NANOPARTICLE ADSORPTION AT FLUID INTERFACES

by

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Abstract

Nanoparticles (NPs) adsorption can add functionality (e.g., catalytic, optical, rheological) to fluid interfaces. NPs can also stabilize fluid interfaces to allow for complex droplet shapes, bijels, and buckled microstructures. Both NPs and surfactants adsorption decreases interfacial tension and stabilizes foams and emulsions. However, unlike surfactants, NP adsorption at fluid interfaces is generally irreversible because their adsorption energy is much larger than the thermal energy, $kT$. However, the distinctions between a surfactant and a NP become blurred as the dimensions of NPs decrease. For example, adsorption of sub-10 nm NPs can be reversible, and dynamic equilibrium can be achieved between a bulk phase and the interface. Therefore, the objective of this dissertation is to uncover the fundamental differences between NPs and surfactants as they adsorb at fluid interfaces. As the distinguishing features between a surfactant and a NP start to vanish, can NPs act as both a particle and a surfactant? In particular, what are the driving forces for NP adsorption and how do they affect the surface pressure? What are the dynamics of NP adsorption to fluid interfaces?

To answer these questions, a material system (ion-pair gold NPs) is selected to show that NPs can achieve dynamic equilibrium between the bulk aqueous phase and its interface with toluene. To demonstrate reversibility of the adsorption process, pendant drop measurements are employed where adsorbed NPs in equilibrium with the bulk phase undergo both mechanical perturbations (compression/expansion) and chemical perturbations (dilution). After perturbations the same equilibrium states are recovered,
indicating that reversible dynamic equilibrium is established between NPs at the interface and in the bulk phase.

With demonstration of a reversible system, a thermodynamically consistent framework is developed to describe the relationship between the bulk NP concentration, adsorbed amount at the interface, and surface pressure. The thermodynamic treatment shows why the Gibbs adsorption isotherm valid for surfactant adsorption does not provide a relationship between surface pressure and adsorbed amount for NPs. Instead the particle-laden interface needs to be treated as a composite material where contributions from both the solid and fluid area in the Helmholtz energy are incorporated. The increase in surface pressure due to particle adsorption originates from both the fluid (surface activity) and the wetting (area replacement) of the particles at the interface. The treatment highlights the fundamental differences between the measured surface pressure caused by particle adsorption compared to the one measured from compression of the interface.

The proposed framework is then tested with the adsorption of ion-pair gold NPs. Independent measurements of the surface pressure and adsorbed amount yields a linear relationship between the surface pressure and surface excess. Such a linear relationship is to be expected if wetting (area replacement) is the main driving force for particle adsorption (while surface activity contributions are negligible). A surface-active species, tetrabutylammonium ion, is then introduced to the system. It is found that when NP and surfactants are present, the surface pressure has two contributions: wetting of the NPs at the interface, as well as surface activity (surfactant-surfactant and surfactant-NP interactions). The proposed model decouples the contributions to the total surface pressure originating from wetting and surface activity. Finally, the thermodynamic model is combined with the
Ward-Tordai model traditionally employed to describe surfactant adsorption dynamics, to successfully predict diffusion-limited adsorption of NPs to the oil-water interface.

These findings elucidate the effects of NP adsorption on interfacial properties. The framework described in this thesis provides a general approach that can be adapted to other experimental systems, and to make predictions as part of guiding experimental designs.
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Dedication

“Love all, trust a few, do wrong to none.”
— William Shakespeare
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1 Introduction

1.1 Particles at oil-water interfaces

The term ‘interface’ refers to the thin boundary layer separating bulk phases from one another. In contrast to “surface”, which often refers to the boundary between a condensed phase and gas phase, the “interface” refers more generally to any phase boundary. As such, one obvious difference between the interface and the bulk phase is that the properties of the interface would be dependent on both phases. As a result, the materials at interface would possess different properties compared to the properties in a bulk phase state. In addition to the self-healing nature of the interfaces, the accessibility to light, availability to materials from both bulk phases, have made the interface a special and attractive platform to investigate. The assembly of particles at fluid-fluid interface has been extensively explored in emulsification, encapsulation, oil recovery, as well as functionalization of the interface. Particles can stabilize emulsions and foams against coalescence, also maintaining different geometry, for example complex droplet shapes, bijels, buckled microstructures. Under these circumstances, the interface behaves as an elastic skin, and the adsorbed particles have a profound effect on interfacial mechanical and rheological properties. For example, viscoelastic Pickering emulsions are superior at preventing coalescence and Ostwald ripening. Recently it has been found that the mechanical property of the interface could be further strengthened by incorporation of surface active additives, such as low MW polymers or surfactants that also adsorb to the interface and/or to the particles, slow the dynamics of the particles within the interface, and lead to jamming. In addition to stability, adsorbed particles can add functionality to fluid-fluid
interfaces based on their material properties and configuration.\textsuperscript{8} For example, NPs can serve as catalysts for reactions between immiscible fluids\textsuperscript{20-21}, optical or plasmonic elements for mirrors or sensing\textsuperscript{22-24}, or promote chemical separation and oil recovery\textsuperscript{25}. Therefore, strategies are needed to control the assembly of particles at oil-water interface. To do so, better understanding of effect on interfacial properties due to particle adsorption is necessary.

The adsorption of particle onto a fluid interface is treated in terms of a decrease in interfacial area. The change in energy $\Delta E$/particle associated with the adsorption of a spherical particle of radius $r_{NP}$ at an oil-water interface is expressed by\textsuperscript{26}:

$$\frac{\Delta E}{\text{particle}} = -\pi r_{NP}^2 \gamma_{OW} \left(1 \pm \cos \theta_{OW}\right)^2.$$  \hspace{1cm} (1.1)

This driving force is due to the replacement of fluid-fluid area with particles that form a contact angle $\theta_{OW}$ at the interface, and is largest when $\theta_{OW} = 90^\circ$.\textsuperscript{26-27} To remain adsorbed at the interface the energy gained from adsorption must be sufficiently larger than $kT$, the thermal energy.\textsuperscript{28} With an adsorption energy of $-10^6 kT$, micron-sized particles usually remain trapped at the oil-water interface once adsorbed, and unless they have partial wettability with one of the bulk phase the interfacial film will buckle during compression of the interface.\textsuperscript{28-29} NPs, in contrast, have a much weaker adsorption energy, which allows for desorption (or reversible adsorption) to happen. In addition, they are also commonly functionalized with surface active ligands, which can introduce ambiguity in their role as a particle or surfactant in decreasing the excess interfacial energy. Even with adsorption energy that could be comparable to $kT$, there are limited reports on reversible adsorption of NP to oil-water interfaces\textsuperscript{30-33}, not to mention robust thermodynamic models capable of
interpreting and predicting the equilibrium partitioning of particles between bulk media and fluid interfaces.

1.2 Outstanding Questions

The equilibrium partitioning of NPs is analogous to the formation of Gibbs monolayers of soluble surfactants, where the surfactants partition between a bulk phase and the interface.\(^{26,34}\) It could have important practical applications. For example, it would be a necessary criteria for the spontaneous formation of Pickering emulsions\(^ {35-36}\), or for recycling and sustainable processes\(^8\), or as part of an additive manufacturing step\(^ {37}\). The weaker adsorption energy allows for dynamic and reversible adsorption of NPs at interface, opening an exciting avenue towards better understanding of thermodynamics of particles at the oil-water interface. In order to better understand the mechanism of NP adsorption at the interface, as well as the influence on interfacial properties upon adsorption, here are the questions to ask:

1. Can NPs adsorbed at a fluid interface maintain dynamic equilibrium with the suspension phase (bulk phase)? At a given temperature, reversible dynamic equilibrium requires both chemical and mechanical equilibrium. In particular, the adsorbed amount should only depend on the chemical potential of the NPs in the bulk (a simple function of NP concentration for dilute systems). For example, the adsorbed amount should remain constant during expansion or contraction of the interfacial area to demonstrate mechanical equilibrium. If these criteria are fulfilled, then the adsorption isotherm and EOS for the NPs at the oil-water interface could be compared to thermodynamic models.
2. Does NPs adsorption alter interfacial tension (IFT) in a similar manner as the surfactants? Quantitative characterization of the dynamic equilibrium between NPs dispersed in the bulk and adsorbed at the interface illustrates the similarities and differences between adsorption of NPs from that of amphiphilic surfactants. The measurement and model of equilibrium EOSs for Gibbs monolayers formed by NPs would help elucidate the role played by particle-particle and particle-interface interactions, change in interfacial area, and IFT on the adsorption dynamic and equilibrium state.

3. Could surfactants adsorption compete with NP adsorption? Competitive adsorption between surfactant mixtures, and surfactant and macromolecule mixtures has been employed as a strategy to control the interfacial properties and composition.\textsuperscript{38-39} Different from those mixtures, the adsorption energy of NPs and surfactant could differ by a lot. Thus the question appear as whether surfactant addition can be utilized to adjust the surface coverage of NP, and / or interfacial properties.

1.3 Dissertation Overview

This dissertation is organized as follows.

Chapter 2 introduces the background of this dissertation, including 1) theoretical background of Gibbs adsorption isotherm and equation of state (EOS), wetting contribution of particle adsorption onto a fluid-fluid interface, and Ward-Tordai model describing mass transfer from a bulk phase to a fluid interface; 2) tools and techniques used throughout this dissertation; and 3) synthesis of the ion-pair gold NP used throughout this work.
Chapter 3 presents the thermodynamic verification of experimental system. Specifically the NPs adsorbed at the interface achieves dynamic equilibrium with the bulk dispersion, demonstrated from both chemical and mechanical perspective.

Chapter 4 illustrate the thermodynamic framework, explaining change in surface pressure of a particle-laden interface due to surface activity (described by GAI) and wetting of NP at the interface (area replacement). The framework highlight the difference in the pressure from NP adsorption compared to pressure from compression of a particle laden interface.

Chapter 5 shows the competitive adsorption of NP and surfactant mixture, demonstrates the capability of controlling surface coverage of NP and interfacial property simultaneously.

Chapter 6 illustrates the applicability of Ward-Tordai model in combination with adsorption isotherm and wetting EOS to describe both NP adsorption dynamics, and NP-surfactant mixture adsorption dynamic.

Chapter 7 shows the general usage of the dynamic model to predict diffusion-limited adsorption dynamics of NPs onto a fluid interface.

Chapter 8 summarizes the conclusions from these chapters, and explains briefly of future work related to this dissertation.
2 Background

2.1 Theory

2.1.1 Thermodynamics of the interface

Gibbs adsorption equation has been widely applied to describe the adsorption of surfactants at liquid-liquid (gas) interface. It is often applied in surfactants at fluid interfaces, to relate the easier measured quantity (interfacial tension, $\gamma$, or surface pressure, $\Pi$) to the unknown property of surface excess, $\Gamma$. To derive the Gibbs adsorption equation from the thermodynamic fundamental equations, we focus on the oil-water interface first.

We use superscript “$\sigma$” to denote parameters or properties of the interface, and superscript “$w$” and “$o$” to denote parameters or properties of the ‘water’ phase and ‘oil’ phase, respectively. We can start from the generalized thermodynamic description of a system with oil-water interface, the Helmholtz free energy, $F$, is given by\(^1\):

$$dF = -SdT - P^o dV^o - P^w dV^w + \gamma dA + \sum \mu_i dn_i .$$

(2.1)

Integral of Eqn. (2.1) while maintaining all the intensive variables constant (here $T$ is constant), would result in the following equation:

$$F = -P^o V^o - P^w V^w + \gamma A + \sum \mu_i n_i .$$

(2.2)

Then we could do a total derivative of Eqn. (2.2), given by:

$$dF = -P^o dV^o - V^o dP^o - P^w dV^w - V^w dP^w + \gamma dA + A d\gamma + \sum \mu_i dn_i + \sum n_i d\mu_i$$

(2.3)
By doing a subtraction of Eqn. (2.1) from Eqn. (2.3), we would obtain the famous Gibbs-Duhem equation\textsuperscript{40} for the whole system, given by:

\[ 0 = SdT - V^o dP^o - V^w dP^w + Ad\gamma + \sum n_i d\mu_i \ . \tag{2.4} \]

Similar procedure can be followed to obtain the Gibbs-Duhem equations for the two phases, oil phase and water phase, respectively, given by:

\[ 0 = S^o dT - V^o dP^o + \sum n^o_i d\mu_i \ , \tag{2.5} \]

\[ 0 = S^w dT - V^w dP^w + \sum n^w_i d\mu_i \ . \tag{2.6} \]

Now we can subtract Eqn. (2.5) and Eqn. (2.6) from Eqn. (2.4), resulting in:

\[ 0 = \left( S - S^o - S^w \right) dT + Ad\gamma + \sum \left( n_i - n^o_i - n^w_i \right) d\mu_i \ . \tag{2.7} \]

Since \( S^\sigma = S - S^o - S^w \), and \( n^\sigma_i = n_i - n^o_i - n^w_i \), we denote \( s^\sigma = S^\sigma / A \), and \( \Gamma_i = n^\sigma_i / A \).

Dividing the two sides of Eqn. (2.7) by the total interfacial area, \( A \), we will obtain:

\[ d\gamma = -s^\sigma dT - \sum \Gamma_i d\mu_i \ . \tag{2.8} \]

At constant temperature \( T \), we would get the Gibbs adsorption equation, given by:

\[ d\gamma = -\sum \Gamma_i d\mu_i \ . \tag{2.9} \]

It can be noted from Eqn. (2.9) that Gibbs adsorption equation relates the surface excess (harder to measure for surfactants) with the interfacial tension (easier to measure) consistently with the thermodynamics of the system.

One of the most commonly used adsorption model dictating equilibrium adsorption is the Frumkin model, which follows the thermodynamic equilibrium criteria described by Gibbs equation. The Frumkin model accounts for non-ideal interactions between adsorbed
species within the interface. The Frumkin adsorption isotherm and the corresponding EOS, which dictates the surface excess, and surface activity of the surfactant \( i \), is given by\(^{1,41}\): \[
C_i(\theta) = a_{l,i} \frac{\theta}{1-\theta} \exp(K_i \theta),
\] (2.10)
\[
\Pi_{i,i} = -kT \Gamma_{i,\infty} \left[ \ln(1-\theta_i) - 0.5K_i \theta_i^2 \right].
\] (2.11)

Here \( i \) is the adsorbed species (surfactants for example), \( C_i \) is the bulk concentration of the species, \( a_{l,i} \) is its dissociation constant characterizing its affinity to the interface, \( \theta_i = \Gamma_i / \Gamma_{i,\infty} \) is the fractional coverage of the surface active species at the interface, with \( \Gamma_{i,\infty} \) being the maximum coverage at the interface. Finally, \( K_i \) can be interpreted the net interaction energy between species \( i \) at the interface relative to thermal energy (i.e., \( kT \)).\(^{42}\)

A positive value for \( K_i \) indicates repulsive interaction and a negative value indicates attraction between adsorbed species.\(^{43}\) When \( K_i = 0 \), the Frumkin adsorption isotherm reduces to Langmuir isotherm, which assumes no interactions at the interface.\(^{44}\) The first term in the bracket in Eqn. (2.11) is the entropic contribution and the second term is the enthalpic contribution caused by the interactions between the surface active species.

### 2.1.2 Wetting EOS of particles at the interface

The driving force for particle adsorption onto a fluid interface is that particle replaces the interfacial area proportional to the particle cross-sectional area, given by\(^{45}\): \[
\frac{\Delta E}{\text{particle}} = -\pi r_{NP}^2 \gamma_{OW} \left(1 \pm \cos \theta_{OW} \right)^2.
\] (2.12)
Du et al. has predicted an increase in the effective surface pressure ($\Pi_{NP}$) due to the adsorption of NP, which is given by\textsuperscript{46}:

$$\Pi_{NP} = |\Delta E| \times \Gamma_{NP}.$$ \hspace{1cm} (2.13)

Here $\Gamma_{NP}$ is the surface excess of NPs at the interface. In this limit, an increase in surface pressure is measured upon their adsorption due to a decrease in the interfacial energy caused by the favorable wetting of the NP at the interface\textsuperscript{47}.

2.1.3 Ward-Tordai model

The adsorption of surfactants onto an initial clean interface is governed by two primary mechanisms, including the diffusion of the species from the bulk phase to the sub-surface regime, as well as the adsorption from the sub-surface region onto the interface, as shown in Figure 2-2.\textsuperscript{48} For diffusion-controlled mass transfer process, assumption is made on the instantaneous equilibrium between the coverage at the interface ($\Gamma$) and the concentration
in the sub-surface region \((c_i)\).\(^{49}\) Thus the rate of adsorption is limited by the diffusion from bulk phase to the sub-surface region, which can be described by Fick’s law of diffusion, given by\(^{50}\):

\[
j_{i} \bigg|_{x \to 0^+} = -D \frac{\partial C}{\partial x} \bigg|_{x \to 0^+}. \tag{2.14}
\]

Here \(j_{i} \bigg|_{x \to 0^+}\) is the flux on the extreme boundary of the bulk phase (\(i.e.,\) the interface).

**Figure 2-2.** Schematic of single component adsorption dynamics, with two fundamental transport process governing the dynamics, including adsorption (black up arrow) and desorption (black down arrow) between the sub-surface region and the interface, as well as diffusion (red arrows) from bulk phase to the sub-surface regime.

Ward-Tordai model (Eqn. (2.16)) can be obtained by solving Fick’s law and one dimensional mass conservation equation, given by\(^{49-50}\):

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}. \tag{2.15}
\]

Details of derivation can be found in Ref.\(^{49}\), where analogy to heat transfer model has been made to capture the mass transfer onto a clean interface. Both simple diffusion
(transient diffusion onto the interface) and back diffusion are considered. The Ward-Tordai model has been employed to capture the diffusion-limited adsorption of various surfactants\textsuperscript{51-52} and macromolecules\textsuperscript{53-54}. In this work pendant drop shape analysis is used and thus the solution under spherical coordinate is applied, which is given by\textsuperscript{55}:

$$\Gamma_i(t) = \frac{D_i}{\pi} \left\{ 2C_i t - \sqrt{t} \int_0^t \frac{c_i(\tau)}{\sqrt{t-\tau}} d\tau \right\} + \frac{D_i}{r_D} \left\{ C_i t - \int_0^t c_i(\tau) d\tau \right\}$$

(2.16)

where $i$ is the surface active species (surfactant for example), $C_i$ is the bulk concentration of the species, $r_D$ is the radius of the pendent droplet, $D_i$ is the diffusivity of the species, which can be estimated using Stokes-Einstein model, given by\textsuperscript{56}:

$$D_{SE} = \frac{kT}{6\pi\mu r_i}$$

(2.17)

where $D_{SE}$ specifically refers to the diffusivity estimated using Eqn. (2.17), $k$ is the Boltzmann constant, $T$ is temperature, $\mu$ is the fluid viscosity, and $r_i$ is the radius of the surface active species.

### 2.2 Tools and Techniques

#### 2.2.1 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) measures the absorption or reflectance in the ultraviolet-visible spectral region. In this work, UV-Vis is employed to measure the absorbance of gold NP dispersions over the range of 350 – 800 nm in a disposable cuvette. Within this spectrum, molecules absorb the energy and undergo electronic transitions. The
UV-Vis spectra for 5 nm gold NPs have a surface plasmon band (SPB) at 530 ± 3 nm, and
535 ± 3 nm SPB for 10 nm NPs. The SPB does not shift with the pH of the aqueous phase.

The bulk concentration of NPs in the aqueous phase is calculated through the Beer-
Lambert law\textsuperscript{47-58} from the adsorption at 450 nm ($A_{450}$) using Eqn. (2.18):

$$C = \frac{A_{450}}{d_0 \varepsilon},$$

(2.18)

where $d_0$ is the width of cuvette (1 cm), and $\varepsilon$ is the extinction coefficient of gold NPs at
450 nm wavelength. To determine the extinction coefficient, NP suspensions are prepared
by dispersing a known mass of dry NPs in a known volume of aqueous solutions. The bulk
concentration of NPs is computed using the core radius of 2.5 nm (or 5 nm for large NPs),
and 19.3 g/mL as the density of gold. The absorbance was measured for a range of known
concentration and compared with the one obtained for aqueous solution in absence of
dispersed NPs. Based on this calibration, the extinction coefficient from the specific
absorbance at 450 nm wavelength can be determined.

