. At large \( N \), the surface assembly of fatty acid resembles the continuous layer, and the spherical shell and raspberry-like form factor models yield similar results (Figure 7.8b and c). We acknowledge that the raspberry-like form factor is strictly applicable only in the case of spherical particles adsorbed onto a larger sphere, the model qualitatively captures the effect of
discrete nature of the surface adsorbed assemblies in the scattering profile, especially at low surface loadings. In our experiments of fatty acid adsorbed on mSiO₂, we observe similar smearing of the primary form factor oscillation at \( R < 0.25 \), highlighting the discrete nature of the fatty acid assemblies formed on mSiO₂ nanoparticles. Upon increasing the counterion concentration to \( R \) above 0.50, the oscillation becomes pronounced, which agrees with the continuous layer of fatty acid molecules on the nanoparticles. At \( 0.25 < R < 0.50 \), the SANS profile shows a behaviour intermediate between discrete patches and continuous layer, which is critical in programming the interfacial binding of the nanoparticle-fatty acid complex (discussed in section 7.4). In summary, the SANS shows that the morphology of the fatty acid adsorbed on the mSiO₂ nanoparticles changes from discrete patches to continuous layer upon increasing \( R \). While the origin of such morphological transitions of the fatty acid self-assemblies is not clear from SANS data, molecular dynamics simulations can provide detailed insight (discussed below).

7.5 Foam stability in fatty acid-mSiO₂ aqueous solution

The form stability of fatty acid soaps in aqueous solution is known to be related to the morphology of fatty acid assemblies at air-water interface. However, the origin of superior foam observed in mixtures of oppositely charged nanoparticles and amphiphiles not well understood. Here we aim to interrelate the state of fatty acid assemblies formed on mSiO₂ nanoparticles with their ability to stabilize air-water interface (i.e. foam). The stability of foams formed by the mixture of fatty acid and mSiO₂ with increasing \( R \) was tested at pH 6. A typical foaming experiment was performed using an aqueous mixture of 0.02 M fatty acid and 1.0 wt. % mSiO₂ with increasing \( R \) from 0.0 to 1.0. The used concentration of fatty acid was equivalent to \( \Gamma_{\text{max}} \) at \( R = 1.0 \). The foam was produced from the fatty acid and mSiO₂ mixture by vigorous shaking, and it was kept undisturbed at room temperature for 18 hours. The change in the foam volume of the mixture after 18 hours is
monitored using digital imaging as shown in Figure 7.9a. The stability of the foam produced by fatty acid-\textit{mSiO}_2 mixture at a given \( R \) is quantified using a foam stability parameter, \( S \), represented as \( S = v_{\text{final}}/v_{\text{initial}} \), where \( v_{\text{initial}} \) and \( v_{\text{final}} \) are the volumes of foam immediately after shaking, and after 18 hours of equilibration, respectively. For \( R = 0 \), the foam stability parameter was equal to zero since no foam could be produced from the pure fatty acids and \textit{mSiO}_2 mixture without counterion (Figure 7.9a). By adding a small amount of counterion (\( R = 0.05 \)), \( S \) increased from 0 to 0.7. By further increasing \( R \), \( S \) reached a plateau value around 0.8 from \( R = 0.2 \) to 0.5. For \( R > 0.5 \), \( S \) decreased to a final value of 0.2 at \( R = 1 \) (Figure 7.9b). From these results, we defined three regions of foam stability. Region I corresponds to low foam stability for \( 0 < R < 0.05 \). Region II, \( 0.05 < R < 0.5 \) corresponds to high foam stability. Region III also corresponds to a low foam stability regime for \( 0.5 < R < 1.0 \). We further investigate the origin of change in foam stability with increasing \( R \) by microscale imaging of the bubbles in all three identified regions for \( R = 0.05, 0.2, \) and \( 1.0 \) (Figure 7.9c-e). In region I, the bubbles were spherical, highlighting the large interfacial tension between air and water. Transforming from region I to region II, the shape of bubbles undergoes a change from smooth sphere to rippled non-spherical. This change in the shape of the bubble upon increasing \( R \) can be attributed to the adsorption of fatty acid-\textit{mSiO}_2 complex at the air-water interface and corresponding interfacial jamming of the nanoparticles. We believe that the partial coating of the \textit{mSiO}_2 with fatty acid makes the nanoparticles partially hydrophobic, driving its interfacial adsorption. Following such interfacial adsorption, the shape transformation of the bubbles is driven by two key factors: (a) Jamming of nanoparticles in the thin films between the bubbles upon liquid drainage hindering the relaxation of the bubbles to spherical shape;\textsuperscript{208,209} and (b) compression of liquid films by nanoparticle jamming causing the buckled and rough appearance of bubble surface.\textsuperscript{13,210} Furthermore, we observe that the shape of
bubbles recover to smooth sphere from rippled perturbed sphere upon increasing $R$ to 1.0 (region III).