2.2.2 Pendent drop shape analysis

Dynamic interfacial tension measurements at the toluene-water interface are conducted
at room temperature using the pendant drop method. A toluene drop is formed in aqueous
solutions of dispersed NPs. The shape of the droplet is fit to the Young-Laplace equation,
which describes the pressure difference, $\Delta P$, between inside and outside the fluid interface
(Laplace pressure). Denote the principal radii of curvature to be $R_i$, the Young-Laplace
equation is given by\textsuperscript{1}: 

\begin{align*}
\Delta P &= \frac{4 \gamma}{R_i} \\
\gamma &= \text{surface tension} \\
R_i &= \text{principal radii of curvature}
\end{align*}
\[ \Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right), \tag{2.19} \]

where \( \gamma \) is the interfacial tension. It needs to be pointed out that the droplet undergoes a force balance between gravitational force and interfacial tension. Since gravity is different depending on height, it gives rise to a pressure gradient on the \( z \)-axis. Denote the bottom of the droplet to be the reference plane, where the principal radii of curvature, \( R_1 = R_2 = R \), also denote the Laplace pressure at this plane to be \( \Delta P_0 \) (Figure 2-3). The Laplace pressure on the in the \( z \)-direction is given by:

\[ \Delta P(z) = \Delta P_0 \pm \Delta \rho g z. \tag{2.20} \]

A geometry relationship can be obtained from Figure 2-3, given by \( R_2 = x / \sin \Phi \). Thus combining the geometry correction with Eqns. (2.19)-(2.20) results in:

\[ \frac{1}{R_1} + \frac{\sin \Phi}{x} = \frac{2}{R} \pm \frac{\Delta \rho g z}{\gamma}. \tag{2.21} \]

A parameter using the arc length, \( s \), of the droplet shape is introduced and Eqn. (2.21) can be recast into a set of first-order differential equations (details in Ref\textsuperscript{25}), that are solvable numerically, the result of which is the interfacial tension of the corresponding droplet shape.
2.3 Ion-Pair Gold NP Synthesis

Ion-pair gold NPs are synthesized and characterized following a previous developed protocol\textsuperscript{32} that is based on the Brust synthesis method\textsuperscript{59-60}.

First of all, 2 mM TPeA–MHA ion-pair solution (MHA : TPeAOH = 1 : 4 in molar ratio) is prepared by mixing 28 mg MHA and 637 µL TPeAOH in 50 mL toluene. Followed by sonication for 20 min before oil bath at 60°C for 4 days. The formation of ion-pair can be verified by FT-IR with the absence of COOH dimer peak (1713 cm\textsuperscript{-1}).

After ion-pair solution is ready, gold NPs can be synthesized. Initially a cleaned 200 mL yellow capped flask with 150 mL toluene is put into oil bath for 45 min in order to equilibrate the temperature of toluene with ion-pair solution temperature. After that, 337
mg TPeACl is added to the 150 mL toluene, and stirred gently with a long stir bar for 10 min until it fully dissolved. Followed by dissolving 92.8 mg HAuCl₄ in 2 mL water, the solution is added to 150 mL toluene, gentle stirring is applied to transfer the gold salt to the toluene phase. After around 25 min stirring, the tiny amount of aqueous solution is clear and toluene phase is yellow, indicating the fully transferring of Au³⁺ to toluene phase. The clear aqueous phase is removed prior to the addition of the 50 mL of 2 mM TPeA–MHA ion-pair solution. Then freshly prepared 0.2 M NaBH₄ (6 mL) solution is added to the reaction flask while vigorously stirring applied. The toluene phase becomes purple right after the addition of NaBH₄. The entire solution preparation and synthesis takes place in an oil bath (60 °C). The reaction takes place for 40 s to obtain 5 nm core diameter gold NPs, and 80 s to obtain 10 nm core diameter gold NPs. The aqueous phase is removed after the reaction and the particles sediment in the remaining toluene phase over a 4 h period, during which the toluene phase becomes clear. After removal of the toluene, the particles are washed at least five times with pure toluene (to remove unbound thiol and excess TPeA cations) before drying in air overnight.

Fourier transform infrared spectroscopy (FTIR, Varian 660-IR spectrometer with DTGS detector) is employed to collect the IR absorbance spectra in transmission mode to determine the chemical functionality on the surface of the gold NPs. A NaCl salt disk (Fisher Scientific) is used initially to obtain the background scan. Gold NPs are dispersed in toluene through 2 min sonication, then 0.5 mL of the dispersion (~0.01 mg/mL) is placed on the NaCl salt disk and left drying at room temperature. For all the NPs investigated here
a 1 : 1 stoichiometric ratio of TPeA : MHA on the surface was confirmed based on a
 correlation between the measured CH\textsubscript{2}/CH\textsubscript{3} IR absorbance intensity and the molar ratio of
 TPeA : MHA\textsuperscript{32, 61} The presence of absorbance peak at 1560 cm\textsuperscript{-1} (COO\textsuperscript{-} stretching), as
well as the absence of COOH dimer peak (1713 cm\textsuperscript{-1}) indicates ion-pair formation.

Transmission Electron Microscopy (TEM, Philips EM 420) is performed at an
acceleration voltage of 100 kV on carbon-coated copper grids (Electron Microscopy
Services, Hatfield, PA). A 5 \textmu L drop of gold NPs dispersion (~0.01 mg/mL in 2-propanol)
is deposited on the TEM grid and allowed to dry in air overnight. The particle size
distribution is obtained from image analysis of at least 200 individual particles. Note here
that the TEM images are taken prior to purification (will be discussed later) and that
aggregates can also form during the drying process and increase the polydispersity.

Dynamic light scattering (DLS, Zetasizer Nano-ZS90, Malvern Instruments) is
performed to determine the size and zeta potentials of the NPs in aqueous solutions. Size
data is collected using disposable plastic cuvettes (4 optical side Polystyrene, Sarstedt AG
& Co) and processed through standard options provided in the Malvern software. The Zeta-
potential of gold NPs is measured in disposable folded capillary cuvettes (1006C, Malvern
Instruments) and the Debye-Hückel equation is used to calculate the zeta potential from
the mobility. Note here that these measurements are at the limit of the resolution of the
instrument and the difference observed with increasing pH might not be significant.
3 Reversible Partitioning of Nanoparticles at an Oil-Water Interface

3.1 Overview

In this chapter, the dynamic equilibrium of ion-pair gold NP is investigated. Equilibrium partitioning is characterized with UV-Vis spectroscopy, while equilibrium surface pressure, dynamic equilibrium are examined via pendant drop shape analysis.

3.2 Introduction

Adsorbed microparticles and nanoparticles (NPs) at fluid interfaces are being used as efficient stabilizers for emulsions and foams since 1903.\textsuperscript{2, 62-63} Particle-laden interfaces play also an important role in technologies such as in catalysis\textsuperscript{64}, sensors\textsuperscript{65-66}, load-bearing foams\textsuperscript{67}, and optics\textsuperscript{22, 68-69}. In addition, the liquid-liquid interface, due to its self-healing nature and its accessibility to light and chemical reagents, is an attractive nanomanufacturing platform to assemble particles. Fluid interfaces hold promise as a well-

\textsuperscript{a} Reprint with permission from Hua, X.; Bevan, M. A.; Frechette, J., \textit{Langmuir}, 2016, 32 (44), 11341-11352. Copyright © 2016 American Chemical Society
defined substrate to engineer NP configurations in a manner that exploits their unique individual and collective properties\textsuperscript{70}. In contrast to dried NP monolayers on solid substrates, which are both static and irreversible, control over reversible adsorption of NPs at oil–water interfaces could allow for \textit{in situ} manipulation of the equilibrium concentration and configuration. The reversible adsorption of NP to oil-water interfaces has been observed experimentally\textsuperscript{30-33}, however robust thermodynamic models capable of interpreting and predicting the equilibrium partitioning of particles between bulk media and fluid interfaces\textsuperscript{8} are still lacking.

While amphiphilic surfactants tend to lower the interfacial tension (\(\gamma_{ow}\)) the adsorption of microparticle or nanoparticle is treated in terms of a decrease in interfacial area. The change in energy \(\Delta E / \text{particle}\) associated with the adsorption of a spherical particle of radius \(r\) at an oil-water interface is expressed by\textsuperscript{47}

\[
\frac{\Delta E}{\text{particle}} = -\pi r^2 \gamma_{ow} \left(1 \pm \cos \theta_{ow}\right)^2. \tag{3.1}
\]

This driving force is due to the replacement of fluid-fluid area with particles that form a contact angle \(\theta_{ow}\) at the interface, and is largest when \(\theta_{ow} = 90^\circ\).\textsuperscript{27,47} To remain adsorbed at the interface the energy gained from adsorption must be sufficiently larger than \(kT\), the thermal energy.\textsuperscript{28} With an adsorption energy of \(\sim 10^6 \ kT\) micron-sized particles usually remain trapped at the oil-water interface once adsorbed, and unless they have partial wettability with one of the bulk phase the interfacial film will buckle during compression of the interface.\textsuperscript{28-29}

NPs, in contrast, have a much weaker adsorption energy. In addition, they are also commonly functionalized with surface active ligands, which can introduce ambiguity in
their role as a particle or surfactant in decreasing the excess interfacial energy. As a result, dynamic equilibrium with one of the fluid phases can be achieved for sub-10 nm particles.\textsuperscript{33} Such partitioning is analogous to the formation of Gibbs monolayers of soluble surfactants, where the surfactants partition between a bulk phase and the interface.\textsuperscript{34, 47} Equilibrium partitioning of NPs between a bulk phase and a fluid interface could have important practical applications. For example, it would be a necessary criteria for the spontaneous formation of Pickering emulsions\textsuperscript{35, 71}, or for recycling and sustainable processes\textsuperscript{8}, or as part of an additive manufacturing step\textsuperscript{37}. The weaker adsorption energy allows for dynamic and reversible adsorption of NPs at interface, opening an exciting avenue towards better understanding of thermodynamics of particles at the oil-water interface.

Modulation of the interactions between the particles, or between the particles and the interface via a change in either applied potential\textsuperscript{72-75}, pH\textsuperscript{31-32, 76-77}, ionic strength\textsuperscript{65, 78}, or other physicochemical interactions\textsuperscript{79-80} is an avenue to shift the dynamic equilibrium between unadsorbed and adsorbed particles. For example Reincke \textit{et al.}\textsuperscript{31} relied on a change in pH to control the adsorption of 6 nm gold NPs at a water-heptane interface, and developed a model based on electrostatic interaction that was in qualitative agreement with the pH-dependent adsorption. A change in the potential at an interface between two immiscible electrolyte solutions has been employed by Su \textit{et al.}\textsuperscript{68, 72-73} to control the adsorption of 1.5 nm gold NPs, and the adsorbed amount was calculated on the basis of the Lippmann equation. Voltage-dependent adsorption of NPs at such interfaces was recently characterized using X-ray scattering and molecular dynamic simulations to highlight how ion correlation on the particles affect their adsorption.\textsuperscript{75, 81}
In our previous work we synthesized gold NPs functionalized with ion pairs ligands.\textsuperscript{32} The ion-pair ligands consist of negatively charged thiol (mercaptohexadecanoic acid, MHA) that are paired with organic cations (tetraalkylammonium, TAA) to form a self-assembled monolayer on the gold particles.\textsuperscript{61, 82-84} The contact angle of the particle at the oil-water interface was estimated from macroscopic wetting measurements to be $\theta_{ow} = 120^\circ$, which gives an adsorption energy of $25-50 \ kT$ for $r = 2.5 - 3.5 \text{ nm}$ NPs. Zeta potential measurements have also shown that the particles are negatively charged in aqueous solutions with $\text{pH} > 10$. We observed that the ion-pair NPs adsorb to the oil-water interface over a wide range of $\text{pH}$ of the aqueous solution, and that an increase in $\text{pH}$ shifts the adsorption equilibrium from the interface to the bulk aqueous phase. We hypothesized that the $\text{pH}$ modulated electrostatic interactions (particle-particle and/or particle-interface), which in turn shifted the dynamic equilibrium between the particles and the oil-water interface.

Even with an adsorption energy that is comparable to $kT$, there are only limited reports of NPs displaying a reversible dynamic equilibrium similar to that of soluble surfactants. At a given temperature, reversible dynamic equilibrium requires both chemical and mechanical equilibrium. In particular, the adsorbed amount should only depend on the chemical potential of the NPs in the bulk (a simple function of NP concentration for dilute systems). For example, the adsorbed amount should remain constant during expansion or contraction of the interfacial area to demonstrate mechanical equilibrium. If these criteria are fulfilled, then the adsorption isotherm and EOS for the NPs at the oil-water interface could be compared to thermodynamic models.
Limits on reversibility have been observed, for example, when adsorption slows down significantly due to crowding prior to reaching equilibrium\textsuperscript{27,85}, when colloidal stability is not maintained at the fluid interface\textsuperscript{86-88}, or when the interactions between the particles adsorbed at the interface lead to the formation of a film with solid-like properties\textsuperscript{89-90}. In these cases, desorption of the particles either due to compression or change in volume fraction in the bulk phase does not occur, and particles remain trapped at the interface. The influence of crowding at the interface on the adsorption dynamics was recently investigated using Monte Carlo simulations by Schwenke and co-workers\textsuperscript{27} where they studied the relationship between adsorption kinetics and the particle configuration at the interface.

There has been instances, however, where reversible behavior has been observed. Garbin \textit{et al.}\textsuperscript{33}, demonstrated mechanical reversibility through the expulsion of NPs from an oil-water interface during the compression of a pendant drop. Lin \textit{et al.}\textsuperscript{91} visualized the exchange between 2.7 nm and 4.6 nm particles adsorbed at the interface using fluorescence microscopy, and Du \textit{et al.}\textsuperscript{46} observed the desorption of NPs due to dilution of the bulk phase. Quantitative characterization of the dynamic equilibrium between NPs dispersed in the bulk and adsorbed at the interface illustrates the similarities and differences between adsorption of NPs from that of amphiphilic surfactants. The measurement and model of equilibrium EOSs for Gibbs monolayers formed by NPs would help elucidate the role played by particle-particle and particle-interface interactions, change in interfacial area, and surface activity on the adsorption dynamic and equilibrium state. For instance, a recent report by Garbin \textit{et al.}\textsuperscript{92} points toward the importance of ligand reorganization at the fluid interface on the stabilization and dynamics of the adsorbed NPs.
In this paper we investigate and model the partitioning of NPs between an aqueous phase and a toluene-aqueous interface. The particles consist of 5 nm gold NPs functionalized with ion-pair ligands for which the adsorbed amount can be modulated by the pH of the aqueous sub-phase. We combine pendant drop measurements and absorbance spectroscopy to evaluate the reversibility of the NP adsorption (see Figure 3-1). We find conditions for dynamic equilibrium with the aqueous bulk phase where a Gibbs monolayer is formed. We measure the EOS of the NPs at the interface under conditions where equilibrium with the bulk aqueous phase is maintained for two different pH. We compare our measurements to the Frumkin model for the adsorption isotherm. We also compare the EOS with both a wetting and Frumkin model.

**Figure 3-1.** Overview of the experimental approach. (Top) UV-Vis measurement is employed to characterize the adsorption of the NP to the water-toluene interface. (Bottom) Pendant drop measurements are employed to determine the surface pressure for a given bulk concentration and to assess mechanical reversibility during expansion and contraction of the droplets.
3.3 Materials and Methods

3.3.1 Reagents and chemicals

All reagents and chemicals were used as received. Potassium hydroxide (KOH, 99.9%) pellets, 16-mercaptohexadecanoic acid (MHA, 99%), gold chloride hydrate (HAuCl₄, >49% Au), sodium borohydride (NaBH₄, >96%), tetrapentylammonium chloride (TPeACl, 99%), tetrapentylammonium hydroxide (TPeAOH, 20wt% 1M aqueous solution) were purchased from Sigma-Aldrich. Sulfuric acid (H₂SO₄, 95.0 to 98.0 w/w %), hydrogen peroxide (H₂O₂, 30.0 to 32.0%), 2-propanol (> 99.9%), toluene (> 99.8%), NaCl salt disk, and RBS 35 Detergent Concentrate were purchased from Fisher Scientific. Deionized water (DIW, 18.2MΩ⋅cm) was obtained from a Milli-Q Gradient system. All glassware, unless otherwise noted, was thoroughly cleaned with piranha solution (4:1 H₂SO₄:H₂O₂), rinsed with DIW and dried overnight in air prior to use. All experiments are performed at 293K.

3.3.2 Synthesis and characterization of ion-pair gold NPs

Ion-pair gold NPs are synthesized following our previous protocol³² that is based on the Brust synthesis⁵⁹. In short, 92.8 mg of HAuCl₄ dissolved in 2 mL water is added to 337 mg TPeACl in 150 mL toluene to transfer the gold salt to the toluene phase. The solution is stirred for 25 min after which 50 mL of 2 mM TPeA–MHA ion-pair solution is added. The ion-pairs were made according to our previously described protocol.⁸⁴ Then freshly prepared 0.2 M NaBH₄ (6 mL) is added to the reaction flask while vigorously stirring. The toluene phase becomes purple right after the addition of NaBH₄. The entire solution preparation and synthesis takes place in an oil bath (60 °C). The aqueous phase is removed
after 40 s and the particles sediment in the remaining toluene phase over a 4 h period, during which the toluene phase becomes clear. After removal of the toluene via evaporation the particles are washed five times with pure toluene (to remove unbound thiol and excess TPeA cations) before drying in air overnight.

Fourier transform infrared spectroscopy (FTIR, Varian 660-IR spectrometer with DTGS detector) is employed to collect the IR absorbance spectra in transmission mode to determine the chemical functionality on the surface of the gold NPs. A NaCl salt disk (Fisher Scientific) is used initially to obtain the background scan. Gold NPs are dispersed in toluene through 2 min sonication, then 0.5 mL of the dispersion (~0.01 mg/mL) is placed on the NaCl salt disk and left drying at room temperature. For all the NPs investigated here a 1:1 stoichiometric ratio of TPeA: MHA on the surface was confirmed (Figure S3-1A-B, Table S3-1) based on a correlation between the measured CH\textsubscript{2}/CH\textsubscript{3} IR absorbance intensity and the molar ratio of TPeA : MHA.\textsuperscript{32, 61} The absorbance peak at 1560 cm\textsuperscript{-1} (COO\textsuperscript{-} stretching) also indicates ion-pair formation (Figure S3-1B).

Transmission Electron Microscopy (TEM, Philips EM 420) is performed at an acceleration voltage of 100 kV on carbon-coated copper grids (Electron Microscopy Services, Hatfield, PA). A 5 μL drop of gold NPs dispersion (~0.01 mg/mL in 2-propanol) is deposited on the TEM grid and allowed to dry in air overnight. The particle size distribution is obtained from image analysis of at least 100 individual particles and is 5 ± 2 nm (Figure S3-1C). Note here that the TEM images were taken prior to purification and that aggregates can also form during the drying process and increase the polydispersity.

Dynamic light scattering (DLS, Zetasizer Nano-ZS90, Malvern Instruments) is performed to determine the size and zeta potentials of the NPs in aqueous solutions. Size
data is collected using disposable plastic cuvettes (4 optical side Polystyrene, Sarstedt AG & Co) and processed through standard options provided in the Malvern software. The Zeta-potential of gold NPs is measured in disposable folded capillary cuvettes (1006C, Malvern Instruments) and the Debye-Hückel equation is used to calculate the zeta potential from the mobility. The radius of the ion-pair gold NPs decreases slightly with increasing pH, with $5 \pm 2$ nm at pH 11.0 and $3 \pm 2$ nm at pH 11.7. These measurements are at the limit of the resolution of the instrument and the difference observed with increasing pH might not be significant. Zeta potential measurements indicate decreasing surface potential at lower pH, -45 ± 3 mV at pH 11.0 compared with -52 ± 2 mV at pH 11.7, in agreement with our previous work.32 Adsorption of TPeA$^+$ ions onto gold NPs surface from the solution at lower pH could also explain the observed change in both the zeta potential and size of the particles.

Throughout the experiments aqueous dispersions gold NPs are maintained at an ionic strength of 5 mM. The pH is controlled while keeping the ionic strength constant by mixing different ratios of 5 mM TPeACl and 5 mM TPeAOH solutions. Prior to characterization the NPs suspensions are purified by removing a layer of adsorbed particles as well as large aggregates from the oil-water interface. This is achieved by shaking vigorously after adding toluene to the aqueous phase. After stirring, particles and aggregates adsorb at the toluene-water interface, which are removed by pipetting out the toluene. The purified particle solution is then placed in a 20 mm glass cuvette (Starna Cell Inc.) with a thin layer of toluene on top.
3.3.3 Adsorption measurements

The absorbance of the gold NPs dispersions is measured by ultraviolet-visible spectroscopy (UV-Vis, Cary 50 spectrophotometer) over the range of 400-800 nm in the same disposable cuvettes as the ones used for DLS measurements. The UV-Vis spectra has a surface plasmon band (SPB) at 530 ± 3 nm (see Supporting Information (SI) Figure S3-1D for the absorption spectra), consistent with our previous work.\textsuperscript{32} The SPB does not shift with the pH of the aqueous phase.