In region I, only few patches of fatty acid molecules are present at the $m\text{SiO}_2$ surfaces (section 7.3) which induce enough amphiphilicity to adsorb at air-water interface. Therefore, hydrophilicity and weak amphiphilic character of the nanoparticles in region I resulted in lack of foam stability. In region II, the number of fatty acid patches at the particle surface was enough to reach an appropriate contact angle value, which leads to the adsorption of particles at the air-water interface. The patchy particles formed a dense layer at the interface protecting the bubbles against coalescence and coarsening due to jamming phenomenon, thus leading to the observed stable foams. In the region III, the fatty acid formed a continuous bilayer structure on the $m\text{SiO}_2$ nanoparticle surface, leading to hydrophilic surface and diminishing the interfacial activity of the nanoparticle-fatty acid complex. This lack of interfacial activity of fatty acid-nanoparticle complex destabilizes the air bubbles, and leads to poor foam stability (sections 7.3). Thus, the fatty acid-$m\text{SiO}_2$ nanoparticles stay in liquid phase and sediment to the bottom of solution due to the fatty acid mediated heteroaggregation of the $m\text{SiO}_2$ nanoparticles (Figure 7.9a, and 7.9e). This absence of nanoparticles at air-water interface spontaneously drives the bubble coalescence, drainage and coarsening without any physical or energetic barrier(s). These foaming experiments highlight a direct relationship between the fatty acid structure on $m\text{SiO}_2$ and their interfacial property. We find that patchy nature of the surface assemblies is necessary for increasing the interfacial activity of fatty acid-$m\text{SiO}_2$ complex and enhancing the corresponding foam stability. We show that the self-assembled state of fatty acid molecules on $m\text{SiO}_2$ directs the interfacial activity of the composite nanostructure and the resulting macroscopic properties such as foam stability. The strong correlation between the self-assembled state of fatty acid molecules on the surface of $m\text{SiO}_2$
nanoparticles and foam stability lead to the formation of controllable foams for which the stability can be tuned by modifying $R$.

Figure 7.9. (a) Photographs of the change in foam volume for the fatty acid-$m$SiO$_2$ mixture with increasing counterion-to-fatty acid molar ratio, $R$. (b) The change in foam stability of fatty acid-$m$SiO$_2$ aqueous solution quantified using foam stability parameter, $S$ as a function of $R$. Three distinct regions of foam stability with increasing $R$ can be identified namely, (I) rapid increase, (II) constant and (III) slow decrease. (c-e) Micrographs of bubbles formed at $R = 0.05$, $R = 0.2$ and $R = 1.0$, respectively, at fixed $m$SiO$_2$ and fatty acid concentration. The images show that the bubbles become non-spherical with the increasing amount of counterion, then recover to spherical shape as more counterion addition. The scale bars correspond to 20 μm. (f) Schematics representing the mechanism of change in foam stability of fatty acid-$m$SiO$_2$ mixtures with increasing $R$.

7.6 Conclusions

This study presents the effect of counterion-to-fatty acid molar ratio, $R$, on the self-assembled state of fatty acid molecules on aminopropyl modified silica nanoparticles. We show that the maximum amount of fatty acid that can be adsorbed on the $m$SiO$_2$ increases with increasing $R$. The increase in the amount of fatty acid molecules adsorbed on positively charged $m$SiO$_2$ nanoparticles is driven by the increase in the number of negatively charged deprotonated fatty acid molecules upon increasing $R$. The increase in the maximum surface excess of fatty acid on $m$SiO$_2$ with increasing $R$ drives a morphological change in the self-assembled state of fatty acids at the nanoparticle
surface from discrete patches to continuous layer. The control over that morphological state of fatty acid on $mSiO_2$ by changing $R$ enables programming the hydrophilic/hydrophobic characteristics of the fatty acid-$mSiO_2$ complex. At low $R$, the fatty acid molecules form large discrete patches on the surface of $mSiO_2$, which decompose and spread on $mSiO_2$ to form a continuous layer at high $R$, evidenced by the analysis of SANS profiles. This morphological change is induced by increased electrostatic interaction between fatty acid and $mSiO_2$ along with decreased van der Waals interaction between fatty acid molecules upon increasing $R$. The self-assembled state of fatty acid on the surface of $mSiO_2$ is strongly correlated with the interfacial activity of the complex. We demonstrated that the foam stability of the mixture can be directed by the altered the adsorbed state of the fatty acid molecules onto $mSiO_2$ by changing the counterion-to-fatty acid molar ratio. This study provides a fundamental basis to comprehend the non-trivial effects of counterion on morphological evolution and phase transition of fatty acid assemblies formed on nanoparticles. Further work on such modified silica nanoparticle and their dispersion with fatty acid can facilitate new principles of designing ultra-stable foams valuable in cosmetics and food industries.\textsuperscript{211,212}
Chapter 8. Production and Stabilization of Foams by Fatty Acid Crystals in High Alcohol Content Solvents