The number density, $\rho$, of NPs in the aqueous phase is calculated through the Beer-Lambert law\textsuperscript{57-58} from the adsorption at 450 nm ($A_{450}$) using Eqn. (3.2)

$$\rho = \frac{A_{450}}{d_0 \varepsilon}, \quad (3.2)$$

where $d_0$ is the width of cuvette (1 cm), and $\varepsilon$ is the extinction coefficient of gold NPs at 450 nm wavelength. To determine the extinction coefficient particle suspensions were prepared by dispersing a known mass of dry NPs in a known volume of aqueous solutions. The number density of NPs was computed using a uniform core radius of 2.5 nm, and 19.3 g/mL as the density of gold. The absorbance was measured for a range of known number density and compared with the one obtained for aqueous solution in absence of dispersed NPs. Based on this calibration we determine the extinction coefficient from the specific absorbance at 450 nm wavelength to be $\varepsilon = 1.9 \times 10^7$ M\(^{-1}\)cm\(^{-1}\), similar to reported literature value\textsuperscript{93}. We determine the adsorbed amount of NPs from the depletion of particles from the bulk phase (as obtained from the change in absorbance) and the known interfacial area. In addition, no plasmon absorption in the UV-Vis absorbance spectrum (or any change in color) is observed in the toluene phase indicating that the AuNPs cannot be dispersed in toluene at all pHs considered here.
3.3.4 Dynamic interfacial tension measurements

Dynamic interfacial tension measurements at the toluene-water interface are conducted at room temperature using the pendant drop method. A toluene drop is formed in aqueous solutions of dispersed NPs, and once the drop is formed the interfacial tension is monitored for 6000 s at every 20 s. All the measurements and fits of the drop shapes to the Young-Laplace equation are performed with a FTA 125 apparatus and software (First Ten Angstroms). Prior to the measurements the glass cuvette, glass syringe (2.5 mL, Model 1002 TLL SYR, Hamilton Company), stainless steel J-needle (20 Gauge, 304SS hub, Cadence Inc.), as well as the tubing (Fisher scientific Co.) are sonicated in 1% v/v dilute RBS solution and rinsed thoroughly with deionized water. The glass syringe, stainless steel J-needle, and the tubing were dried with N$_2$ and stored in toluene overnight while the glass cuvettes are stored in deionized water. Right before the measurements the cuvette is rinsed thoroughly with the gold NPs solution and the needle and tubing with toluene. All connections are sealed with Teflon tape (Fisher scientific Co.) first and then Parafilm (Parafilm M). For expansion of the drops a rate of 0.1 mL/min was employed, while for the contraction we used 5 $\mu$L/min. The lower contraction rate was necessary due to experimental limitations of our apparatus.

3.4 Results and Discussions

3.4.1 Adsorption isotherm

Adsorption isotherms for the NPs are obtained from UV-Vis spectroscopy for adsorption from aqueous solutions at pH 11.0 and at pH 11.7. In Figure 3-2 the adsorbed amount is obtained from the change in the bulk NP concentration after the addition of
toluene to an aqueous particle suspension. In our analysis, we assume that particles do not adsorb to the air-water interface, in agreement with pendant drop measurements (see SI Figure S3-3 for the surface tension measurement at the air-water interface). We also assume that the decrease of the NP concentration in the bulk aqueous phase upon the addition of toluene, as measured from absorbance, is due to adsorption to the toluene-water interface. Note that the toluene phase is added gently (no shaking/stirring). Preliminary results show that vigorously stirring the solution leads to slightly higher adsorption than the one we obtain under quiescent conditions, especially in the high-coverage region. This discrepancy is likely due to the increase in the meniscus area via pinning of the contact line during stirring. The absorbance measurements are performed 24 hours after the addition of the toluene phase. The area used to calculate surface density is 1.4 cm², which is the meniscus area of the solution in the glass vials used in experiments (see SI Figure S3-4 for the image and calculation of the meniscus area). A particle radius of 3.5 nm is assumed to obtain the area fraction of NPs at the interface, this value includes an average core radius of 2.5 nm and an additional 1 nm for the ligand on the surface. Assuming the NPs form a contact angle of 90º with the oil-water interface gives the maximum area fraction for the NPs in a 2D plane. The exact location of this 2D plane might be slightly above or below the fluid interface depending on the true contact angle of the particles at the oil-water interface (estimate of θ_{ow} = 120º are based on macroscopic wetting measurements).

For the two pH investigated, the adsorption of the NPs at the toluene-water interface increases with increasing bulk concentration and then reaches a plateau (Figure 3-2). For bulk NP concentrations that spans over three orders of magnitude our measurements indicate that we always maintain sub-monolayer coverage; the area fractions are always
less than the hard disk limit of 0.907. For a given volume fraction of NPs in the bulk phase we find a larger adsorbed amount at pH 11.0 than at pH 11.7. This observation is consistent with our previous work where we showed that an increase in pH leads to desorption of the ion-pair NPs from the oil-water interface. Partitioning of particles between a bulk phase and an interface has been shown previously, but to the best of our knowledge, this is the first complete equilibrium adsorption isotherm for Gibbs monolayers of NPs at an oil-water interface.

![Figure 3-2](image)

Figure 3-2. Adsorption isotherms obtained at pH 11.0 (red circles) and pH 11.7 (black triangles). Dashed lines are sigmoidal fits of the experimental data used for Figure 3-7 (described in the SI Eqn. (3.11)). A core NP diameter of 5 nm is employed to get the surface excess from the absorbance. The area fraction is calculated based on a diameter of 7 nm to account for the size of the ligand on the surface of the NPs.

3.4.2 Dynamic interfacial tension measurements

Dynamic interfacial tension measurements are an effective means to study transport and adsorption dynamics of dispersed particles to oil-water interfaces.
of a Gibbs monolayers via the adsorption of NPs to an oil-water interface decreases the effective tension of the interface, and as the adsorption proceeds the decrease in interfacial tension reaches a plateau (see Figure 3-3). This decrease can be understood in terms of a 2D osmotic pressure (or surface pressure, \( \Pi = \gamma_0 - \gamma \)) between a bare and a particle-laden interface due to their entropic and enthalpic differences.\(^8\)\(^,\)\(^9\) For a reversible process at equilibrium with a bulk phase, the surface tension reaches a plateau once dynamic equilibrium is established between adsorbed particles and the bulk suspension (i.e., when the rate of adsorption is equal to the rate of desorption).

Here we measure the interfacial tension of a pendant drop of toluene in aqueous TPeA\(^+\) solutions at either pH 11.0 or at pH 11.7 for a range of known NP volume fractions in the bulk aqueous phase (as measured via absorbance spectroscopy), see Figure 3-3. We see that a plateau in interfacial tension is reached at long times for all the concentration of NPs investigated. We also find that an increase in the concentration of NPs leads to a decrease in the equilibrium interfacial tension, consistent with an increase in the adsorbed amount. For the highest bulk concentrations (viii-ix for both pH for example) the surface tension no longer decreases with increasing of the bulk NP concentration. This behavior can be due to kinetic limitations or saturation of the interfacial layer. This paper focuses on the equilibrium behavior, and as such, modeling of the transient dynamic data will be revisited in future work.
Figure 3-3. Dynamic interfacial tension of a pendant toluene drop formed in aqueous solutions with dispersed NPs at (A) 5 mM pH 11.0 TPeA\(^+\) solution, and (B) 5 mM pH 11.7 TPeAOH. The NP number densities in (A) are: (i) 0, (ii) \(2.1 \times 10^{11}\) /mL, (iii) \(3.7 \times 10^{11}\) /mL, (iv) \(6.6 \times 10^{11}\) /mL, (v) \(1.1 \times 10^{12}\) /mL, (vi) \(1.9 \times 10^{12}\) /mL, (vii) \(2.3 \times 10^{12}\) /mL, (viii) \(1.1 \times 10^{13}\) /mL, (ix) \(1.7 \times 10^{13}\) /mL. The NPs number densities in (B) are: (i) 0, (ii) \(2.4 \times 10^{11}\) /mL, (iii) \(6.0 \times 10^{11}\) /mL, (iv) \(6.3 \times 10^{11}\) /mL, (v) \(1.1 \times 10^{12}\) /mL, (vi) \(3.5 \times 10^{12}\) /mL, (vii) \(5.2 \times 10^{12}\) /mL, (viii) \(1.0 \times 10^{13}\) /mL, (ix) \(1.6 \times 10^{13}\) /mL.

Dynamic equilibrium, irreversible adsorption, or dynamic arrest in the adsorbed layer (e.g., due to packing effects at high coverages or aggregation via interparticle attraction)
could all lead to the plateaus observed in the interfacial tension. Testing for path-independent mechanical reversibility can help assess if equilibrium is reached in the adsorption process after the interfacial tension reaches a plateau. At a given bulk NP concentration, path-independent mechanical reversibility implies that an equilibrated value of the interfacial tension is recovered after either expansion or contraction of the drop if sufficient time is allowed for equilibration (in contrast, NPs that are irreversibly adsorbed, aggregated, or dynamically arrested would not achieve the same plateau with either expansion or contraction). Expansion of a drop creates new bare oil-water interfacial area, and adsorption of NPs is required to recover the original interfacial tension. Similarly, desorption of NPs is necessary to maintain a constant surface concentration after the contraction of a drop. This desorption step can be hindered because of possible particle aggregation at the interface, irreversible adsorption of large NPs, or particle-particle attraction, all of which can prevent the expulsion of particles from the interface.

To characterize the mechanical reversibility of the measured surface pressures, a toluene droplet is formed in aqueous solutions with a known concentration of dispersed NPs. Once the interfacial tension reaches a plateau, the pendant drop is mechanically disturbed either by increasing or decreasing the droplet area. After the perturbation, the droplet is allowed to stabilize in the solution until the interfacial tension reaches a plateau. We considered the adsorption to be mechanically reversible if, after an increase or reduction of the interfacial area by 30%, the interfacial tension remained within 0.5 mN/m of the initial plateau value. We performed these experiments for increasing bulk NP concentrations and show, in Figure 3-4, the highest bulk concentration (for each pH) at which reversible behavior is observed. We did not observe buckling of the interface in any
of our compression experiments, indicating that the work done during compression can overcome the adsorption energy of the particle to the interface. In the case where mechanical reversibility is observed, desorption of the nanoparticles is favored over increasing the interfacial area via buckling. For pH 11.7 we could not find a bulk concentration where the adsorbed layer did not display mechanical reversibility, but at higher bulk concentrations than the one reported in Figure 3-4, we could not decrease the area by 30% and maintain a stable droplet (i.e., avoid drop breakup or detachment). As a result, reversibility of the two highest concentrations at pH 11.7 could not be evaluated. Nevertheless, when comparing between the two pH we find that reversibility can be obtained with higher bulk NPs density at pH 11.7 than at pH 11.0.

![Figure 3-4. Dynamic interfacial tension recorded every 20 s for 6000 s for a toluene drop formed in an aqueous solution at (top) 5 mM TPeA<sup>+</sup> pH 11.0 with NPs number density of 1.9×10<sup>12</sup> /mL, and at (bottom) 5 mM TPeAOH pH 11.7 with NPs number density of 5.2×10<sup>12</sup> /mL. (A, D) Initial stabilization of the interfacial tension of a bare toluene droplet in an aqueous solution with dispersed NPs. (B, E) After the interfacial tension reaches its steady-state value, a second measurement is started. (B, E) Stabilization of the interfacial tension.](image-url)
tension after an increase in area of the droplet of (top) 29%, and (bottom) 38% at 0.1 mL/min. (C, F) Stabilization of the interfacial tension after a decrease in area of the droplet of (top) 35%, and (bottom) 32% at 5 μL/min. Schematics of the processes are shown in the insets.

At pH 11.0 we are able to evaluate the mechanical reversibility for all bulk NP concentrations. We find that for the three highest bulk NP concentrations the interfacial tension does not recover to its initial value after compression of a pendant drop (see Figure 3-5), suggesting that dynamic equilibrium is not reached at these concentrations. In the absence of mechanical reversibility, NP adsorption leads to plateau values that are path and size dependent. For example, Figure 3-5 shows the time evolution of the interfacial tension of a toluene drop once it has been compressed to different extents. Prior to compression, the interfacial tension of the drops were the same, and stable at a value shown by the dashed line. The more the area is decreased, the lower is the final interfacial tension, and the more it deviates from its initial value. Again, the loss of mechanical reversibility could result from particle aggregation, arrest, or irreversible adsorption at the interface, which could all occur during the initial adsorption process or during compression (owing to the rather severe 30% reduction in interfacial area).29,103
Figure 3-5. Interfacial tension (IFT) measured after the area of NP-laden toluene droplets is reduced in aqueous solution at pH 11.0 with NPs number density $1.1 \times 10^{13}$ /mL. The droplet area is decreased by 23% (circle), 31% (triangle), and 40% (square) respectively at 5 μL/min after interfacial tension reached equilibrium. Black dashed line is the equilibrium interfacial tension used as a reference line.

The equilibrated surface pressure as a function of bulk concentration of NPs is shown in Figure 3-6 for the two aqueous solution pHs. The equilibrium surface pressure ($\Pi$) is calculated from $\Pi = \gamma_{0} - \gamma_{eq}$ using the equilibrium plateau values of the interfacial tension ($\gamma_{eq}$) in Figure 3-2.¹ We see that for both pH the curves follow the same qualitative behavior, but that for a given concentration of NPs the surface pressure is always higher at pH 11.0 than at pH 11.7, which is consistent with a higher surface coverage at lower pH. Also shown in Figure 3-6 are the steady-state surface pressures for the bulk NP concentrations where the adsorbed layer is not in mechanical equilibrium with the aqueous phase. These are $\Pi$ values inferred from non-equilibrium plateau $\gamma$ values, but care must be taken in their interpretation as we discuss in the following. For pH 11.7 the limit of
reversibility could not be tested for the last two points (again, because drops became unstable). Mechanical reversibility was confirmed for all the other NP concentrations.

Once the surface pressure reaches $\Pi = 13.5 \text{mN/m}$ for the experiments performed at pH 11.0 and $\Pi = 12 \text{mN/m}$ for the experiments performed at pH 11.7, an increase in bulk concentration no longer lead to an increase in surface pressure. It is interesting to compare these limiting values in surface pressure to the ones obtained by Garbin et al.\textsuperscript{33} where they found, that $\Pi = 13 \text{mN/m}$ was the maximum surface pressure that could be attained during compression to avoid expulsion from the interface of 4.6 nm gold NPs functionalized with a very different ligand. They hypothesized that for $\Pi > 13 \text{mN/m}$ ligand-mediated steric repulsion between particles was sufficiently strong to favor expulsion of the particles to the bulk phase. Brownian dynamic simulations were in quantitative agreement with this argument.\textsuperscript{92} The ligands employed here are completely different than the ones employed in their work but we reach a very similar limiting surface pressure.
Figure 3-6. Equilibrium surface pressure ($\Pi$) of a NP-laden toluene-water interface as a function of bulk NPs number density at pH 11.0 (red circles) and pH 11.7 (Black triangles). $\Pi = \gamma_0 - \gamma_{eq}$, where $\gamma_0$ is the interfacial tension for the pure solvent. Here $\gamma_0 = 23.2$ mN/m at pH 11.0, and $\gamma_0 = 23.0$ mN/m at pH 11.7. Hollow spheres mark the high concentration of gold NPs at pH 11.0 where mechanical reversibility cannot be obtained. Grey triangles stand for the concentrations at pH 11.7 where the mechanical reversibility cannot be tested due to instability of pendant droplet during experiments. Dashed lines are to guide the eye.

The Gibbs adsorption equation (GAE) relates the surface pressure to the adsorbed amount (and vice versa). The simplest form of the GAE is given in Eqns. (3.3)-(3.4) for the case of a single species $i$ that adsorbs to an interface from a dilute bulk solution.

$$d\Pi = \sum \Gamma_i d\mu_i,$$

$$d\mu_i = kTd\ln(f_i \rho_i) = kTd\ln\rho_i.$$
In Eqn. (3.4) the term $\mu_i$ refers to the chemical potential of species $i$, $f_i$ is its activity coefficient, $k$ is the Boltzmann constant, and $T$ is the temperature. The GAE is a thermodynamic requirement for the dynamic equilibrium between adsorbing species and a bulk phase for a constant interfacial area $A$. If we apply the GAE to the pressure isotherms shown in Figure 3-6, we obtain adsorbed amounts that are physically unrealistic (by orders of magnitude) and beyond our experimental error. We suggest that this discrepancy can be understood by the fact that the mechanism for the reduction of the surface pressure during the adsorption of NP is mainly a reduction in interfacial area and not due to surface activity$^{46,97}$. The GAE in its simplest form of Eqns. (3.3)-(3.4) might be better suited for the adsorption of amphiphilic surfactants than of NPs. In addition, we likely also have co-adsorption of the surface active tetraalkyl ammonium ions from the aqueous NP solution (to maintain charge neutrality at the interface, for example). In terms of precedent, we could only find a limited number of literature studies where the adsorption of NPs to a fluid interface was tested against the GAE. The 3D distribution of nanocrystals to a fluid interface was measured via cryogenic electron tomography in conjunction with surface tension measurements by van Rijssel$^{104}$. The authors did not find agreement between the adsorption of the nanocrystals and the GAE and attributed the differences to the adsorption of surface active species that had a stronger effect on the interfacial tension than the adsorption/desorption of the nanocrystals. Kutuzov and coworkers extracted an adsorbed amount that were between 1-10 monolayers by differentiating their pressure isotherms.$^{95}$ Although the calculated adsorbed amount ($\Gamma$ vs. $\rho$) was not verified independently, their results also question the use of the validity of the GAE for their experimental system.
3.4.3 EOS for a Gibbs monolayer of NPs

We analyze together the surface pressure data (Figure 3-6) and adsorption isotherm data (Figure 3-2) to obtain the EOS for the adsorbed NPs in equilibrium with an aqueous dispersion at pH 11.0 and pH 11.7. It is important to note that the adsorption and surface pressure isotherms are independent data sets; we do not infer the adsorbed amount from the surface pressure. To the best of our knowledge this is the first report of the measurements of EOS for adsorbed NPs in chemical and mechanical equilibrium with a bulk phase (i.e., where fluxes re-establish dynamic equilibrium following a chemical or mechanical disturbance). The EOS shown in Figure 3-7 are obtained as follows: first we fit the adsorption isotherm (Figure 3-2) with a sigmoidal curve (dashed lines in Figure 3-2 and see the SI for details of the sigmoidal fits). We then used the fitted curve to map the adsorbed amount to the surface pressure isotherm ($\Pi(\rho)$, Figure 3-6) to obtain the corresponding EOS (i.e. $\Pi(\Gamma)$, Figure 3-7). The open points for pH 11.0 represent measurements where the equilibrium surface pressure were not in mechanical equilibrium with the bulk phase.

The measured EOS indicate that the surface pressure is a function of both the NP area fraction and the pH of the aqueous phase. The fact that the surface pressure is significant even at large areas per particle (i.e., reciprocal of #/area (abscissa in Figure 3-7) >> core particle cross sectional area) indicates that the particle-particle interactions are repulsive and relatively long-ranged. For both pH investigated the EOS display the same qualitative features: first, at low coverage ($\eta < 0.2$) the surface pressure is significant and builds up rapidly and linearly with the increase in the adsorbed amount, then at higher coverage (
the surface pressure increases much more slowly, almost reaching a limiting value.

It is interesting to compare and contrast the EOS for pH 11.0 and pH 11.7. In the low coverage region (see inset of Figure 3-7), the adsorbed layer in equilibrium with an aqueous phase at pH 11.7 has a higher surface pressure for a given area fraction than an adsorbed layer in equilibrium with a solution of pH 11.0. This difference between the two isotherms at low coverage implies different particle-particle interactions at the interface at pH 11.7. Note that the adsorption isotherm shown in Figure 3-2 reaches a significantly lower maximum coverage for particles in equilibrium with a solution at pH 11.7 than at pH 11.0. Similarly, at a given surface pressure the area fraction for the layer in equilibrium with a solution at pH 11.7 is lower than for a monolayer in equilibrium with a solution at pH 11.0. All of these observations taken together suggest the repulsion between NPs within the interface is longer-ranged at pH 11.7 than at pH 11.0. In the region where the pressure increases more slowly with area fraction (\( \eta > 0.2 \)), we observe that the effect of pH on the EOS essentially disappears and the two curves overlap with each other.

Previous pressure-area measurements for adsorbed NPs point out the importance of steric repulsion at high coverage.\textsuperscript{33,102} If the near-limiting values in surface pressure are due to steric repulsion, having the curves overlap at high \( \eta \) suggests similar core sizes for the particles in equilibrium with the aqueous solution at pH 11.0 and at pH 11.7. Note here that the particles are likely too far apart for the ligand to touch, but the bulky cation employed here (TPeA\textsuperscript{+}) is also amphiphilic, and co-adsorbs on the particles and at the interface. Co-adsorption and/or exchange between the NPs and cations at the interface could possibly explain the decrease in slope of the EOS, and could contribute to the
repulsive interactions in the high coverage region. This possibility is not unlike the recent work by Bera et al.\textsuperscript{75} who demonstrated that ion condensation on the particles altered their equilibrium configuration at the interface.