8.1 Introduction

In early 2020, the World Health Organization (WHO) declared a global pandemic due to COVID-19. The rapid spread of this pandemic has highlighted the importance of disinfectants for personal and household hygiene. One of many ways to reduce the transmission of contagious bacteria and viruses is frequent and effective hand sanitization by the traditional handwashing or using alcohol-based hand sanitizers. The WHO recommends formulating alcohol-based hand sanitizers using at least 80% by volume (v/v) ethanol or 75% isopropyl alcohol. Alcohol-based hand sanitizers are known to dissolve lipids from the Stratum Corneum, the uppermost layer of the skin, leading to discomfort and cracking of skin, which opens routes for the entry of pathogens. Moreover, these formulations alone are low-viscosity Newtonian liquids, thus pouring and rubbing these on hands is difficult. Specially designed synthetic polymers lead to the gelling of such alcohol-water solution, but require a precise control over the pH, which is sometimes not feasible at industrial scale. Additionally, the short- and long-term impact of these synthetic polymers on skin (irritation) and on the virus inactivation are currently unknown. Recently, foam-type disinfectant formulations have been introduced in the market to address the issues of solution dripping, runoff, and difficulty to cover the entire hand surface during the use. Foams can be visually spread on the skin and are easier to handle and spread than traditional gels. However, the formation and stabilization of foams using high ethanol content solvents such as the one recommended by WHO remains a challenge. Despite low surface tensions, the absence of

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disjoining pressure between the bubbles formed by alcohol-water mixtures is responsible for film collapse when it thins due to the drainage\textsuperscript{216}. The scientific challenge is to stabilize the bubbles against coalescence and to avoid thin film collapse thus providing a foam-based alternative to currently used hand sanitizers, which is easy to apply, and assists with limiting the spread of pathogens.

A recent study showed that foams from alcohol-water mixture containing 40 % ethanol can be stabilized using a mixture of sodium dodecyl sulphate (SDS) and long chain alcohol\textsuperscript{63}. Another study showed that a short chain perfluorosurfactant enabled the formation and short-term stabilization of foams from ethanol-water mixture with maximum ethanol content of 50 %\textsuperscript{64}. These initial studies on ethanol-water foams have three major limitations: (i) Alcohol content in the foam is significantly lower than the 80 % concentration as recommended by WHO for adequate hand sanitization, (ii) There is lack of long-term foam stability, and (iii) The precursors used in the foam production are synthetic and may adversely affect skin. In this article, we overcome these limitations by using crystalline particles of natural fatty acids as foam stabilizers. We demonstrate the formation and long-term stability of foams formed using high alcohol content solvents (up to 100 % ethanol and isopropanol) and call these formulations as \textit{Foamitizer}. In our case, the formation of foam is associated with the adsorption of fatty acid (FA) crystals at air-water surface protecting the bubbles against coalescence rather than lowering the surface tension. These FA crystalline particles have never been applied to form and stabilize foams using high alcohol content solvents\textsuperscript{217}.

\textbf{8.2 Generation of stearic fatty acid foams}

We demonstrate the principle of using FA crystalline particles as foam stabilizers on a series of linear saturated fatty acids with number of carbon atoms ranging from 14 to 22. We specifically
focus on stearic acid \((\text{C}_{17}\text{H}_{35}\text{COOH} \text{– C18})\) as foam stabilizer, as it is one of the major component of the Stratum Corneum and currently used in cosmetic formulations as a moisturizing agent\(^2\). 