**Figure 3-7.** EOSs for NPs adsorption at the oil-water interface. The data points are obtained by combining the data of Figure 3-2 and Figure 3-6. Red circles are experimental data for an aqueous phase at pH 11.0 and black triangles represent experimental data for pH 11.7. Hollow symbols at pH 11.0 indicate that the corresponding data points did not display mechanical reversibility. The dashed lines are results for fitting $\Pi(\Gamma)$ to the Frumkin equation of state (Eqn. (3.8)) using the parameters shown in Table 3-1. The solid lines are results for fitting to the EOS based on an adsorption energy model (Eqn. (3.9)) using only the 4 lowest $\Pi(\Gamma)$. The inset shows the EOS in the low coverage region, and the axes titles are the same as the ones in the main figure.
Comparison with adsorption isotherm and EOS models

The Frumkin adsorption isotherm, which is often applied for the adsorption of soluble surfactants\textsuperscript{105}, is employed here to describe the adsorption of NPs to the toluene-water interface. However, in contrast to surfactant adsorption, the area taken by an adsorbed NP is significantly larger from that of the other species in solution (water, salt). In an attempt to take into account this size difference, we employ a form of the Frumkin adsorption isotherm that is derived for the case where the adsorbed species has a much larger cross-section than the one of the solvent molecules, as given by Eqns. (3.5)-(3.7):

$$\rho = a \frac{\theta_{NP}}{n_i (1-\theta_{NP})^\eta} \exp[Kn_i \theta_{NP}] ,$$  \hspace{1cm} (3.5)

$$\theta_{NP} = \Gamma \omega_1 ,$$  \hspace{1cm} (3.6)

$$n_i = \omega_i / \omega_0 ,$$  \hspace{1cm} (3.7)

where $\rho$ is the number density of NPs in bulk phase, $a$ is the dissociation constant\textsuperscript{106}, $\Gamma$ is the surface excess of NP, $\omega_1$ is the cross-sectional area of a NP at the interface, the surface area fraction is $\theta_{NP}$, and the solvent molecular area at the interface is $\omega_0$. In Eqn. (3.7) a smaller $a$ represents stronger attraction between particles and the interface. The interaction between adsorbed species within the interface is captured by $K$, where a negative $K$ represents attraction and a positive value repulsion. The Frumkin EOS shares the same parameters as the Frumkin adsorption isotherm and is shown in Eqn. (3.8).\textsuperscript{106} Together the EOS of Eqn. (3.8) and the adsorption isotherm of Eqn. (3.5) satisfy thermodynamic equilibrium between the interface and the bulk phase\textsuperscript{106-107} and obeys the GAE (Eqn. (3.3)). An analogous form of Eqn. (3.8) was employed to describe pressure-area measurements of NPs irreversibly adsorbed to an air-water interface.\textsuperscript{99}
\[
\Pi = -\frac{kT}{\omega_0} \left[ \ln(1 - \theta_{NP}) + (1 - \frac{1}{n_1})\theta_{NP} - 0.5K\theta_{NP}^2 \right]. \quad (3.8)
\]

Alternatively, Du et al.\textsuperscript{46} derived an EOS where the surface pressure is caused by the replacement of fluid-fluid interfacial area by NPs, as shown in Eqn. (3.9):

\[
\Pi = \Gamma \Delta E. \quad (3.9)
\]

In Eqn. (3.9) \( \Delta E \) is an adsorption energy/particle (or an effective adsorption energy), such as the one shown in Eqn. (3.1). This EOS neglects any particle-particle interactions, and as such its validity should be limited to low area fraction. Also, Eqn. (3.9) has not been derived in the context of phase equilibria between the adsorbed and dispersed NPs. The dependence of \( \Delta E \) on the particle cross section area has been validated by assuming a limiting area fraction of 0.907.\textsuperscript{46,108} Simulations using dissipative particle dynamics have highlighted the importance of incorporating particle-particle interactions along with Eqn. (3.9).\textsuperscript{97} Finally, this second EOS has not been tested in experiments where \( \Pi \) and \( \Gamma \) have been measured independently.
Figure 3-8. Fits of the experimental data to (A) Frumkin adsorption isotherm (Eqn. (3.5), dashed lines) and (B) pressure isotherm (Eqns. (3.5) and (3.9), solid lines). The fitting parameters for Eqn. (3.5) are given in Table 3-1. Red circles are experimental data for pH 11.0, and black triangles represent experimental data for pH 11.7. Hollow symbols indicate data points not used for in the fitting algorithm.

We fit the adsorption isotherm to Eqn. (3.5) and the EOS to Eqn. (3.8), and the best fitting parameters for both curves are shown in Table 3-1. To better capture the low area fraction and dissociation constant of the adsorption isotherm, the adsorption data from the
plateau in Figure 3-8A was not included in the fits. Similarly, the fits to the EOS were limited to the points where reversible behavior was observed. The fitting parameters for the two curves should be the same for thermodynamic equilibrium with a surface active species (and in the absence of co-adsorbing species). It is obvious from the reported values in Table 3-1 that the values for the fitting parameters for the two curves are different. In particular, the difference in the relative size between the particles and the solvent molecules (captured by $n_1$) is drastically different when comparing the fits to the EOS with the ones for the adsorption isotherm at a given pH. Note here that $\omega_i$ is not a fitting parameter since $n_1 = \omega_i / \omega_0$. For both pH we find that the value of $n_1$ increases significantly between the EOS and adsorption isotherm. A possible explanation is that for the adsorption isotherm we only measure the core size of the adsorbed particles. Our experiments would not be able to detect if the particles bring along ions during the adsorption process (to maintain charge neutrality for example). Such an effect could possibly lead to different values for $n_1$ at a given pH.

Table 3-1. Parameters obtained from fitting the $\Pi(\rho)$ and $\Gamma(\rho)$ curves (dashed lines in Figure 3-7 and Figure 3-8A) using Eqn. (3.5) for the adsorption isotherm and Eqn. (3.8) for the EOS. $^a \omega_i = n_1 \times \omega_i$

<table>
<thead>
<tr>
<th></th>
<th>pH 11.0</th>
<th></th>
<th>pH 11.7</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>Adsorption isotherm</td>
<td>EOS</td>
<td>Adsorption isotherm</td>
<td>EOS</td>
</tr>
<tr>
<td>$a$ ($10^{20} \text{ m}^3$)</td>
<td>5.0</td>
<td>N/A</td>
<td>12.5</td>
<td>N/A</td>
</tr>
<tr>
<td>$\omega_0$ ($10^{-18} \text{ m}^2$)</td>
<td>0.33</td>
<td>0.30</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>$n_1$</td>
<td>8.0</td>
<td>350</td>
<td>9.1</td>
<td>750</td>
</tr>
<tr>
<td>$K$</td>
<td>5.5</td>
<td>8.0</td>
<td>6.6</td>
<td>10.0</td>
</tr>
<tr>
<td>$\omega_i$ ($10^{-18} \text{ m}^2$) $^a$</td>
<td>2.64</td>
<td>105</td>
<td>2.73</td>
<td>150</td>
</tr>
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</table>
Overall, the adsorption isotherm is well-described by the Frumkin equation over most of the range of NP concentrations investigated here (Figure 3-8A). We find that the most significant difference between adsorbed particles in equilibrium with a solution at pH 11.0 from those in equilibrium with a solution at pH 11.7 is the smaller dissociation constant, $a$, which is consistent with stronger particle attraction to the interface at pH 11.0. Wetting of the core particle produces attraction to the interface and hence adsorption (whereas interactions within interface will depend on lateral electrostatic interactions). We also find that the maximum packing is larger at pH 11.0 ($\eta = 0.62$) than at pH 11.7 ($\eta = 0.43$). However the plateau value is not well-described by the Frumkin isotherm, which could be due to the same kinetic limitations that limit reversibility in the pendant drop experiments performed at higher bulk NP concentration.

On the other hand, the EOS (Eqn. (3.8)) captures the general magnitude of the $\Pi(\Gamma)$ curve, the agreement is not excellent even in the low area fraction (see inset of Figure 3-7). The deviations become even more significant when the surface pressure is greater than approx. 10 mN/m and when $\eta > 0.2$. When looking at the effect of pH in the values of the fitted parameters, the differences between the two EOS in Figure 3-7 cannot be attributed to differences in dissociation constant (the equation of state does not depend on the dissociation constant.) Therefore, based on this model, the most significant differences between the two pHs is the change in $n_1$, the ratio between the area taken by the particle to that of a solvent molecule, which increases with pH.

We also compared our measurements to the EOS of Eqn. (3.9) by forcing a straight line from the origin through the low coverage region of Figure 3-7 for the data at each pH. As shown in the inset of Figure 3-7, the EOS is linear in the low coverage region ($R^2 = 0.90$ at
pH 11.0 and $R^2 = 0.93$ at pH 11.7). The slope of the lines correspond to an adsorption energy. We obtain $\Delta E = 552kT$ for pH 11.0 and 941 $kT$ for pH 11.7. If we assume $\theta_{ow} = 90^\circ$ in Eqn. (3.1) we obtain a radius of 5.5 nm at pH 11.0 and 7.3 nm at pH 11.7, about 1.5-2.0 times the value we obtain based on TEM or DLS. While the effective size of the NPs obtained are not unreasonable, the values of $\Delta E$ are much larger than what would be expected for a reversible process. It is possible that the NPs employed here are both surface active (due to the amphiphilic ligands) and act to replace oil-water interfacial area during the adsorption process. Therefore a thermodynamic model that incorporates both effects, along with particle-particle interactions might be necessary to fully capture the measured EOS.

At higher surface coverage we observe significant deviations when we compare the measured EOS to either Eqn. (3.8) or Eqn. (3.9). Similar deviations are observed in the surface pressure isotherm taken at higher bulk concentrations. In this region a more complex model (perhaps based on non-equilibrium effects) appears to be necessary to describe our experiments. For example, competitive adsorption between co-ions and the NPs could also explain the self-limiting behavior observed at higher area fraction. In that case replacement between adsorbed ions and NPs could explain the increase in adsorption as measured from the adsorption isotherm while maintaining a near constant pressure in the pressure isotherm. Similarly, polydispersity and deviations from a spherical shape could also have an effect on the EOS that is not considered here. In this case, a more complex adsorption model would then be necessary to model our experimental results.

The effect of pH on the values of the Frumkin parameters shown in Table 3-1 lead to significant differences in the adsorption & pressure isotherms as well as in the EOS. It is
interesting that a change in pH in the bulk phase (at constant ionic strength) has such an impact on the adsorbed nanoparticles. A change in pH can modify the electrostatic interactions between adsorbed particles (captured by $K$) as well as between the particles and the interface (captured by $a$). The pH could also have an effect on the ligands on the particles. Indeed we observe a small change in the zeta potential with pH (see our previous work\textsuperscript{32} for more details). Our results indicate that modulation of interactions (electrostatics, van der Waals, steric) between adsorbed particles and between the particles and the interface can be sufficient to compete with the adsorption energy to shift the equilibrium behavior of adsorbed particles. Such strategies could be employed, for example, toward controlling continuously the assembly and configurations of NPs at oil-water interfaces. Our experiments could also help test models for adsorption and EOS that include a particle-level description of the interactions (\textit{i.e.}, particle-particle and particle-interface potentials).

3.5 Conclusion

We characterized the formation of Gibbs monolayers of NPs that adsorb to a toluene-water interface from a bulk aqueous phase. We compared and contrasted the NP adsorption to the formation of Gibbs monolayers of soluble surfactants. We showed similarities between NPs and surfactants in terms of the adsorption isotherm, and in terms of mechanical reversibility of the adsorbed NPs. We find that the adsorption isotherm can be well-described by the Frumkin adsorption isotherm up to (but not including) saturation. In contrast the EOS shows strong deviation from the Frumkin description. Comparison with the Frumkin EOS shows reasonable agreement at low area fraction, and the fitted parameters indicate a large size difference between the adsorbed particles and the solvent.
molecules, and this difference becomes more pronounced as the pH increases. Alternatively, a linear model for the EOS that is based on the replacement of the interfacial area by NPs can capture the low area fraction portion of the EOS very well, but yields an effective adsorption energy that is too large for a reversible process. In addition to these deviations, when the area fraction is greater than 0.2 the surface pressure hardly changes with the adsorbed amount, likely due to non-equilibrium effects. Our results highlight the need to develop EOS that combine the amphiphilic nature of the NPs with their capability to replace oil-water interfacial area, as well as explicit particle-particle interactions within the fluid interface.

3.6 Supporting Information

3.6.1 Characterization of ion-pair gold NPs

Fourier transform infrared (FTIR) spectroscopy is employed to characterize the ligands on the gold nanoparticles. As described in our previous work\textsuperscript{32}, the presence of TPeA\textsuperscript{+} as part of the ligands on the nanoparticles leads to asymmetric and symmetric CH\textsubscript{3} stretching bands at 2955 ± 3 cm\textsuperscript{-1} and 2870 ± 2 cm\textsuperscript{-1}, respectively (Figure S3-1A). Deprotonation of the carboxylate group is evident from the presence of a band at 1560 cm\textsuperscript{-1} (asymmetric COO\textsuperscript{-} stretch), and consistent with the presence of ion-pairs between TPeA\textsuperscript{+} ions and deprotonated MHA bound on the gold surface (Figure S3-1B). We previously calibrated the CH\textsubscript{2}/CH\textsubscript{3} infrared absorbance intensity\textsuperscript{32} to quantify the stoichiometry between TPeA\textsuperscript{+} and MHA on the surface of gold nanoparticles. Using the same calibration here we find that the ligands on the particles employed in the experiments have a stoichiometric ratio that is also very close to 1 : 1 TPeA\textsuperscript{+} : MHA (Table S3-1).
Gold nanoparticles were imaged using transmission electron microscopy (TEM) (Figure S3-1C) right after synthesis. Prior to electron microscopy the nanoparticles are dispersed in 2-propanol by sonication for 5 min, after which 5 μL of the solution is dispensed on carbon-coated copper grids (Electron Microscopy Services, Hatfield, PA). The grid is left to dry at room temperature overnight before imaging, which caused some aggregation of nanoparticles on the grid. Ultraviolet-visible spectroscopy is employed to characterize the size and concentration of gold nanoparticles dispersed in 5 mM TPeA\(^+\) solution at both pH 11.0 and at pH 11.7. A surface plasma band (SPB) peak at 530 ± 3 nm (Figure S3-1D) indicates the size of gold nanoparticles in aqueous solution around 5 nm according to our previous characterization.\(^{32}\)

Table S3-1. Measured composition of ion-pair gold nanoparticles as synthesized. Molar ratio of TPeA : MHA was calculated using the calibration for the CH\(_2\)/CH\(_3\) intensity ratio.\(^{32}\)

<table>
<thead>
<tr>
<th>TPeA : MHA molar ratio</th>
<th>Asym. CH(_2)/CH(_3)</th>
<th>Sym. CH(_2)/CH(_3)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1.0 ± 0.2</td>
<td>0.9 ± 0.1</td>
</tr>
</tbody>
</table>
Figure S3-1. Characterization of gold nanoparticles. (A-B) FT-IR characterization of ion-pair gold nanoparticles as synthesized. (C) TEM imaging: gold nanoparticles are dispersed in 2-propanol using sonication and dispersed on TEM grid prior to purification. (D) UV-Vis absorption spectrum of NPs dispersed in aqueous solution at pH 11.7.

3.6.2 Effect of purification process on adsorption at oil-water interface

As described in the main text, NPs are purified prior to experiments by using the interface as a selective filter to remove aggregates and large size particles from synthesis. Figure S3-2 shows the effect on UV SPB before and after this purification process in reducing NPs polydispersity (left). The removal of aggregates/large particles have a
significant effect on adsorption of NPs at oil-water interface, likely due to the preference of aggregates to adsorb compared to single nanoparticles.

**Figure S3-2.** (Left) UV-Vis spectra for NPs prior to (black solid line) and after (red dashed line) purification process. (Right) Adsorption prior to (Red cycles) and after (Black triangles) purification process. Dashed lines are to guide the eye.

### 3.6.3 Adsorption of gold NPs at air-water interface

A key assumption in the determination of the adsorption isotherm is that there is negligible adsorption of nanoparticles at the air-water interface. We verified this assumption by performing control experiments using pendant drop tensiometry. In the control experiments, first the interfacial tension of pure air-water interface is obtained, and a value of 72.8 ± 0.2 mN/m (black cycles in Figure S3-3) is obtained in agreement with a known reported values for a clean air-water interfaces. Subsequently, we measured the interfacial tension of 5 mM pH 11.0 and pH 11.7 TPeA⁺ aqueous solutions without gold nanoparticles (Figure S3-3, red hollow cycle representing pH 11.0, and black hollow triangle standing for pH 11.7 aqueous solution). It is obvious from Figure S3-3 that increasing the pH and adding TPeA⁺ ions to the aqueous solution decreases the surface
tension to around 65.4 ± 0.4 mN/m (we did not observe a significant effect of pH on the surface tension based on similar measurements with KOH solutions). Finally, we repeated the measurements but with the addition of gold nanoparticles at a number density of $3.5 \times 10^{12}$/mL in the aqueous phase. As shown in Figure S3-3, the air-water interfacial tension does not change when particles are present in the aqueous phase (Figure S3-3, red cycles for pH 11.0 case, and black triangles showing pH 11.7 case), confirming that the gold nanoparticles investigated here do not adsorb at the air-water interface during the experimental time scale.

**Figure S3-3.** Interfacial tension measurements at the air-water interface. (black solid circle) air-water interface, (black hollow circle) air-water interface with 5 mM pH 11.0 aqueous solution, (black hollow triangle) air-water interface with 5 mM pH 11.7 aqueous solution, (black hollow square) air-water interface with gold nanoparticles dispersed in 5 mM pH 11.0 aqueous solution, (black solid triangle) air-water interface with gold
nanoparticles dispersed in 5 mM pH 11.7 aqueous solution. Black dashed line marking 72.8 mN/m is used as a reference for pure air-water interface tension.

3.6.4 Estimating meniscus area

The glass vials employed for nanoparticle adsorption have a diameter of 1.3 cm. The curvature of the meniscus formed at the toluene-water interface increases the nominal interfacial area. We imaged the toluene-water interface after equilibration with NPs dispersions (Figure S3-4A, B). We observe that the contact angle between interface and the cylinder wall is close to 90°, indicating that the interface is approaching a flat surface. The meniscus area was calculated by solving for the height, \( h(r) \), against the wall, by following Eqn. (3.10) and integrating for the whole cylindrical wall (which is the glass vial here).

\[
\gamma \left\{ \frac{h^*(r)}{\left[1+(h'(r))^2\right]^{3/2}} + \frac{h'(r)}{r\left[1+(h'(r))^2\right]^{1/2}} \right\} + \Delta \rho gh(r) = 0, \quad (3.10)
\]

where \( \gamma \) is the interfacial tension of the two immiscible solvents, \( r \) is the horizontal distance of interface away from center of cylinder cross-section, \( \Delta \rho \) is the density difference between two solvents, \( g \) is the gravitational acceleration. The meniscus area can then be solved as a function of contact angle between interface and the cylindrical wall (Figure S3-4C). Since the imaging indicates a contact angle approaching 90°, and meniscus area is reaching a plateau with contact angle greater than 70°, we use the meniscus area of 1.4 cm², corresponding to a contact angle of 70°.
Figure S3-4. Image of the toluene-water interface at pH 11.0 (A), and pH 11.7 (B). (C) Calculated meniscus area at different contact angles between interface and the wall.

3.6.5 Effect of TPeA$^+$ ions on interfacial tension

It has been noticed that with TPeA$^+$ ions only, interfacial tension varies from 35 mN/m (pure toluene-water interfacial tension) to 23.0 mN/m (toluene-5 mM TPeAOH solution interfacial tension). Dynamic interfacial tension was measured in the absence of nanoparticles at the toluene-5mM solution interface. The 5mM solution is a mixture of 5 mM KOH (pH 11.7) and 5mM TPeAOH (pH 11.7) at different ratios, so that a constant pH and ionic strength can be maintained. It is obvious from Figure S3-5 that as the concentration of TPeA ions increases, the interfacial tension decreases from 33.6 mN/m (5 mM KOH solution) to 23.0 mN/m (5 mM TPeAOH solution).
Figure S3-5. Interfacial tension at toluene-5 mM pH 11.7 solution interface vs. TPeA$^+$ ions concentration in solutions.

3.6.6 Function to describe the adsorption isotherm

A sigmoidal function is used to map the adsorption isotherm data to create the equation of state in Figure 3-6. We employed the Chapman function (see Eqn. (3.11)).

$$
\Gamma(\rho) = y_0 + a \times \left[1 - \exp\left(-b \times \rho\right)\right].
$$

(3.11)

Table S3-2. Fitting parameter for the sigmoidal fit used to map the adsorption isotherm in Figure 3-1.

<table>
<thead>
<tr>
<th></th>
<th>pH 11.0</th>
<th>pH 11.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$ (1/nm$^2$)</td>
<td>-2.7864×10$^4$</td>
<td>3.4610×10$^{-5}$</td>
</tr>
<tr>
<td>$a$ (1/nm$^2$)</td>
<td>0.0160</td>
<td>0.0105</td>
</tr>
<tr>
<td>$b$ (1/mL)</td>
<td>8.5945×10$^{-14}$</td>
<td>9.2449×10$^{-14}$</td>
</tr>
<tr>
<td>$c$</td>
<td>0.5585</td>
<td>0.8257</td>
</tr>
</tbody>
</table>

3.6.7 Fitting adsorption isotherm and EOS to Frumkin equations

The adsorption isotherm at low concentration and the low concentration data in the EOS (first four data points of each pH) were fit to the Frumkin equation using MATLAB...
2015b by minimizing the distance between each of the data points and the theoretical curve, that is, to minimize the following Eqn. (3.12):

\[ d = \frac{1}{m} \sum_{i=1}^{m} (X_i - \tilde{X}_i), \]

where \( X_i \) is the experimental data and \( \tilde{X}_i \) is the theoretical predicted value. In the adsorption isotherm, \( X \) is the bulk NPs density, in EOS, \( X \) is the surface pressure \( \Pi \). As described by the Eqns. (3.5)-(3.8) in main text, the fitting parameters for the adsorption isotherm are \( a \), \( K \), \( n \), and \( \omega_0 \), while for the EOS, the fitting parameters are \( K \), \( n \), and \( \omega_0 \).
4 Thermodynamic Analysis of Nanoparticle Adsorption at Fluid Interface

4.1 Overview

This chapter elucidates the effect of NPs adsorption on interfacial properties from a thermodynamic perspective. A thermodynamically consistent framework is developed to relate bulk concentration, adsorbed amount at the interface, and surface pressure. Differences in surface pressure due to adsorption and compression is also highlighted in this chapter.