Our strategy to produce high ethanol content foams was to use the concentration of FA in significant excess of its solubility limit in the respective ethanol-water mixture. The foams are obtained in two steps as shown in Figure 8.1. In the first step, a large amount of C18 (concentration >> solubility limit) is added to aqueous solvent containing 85% ethanol. This mixture is heated above the phase transition temperature to obtain molecularly dissolved fatty acid in the solvent. Then, by cooling down the mixture below the phase transition temperature, the solution becomes supersaturated leading to the formation of C18 crystalline particles. In the second step, foam is produced from the crystalline particles by introducing gas in the dispersion by two-syringes method: where one syringe is filled with air and the other one filled with the liquid phase and connected by a constriction\(^3\).

![Figure 8.1](image_url)

Figure 8.1. Schematic of the limpid sample containing molecularly dissolved fatty acids (FA) in the solvent at temperature above the melting temperature \((T_m)\). Below \(T_m\), crystals are formed by cooling, and turbid dispersion is obtained. By introducing air into the crystals dispersion, foams are formed due to the bubbles stabilization by the FA crystals. By heating the foam above \(T_m\), crystals melt and the foam disappear leading to the initial limpid solution of FA molecules. The scale bar is 5 mm.
8.3 Solubility and phase transition temperature of C18 in ethanol-water mixture

The presence of crystalline particles in ethanol-water mixture is a pre-requisite to produce foam. The solubility of C18 in the ethanol-water mixture containing 85 % ethanol was determined by monitoring the change in transmittance. First, we determined the solubility limit by measuring the transmittance of C18 with increasing concentration from 0.2 to 2.0 wt.% at 25°C (Figure 8.2a). The solubility limit of C18 at 25 °C is ~ 1 wt.%. Below 1 wt.%, the transmittance was ~100% and the samples remained limpid. Above 1 wt.%, we observed the transition from a liquid limpid dispersion into a white turbid dispersion leading to a decrease in transmittance. By optical and crossed polarized microscopy, we observed the presence of platelet-shape FA crystalline particles within size range ~40-70 µm (Figure 8.2a inset, 8.3). Then, we determined the melting temperature (T_m) of the crystals corresponding to the phase transition for C18 at 10 wt.% in the ethanol-water mixture using transmittance measurements (Figure 8.2b). C18 shows a first order phase transition from a crystalline (turbid) to liquid phase (limpid) at 42 °C. The molecular ordering of C18 within the crystalline particles was determined by Wide-Angle X-ray Scattering (WAXS) as a function of the temperature in the range 0.1 < Q < 1.0 Å⁻¹; where Q is the wave vector (Figure 8.2c). From 25 °C to 40°C, i.e. below the phase transition temperature, one intense peak at 0.155 Å⁻¹ corresponding to a d-spacing of ~40.5 Å, followed by additional higher order Bragg peak were detected. Below the melting temperature, C18 crystals had a double layer structure and crystallized into the C-polymorphic form, which is known to be its most stable form. From 42°C corresponding to T_m, no Bragg peaks were observed in WAXS, indicating the melting of the crystals and the presence of molecularly dissolved C18 in the solvent (Figure 8.2c).
Figure 8.2. (a) Evolution of the transmittance as a function of fatty acid concentration in 85 % of ethanol at 25 °C. (b) Evolution of the transmittance as a function of temperature for C18 at 10 wt.% in 85 % of ethanol. (c) WAXS spectra for C18 at 10 wt.% in 85 % of ethanol as a function of temperature. The spectra are shifted in intensity for clarity.
Figure 8.3 Bright field microscopy images showing the crystals of C18 fatty acid. The numbers in the image indicate the length of the corresponding double headed arrow. The scale bar is 45 µm.

8.4 Foamability and Foam stability of C18

Foams were prepared at 25 °C as a function of C18 concentration and characterized for both foamability and foam stability. Below the solubility limit of 1 wt.% no foam was produced since no crystal were present. However, from 2 wt.% to 10 wt.% the surface-active C18 crystals were present in the ethanol-water solvent and foams were obtained (Figure 8.3a). The initial quantity of foams produced increased by increasing C18 concentration (Table 8-1).
Figure 8.4 (a) Photographs of the change in foam volume as a function of C18 concentration just after foam formation and after 48 hours at rest at 25°C. The scale bar is 5 mm. (b) Change in foam stability quantified using the foam stability parameter ($S$) as a function of C18 concentration at 25°C. (c) Photographs of a foam made with C18 at 10 wt.% just after foam formation and after conservation of the foam for 30 days at 25°C, with the corresponding microscopy picture showing the bubbles coverage by fatty acid crystalline particles and the non-spherical shape of the air bubbles. The scale bar in c is 100 µm (30 µm in inset). (c) WAXS spectra of the foam and the drained limpid liquid at 25°C.