4.1 Introduction

The adsorption of surfactants are usually described by the GAI,\(^1\) that relates an experimentally accessible quantity, interfacial tension (\(\gamma\)), to surface excess (\(\Gamma\)), which is more difficult to measure directly.\(^{41,109}\) The GAI is obtained from the Gibbs-Duhem equation (Eqn. (4.12)) that is applied to an interface.\(^{40}\) In the case of surfactants, measurements of a pressure isotherm can be converted to a surface excess via the GAI, where the resulting pressure-surface excess data can be employed to test equations of state (EOS) for adsorbed molecules at fluid interfaces.\(^{110-111}\)

Experimental data characterizing the adsorption of particles at fluid interface strongly suggests that employing the GAI to a pressure isotherm will not give the correct surface excess.\(^{46,112-113}\) In fact, prior results show that the GAI largely overestimates the surface excess for particle adsorption at fluid interfaces, and either predicts multilayer adsorption or a negligible change in interfacial tension upon particle adsorption.\(^{108,112-113}\) It has been
proposed that the effect of particle attachment to a fluid interface is better interpreted in terms of an area replacement, where some fluid-fluid area is replaced by particle-fluid area due to the favorable wetting of the particles at the interface. The decrease in energy caused associated with this area replacement is given by\textsuperscript{45,47}:

$$\Delta E = -\pi r_p^2 \gamma_{\text{OW}} \left( 1 \pm \cos \theta_{\text{OW}} \right)^2,$$

where $\Delta E$ is the adsorption energy per particle, $r_p$ is the particle radius, $\gamma_{\text{OW}}$ is the interfacial tension of the clean interface, $\theta_{\text{OW}}$ is the contact angle of particle at the fluid interface. Du \textit{et al.} proposed that favorable wetting of the particles to a fluid interface will result in a linear relationship between the surface pressure, $\Pi = \gamma_{\text{OW}} - \gamma$, and the surface excess, $\Gamma$, given by\textsuperscript{45}:

$$\Pi = \Gamma |\Delta E|. \quad (4.2)$$

The relationship of Du \textit{et al.}\textsuperscript{46} does not relate the measured surface pressure to the particle bulk concentration. Moreover, it suggests that the adsorbed particles are not surface active (\textit{i.e.} they do not intrinsically change the interfacial tension) and neglects particle-particle interactions. The relationship of Eqn. (4.2) also does not connect to other interfacial thermodynamic relationships such as the GAI. Doing so would help better understand the relationship between measured IFT and the attachment of particles to a fluid interface.

In addition, whether or not particles affect interfacial tension is still under debate. Although a large body of work now shows that the area replacement term of Eqn. (4.2) is a good approximation for the measured surface pressure.\textsuperscript{112-113} On the other hand, many reports also indicate that surface pressure is not particularly sensitive to the
compression/expansion of a fluid interface unless the area fraction of particles is large.\textsuperscript{8, 28} Therefore there is a need for a thermodynamically consistent framework, alike the GAI, to describe the relationship between surface excess ($\Gamma$), bulk particle concentration ($C$), and interfacial tension ($\gamma$). Such a framework would help settle ongoing debate on how the presence of particles affect interfacial tension.

Here we show the relationship between the pressure isotherm, adsorption isotherm and equation of state (EOS) for particle-laden interface. We show that particle adsorption is fundamentally different from that of surfactants. We also discuss why applying the GAI to a pressure isotherm of particle adsorption will not result in the surface excess. We validate our treatment using experimental results along with prior work in the literature as well. Finally, we show that the same set of equations can be employed to describe both the measured surface pressure due to particle adsorption as well as during compression or expansion.
Figure 4-1. Schematic of the capillary system, with two immiscible bulk phases (water phase and oil phase), the corresponding interface with area of $A$, and interfacial tension of $\gamma$, and surface-active particles with radius $r_p$, dispersed in only one of the bulk phases (water phase), and capable of adsorbing to the interface.

4.2 Theoretical Development

Consider an open multicomponent system harboring a fluid interface, as illustrated in Figure 4-1.\(^1\) We first assume that the change in fluid volume caused by the adsorption of the particles to the interface is negligible. Therefore, the adsorption of particles is not doing expansion/contraction work on the system. We also assume that we reach equilibrium between phases, for instance, the particle-laden interface is at equilibrium with the particles dispersed in the bulk phase, indicating the formation of a Gibbs monolayer.
Here we follow the derivation for the GAI given by Berg\textsuperscript{1}. The work considered for the system include expansion/contraction, change in the interfacial area, which is commonly considered for surfactants adsorption, given by\textsuperscript{1,40}:

$$\delta W = -P^o dV^o - P^w dV^w + \gamma dA ,$$

(4.3)

where $P$ is the pressure, and $V$ is the volume. The superscript “$o$” is used to demote parameters or properties of the interface, and superscripts “$w$” and “$o$” are used to denote parameters or properties of the ‘water’ phase and ‘oil’ phase, respectively. $A$ is the area of the interface. In addition, NPs adsorption is also doing work to the system by wetting the interface, given by\textsuperscript{46}:

$$\delta W_{np} = \Delta E n_p^\sigma ,$$

(4.4)

where $n_p^\sigma$ is the number of particles at the interface, $\Delta E$ is the adsorption energy (Eqn. (4.1)). We can then express the generalized thermodynamic description of the capillary system shown in Figure 4-1. Specifically, the Helmholtz free energy, $F$, can be given by\textsuperscript{1}:

$$dF = -SdT - P^o dV^o - P^w dV^w + \gamma dA + \Delta E n_p^\sigma + \sum \mu_i n_i ,$$

(4.5)

where $S$ is the entropy, $T$ is the temperature of the system, $\mu_i$ is the chemical potential of species $i$, and $n_i$ is the number of species $i$. Here $i$ can be surface active species, for example surfactants\textsuperscript{109}, macromolecules\textsuperscript{114}, or particles. Integral of Eqn. (4.5) while maintaining all the intensive variables constant (here $T$ is constant), would result in the following equation:

$$F = -P^o V^o - P^w V^w + \gamma A + \Delta E n_p^\sigma + \sum \mu_i n_i .$$

(4.6)

A total derivative of Eqn. (4.6), would result in:
\[
dF = -P^o dV^o - V^o dP^o - P^w dV^w - V^w dP^w + \gamma dA + Ad \gamma + \Delta E n^\sigma d(\Delta E) + \sum \mu_i dn_i + \sum \eta_i d \mu_i
\]  
(4.7)

By doing a subtraction of Eqn. (4.5) from Eqn. (4.7), the following Eqn. (4.8) can be obtained, express as:

\[
0 = SdT - V^o dP^o - V^w dP^w + Ad \gamma + n^\sigma d(\Delta E) + \sum \eta_i d \mu_i
\]  
(4.8)

Note here the term \(n^\sigma d(\Delta E)\) would vanish since \(\Delta E\), the adsorption energy per particle, is a constant that is independent of particle number in the system, which indicates \(\Delta E\) plays the same role as an intensive parameter of the system. By removing this term, the famous Gibbs-Duhem equation\(^{40}\) for the whole system can be achieved, given by:

\[
0 = SdT - V^o dP^o - V^w dP^w + Ad \gamma + \sum \eta_i d \mu_i .
\]  
(4.9)

Similar procedure can be followed to obtain the Gibbs-Duhem equations for the two phases, oil phase and water phase, respectively, given by:

\[
0 = S^o dT - V^o dP^o + \sum n^o_i d \mu_i .
\]  
(4.10)

\[
0 = S^w dT - V^w dP^w + \sum n^w_i d \mu_i .
\]  
(4.11)

Now we can subtract Eqn. (4.10) and Eqn. (4.11) from Eqn. (4.9), resulting in:

\[
0 = \left(S - S^o - S^w\right) dT + Ad \gamma + \sum \left(n_i - n^o_i - n^w_i\right) d \mu_i .
\]  
(4.12)

Since \(S^\sigma = S - S^o - S^w\), and \(n^\sigma_i = n_i - n^o_i - n^w_i\), we denote \(S^\sigma = S^\sigma / A\), and \(\Gamma_i = n^\sigma_i / A\). Dividing the two sides of Eqn. (4.12) by the total interfacial area, \(A\), we will obtain:

\[
d\gamma = -s^\sigma dT - \sum \Gamma_i d \mu_i .
\]  
(4.13)

At constant temperature \(T\), we would get the Gibbs adsorption equation, given by:

\[
d\gamma = -\sum \Gamma_i d \mu_i .
\]  
(4.14)
It can be noted from the above derivation that the GAI predicts only the change in $\gamma$ due to surface activity, instead of change in $\gamma$ due to change in surface free energy.

*Wetting contribution does show up in adsorption*

However, if starting from the definition of interfacial energy (or surface pressure), different result would be obtained. Interfacial energy (here $\gamma'$ is used to avoid confusion with previous derivation), is defined by:

$$\left. \frac{\partial F}{\partial A} \right|_{T,V,V',n_i} \equiv \gamma' . \quad (4.15)$$

Thus, Eqn. (4.5) will result in the following expression:

$$\left. \frac{\partial F}{\partial A} \right|_{T,V,V',\gamma',n_i} = \gamma + \Delta E \frac{dn_p^\sigma}{dA} . \quad (4.16)$$

Here we denote the surface coverage of particles, $\Gamma_p$, to be $\Gamma_p = n_p^\sigma / A$, and area fraction of particles at the interface, $\eta_p = n_p^\sigma \times \pi r_p^2 / A$, from which $dn_p^\sigma / dA = \eta_p / \pi r_p^2 = \Gamma_p$ would be obtained. As a result, Eqn. (4.16) would become:

$$\left. \frac{\partial F}{\partial A} \right|_{T,V,V',\gamma',n_i} = \gamma + \Delta E \times \eta_p / \pi r_p^2 . \quad (4.17)$$

Combining Eqn. (4.15) and Eqn. (4.17), the following Eqn. (4.18) can be obtained, given by:

$$\gamma' = \gamma + \Delta E \times \eta_p / \pi r_p^2 . \quad (4.18)$$

This gorgeous Eqn. (4.18) demonstrates that the interfacial energy, $\gamma'$, which is also what can be measured at the interface due to particle adsorption, consists of two contributions, one is from the change in surface activity ($\gamma$) similar to the effect of surfactants adsorption, the other is due to particle wetting the interface (changing in
interfacial energy). It shows that the contribution from particle wetting the interface is thermodynamically consistent compared to the surface activity component, which suggests that the particle-laden interface is a “composite” material, in contrast to surfactant-coated interface, where mixing happens on a molecular level. Moreover, instead of a function of particle size, the contribution from particle wetting the interface is only dependent of the area fraction at the interface ($\theta_{OW}$ corrects for the actual area replaced by particles).

*Pressure from adsorption vs. compression*

The total surface pressure ($\Pi_T$) can be expressed by:

$$
\Pi_T = \gamma_{OW} - \gamma' = \Pi_{SA} + \Pi_{WT}.
$$

(4.19)

Eqn. (4.19) again highlights the contributions to surface pressure due to particle adsorption, including particle wetting the interface ($\Pi_{WT}$), and particle surface activity ($\Pi_{SA}$), given by:

$$
\Pi_{WT} = \left(1 \pm \cos \theta_{OW}\right)^2 \gamma_{OW} \times \eta_p,
$$

(4.20)

$$
\Pi_{SA} = \gamma_{OW} - \gamma.
$$

(4.21)

Note that $\Pi_{SA}$ can be described by EOSs that associated with the adsorption isotherms. For example, the simplest case is the Langmuir model, which assumes idea mixing and ideal interactions, while Frumkin model considers idea mixing but non-ideal interactions. Here to simplify the problem, we use the Langmuir EOS to predict the surface activity contribution to pressure, which is given by:

$$
\Pi_{SA} = -kT \Gamma_\infty \ln\left(1 - \Gamma / \Gamma_\infty\right).
$$

(4.22)
Here $\Gamma_\alpha$ is the maximum surface excess of particle, which has an upper limit of 0.907 / $\pi r_p^2$.

It needs to be pointed out that the pressure from adsorption is different from the pressure accumulated during compression of the particle-laden interface (assuming no desorption happening during compression), which is generally originated from particle-particle interactions within the interface.\(^{47}\)

### 4.3 Results and Discussions

#### 4.3.1 Predictions

As has been discussed above, the wetting contribution, $\Pi_{\text{WT}}$ (Eqn. (4.20)) is independent of particle size, yet the surface activity contribution, $\Pi_{\text{SA}}$ (Eqn. (4.22)) would be affected by particle size. Figure 4-2 shows the prediction of the two contributions at toluene-water interface ($\gamma_{\text{OW}} = 35.8$ mN/m), contact angle $\theta_{\text{OW}}$ is assumed to be 90º to simplify the case. To predict $\Pi_{\text{SA}}$, assumption is made such that $\Gamma_\alpha = 0.907 / \pi r_p^2$, and three particle radius is used, including 0.5 nm (black solid line), 1.5 nm (red medium dashed line), and 2.5 nm (green short dashed line). It is obvious from Figure 4-2 that unless the particle is really small ($< 2$ nm in radius), $\Pi_{\text{SA}}$ would have negligible effect on the total surface pressure. In other words, the main contribution to $\Pi_T$ would be from particle wetting the interface ($\Pi_{\text{WT}}$). Consistent result of surface pressure increasing linearly with area fraction has been observed experimentally. For example, Zhang \textit{et al.}\(^{113}\) has reported the adsorption of EC particles could lead to surface pressure increasing proportionally with...
increasing area fraction up to 0.9. More comparison with literature reports will be discussed later.

**Figure 4-2.** Surface pressure contributed from wetting ($\Pi_{WT}$, Eqn. (4.20)) and surface activity ($\Pi_{SA}$, Eqn. (4.22)) at toluene-water interface, $\theta_{ow}$ is assumed to be 90º. Different radius is used to predict $\Pi_{SA}$, including $r_p = 0.5$ nm (black solid line), $r_p = 1.5$ nm (red medium dashed line), $r_p = 2.5$ nm (green short dashed line).

The difference in pressure from particle adsorption and from compression of particles within the interface (assuming no desorption/adsorption happening during compression) has been highlighted in the above derivation, with predictions are shown in Figure 4-2. It needs to be pointed out that increasing of surface pressure may only be observed at high area fraction, depending on the materials of the particles.$^{8,28-29}$
4.3.2 Experimental validation

Previously we have demonstrated experimentally that the 5 nm and 10 nm ion-pair gold nanoparticle (NP) adsorption at toluene-water interface can reach equilibrium with the bulk phase.\textsuperscript{32, 112, 115} Moreover, we have measured both the pressure isotherm via pendant drop shape analysis and the adsorption isotherm via UV-Vis of the two sized NP.\textsuperscript{112} Combining the two isotherms, EOS for particle adsorption can be obtained. In addition, when the adsorption reaches equilibrium with the bulk phase, compression of the particle-laden interface (here specially refers to pendant drop surface) is conducted at 5 \( \mu \)l/min to ensure no adsorption/desorption during the measurements. Figure 4-3 shows the two EOS for 5 nm (A) and 10 nm (B) NPs at toluene–5 mM KOH solution interface. As can be expected from the theoretical predictions, the pressure due to NP adsorption increases linearly with NP surface coverage, while the pressure due to compression builds up slowly at low coverage and increases dramatically at high coverage. Eqns. (4.20) is used to predict the adsorption EOS (solid lines in Figure 4-3), good agreements with experiments are reached for both 5 nm and 10 nm NPs. Additionally, efforts have been made to describe the EOS due to compression with Eqn. (4.22), resulting in a maximum area fraction of 0.45 for 5 nm NP and maximum area fraction of 0.38 for 10 nm NP. The results is not unreasonable considering the ion-pair surface functional groups would result in an additional 1 nm on the radius of NPs,\textsuperscript{61} which gives rise to the radius of NPs to be 3.5 nm and 6 nm.
Figure 4-3. Comparison between EOS of NP adsorption and EOS of compression of particle-laden interface, with 5 nm ion-pair gold NP (A) and 10 nm ion-pair gold NP at toluene–5 mM KOH solution interface. Solid symbols shows the measured EOS of NP adsorption, open symbols shows the EOS during compression of the droplet surface, where the initial pressure due to wetting is subtracted.

4.3.3 Interpretation of prior literature reports

It would be more convincing to compare the theory to prior literature reports. Below Table 4-1 shows prior literature reports on the change in interfacial tension (or pressure, $\Pi_{\Pi_T}$) during adsorption, which can be modeled and predicted using Eqn. (4.20), while Table 4-2 listed prior reports on the pressure built during compression ($\Pi_{Sl}$), which can be generally predicted by Eqn. (4.22) (or other EOS describing surface activity dependent on specific experimental conditions), while difference exists due to particles with different material interactions within the interface. Other EOSs (for example, van der Waals EOS,$^{28}$ Frumkin EOS,$^{41}$ hard disk EOS,$^{116-117}$ etc.) may also apply depending on different cases.
Figure 4-4 shows an example of surface pressure due to adsorption vs. compression reported by two different groups. The solid circles representing EOS due to adsorption of 91 nm latex NP onto air-water interface, which can be well described by the wetting EOS (Eqn. (4.20), solid line in Figure 4-4). Meanwhile the compression of 2.6 μm latex NP at octane-water interface is shown in open circles, and the $\Pi_{SA}$ is adapted from original literature report (Eqn. 6 in ref 28). Again, the difference in surface pressure due to adsorption and compression is highlighted here. Consistency can be found between our system and prior literature reports.

**Figure 4-4.** Literature reports on surface pressure due to latex particle adsorption compared to compression. Note the two sets of data are from different groups: adsorption of 91 nm latex NP onto air-water interface (solid circles) is reported by Okubo, and compression of 2.6 μm latex NP at octane-water interface (open circles) is reported by Aveyard et al. Solid line is fitting to the EOS of adsorption using Eqn. (4.20) assuming $\theta_{ow} = 90^\circ$. Dashed line is adapted from original fitting using the Eqn. 6 reported in the original literature.28
Table 4-1. Prior literature reports of IFT in the presence of particles dispersed in one of the bulk phases.

<table>
<thead>
<tr>
<th>Material</th>
<th>Size</th>
<th>Adsorbs from</th>
<th>Measurements</th>
<th>Predict IFT</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe-TOPO NP</td>
<td>2.3 nm, 6 nm</td>
<td>Aqueous phase</td>
<td>Pendant drop</td>
<td>Eqns. (4.20)-(4.22)</td>
<td>95, 119</td>
</tr>
<tr>
<td>EC NP</td>
<td>42 nm, 44±5 nm, 89.1 nm</td>
<td>Aqueous phase</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>108, 120-122</td>
</tr>
<tr>
<td>Gold NP</td>
<td>4.6 nm</td>
<td>Aqueous phase</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>33, 123</td>
</tr>
<tr>
<td>Ion-pair gold NP</td>
<td>5 nm, 10 nm</td>
<td>Aqueous phase</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>112, 115</td>
</tr>
<tr>
<td>Superparamagnetic iron oxide core, with PEG shell</td>
<td>8.4±1.4 nm</td>
<td>Aqueous phase</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>124</td>
</tr>
<tr>
<td>Silica core</td>
<td>~500 nm</td>
<td>Aqueous phase</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>113</td>
</tr>
<tr>
<td>Silica core coated with HMS</td>
<td>510 nm, 770 nm</td>
<td>Particle pinned at emulsion interface prior to measurements</td>
<td>Micropipet Tensiometer</td>
<td>γ constant</td>
<td>125</td>
</tr>
<tr>
<td>PMMA-HPs</td>
<td>156.9±0.5 nm (CA: 76º)</td>
<td></td>
<td></td>
<td>γ constant, IT constant during compression</td>
<td>126</td>
</tr>
<tr>
<td>Silica-FPs</td>
<td>216±16 nm (CA: 94º)</td>
<td></td>
<td>Dispersed in methanol and deposited onto interface</td>
<td>Pendant drop</td>
<td>126</td>
</tr>
<tr>
<td>Ag-JPs</td>
<td>210±18 nm (CA: 86º)</td>
<td></td>
<td></td>
<td>Eqn. (4.20) for adsorption; Eqn. (4.22) for compression</td>
<td>126</td>
</tr>
<tr>
<td>Hydrophilic silica NP</td>
<td>150 nm (CA: 60º)</td>
<td>Aqueous solution</td>
<td>Pendant drop</td>
<td>IFT constant</td>
<td>127</td>
</tr>
<tr>
<td>Hydrophobic silica particle</td>
<td>12 nm</td>
<td>Paraffin oil</td>
<td>Pendant drop</td>
<td>IFT constant</td>
<td>128</td>
</tr>
<tr>
<td>Particle Type</td>
<td>Diameter(s)</td>
<td>Medium</td>
<td>Measurement Method</td>
<td>Equation No.</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>---------------------</td>
<td>-----------</td>
<td>----------------------------------</td>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>TiO2 particle</td>
<td>470 nm</td>
<td>Aqueous solution</td>
<td>Kruss K12 processor tensiometer</td>
<td>Eqn. (4.20)</td>
<td>129</td>
</tr>
<tr>
<td>Partially hydrophobic silica particle</td>
<td>20 nm</td>
<td>Aqueous solution</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>130</td>
</tr>
<tr>
<td>Au-cit</td>
<td>5 nm, 10 nm, 20 nm</td>
<td>Aqueous solution</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>46</td>
</tr>
<tr>
<td>Carbon-black particle</td>
<td>Primary 10-20 nm, aggregates into 120 nm</td>
<td>Aqueous solution</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>131</td>
</tr>
<tr>
<td>Silica core with HGD and MGD brushes</td>
<td>20 nm core</td>
<td>Aqueous solution</td>
<td>Micro-tensiometer</td>
<td>Eqn. (4.20)</td>
<td>17</td>
</tr>
<tr>
<td>Latex particle</td>
<td>38-460 nm</td>
<td>Deposition</td>
<td>Wilhelmy-type surface tensiometer</td>
<td>Eqn. (4.20)</td>
<td>118</td>
</tr>
<tr>
<td>Janus particle</td>
<td>50 nm-300 nm</td>
<td>Aqueous solution</td>
<td>Pendant drop</td>
<td>Eqn. (4.20)</td>
<td>132</td>
</tr>
<tr>
<td>Silica</td>
<td>7-20 nm</td>
<td>Spreading</td>
<td>Du Nouy balance</td>
<td>Eqn. (4.20)</td>
<td>133</td>
</tr>
</tbody>
</table>
Table 4-2. Prior literature reports of pressure during compression of a particle-laden interface.

<table>
<thead>
<tr>
<th>Material</th>
<th>Size</th>
<th>Adsorbs from</th>
<th>Method</th>
<th>Predict II</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica core with PNIPAM shell</td>
<td>88 nm</td>
<td>Spreading to interface</td>
<td>Langmuir trough</td>
<td>Eqn. (4.22)</td>
<td>134</td>
</tr>
<tr>
<td>Latex particle</td>
<td>0.2-2.6 μm</td>
<td>Spread to interface with IPA</td>
<td>Langmuir trough</td>
<td>Eqn. (4.22)</td>
<td>28</td>
</tr>
<tr>
<td>Sulfated PS particle</td>
<td>2.4 μm</td>
<td>Spread to interface</td>
<td>Langmuir trough</td>
<td>Eqn. (4.22)</td>
<td>135</td>
</tr>
<tr>
<td>Silica particle</td>
<td>1 μm</td>
<td>Spread to interface</td>
<td>Langmuir trough</td>
<td>Eqn. (4.22)</td>
<td>29</td>
</tr>
</tbody>
</table>

4.4 Conclusions

We elucidated the consistency of particle wetting the interface and surface activity contributions to the surface pressure thermodynamically. We explained the reason that wetting terms is absent in the GAI, and thus highlighted the need of corrections to GAI in order to describe particle adsorption at fluid interfaces. We compared the wetting and surface activity contributions during adsorption, and found that wetting contribution dominate during adsorption, unless particle is extremely small (< 1 nm in diameter). The surface pressure during compression of the interface is attributed only to surface activity. Experimental results are employed to validate our theoretical derivations, along with prior literature reports of pressure due to adsorption and pressure due to compression. Both show qualitative consistency with our theory.
5 Controlling Nanoparticle Adsorption and Surface Pressure at the Oil-Water Interface via Competitive Adsorption

5.1 Overview

Surfactants are introduced to investigate the competitive adsorption of NP-surfactant mixture. Single component adsorption is studied first and parameters describing the two components adsorption are obtained by modeling using Frumkin adsorption isotherm and wetting EOS. Followed by the characterization and modelling of binary mixtures.

5.2 Introduction

Nanoparticles (NPs) can stabilize emulsions and foams against coalescence\textsuperscript{9-11}. Beyond stability, adsorbed NPs can add functionality to fluid interfaces based on their material properties and configuration. For example, NPs can serve as catalysts for reactions between immiscible fluids\textsuperscript{20-21}, optical or plasmonic elements for mirrors or sensing\textsuperscript{22-24}, or promote chemical separation and oil recovery\textsuperscript{25}. Adsorbed particles also have a profound effect on interfacial mechanical and rheological properties\textsuperscript{15-16}. For example, viscoelastic Pickering
emulsions are superior at preventing coalescence and Ostwald ripening. Therefore, strategies are needed to simultaneously control functionality and mechanical properties of NP-laden oil-water interfaces. To do so, it is necessary to have a better grasp of the mechanisms driving NPs to fluid interfaces and of how NPs affect interfacial properties.

A recent strategy to control the mechanical properties of a particle-laden interface has been the incorporation of surface active additives, such as low MW polymers or surfactants that also adsorb to the interface and/or to the particles, slow the dynamics of the particles within the interface, and lead to jamming. In these system the oil-water interface acts as an elastic skin, which can lead to complex droplet shapes, bijels, buckled microstructures, and highly stable foams and emulsions. To the author’s knowledge, prior studies are limited to cases where either particles or the surface active species (or both) are irreversibly adsorbed to the fluid interface (or to the particles), which limits the potential for dynamic modulation of interfacial properties.

In contrast to larger particles, sub-20 nm NPs can reversibly partition between a bulk phase and the interface leading to the formation of Gibbs monolayers. Such reversible partitioning can be modulated via external fields or solution conditions, and can enable new technologies such as tunable plasmonic elements, recycling and sustainable processes, or additive manufacturing. We previously demonstrated that reversible partitioning led to control of the area fraction of NPs and reflectivity of an oil-water interface by changing the ionic strength and pH of the aqueous sub-phase. Similar control of the area fraction of NPs at an oil-water interface via change in ionic strength was also reported recently by Chai et al. However, despite these opportunities, it remains poorly
understood how sub-20 nm NPs reversibly adsorb to fluid interfaces and determine their emergent interfacial properties.

The presence of surface active additives with reversible binding to interfaces could bring additional means to control properties of particle-laden interfaces.\textsuperscript{139-141} For example, mixtures of NPs and surfactants have been employed to design switchable emulsions. Binks \textit{et al.}\textsuperscript{142} achieved the double inversion of silica particle stabilized emulsions via irreversible adsorption of surfactants on the NPs surfaces. The adsorption of surfactant to NPs can also facilitate the adsorption & desorption of NPs from oil-water interfaces, as well as adjusting NP coverage within the interface.\textsuperscript{136, 143-145} In all these cases, the underlying mechanism is adsorption of surfactants \textit{to the particles} (often irreversibly), thereby changing the NPs surface properties and their affinity for the oil-water interface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Schematic of single component (NP and TPeA\textsuperscript{+} ion) reversible adsorption at the toluene-water interface (left panel), and the reversible and competitive adsorption of NP and TPeA\textsuperscript{+} ion mixture (right panel). Inset shows the legend of NP and TPeA\textsuperscript{+} ion. Note here TPeA\textsuperscript{+} ion is also part of the ion-pair coated on NP surface during synthesis.}
\end{figure}
Here we demonstrate how the reversible and competitive adsorption between NPs and surfactants for a fluid interface can lead to independent control of the adsorbed amount and surface pressure (Figure 5-1). In contrast to prior work, both species investigated (NPs and surfactants) interact reversibly with the interface and without the surface active species binding to the NPs. The surface active species in solution is tetrapentylammonium cations (T PeA⁺). This surface active cation is also part of the ion-pair ligands bound to the NPs (inset of Figure 5-1). As a result, control of NPs adsorption is not achieved via binding of the surfactant to the NPs. We characterize and model the adsorption of NPs to a toluene-water interface in the absence and presence of the surface active species. The experiments are performed with NPs of two different sizes, at two pH values, and across a wide range of T PeA⁺ and NP bulk concentrations. We show that the presence of free surface active ions competes with the NPs for the interface and gives rise to larger surface pressure upon the adsorption of NPs. Through a competitive adsorption model, our experiments elucidate and isolate the contributions of different mechanisms (adsorption of the NPs to the interface and surface activity) on the measured surface pressure. We also demonstrate reversible tuning of adsorbed amount via changes in the surfactant concentration or pH of the aqueous phase. Competitive adsorption allows for independent control over both area fraction of NPs and surface pressure at the oil-water interface.

**Background on the role of NPs adsorption on surface pressure**

Whether or not NPs are surface active and reduce interfacial tension upon adsorption is still debated (see Ref. 18, 146 for an overview). A proposed mechanisms is that NPs are generally not amphiphiles; instead, an increase in surface pressure is measured upon their adsorption due to a decrease in the interfacial energy caused by the favorable wetting of
the NP at the interface\textsuperscript{47} (see Figure 5-2A). In this limit, Du\textit{ et al.}\textsuperscript{46} predict an increase in the effective surface pressure ($\Pi_{NP}$) due to the adsorption of NPs given by:

$$\Pi_{NP} = |\Delta E| \times \Gamma_{NP}, \quad (5.1)$$

where $\Delta E$ can be interpreted as the change in energy of the oil-water interface (per adsorbed particle) caused by the favorable wetting of the NPs at the interface. $\Gamma_{NP}$ is the surface excess of NPs at the interface. The wetting of the NPs at the oil-water interface leads to a change in energy for the adsorption of a spherical particle of radius $r_{NP}$ expressed by:\textsuperscript{47}

$$\frac{\Delta E}{\text{particle}} = -\pi r_{NP}^2 \gamma_{OW} \left(1 \pm \cos \theta_{OW}\right)^2. \quad (5.2)$$

This decrease in energy is due to the replacement of fluid-fluid area with particles that form a contact angle $\theta_{OW}$ at the interface, and is largest when $\theta_{OW} = 90^\circ$.\textsuperscript{27,47} Based on this description, the surface pressure ($\Pi_{NP}$) is directly proportional to the area fraction of adsorbed NPs ($\eta_{NP} = \pi r_{NP}^2 \Gamma_{NP}$) and independent of particle-particle interactions. Zhang\textit{ et al.}\textsuperscript{113} recently reported that the EOS of 200 nm ethyl cellulose NPs could be fully described by Eqn. (5.1) to the hard disk limit of 0.907 with no effect of NP interactions.

Instead of a wetting argument, it has also been proposed that NPs can be surface active, directly affect the interfacial tension ($\gamma_{OW}$), and display amphiphilicity in a manner analogous to surfactants, as illustrated in Figure 5-2B.\textsuperscript{17,99} In that case, thermodynamic equilibrium dictates that the relationship between the adsorption isotherm and the EOS would obey the Gibbs adsorption isotherm.\textsuperscript{1,147} The Frumkin model, which accounts for non-ideal interactions between adsorbed species within the interface, is thermodynamically consistent and can describe the adsorption, Eqn. (5.3) and EOS, Eqn. (5.4), of a species to an interface.\textsuperscript{41}
\begin{align*}
C_i (\theta_i) &= a_{L,i} \frac{\theta_i}{1-\theta_i} \exp(K_i \theta_i), \quad (5.3) \\
\Pi_{i-i} &= -kT \Gamma_{i,\infty} \left[ \ln(1-\theta_i) - 0.5K_i \theta_i^2 \right]. \quad (5.4)
\end{align*}

The EOS in Eqn. (5.4) gives the surface pressure ($\Pi_{i-i}$), which can also be defined as:
\[ \Pi_{i-i} = \gamma_o - \gamma(\Gamma_i), \quad (5.5) \]
when the pressure is associated with the adsorption of species $i$ to the interface, and defined as the difference between the interfacial tension of the bare oil-water interface ($\gamma_o$) and the interfacial tension with adsorbed species ($\gamma$). In Eqns. (5.3)-(5.4), $i$ is the adsorbed species (NP for example), $C_i$ is the bulk concentration of the species, $a_{L,i}$ is its dissociation constant characterizing its affinity to the interface, $\theta_i = \Gamma_i / \Gamma_{i,\infty}$ is the fractional coverage of the surface active species at the interface, with $\Gamma_{i,\infty}$ being the maximum coverage at the interface. Finally, $K_i$ can be interpreted the net interaction energy between species $i$ at the interface relative to thermal energy (i.e., $kT$). A positive value for $K_i$ indicates repulsive interaction and a negative value indicates attraction between adsorbed species. When $K_i = 0$, the Frumkin adsorption isotherm reduces to Langmuir isotherm, which assumes no interactions at the interface. The Frumkin model is also routinely used to describe the adsorption of charged surfactants. The first term in the bracket in Eqn. (5.4) is the entropic contribution and the second term is the enthalpic contribution caused by the interactions between the surface active species.

We previously characterized the reversible adsorption of 5 nm ion-pair gold NPs. Our results demonstrated the formation of Gibbs monolayer of NPs at the interface. The EOS followed a linear relationship analogous to Eqn. (5.1) at low surface coverage, but with a slope that was higher than predictions based on Eqn.(5.2). We also observed strong
deviations in the EOS at higher area fraction. However, attempts to model the adsorption isotherm and EOS showed that models based either on an adsorption energy (Eqns. (5.1)-(5.2)) or on surface activity (Eqns. (5.3)-(5.4)) alone were not able to capture the measured data over the whole range of area fraction. We suggested the need to develop models that combine surface activity with the reduction of interfacial area.

![Figure 5-2](image.png)

**Figure 5-2.** (A) Schematic of NP wetting the interface: NP contributes to surface pressure by replacing the interfacial area (wetting the interface), described by Eqn. (5.1). (B) Schematic of other contributions to surface pressure from surface activity, include NP-NP interactions ($\Pi_{NP-NP}$), ion-ion interactions ($\Pi_{I-I}$), as well as NP-ion interactions ($\Pi_{NP-I}$) within the interface.

### 5.3 Materials and Methods

#### 5.3.1 Reagents and chemicals

All reagents and chemicals are used as received. Potassium hydroxide (KOH, 99.9%) pellets, potassium chloride (KCl, 99.9%), 16-mercaptohexadecanoic acid (MHA, 99%), gold chloride hydrate (HAuCl$_4$, >49% Au), sodium borohydride (NaBH$_4$, >96%), tetratryptylammonium chloride (TPeACl, 99%), tetratryptylammonium hydroxide (TPeAOH, 20wt% 1 M aqueous solution) are purchased from Sigma-Aldrich. Sulfuric acid
(H₂SO₄, 95.0 to 98.0 w/w %), hydrogen peroxide (H₂O₂, 30.0 to 32.0%), 2-propanol (> 99.9%), toluene (> 99.8%), NaCl salt disk, and RBS 35 Detergent Concentrate are purchased from Fisher Scientific. Deionized water (DIW, 18.2 MΩ·cm) is obtained from a Milli-Q Gradient system. All glassware, unless otherwise noted, is thoroughly cleaned with piranha solution (4:1 H₂SO₄:H₂O₂), rinsed with DIW and dried overnight in air prior to use. All experiments are performed at 295 K.

5.3.2 Synthesis and characterization of ion-pair gold NPs

Ion-pair gold NPs are synthesized and characterized following the same protocol described in our previous work.¹¹² Note here, for the small NPs (5 nm core diameter), the same purification protocol is applied, where NPs are dispersed in solution initially, followed by addition of toluene and vigorously shaking to accelerate the adsorption of the larger particles. The solution is then allowed to settle for 12 h to ensure that large aggregates and particles stay at the interface while most NPs desorb from the interface, before being used in experiments. We did not conduct the same purification protocol for the large NPs (10 nm core diameter).

The stoichiometry of the ion-pair surface functional groups is characterized with Fourier transform infrared spectroscopy (FTIR, Varian 660-IR spectrometer with a DTGS detector) following our prior protocol.¹¹² Absorbance spectra in transmission are collected to determine the stoichiometric ratio of TPeA/MHA on the surface based on a calibration curved developed previously.³² The formation of ion-pairs is further indicated by the absorbance peak at 1560 cm⁻¹ (COO⁻ stretching).

Transmission electron microscopy (TEM, Philips EM 420) is employed to determine NPs size. A 5 μL 2-propanol droplet with dispersed NPs is deposited on a TEM grid
(Electron Microscopy Services, Hatfield, PA) and allowed to dry overnight in air. The particle size distribution is obtained via image analysis of at least 200 individual particles, giving a result of 5.2 nm ± 1.3 nm for the small NPs, and 10.4 nm ± 2.7 nm for the large NPs. Note that TEM imaging is taken prior to purification. Also aggregates can form during the drying process via capillary forces, which could increasing the polydispersity and morphology of NPs.

The NPs size in solution and their zeta potential is measured using dynamic light scattering (DLS, Zetasizer Nano-ZS90, Malvern Instruments). Disposable plastic cuvettes are used (4 optical side polystyrene, Sarstedt AG & Co) to collect the size data, during which standard options provided in the Malvern software is used. Disposable folded capillary cuvettes (1006C, Malvern Instruments) are used for zeta potential measurements, and the Debye-Hückel equation is used to calculate the zeta potential from the mobility (values are shown in supporting information in Table S5-3).

5.3.3 Solution conditions used to disperse NPs for all experiments

Throughout the experiments, the ionic strength of all aqueous solutions is maintained constant at 5 mM. The pH of the aqueous phases is adjusted by mixing different ratios of 5 mM KOH/KCl, or different ratios of 5 mM TPeAOH/TPeACl. The TPeA⁺ ion concentration at a fixed aqueous pH is adjusted by mixing different ratios of pH 11.0 KOH/KCl solutions and pH 11.0 TPeAOH/TPeACl solutions, or mixing different ratios of pH 11.7 KOH and pH 11.7 TPeAOH solutions.

5.3.4 Adsorption & pressure isotherms measurements

Adsorption isotherms are measured with ultraviolet-visible spectroscopy (UV-Vis, Cary 50 spectrophotometer), following the same protocol described in our previous
work. The adsorbed amount is obtained from the bulk NP density difference before and 24 h after the addition of toluene. Note here for high bulk concentrations of NPs (absorbance exceeds 1 in the measurements), the solutions are diluted before conducting UV-Vis measurements to ensure the absorbance is within the measurable range. The area used to calculate surface density is 1.4 cm², which is the meniscus area of the solution in the glass vials. We assumed that NPs do not adsorb to air-water interface, which we verified in our previous work. The extinction coefficient for large NPs (5 nm core radius) at 450 nm wavelength is calibrated to be $6.1 \times 10^7$ M$^{-1}$ cm$^{-1}$, by assuming a monodispersed radius of 5 nm and density of gold to be 19.3 g/mL.

Pressure isotherms are obtained from pendant drop shape analysis (First Ten Angstroms), as described in our previous work. During the measurement, a toluene droplet is created in aqueous solutions with different densities of NPs at a given TPeA$^+$ concentration at a given pH, when the adsorption takes place. The droplet is allowed to stay in the solution for at least 3 h, during which the interfacial tension is recorded, until the change in interfacial tension is less than 0.5 mN/m (resolution of the apparatus) for more than 5000 sec. After that, the equilibrium interfacial tension ($\gamma_{eq}$) is obtained by taking the average of the measurements during the last 5000 sec, and surface pressure is obtained with $\Pi = \gamma_0 - \gamma_{eq}$, where $\gamma_0 = 34$ mN/m (the value of 5 mM KOH-toluene interfacial tension, see Figure S5-2 in Supporting Information).
5.4 Results and Discussions

5.4.1 Single component adsorption

*Adsorption of NPs to the toluene-water interface.* The NPs studied here are functionalized with a self-assembled monolayer of ion-pair ligands. These ligands consist of a negatively charged thiol (deprotonated mercaptohexadecanoic acid, MHA) paired with an organic cations (tetrapentylammonium, TPeA⁺, see Figure 5-1) prior to the covalent attachment of the thiol group to the gold NPs. We have previously shown that these ion-pairs form a robust self-assembled monolayer on the gold surfaces (Figure 5-1).61,82-84 We have shown that these 5 nm ion-pair gold NPs partition reversibly at the toluene-water where the partitioning can be modulated with the pH of the aqueous sub-phase.32 At low pH (pH < 11.0) the NPs adsorbed at the interface to form a reflective layer, indicative of high area fraction and close proximity of the adsorbed NPs. As the pH increases, the NPs desorb from the interface and the interface becomes transparent, indicative of a lower area fraction and larger NP-NP separation. Further study demonstrated the equilibrium partitioning of the 5 nm ion-pair gold NPs between an aqueous subphase and the toluene-water interface. The EOS of the NPs was characterized and showed the formation of Gibbs monolayer at both pH 11.0 and pH 11.7.112

We use UV-Vis spectroscopy to obtain the adsorption isotherms of gold NPs to the aqueous-toluene interface, as shown in Figure 5-3. The composition of the aqueous phase is a mixture of KCl/KOH selected to keep the ionic strength constant at 5 mM and the pH either at pH 11.0 or pH 11.7. The composition of the aqueous phase is also selected because the cation (K⁺) does not have a significant surface activity: the presence of salt reduces toluene-water interfacial tension by less than 2 mN/m, from 35.8 mN/m, to 34.0 mN/m.
The area fraction is calculated from the surface excess following \( \eta_{NP} = \pi r_{NP}^2 \Gamma_{NP} \) and evaluated at the equator of the NPs (assuming the contact angle of the NPs at the toluene-water interface is 90°, resulting in a maximum area fraction for the NPs at the interface). We use a radius \( (r_{NP}) \) of 3.5 nm for the small NPs that includes the core size of 2.5 nm and an additional 1 nm for the ligand on the surface when converting the NP surface excess \( (\Gamma_{NP}) \) to NP area fraction \( (\eta_{NP}) \). Similarly, for the larger particle we use a radius of 6 nm to include the 5 nm core size and an additional 1 nm for the ligand. Note that the nm thickness for the ligand is a rough estimate based on the comparison of the decrease in the attenuation of the Au4f photoelectrons emitted from the underlying gold substrate for ion-pair monolayers (compared to a full MHA monolayer).