Table 8.1. Initial foam volume obtained just after foam formation

<table>
<thead>
<tr>
<th>C18 concentration in wt.%</th>
<th>Initial foam volume (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>0.7</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.7 ± 0.04</td>
</tr>
<tr>
<td>3</td>
<td>0.9 ± 0.07</td>
</tr>
<tr>
<td>4</td>
<td>1.4 ± 0.08</td>
</tr>
<tr>
<td>5</td>
<td>1.6 ± 0.04</td>
</tr>
<tr>
<td>7</td>
<td>3.6 ± 0.2</td>
</tr>
<tr>
<td>10</td>
<td>4.6 ± 0.3</td>
</tr>
</tbody>
</table>

The stability of the foam was quantified using a foam stability parameter, $S$, represented as $S = v_{initial}/v_{final}$, where $v_{initial}$ and $v_{final}$ are the volumes of foam immediately after foam production, and after 48 hours of equilibration at 25 °C, respectively. Here $S = 0$ represent
unstable foam and $S = 1$ is ultrastable foam. For C18 in ethanol-water mixture, $S$ increases from 0.2 to 0.98 upon increasing the fatty acid concentration from 2 wt.% to 10 wt.% (Figure 8.4b). The foam stability increases with C18 concentration due to an increase in the amount of crystalline particles in the solution, as shown by microscopy both at bubble surfaces and in bulk (Figure 8.4c and Figure 8.5). We followed the foam stability for one month, and no change was observed in terms of foam volume and bubbles size. This foam could be considered as ultrastable. Note that the liquid fraction was high around 40-45 %, corresponding to very wet foams, and the drainage was stopped quickly after foam formation. Similar observations were made for aqueous foams stabilized by SDS crystalline particles.

Figure 8.5 Microscope images for foams based on C18 with its increasing concentration in 85 % ethanol. (a) The foam images show an increase in bubbles quantity by increasing C18 concentration from 2 wt.% to 10 wt.%. A change from spherical bubbles not well covered by crystals to fully covered bubbles with non-spherical shapes is visible by increasing C18 concentration. Much more crystals in bulk are also visible in the background between the bubbles by increasing the C18 concentration. The scale bar is 200 μm. (b) By zooming into the foams at the bubble scale level, the microscope images show that the area occupied by the crystals and the coverage increased by increasing C18 concentration. No bubble and crystal are visible for 0.2 wt.% and 0.7 wt.%. Only crystals are present at 1 wt.%. At 2 wt.%, the bubble is spherical with only few crystals on the surface. From 5 wt.%, all the bubbles are well covered. The scale bar is 40 μm.
To understand the foam stabilization mechanisms, we performed multi-scale characterization using contact angle measurements, microscopy and WAXS experiments. The key parameter for crystals to adsorb at the air-solvent surface is to exhibit a suitable contact angle below $90^\circ$. The contact angle of a drop of ethanol-water mixture in air on a C18 crystals was $\sim 32^\circ$, consistent with adsorption of the crystalline particles to air bubble surface (Figure 8.6).

Figure 8.6 Photograph of the contact angle measurement for the C18 acid crystal.

The driving force for the adsorption of C18 crystals is to reduce the surface energy of the air-solvent surface. The crystalline particles adsorbed onto bubble surfaces were clearly observed by bright-field and crossed-polarizer microscopy as shown in Figure 8.4c. The bubble surface was rough and textured due to the adsorption of the crystalline particles at the surface. Some bubbles were also non-spherical which is characteristic of particle-coated interfaces leading to solid-like interfaces. By WAXS, we determined that the crystals structure of C18 was the same in bulk and inside the foam (Figure 8.4d). Coarsening and the coalescence of bubbles was arrested by the presence of C18 crystals. The crystals delayed the drainage by accumulating in the foam liquid channels between bubbles thus restricting film collapse, which was one of the main
challenges to stabilize foams with high alcohol content. Therefore, foams were stable for months after production (Figure 8.4c).