For all the isotherms, we observe that the adsorbed amount of NPs at the toluene-water interface increases with increasing bulk NP number densities, and then reaches a plateau (Figure 5-3). For a range of bulk NP concentrations that span 4 orders of magnitude in number density, we observe coverages up to nearly monolayer coverages (area fraction less than the hard disk limit of 0.907). The dependence of the adsorbed NPs with the bulk NPs concentration is indicative of the formation of a Gibbs monolayer at the toluene-water interface, consistent with our previous work. Comparing the adsorption of 5 nm NPs at the two pH values we observe that for the same bulk NP concentration, more NPs adsorb to the interface at pH 11 than at pH 11.7, similar to our previous findings showing increasing pH causes NPs desorption. Moreover, when maintaining constant pH at pH 11.7, we find that a higher area fraction (Figure 5-3B) is obtained for the larger particles given a NP bulk concentration, especially at high NP concentration. Note that the coverage of 10 nm NPs at high concentration reaches a maximum coverage slightly higher than one
monolayer (area fraction ~0.95), likely due to polydispersity of NPs. Through investigating NPs adsorption at two different pH values and with two different sized NPs, we demonstrate the capability of adjusting NP surface coverage via NP bulk density, solution pH, and NP size.

In fitting the adsorption isotherm data to the Frumkin model of Eqn. (5.3), we did not include the data at high coverage (open symbols in Figure 5-3) due to effects caused by polydispersity (shown in Figure 5-3). However, values for the parameter are almost identical if the full set of data is used and the resulting conclusions remain unchanged (see Table S5-2 in Supporting Information for the parameters using all the points). The parameters obtained from fits to the data (least squared error) are given in Table 5-1. As seen from Figure 5-3 the adsorption of the NPs is well-described by the Frumkin model.
Figure 5.3. Adsorption isotherms (A) and pressure isotherms (B) of 5 nm NPs in 5 mM KOH solutions at pH 11.0 (cyan dotted circles) and pH 11.7 (green squares), as well as 10 nm NPs in 5 mM pH 11.7 KOH solution (blue triangles). Only the solid symbols are used for fitting the data to the Frumkin model. Dashed lines are best fits to the Frumkin adsorption isotherm (Eqn. (5.3)) with fitting parameters listed in Table 5-1. Inset in (B) is the predicted surface pressure from the Frumkin EOS by Eqns. (5.3)-(5.4) with parameters listed in Table 5-1.

Table 5-1. Parameters obtained from fitting $\Gamma_{NP}(C_{NP})$ for the adsorption isotherms of NPs at low surface coverage (shown in Figure 5-3) at the toluene-water interface at pH 11.0 and pH 11.7 using Frumkin adsorption isotherm in Eqn. (5.3).

<table>
<thead>
<tr>
<th>pH</th>
<th>$r_{NP}$ (nm)</th>
<th>$a_{L,NP}$ (#/mL)</th>
<th>$K_{NP}$</th>
<th>$\Gamma_{NP,\infty}$ (#/nm$^2$)</th>
<th>$\eta_{NP,\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 11.0</td>
<td>3.5</td>
<td>$1.6 \times 10^{12}$</td>
<td>0</td>
<td>0.022</td>
<td>0.85</td>
</tr>
<tr>
<td>pH 11.7</td>
<td>3.5</td>
<td>$3.1 \times 10^{12}$</td>
<td>-0.3</td>
<td>0.018</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>$2.7 \times 10^{12}$</td>
<td>-1.6</td>
<td>0.008</td>
<td>0.95</td>
</tr>
</tbody>
</table>
When comparing the fitting parameters at different pH values and NP sizes, a common feature is that the NP-NP interaction parameter within the interface is small ($K_{NP} \sim 0$) for the smaller particles and comparable to the thermal energy for the larger particles. We find that increasing the pH of the aqueous phase affects the affinity between NPs and the interface as indicated by higher dissociation constant, $a_{L,NP}$. The higher dissociation constant at higher pH, indicates that NPs have higher affinity with the interface at pH 11.0 than at pH 11.7. Hydroxyl ions (OH⁻) tend to adsorb to the oil-water interface, and considering that the NPs have a negative zeta potential, a lower concentration of OH⁻ should lead to less repulsion between the NPs and the interface at lower pH and more NPs adsorbed. The dissociation constant is only slightly smaller for large NPs (higher affinity for interface), despite the higher adsorption energy (Eqns. (5.1)-(5.2)). However, a larger maximum area fraction is achieved with the larger NPs. Based on the Frumkin model of Eqn. (5.3) we can evaluate the surface pressure that can be attributed to NP-NP enthalpic and entropic contributions using the Frumkin EOS\(^4^1\) (Eqn. (5.4)). The estimated pressure isotherms are shown in the inset of Figure 5-3. Based on the parameters obtained from the adsorption isotherms, our results indicate that the NPs should not lead to a significant change in the oil-water interfacial tension (i.e., no surface activity of the NPs). We obtain the pressure isotherm caused by NP adsorption using pendant drop tensiometry (Figure 5-3B). As discussed in our previous work we see that the surface pressure is a strong function of the bulk concentration of NPs. We also observe that the change in surface pressure is much more significant than predictions based on surface activity. We also find that at a given bulk NP concentration, the surface pressure is slightly higher for the larger NPs.
We combine the pressure and adsorption isotherms to get the EOS of NPs at the oil-water interface (Figure 5-4). Note here that both sets of data are obtained separately. To obtain the EOS, first we fit the adsorption isotherm and the pressure isotherm with an individual sigmoidal curves. Then, using the sigmoidal curve we find the surface excess that corresponds to every bulk NP concentration in the pressure isotherm and get the EOS.

For the surface pressure, we use the toluene-5 mM KOH solution interfacial tension as the reference state with $\gamma_{OW}$ (34 mN/m). We assumed a contact angle, $\theta_{OW}$ to be 90º to have an upper limit of pressure from NPs wetting the interface. We see that the EOS is independent on NP size and pH of the aqueous solution when the surface excess is converted into an area fraction (Figure 5-4B).

Predictions for the EOS based on Eqns. (5.1)-(5.2) and based on Eqns. (5.3)-(5.4) are shown along with the measured data in Figure 5-4. Our measurements again confirm that the contribution due to surface activity are negligible compared to that of wetting of the particles. We also see that the EOS for the two NP sizes collapse when plotted with respect to the area fraction. The EOS based on Eqns. (5.1)-(5.2) predicts a linear relationship between the measured surface pressure and the surface excess, and we observe such a linear dependence at low coverage ($\eta_{NP} < 0.3$). In addition, the effective size in the linear regime obtained from finding the value of the radius that best fits the data is almost equal to the actual size of the NPs (6.8 nm vs. 6 nm, and 3.8 nm vs. 3.5 nm). At higher coverage the surface pressure measured is less than the estimated value using the actual NPs size. However, the “effective radius” obtained from fitting the data to Eqns. (5.1)-(5.2) is still quite close to the actual size. According to the size distribution from TEM imaging, small NPs have a diameter distribution of 5.2 nm ± 1.4 nm, and the large NPs have a diameter
distribution of 10.4 nm ± 3.3 nm (Figure S5-1C-D in Supporting Information). We suspect that initially larger particles adsorb to the interface (the points are lightly above the straight line) or displaced smaller adsorbed NPs. Then, as the coverage increases, smaller NPs preferentially adsorb to the interface. Favoring the adsorption of smaller particles at higher coverages could be energetically favorable (e.g., as in binary or polydispersed NP adsorption)\textsuperscript{148-149}, or possibly be due to kinetic limitations\textsuperscript{19,27,150}. As the surface coverage increases, the energetic cost to rearrange the NPs to make place for a new NP might be slower or more costly compared to the rate of adsorption. In this limit, adsorption of smaller NPs would be favored, even if the decrease in energy due to the reduction in area is lower.

\textit{Adsorption of TPeA\textsuperscript{+} at toluene-water interface.} In the next set of experiments, we characterize the surface activity of the tetrapentylammonium (TPeA\textsuperscript{+}) cation in the aqueous phase in the absence of NPs. Similar quaternary ammonium salts have been employed to facilitate the adsorption of NPs to a fluid interface,\textsuperscript{145} to stabilize emulsions along with NPs,\textsuperscript{151-152} or used as spacer for surfactant/DNA complex assembly at air water interface\textsuperscript{153}. As a reminder, TPeA\textsuperscript{+} are at the terminal end of the ligands on the NPs surface.
**Figure 5-4.** EOS shown in terms of (A) the surface excess ($\Gamma_{\text{NP}}$) and (B) the area fraction of NPs ($\eta_{\text{NP}}$) for the 5 nm NPs in 5 mM KOH solutions at pH 11.0 (cyan dotted circles) and pH 11.7 (green squares), as well as 10 nm NPs in 5 mM pH 11.7 KOH solution (blue triangles). Dashed lines are to guide the eye. Dotted lines are upper and lower limits of NPs contribution to surface pressure, described by Eqns. (5.1)-(5.2) with $\gamma_{\text{OW}} = 34\text{mN/m}$, and $\theta_{\text{OW}} = 90^\circ$. Solid lines are contribution to surface pressure from the actual radius, labelled
with $r$. The radius variation, $\Delta r$, is obtained from finding the range of radii that encompasses all the data as fitted to Eqns. (5.1)-(5.2) (the values of $r$ are shown in inset of Figure 5-4A). The inset of Figure 5-4B shows the pressure from NP-NP interactions, estimated using Eqn. (5.4) with parameters listed in Table 5-1.

As shown in Figure 5-5, the presence of TPeA$^+$ in the aqueous phase reduces the interfacial tension of the toluene-water interface significantly, by more than 10 mN/m at both pH 11.0 and pH 11.7, consistent with reported results$^{154}$. A comparison between Figure 5-5 and Figure 5-6B shows that both NPs and TPeA$^+$ lead to change in surface pressure that are similar in magnitude. Using a mixture of different ratios of 5 mM TPeAOH and 5 mM TPeACl solutions, we can adjust the pH of the aqueous phase while maintaining a constant TPeA$^+$ concentration in the bulk. We see that for the same TPeA$^+$ concentration, a slightly higher surface pressure is achieved at pH 11.7 than at pH 11.0.

![Figure 5-5](image)

**Figure 5-5.** Surface pressure (given by Eqn. (5.5) with $\gamma_0 = 34$ mN/m) of TPeA$^+$ ions in 5 mM, pH 11.0 solution (pink triangles) and pH 11.7 solution (black circles) measured via
pendant drop shape analysis. The lines are the corresponding fits using Frumkin model described by Eqns. (5.3)-(5.4). The fitting parameters are listed in Table 5-2.

We also model the adsorption of TPeA$^+$ to the toluene-water interface using the Frumkin model\textsuperscript{41} given in Eqns. (5.3)-(5.4), where component $i$ now represents the TPeA$^+$ ion (I). The Frumkin model accurately represents the data, as shown in Figure 5-5, and the fitting parameters are listed in Table 5-2. Based on the parameters in Table 5-2, we see that there is a strong repulsion between TPeA$^+$ ions adsorbed at the interface (for example, the interaction parameter for SDS at oil-water interface is $\sim$8\textsuperscript{41}), and that this repulsions is similar for the two pH investigated. The maximum coverage at the interface is also similar between the two pH values, and assuming a radius of 0.5 nm\textsuperscript{61} we can estimate the maximum area fraction to be around 0.16. Difference in the dissociation constants capture the main differences between the curves show in Figure 5-5. The adsorption at pH 11.7 is described by a much smaller dissociation constant than at pH 11.0, indicating stronger affinity between TPeA$^+$ and the interface at higher pH. This is consistent with the fact that the OH$^-$ groups tend to adsorb at oil-water interface and result in a negatively charged interface.\textsuperscript{155}

<table>
<thead>
<tr>
<th>$pH$</th>
<th>$a_{L,1} (mM)$</th>
<th>$K_I$</th>
<th>$\Gamma_{L,\infty} (&gt;$/nm$^2$)</th>
<th>$\eta_{L,\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 11.0</td>
<td>$1.00 \times 10^{-6}$</td>
<td>6.00</td>
<td>0.20</td>
<td>0.160</td>
</tr>
<tr>
<td>pH 11.7</td>
<td>$2.45 \times 10^{-7}$</td>
<td>6.57</td>
<td>0.21</td>
<td>0.163</td>
</tr>
</tbody>
</table>

Table 5-2. Parameters obtained from fitting the pressure isotherm for the TPeA$^+$ adsorption at toluene-water interface at pH 11.0 and pH 11.7 shown in Figure 5-5 to the Frumkin adsorption model described by Eqns. (5.3)-(5.4). A TPeA$^+$ radius of 0.5 nm\textsuperscript{61} is assumed to estimate the maximum area fraction of TPeA$^+$ at the toluene-water interface.
5.4.2 Competitive adsorption between NPs and TPeA$^+$ ions

Adsortion & pressure isotherms. Figure 5-6 shows the adsorption isotherms of NPs in the presence (black circles and red triangles) and absence (green squares) of TPeA$^+$. NP surface coverage decreases in the presence of TPeA$^+$ ions. It is clear from Figure 5-6 that the presence of the TPeA$^+$ ion limits the adsorption of NPs at all NPs concentration, and leads to a lower maximum area fraction at high bulk NP concentrations.

We hypothesize that the decrease in adsorbed NPs is due to competitive adsorption between the NPs and the surface active ions. Increasing the bulk TPeA$^+$ concentration from 0 mM, to 0.01 mM, and then 5 mM, increases the adsorbed amount of ions and, in turn, decreases the adsorbed NPs. Competitive adsorption at fluid interfaces has been reported for combinations of surface active molecules such as alkanes and surfactants$^{156}$ or macromolecules and surfactants$^{157}$. However, to the best of our knowledge competitive reversible adsorption between NPs and a surface active molecule has yet to be reported.

The apparent competitive adsorption suggested by Figure 5-6 is surprising considering both the difference in size between the molecules ($\sim$1 nm in diameter) and the particles ($\sim$5 nm in diameter), and the fact that particles do not exhibit significant surface activity (inset of Figure 5-3B and Figure 5-4B).

We rule out that the decrease in NP adsorption with the addition of TPeA$^+$ is due to a change in the surface property of the NPs. Based on zeta potential measurements, the NPs and TPeA$^+$ are oppositely charged. The zeta-potential of NPs in different solution conditions (Table S5-3 in supporting information) shows a slight increase in NPs zeta-potential in the presence of TPeA$^+$. However the change in zeta potential ($\sim$15% change) is equivalent to adding only one 1 extra TPeA$^+$ on the NP surface, which is insufficient to
describe our experimental results. In addition, the hydrodynamic size of NPs (size measured with dynamic light scattering) in different solution conditions (Table S5-4 in supporting information) shows no change upon addition of TPeA$^+$ in solutions. Since both hydrodynamic radius and zeta potential are commonly employed to determine surfactant adsorption on NPs, and such a change is absent here, it appears that the shift in NP equilibrium is not due to a variation in NP’s surface property.

**Figure 5-6.** Adsorption isotherms (A) and pressure isotherms (B) of 5 nm NPs in pH 11.7 solutions with 0 mM TPeAOH (green squares), 0.01 mM TPeAOH (red down triangles), and 5 mM TPeAOH (black circles). Dashed lines in (A) are to guide the eye. Black and red
dashed lines in (B) are best fits to the combination of NPs wetting the interface (Eqn. (5.1)) and the binary Frumkin model described by Eqns. (5.6)-(5.8) with parameters listed in Table 5-1 and Table 5-4. Green dashed line is to guide the eye. Total ionic strength of the solution is 5 mM.

The presence of TPeA$^+$ in the aqueous phase also has a significant effect on the interfacial tension in the presence of NPs. Shown in Figure 5-6B are the pressure isotherms of dispersions of 5 nm NPs in the presence and absence of TPeA$^+$ in pH 11.7 and ionic strength of 5 mM (as measured via pendant drop shape analysis). Increasing the concentration of TPeA$^+$ shifts the pressure isotherms to higher values, consistent with the decrease in interfacial tension caused by the adsorption of TPeA$^+$ to the interface, as shown in Figure 5-5 (higher $\gamma$-intercept). Moreover, the addition of TPeA$^+$ increases the total surface pressure at the same bulk NP concentration. However, the curves are not simply shifted upward, indicating that the total surface pressure is not simply a superposition of the contribution of the NPs and TPeA$^+$, also suggesting competitive adsorption between the species.

5.4.3 Equation of state

We combine the pressure and adsorption isotherms to get the EOS for the binary adsorption (NPs and TPeA$^+$, Figure 5-7) using the same approach as for the NPs in the absence of TPeA$^+$ (Figure 5-4). The EOS for the binary system (TPeA$^+$ and NPs) is obtained by combining the adsorption and pressure isotherms for the 5 nm NPs (pH 11.7) solutions with different TPeA$^+$ concentrations (Figure 5-7A). Note that both sets of data are obtained independently.
The intercepts of the binary systems (where NPs are absent) agrees well with the value of the surface pressure determined from the EOS of the TPeA\(^+\) alone at the toluene-pH 11.7 solution interface shown in Figure 5-5. Moreover, at low coverage \(I_{NP} < 0.003 \text{ #/nm}^2\) we observe a linear relationship in the EOS, after which the EOS reaches a plateau. Focusing on the low coverage (linear) regime of EOS (Figure 5-7B), we see that the slopes in the presence of TPeA\(^+\) (black and red dashed lines) are larger than in the case of adsorption from a KOH aqueous solution. In addition, the slope of the EOS in the presence of TPeA\(^+\) would suggests a larger size (shown in Table 5-3) if they were to be interpreted solely by wetting of the NPs to the oil-water interface as in Eqn. (5.2). However, DLS size measurements (Table S3-2 in supporting information) do not show a dependence of the size of the NPs on the solution conditions. A larger slope in the EOS was also observed at pH 11.0 in our previous work.\(^{112}\)

**Table 5-3.** Parameters used to fit the measurements of 5 nm NPs EOS at low coverage shown in Figure 5-7B with Eqns. (5.1)-(5.2), by assuming a contact angle of 90º, and using the measured IFT of 5 mM KOH-toluene, 34 mN/m, as the pure interfacial tension, \(\gamma_{ow}\).

<table>
<thead>
<tr>
<th>[TPeA(^+)] (mM)</th>
<th>(r_{eff} \text{ (nm)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.79</td>
</tr>
<tr>
<td>0.01</td>
<td>5.64</td>
</tr>
<tr>
<td>5</td>
<td>5.53</td>
</tr>
</tbody>
</table>
Figure 5-7. (A) EOSs of 5 nm NPs adsorption from pH 11.7 solutions with 0 mM TPeAOH (green squares), 0.01 mM TPeAOH (red down triangles) and 5 mM TPeAOH (black circles). Black and red dashed lines are fitting to binary Frumkin model, green dashed line is to guide the eye. (B) Zoom in of the low surface coverage (equivalent to area fraction < 0.3). Dashed lines are fits to the experimental data at low coverage to Eqn. (5.1) with the fitting parameters listed in Table 5-3. Shaded region represents $r_{ef} = r_{NP} \pm 0.25r_{NP}$, using the variation obtained from Figure 5-4A.