The principle of using FA crystals to stabilize foams can be extended to solvents with 100% alcohol content. We increased the ethanol content of the liquid phase from 75 % to 100 % and kept the concentration of C18 at 10 wt.% at 25 °C. For all tested ethanol amounts, foams were obtained due to the presence of C18 crystals (Figure 8.7a). The foam stability parameter, $S$, show a slight decrease from 0.98 to 0.86 upon increasing the ethanol content from 75% to 100%. We extended our approach to produce ethanol-based foams using isopropanol, which is the other solvent recommended by WHO for hand sanitization product\textsuperscript{214}. Foams were produced from 75 % to 100 % of isopropanol. For C18 at 10 wt.% at 25 °C stable foams were obtained with aqueous mixtures containing 75 % to 100 % of isopropanol (Figure 8.7a). These results show that the main parameter to design stable foams from solvents such as ethanol and isopropanol was the presence of surface-active C18 crystals, since SDS cannot stabilize such type of foams (Figure 8.7a and Figure 8.8).
Figure 8.7 (a) Evolution of the foam stability parameter \((S)\) for C18 at 10 wt.% and SDS at 10 wt.% with an amount of alcohol varying from 75 % to 100 % at 25°C. Stabilization/destabilization of a foam made with C18 at 10 wt.% in 85 % of ethanol during heating/cooling cycles: (b) Evolution of the foam volume as a function of time. (c) Photographs of foams with the corresponding Infrared images. The scale bar is 5 mm.
Figure 8.8 Evolution of the foam stability for 10 wt.% SDS at 25 °C showing the very low stability of the foams and the low initial quantity of the foam formed.

Foams were also obtained using crystals of other FA such as myristic acid (C14), palmitic acid (C16) and behenic acid (C22). They formed surface-active platelet-shape crystals in the solvents above their respective solubility limit, leading to the formation and stabilization of foams (Figure 8.9-8.12). First, we determined the evolution of the transmittance as a function of fatty acids concentration after 24 hours of equilibration to determine the minimum concentration to obtain crystalline particles at 25°C for C14, C16, C18 and C22 (Figure 8.9)
Figure 8.9 (a) Evolution of the transmittance as a function of fatty acids concentration for C14, C16, C18 and C22. (b) Evolution of the transmittance as a function of temperature for C14 at 30 wt.%, C16 at 20 wt.%, C18 at 10 wt.% and C22 at 5 wt.%.

For C14, above 18 wt.%, we observed the transition from a liquid limpid dispersion into a white turbid dispersion by naked eyes, which was correlated with an increase of transmittance. For C16, above 3 wt.%, we observed the transition and the formation of crystals. For C22, the formation of crystals and the increase of transmittance happened above 0.05 wt.%. By optical and crossed polarized microscopy, we observed the presence of surface fatty acids crystalline particles (Figure 8.10). Then, we determined the melting temperature of the crystals corresponding to the solubility limit by spectrophotometry as a function of fatty acids as illustrated in Figure 8.9b. The crystals melt at around: 34 °C, 39°C, 42 °C, and 52 °C for C14 at 30 wt.%, C16 at 20 wt.%, C18 at 10 wt.% and C22 at 5 wt.% respectively.
Figure 8.10 Cross polarized light microscopy images showing the presence of surface-active crystals in bulk for: (a) C14 at 30 wt.%, (b) C16 at 20 wt.%, (c) C18 at 10 wt.% and (d) C22 at 5 wt.%.

The crystals structure was determined by WAXS measurements from wave vector (Q) 0.1 to 1 Å\(^{-1}\) as a function of temperature for C14, C16 and C22 (Figure 8.11). For C14, at 20°C, below the solubility limit, one intense peak was detected at 0.195 Å\(^{-1}\) corresponding to a d-spacing of around 32.2 Å (Figure 8.11a). This peak was followed by additional higher order reflections peak visible on the spectra showing only one molecular packing arrangement. At 27°C corresponding to the melting temperature of C14, no peak was observed in the scattering spectra showing the melting of the crystals and only the presence of C14 molecularly dissolved in the solvent. For C16, at 25°C, one intense peak followed by its harmonics was detected at 0.175 Å\(^{-1}\) corresponding to a d-spacing of around 35.9 Å (Figure 8.11b). No peak was detected at 40°C above the melting temperature of the crystals. For C22, at 25°C, one intense peak followed by its harmonics was
detected at 0.129 Å⁻¹ corresponding to a d-spacing of around 48.7 Å (Figure 8.11c). At 60°C, above the melting temperature, peak disappeared. By comparing with data in the literature, we conclude that below the solubility limit, all the fatty acids formed crystals with a double layer structure associated with a possible β-form²²⁰.

Figure 8.11 WAXS spectra as a function of temperature of fatty acids: (a) C14 at 30 wt.%, (b) C16 at 20 wt.% and (c) C22 at 5 wt.%. The stability of the foam was quantified using the foam stability parameter $S$ (Figure 8.12). For C14 at 30 wt.% in ethanol-water mixture, $S$ was 0.96 and the initial foam volume was $6 \pm 0.1cm^3$. For C16 at 20 wt.%, $S$ was 0.96 and the initial foam volume was $4 \pm 0.1 cm^3$. For C22 at 5 wt.%, $S$ was 0.92 and the initial foam volume was $2.6 \pm 0.1 cm^3$. 

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Figure 8.12 Photographs of the change in foam volume as a function of fatty acid concentration in 85 % (v/v) ethanol in water just after foam formation and after 48 hours at rest at 25°C: (a) C14 at 30 wt.%, (b) C16 at 20 wt.% and (c) C22 at 5 wt.% The scale bar is 10 mm.

8.5 Destabilization of foam

The destabilization of the foams can be triggered by heating the foams and melting the fatty acid crystals. We studied the foam stability as a function of temperature using visible and infrared imaging (Figure 8.7b-c). The foams formed by C18 in the ethanol-water mixture at 25 °C were quickly destabilized above $T_m$ of the crystals (Figure 8.7c). We monitor the effect of crystal melting by optical microscopy, where we observe that the C18 crystals stabilizing the bubbles and dispersed in bulk disappear at $T_m$ leading to rapid destabilization of foam. The foam destabilization process could be arrested by cooling down the foam below its melting temperatures before all the foam disappeared. This is demonstrated in Figure 8.7c, where the change in foam volume could be controlled by instantaneous cooling of the foam. The foam could be destabilized/stabilized at will, just by tuning the temperature below or above the corresponding $T_m$ of the crystals. The foam
destabilization temperature depends only on the $T_m$ of the fatty acid, which is governed by the alkyl chain length of fatty acid, its concentration and the nature of the solvent.

8.6 Conclusion

The COVID-19 pandemic crisis has exposed significant scientific gaps in different fields such as in soft matter \(^{215}\). Here, we took the opportunity to fill one of these gaps concerning the production and stabilization of foams using high alcohol content solvents. This is an important issue both from fundamental and applied standpoint, where new formulations are required for better hand sanitization and limit the transmission of pathogens. We show for the first time how foams with high content of alcohols such as ethanol or isopropanol can be formed using fatty acid crystalline particles, which are critical for skin nourishment. This new route to synthesize foams from high alcohol content solvents would help to tackle the disadvantages of commercial hand sanitizers.
Chapter 9. Summary and Outlook

This Ph.D. dissertation provides a better understanding of adsorption and morphological change of nanostructures at solid-liquid and liquid-air interfaces. We showed that the adsorption and reorganization of nonionic surfactant and fatty acid adsorbed on silica-based adsorbent in aqueous solution. Further, the effect of pore size and salinity on the adsorption and catalytic activity of gold nanoparticles under silica confinements was studied. We demonstrated that the uptake and morphological change of nanostructures was governed by the intermolecular and intramolecular interactions including van der Waals, hydrogen bonding, and electrostatic interactions. In addition, the aqueous foam in alcohol-water mixture was studied in order to generate the ultra-stable foam in high alcohol content solvent. In this Chapter, we concluded the results of each project and provided their significance to uncover the nanostructures adsorbed at the heterogenous interfaces.

In Chapter 4, we show the impact of temperature on the adsorption and reconfiguration of C₆E₃ surfactant in silica pores. The adsorbed amount of C₆E₃ in silica pore wall is investigated using adsorption isotherms, and it is found that the maximum loading amount of C₆E₃ in pore is increasing with temperature. The morphological change of C₆E₃ in silica pore is probed using SANS, and we present that the C₆E₃ aggregates transform from shell to globule on the pore wall upon increasing temperature. We further demonstrate that the C₆E₃ micelles in porous silica exhibit the reversible adsorbed-desorbed ability from pore with heating-and-cooling cycles. This study provides insight into the assembly of nonionic surfactant in hard confinement, which enables the development of new multiresponsive materials for isolating and recovering molecules.

In Chapter 5, we extended a SANS analysis model to study the morphology of adsorbates in porous materials. We use mathematical method to uncover the influence of pore size, number of adsorbate and lattice parameter of hexagonal pore on the SANS profiles. The model quantitively
represents the scattering profiles of AuNPs and C₆E₃ surfactant in mesoporous silica material. This new SANS analysis model enables a development for elucidating the structures of nano-assemblies inside nanopores. In Chapter 6, we showed the effect of pore size and salinity on the adsorption and assembled state of AuNPs in propylammonium-functionalized porous silica materials (mSiO₂). We show an increase maximum surface excess of AuNPs in mSiO₂ upon increasing pore size. This increase origins from the decreased physical barrier for AuNPs diffusing to the pore space. The catalytic activity of AuNPs in pore is also impacted by the pore diameter. Increasing the pore size increases the reaction rate of reduction of 4-nitrophenol to 4-aminophenol due to the reduced restriction of the chemicals in and out the silica pore. We also present that the AuNPs adsorbed on the silica pore wall remain the stable state and catalytic activity under extremely high salinity solution. This Chapter establishes the important role of nanopore and dispersion salinity on the uptake and catalytic activity of NPs.

In Chapter 7, we investigated the self-assembled state and adsorption of fatty acid on propylammonium-functionalized silica (mSiO₂) surface with different counterion-to-fatty acid molar ratio (R). We found that the amount of deprotonated fatty acid molecules increases upon increasing R value, and this change results into the increase of the maximum surface excess of fatty acid on positively charged mSiO₂ at pH 6. The increase of maximum adsorbed amount with R induces the structural transformation of fatty acid assemblies on mSiO₂ surface from individual aggregates to the continuous layers. In addition, we demonstrated that the self-assembled state of fatty acid molecules on mSiO₂ governs the ability to stabilize the foam formed by the mixture of fatty acid and mSiO₂. This project provides a better understanding of self-assembled state of fatty acid on silica surface by varying counterion-to-fatty acid molar ratio, and develops a strategy to design the multifunctional foam utilized in medical and cosmetic industries.
In Chapter 8, we developed a method to form ultra-stable aqueous foam in high alcohol content solvents using fatty acid crystals. We found that the platelet shape crystalline particles are adsorbed at liquid-air interface preventing the bubbles from coalescence. The destabilization mechanism is activated by heating up the foam above the phase transition temperature of fatty acid crystals on bubble films. This destabilization of foam results from the melting of crystals on the liquid-air interfaces, and the bubbles thus lose the protection from collapse. This study exhibits in this Chapter provides an innovative approach to generate the thermostimulable high alcohol content foam, which are critical for designing a better hand sanitizer to limit the spread of pathogens and to nourish the hand skin.

My future research interests focus on producing ultra-stable foam emulsion using fatty alcohol crystalline for topical drug delivery. Crystalline particles including glycerides, long chain alcohol and fatty acid were used as foam stabilizer in oil foams. The crystalline particles in oil foam are achieved by heating-and-cooling procedure which leads to crystals dispersed inside a continuous liquid oil phase. We extended this concept to Chapter 8, and the ultra-stable aqueous foams based on ethanol are generated from fatty acids crystalline particles. However, the preparation procedure to obtain crystalline particles involved complicated heating and cooling steps. In order to overcome this limitation, we will propose the anti-solvent precipitation method which has never been used to produce crystalline particles for foam stabilization. We plan to form long-term stable foam emulsion using fatty alcohols and mineral oil, which are widely used in cosmetic and pharmaceutical applications for their moisturizing effect. The foam emulsion is generated in ethanol-based aqueous solution because ethanol can be used as a skin penetration enhancer, and thus improves the efficacy of topical drug delivery. The work presented in this Ph.D.
dissertation will provide strategies for fabricating multifunctional materials in cosmetic, and pharmaceutical applications.
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Foamitizer: High ethanol content foams using fatty acid crystalline particles
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Vita

Yingzhen Ma was born in Fushun, Liaoning, China. He majored in chemical engineering in Liaoning Shihua University and earned his bachelor’s degree in fall 2014. After his undergraduate study, he moved to the United States and started his master study in the State University of New York at Buffalo (SUNY Buffalo), where he investigated the ionic liquid and salt effects on the thermodynamics of amphiphile micellization in water. In 2017 fall, Yingzhen joined Prof. Bhuvnesh Bharti’s group in Louisiana State University, and his research focused on understanding the adsorption and morphology of soft and hard nanomaterials at the heterogenous interfaces.

Publications


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