We use a binary Frumkin model\textsuperscript{156} to describe the enthalpic and entropic contributions to the surface pressure caused by the competitive adsorption of both NPs and TPeA\textsuperscript{+} to the oil-water interface. The binary Frumkin model accounts for interactions between individual species ($K_{NP}$ and $K_{I}$), as well as interactions between species (i.e., ion-NP interactions, here $K_{NP,I}$) within the interface, and is given by Eqn. (5.6):
\[ \Pi_{\text{Bin}}(\theta_I, \theta_{\text{NP}}) = -kT \Gamma_\infty \left[ \ln \left(1 - \theta_I - \theta_{\text{NP}}\right) - 0.5K_{\text{NP}}\theta_{\text{NP}}^2 - 0.5K_I\theta_I^2 - K_{\text{NP} \cdot I}\theta_{\text{NP}}\theta_I \right], \quad (5.6) \]

where \( \Gamma_\infty = \left(\Gamma_I + \Gamma_{\text{NP}}\right) / \left(\theta_I + \theta_{\text{NP}}\right) \) is the total surface coverage, allowing for different maximum coverage for each of the individual components. The maximum coverage of TPeA^+ is about 0.2 molecules/nm^2 (Table 5-2), which is more than 10 fold larger than the maximum coverage of NPs (0.01 – 0.02 NPs/nm^2 depending on solution condition, Table 5-1), thus, we cannot assume the same \( \Gamma_\infty \) in the binary Frumkin model to describe the two component. The corresponding binary adsorption isotherms are given by:

\[ C_{\text{NP}}(\theta_I, \theta_{\text{NP}}) = a_{L,\text{NP}} \frac{\theta_{\text{NP}}}{1 - \theta_I - \theta_{\text{NP}}} \exp\left(K_{\text{NP}}\theta_{\text{NP}} + K_{\text{NP} \cdot I}\theta_I\right), \quad (5.7) \]

\[ C_I(\theta_I, \theta_{\text{NP}}) = a_{L,I} \frac{\theta_I}{1 - \theta_I - \theta_{\text{NP}}} \exp\left(K_I\theta_I + K_{\text{NP} \cdot I}\theta_{\text{NP}}\right). \quad (5.8) \]

This model describes the surface activity of the oil-water interface, and how adsorption changes the inherent interfacial tension of the oil-water interface. This Frumkin competitive model has been used to describe theoretically the competitive adsorption between surfactants and other large molecules, including alkanes, proteins, etc. Unfortunately there are very limited comparison between the model and experimental data. One challenge that can prevent experimental validation lies in the difficulties in measuring surface excess of one or both species. In the case of the adsorption of NPs, the binary Frumkin model also does not include the wetting contribution of the NPs to the oil-water interfacial energy as given by Eqns. (1)-(2).

Here we propose that the measured surface pressure originates from both the wetting of the NPs (\( \Pi_{\text{NP}} \), given by Eqn. (5.1)) and from surface activity (\( \Pi_{\text{Bin}} \), given by Eqn. (5.6)). Further, we suggest the two contributions are additive as given by:

\[ \Pi_{\text{Total}} = \Pi_{\text{NP}}(\Gamma_{\text{NP}}) + \Pi_{\text{Bin}}(\theta_{\text{NP}}, \theta_I). \quad (5.9) \]
To employ the model, we need the properties of the pure single components (here the NPs and the TPeA$^+$ ions). For the surface active ion, we characterized the pressure isotherms of TPeA$^+$ adsorption at toluene-water interface (Figure 5-5, Eqns. (5.3)-(5.4)), and obtained the necessary parameters for the TPeA$^+$, see Table 5-2. Similarly the data in Figure 5-3 and Figure 5-6 as well as the EOS of NPs in the absence of TPeA$^+$ give us all the necessary parameter (Table 5-1) to describe the adsorption of the NPs in the absence of TPeA$^+$.

Because we characterized the adsorption of the pure components independently, the only unknown parameter necessary to model the competitive adsorption is $K_{NP-I}$, which describes the interactions between ions and NPs within the interface. While we measure directly the adsorption of NPs in the presence of TPeA$^+$, we do not measure the adsorption of TPeA$^+$ when NPs are present. Here we used the least square fitting to minimize the error between individual data points in the binary pressure isotherms and the predictions using Eqns. (5.6)- (5.9) (see the supporting information for details on fitting). Using this method we can obtain the only unknown fitting parameter $K_{NP-I}$, shown in Table 5-4 for the different experimental conditions. With the value of $K_{NP-I}$ we can predict the ion surface coverage based on Eqn. (5.8), see Figure 5-8.
**Figure 5-8.** TPeA$^+$ area fraction, $\eta_i$ (open symbols), 5 nm NP area fraction $\eta_{NP}$ (solid circles and triangles), and total area fraction, $\eta_{Total} = \eta_i + \eta_{NP}$ (solid diamonds), as the number density of NPs increases in 5 mM TPeAOH solution (black circles) and in 0.01 mM TPeAOH solution (red triangles). The ions and total area fraction is obtained from fitting the pressure isotherms (Figure 5-6B) to the binary Frumkin model, with the fitting parameters in Table 5-4. Green dashed line is a reference for ion area fraction in KOH solution since no TPeA$^+$ ions are present. Red and black dashed lines are fits to the binary model, solid lines are to guide the eye. Total ionic strength of the solutions is 5 mM.

The binary adsorption model shows good agreement with the measured data, see Figure 5-6B and Figure 5-8. In Figure 5-8 we also show that competitive adsorption causes the surface coverage of the TPeA$^+$ cations to decrease as NP bulk density increases. As NPs adsorb to the interface the ion surface density decreases. The adsorption of NPs shifts the equilibrium partitioning between the adsorbed ions and ions in the bulk. Note here, the ion surface coverage is calculated based on the total area of the interface, and would increase
if instead we removed the area occupied by the NPs. Regardless, the ion area fraction decreases in the presence of NPs whether or not it is compared to the total or fluid interfacial area (see Figure S5-3 in Supporting Information). The NP-Ion interaction parameter is comparable across the different solution conditions investigated and between different NP sizes. Based on the parameters listed in Table 5-4 we see that the NP-ion interaction parameter is a relatively strong attraction (the parameter $K_{NP-I}$ is normalized with the thermal energy $kT$). This attraction is consistent with the charge on the NPs being opposite to the charge of the TPeA$^+$ cations (Table S5-4 in supporting information) even if the TPeA$^+$ cations are part of the ligands on the NPs. The strong attraction parameter between the ion and NPs is in sharp contrast with the weak attraction for the NP-NP interaction parameter, and the strong repulsion between ions. Note here that the interaction parameter represents an integration over an interaction potential that can vary spatially between attractive and repulsive interactions. For single components a phase transition at the interface is expected when $K_i < -4$, and $\theta_i = 0.5$. To our knowledge, the interfacial phase behavior for binary mixtures as a function of the Frumkin parameters has not been quantified.

**Table 5-4.** Parameters obtained from fitting the NPs pressure isotherms, $\Pi(C_{NP})$ in the binary system (Figure 5-6B) using Eqns. (5.6)-(5.9).

<table>
<thead>
<tr>
<th>$pH$</th>
<th>$r_{NP}$ (nm)</th>
<th>$[TPeA^+]$ (mM)</th>
<th>$K_{NP-I}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 11.0</td>
<td>3.5</td>
<td>5</td>
<td>-6.8</td>
</tr>
<tr>
<td>pH 11.7</td>
<td>3.5</td>
<td>0.01</td>
<td>-7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>-7.6</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>5</td>
<td>-7.9</td>
</tr>
</tbody>
</table>
The individual contributions of surface activity and wetting of the NPs are shown in the EOS of Figure 5-9. The light yellow area represents increase in the measured surface pressure due to the wetting of the NPs to the interface. The blue area corresponds to the contribution of surface activity: ion-ion interactions, ion-NP interactions, and NP-NP interaction (negligible here, see inset of Figure 5-3A and Figure 5-4). More importantly, note that while the EOS for the NPs in the presence of ions is linear with respect to the surface excess as low area fraction, as would be predicted by Eqn. (5.1), it does not follow Eqn. (5.1). In fact, the surface activity due to ion-NPs interactions plays a very important role in the surface pressure and it would be a mistake to interpret the linear regime as a change in interfacial area. Our measurements provide insight into the interpretation of pendant drop measurement performed during the adsorption of NPs. Efforts often involve trying to attribute the change in interfacial tension as either area replacement or surface activity. Our measurements clearly indicate that both can occur simultaneously, and how each mechanism can be isolated. We find that NPs-ions and ions-ions interactions contribute significantly to the total surface pressure measured during the adsorption on NPs and that their contribution is comparable to the surface pressure caused by the wetting of the NPs to the interface. We demonstrate that ions and NPs adsorption is competitive and reversible for both species. As far as we know, we are the first to demonstrate the competitive adsorption between ions and NPs at oil-water interface.
Figure 5-9. Surface pressure ($\Pi_{Total}$) of 5 nm NPs adsorption in pH 11.7 solutions with 5 mM TPeAOH. $\Pi_{Total}$ contributed from NPs reducing area ($\Pi_{NP}$, solid line, light yellow area), and the contribution from binary interactions ($\Pi_{Bin}$, light cyan area) including ion-ion interaction, NP-NP interaction and ion-NP interaction. The shaded regime is to label the upper and lower limit accounting for NPs polydispersity. Dashed black curve is to guide the eye.

Note that polydispersity may affect the contributions from wetting of the NPs as well (similar to the single component case described earlier). Thus a lower limit of pressure from area reduction is marked here but would not affect the main conclusions. The effect of polydispersity will only affect the ion surface coverage by a negligible amount. This is
due to ion surface coverage is close to saturation value, thus little change in ion surface
corcentration would impart a large change in surface pressure. Not only can the
competitive adsorption model apply to the adsorption of 5 nm NPs from pH 11.7 solutions,
it also applies to other pHs and NP sizes (see Supporting Information, Figure S5-4).

5.4.4 Demonstration of tunability

We use the addition of TPeA$^+$ ions to an interface with adsorbed NPs to demonstrate
that the competitive adsorption can cause desorption of NPs from the toluene-water
interface (see Figure 5-10). Initially NPs were dispersed in 5 mM KOH solutions at pH
11.7, and once toluene is added. The NPs adsorb to the toluene-water interface. After
adsorption under quiescent conditions (12 h) we measure the absorbance (solid black line
in Figure 5-10B). We then add a small volume (2.4 $\mu$L) of concentrated TPeAOH solution
(6.34 mM) to achieve a TPeA$^+$ concentration of 0.01 mM, and total ionic strength is 5.01
mM. After waiting for another 12 h, the third measurement (red dashed line in Figure
5-10B) is taken to obtain the NP bulk density after addition of TPeA$^+$. The difference
between the two measurements is the change of NPs surface coverage upon adding ions. It
is obvious from Figure 5-10B and Table 5-5 that upon the addition of ions the area fraction
of NPs decreases from 0.35 to 0.12, which an important change and agrees with the
equilibrium measurement where the adsorption of ions and NPs occur simultaneously
(Figure 5-6). These experiments therefore demonstrate that the adsorption of ions and NPs
are competitive, reversible, and tunable: addition of ions shifts the equilibrium partitioning
of NPs (desorbing NPs from the interface).
Table 5-5. The NPs bulk density and area fraction of NPs calculated from measurements 1-3 (M1-M3), by assuming a radius of 3.5 nm.

<table>
<thead>
<tr>
<th>$C_{NPs} (10^{12}/mL)$</th>
<th>M1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.82</td>
<td>2.35</td>
</tr>
<tr>
<td>$\eta_{NP}$</td>
<td>0.35</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Figure 5-10. (A) Schematic of the effect of TPeAOH on NPs desorption from the interface. (B) UV-Vis spectrum of the initial 5 nm NPs dispersed in 5 mM KOH solution 12 h after addition toluene to the system (black solid line), and the absorbance 12 h after addition 2.4 $\mu$L of 6.34 mM concentrated TPeAOH solution (red dashed line). The corresponding bulk density and NPs area fraction are listed in Table 5-5.

Additional experiments were conducted using pendant drop shape analysis to demonstrate that addition of TPeA$^+$ leads to desorption of NPs from the interface. Initially a bare toluene droplet is created in 5 mM KOH solution at pH 11.7 with 5 nm NPs dispersed in the aqueous phase. We monitor the interfacial tension until equilibrium is reached. We
then add a small volume of concentrated TPeAOH solution to get a TPeA$^+$ concentration to 0.01 mM. Upon the addition of TPeA$^+$ the IFT decreased, also consistent with earlier measurements indicating that TPeA$^+$ is highly surface active and can displace NPs from the interface. After the dynamic IFT reaches a plateau (Figure 5-11), we create a new bare toluene droplet and again monitor the IFT (Figure 5-11). If we compare the equilibrium IFT between the two cases where the order of adsorption is different we see that the same equilibrium value is obtained, suggesting that the binary adsorption reaches equilibrium (final value independent on pathways). In addition, by comparing the first plateau value in Figure 5-11 (~23 mN/m) and the plateau value in Figure 5-11 (~19.5 mN/m) to the equilibrium measurements, we find that the surface pressures are nearly identical, independent of the order of adsorption. The equilibrium measurements showed that the surface excess of NPs surface coverage is smaller in presence of TPeA$^+$, here we prove that addition of ions can desorb NPs from interface.

**Figure 5-11.** A droplet was immersed in 5 mM KOH solution with 5 nm NPs dispersed, the interfacial tension was monitored till a plateau was reached (black circles), then adding
2.4 μL 63.4 mM concentrated TPeAOH solution, monitor the interfacial tension (red circles) until equilibrium reached. A new created droplet was immersed in the above solution (same NPs density, 0.01 mM TPeAOH solution, total ionic strength is 5.01 mM) and monitor the interfacial tension (blue circles). Insets show the schematic of above described pathway.

The adsorption energy of the 5 nm NPs that we used in the experiments, is around -162 kT (based on Eqn. (5.2)), which is much larger than thermal fluctuations. With such a large adsorption energy one could expect that the adsorption of NPs would be irreversible. However, here the energy associated with the adsorption of the surface active ions is probably comparable to that of the NPs. As a consequence, the ions can cause the NPs to desorb from the interface. We show that adding NPs can desorb the ion, and also that the ions can desorb the NPs, with both processes being reversible (and path independent). Similar displacement has been observed between proteins (macromolecules) and surfactants, where surfactants can partly or even completely displace proteins from the interfaces.

Overall, looking back at the EOS of Figure 5-6, we see that we can see that the competitive adsorption of ions allow us to control both the area fraction of NPs at the oil-water interface and the surface pressure of the interface independently. The concentration of ions and NPs in the aqueous phase act as an external knob, allowing us to obtain different surface pressure while maintaining the NP surface coverage constant (see Figure 5-7). Similarly, we can also keep the surface pressure the same while changing NP surface coverage by changing the ion concentration (Figure 5-6 and Figure 5-7A). This

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independent control of both area fraction and surface pressure is fully described by the competitive adsorption model presented here.

5.5 Conclusion

We characterized the competitive adsorption of NPs and surfactants at the oil-water interface. The particles were 5 nm and 10 nm gold NPs functionalized with ion-pair ligands, while the surface active species was tetraptentyl ammonium cation (TPeA\(^+\)). In contrast to prior work, the competitive adsorption for the oil-water interface occurred without significant binding of the surface active species to the NPs. Throughout our measurements the adsorption of the ions and NPs at the oil-water interface was reversible. We obtained the equation of state (EOS) of the fluid interface through independent measurements of the adsorption and pressure isotherms of the NPs. We presented and validated a competitive adsorption model that takes into account the wetting of the particles at the oil-water interface as well as their surface activity caused by interactions (particle-particle, particle-surfactant, and surfactant-surfactant). The key findings of our work can be summarized as follows:

- The presence of free surface active ions competes with the NPs for the interface, and higher surface pressures are obtained for the binary systems than for the NPs and surfactants individually (Figure 5-6).

- The competitive adsorption model elucidates and isolates how the surface pressure arises from a combination of wetting of the NPs to the interface and the surface activity of the adsorbed species. The independent measurement of the surface
excess and surface pressure allow us to validate the competitive adsorption model. (Figure 5-9)

- Our measurements and thermodynamic model are the first to demonstrate that the adsorption of surfactants and NPs is competitive, reversible, and tunable. We show that adding NPs can cause ions to desorb, and also that the ions can NPs to desorb, with both processes being reversible (and path independent). (Figure 5-8, Figure 5-10, and Figure 5-11).

- Competitive adsorption enables independent control over both area fraction of NPs and surface pressure at the oil-water interface. The concentration of ions and NPs in the aqueous phase can be used to control both parameters (Figure 5-6 and Figure 5-7A).

5.6 Supporting Information

5.6.1 Characterization of ion-pair gold NPs

Fourier transform infrared (FTIR) spectroscopy is used to characterize the surface functionality of the ligands on the 5 nm and 10 nm NPs. As described in our previous work\textsuperscript{32,112}, the ion-pair of TPeA/MHA on the NPs surface will lead to asymmetric and symmetric CH\textsubscript{3} stretching bands at 2955 ± 3 cm\textsuperscript{-1} and 2870 ± 2 cm\textsuperscript{-1}, respectively (Figure S5-1A). Deprotonation of the carboxylate group is evident from the presence of a band at 1560 cm\textsuperscript{-1} (asymmetric COO\textsuperscript{-} stretch), and consistent with the presence of ion-pairs between TPeA\textsuperscript{+} ions and deprotonated MHA bound on the gold surface (Figure S5-1A). We previously calibrated the CH\textsubscript{2}/CH\textsubscript{3} infrared absorbance intensity\textsuperscript{32} to quantify the stoichiometry between TPeA\textsuperscript{+} and MHA on the surface of gold NPs. Using the same
calibration here we find that the ligands on the particles employed in the experiments have a stoichiometric ratio that is also very close to 1 : 1 TPeA\(^+\) : MHA (Table S5-1).

Ultraviolet-visible (UV-Vis) spectroscopy is employed to characterize the size and concentration of both 5 nm and 10 nm gold NPs dispersed in aqueous solutions. A surface plasma band (SPB) peak at 530 ± 3 nm and 538 ± 2 nm (Figure S5-1B) indicates the size of gold NPs in aqueous solution to be around 5 nm and 10 nm according to our previous characterization.\(^{32}\)

The gold NPs are imaged using transmission electron microscopy (TEM) (Figure S5-1C-D) right after synthesis. Prior to electron microscopy the NPs are dispersed in 2-propanol by sonication for 5 min, after which 5 \(\mu\)L of the solution is dispensed on carbon-coated copper grids (Electron Microscopy Services, Hatfield, PA). The grid is left to dry at room temperature overnight before imaging, which could cause some aggregation of NPs on the grid. Insets show the size distribution of the 5 nm and 10 nm NPs by analyzing at least 200 NPs from TEM imaging.

<table>
<thead>
<tr>
<th>TPeA : MHA molar ratio</th>
<th>Asym. CH(_2/CH_3)</th>
<th>Sym. CH(_2/CH_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm NPs</td>
<td>0.91 ± 0.2</td>
<td>1.12 ± 0.1</td>
</tr>
<tr>
<td>10 nm NPs</td>
<td>0.96 ± 0.3</td>
<td>1.09 ± 0.2</td>
</tr>
</tbody>
</table>

Table S5-1. Measured composition of ion-pair gold nanoparticles as synthesized. Molar ratio of TPeA : MHA was calculated using the calibration for the CH\(_2/CH_3\) intensity ratio.\(^{32}\)
Figure S5-1. Characterization of gold nanoparticles. (A) FT-IR characterization of 5 nm (black curve) and 10 nm (red curve) ion-pair gold nanoparticles as synthesized. (B) UV-Vis absorption spectrum of 5 nm (black curve) and 10 nm (red curve) ion-pair gold nanoparticles as synthesized. TEM imaging: 5 nm gold nanoparticles (C) and 10 nm gold nanoparticles (D) are dispersed in 2-propanol using sonication and dispersed on TEM grid. The inlets are size distribution of gold NPs with image analysis.

The size of the NPs in solution is measured with dynamic light scattering (DLS, Zetasizer Nano-ZS90, Malvern Instruments) using disposable plastic cuvettes (4 optical
side polystyrene, Sarstedt AG & Co) and the standard options provided in Malvern software. Results of the measurements for the two difference sizes are shown in Table S5-2.

**Table S5-2.** Size measurements using DLS of NPs dispersed in different solution conditions.

<table>
<thead>
<tr>
<th>pH</th>
<th>[TPeA⁺] / mM</th>
<th>Small NPs Diameter (nm)</th>
<th>Large NPs Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 11.0</td>
<td>0</td>
<td>5.5 ± 1.5</td>
<td>10.6 ± 1.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.9 ± 1.2</td>
<td>10.8 ± 1.7</td>
</tr>
<tr>
<td>pH 11.7</td>
<td>0</td>
<td>4.6 ± 1.9</td>
<td>10.2 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.7 ± 1.7</td>
<td>10.3 ± 1.9</td>
</tr>
</tbody>
</table>

5.6.2 *Fitting single component adsorption isotherms to Frumkin model with all data*

The adsorption isotherms of NPs in different solution conditions are fit to Frumkin adsorption isotherm using only the data at low coverage to reduce the possible effect of polydispersity on the fitting parameters. However, compared to using only data at low coverage, incorporating all data into fitting does not change the fitting parameters by much (shown Table S5-3).

The Frumkin adsorption isotherm is given by:

\[
C_{NP}(\theta_{NP}) = a_{L,NP} \frac{\theta_{NP}}{1 - \theta_{NP}} \exp(K_{NP,\theta_{NP}}),
\]

where \(C_{NP}\) is the bulk number density of NPs in #/mL, \(a_{L,NP}\) is the dissociation constant characterizing the affinity of NPs to toluene-water interface, \(\theta_{NP} = \Gamma_{NP}/\Gamma_{NP,\infty}\) is the fractional coverage of NPs at the interface, and \(\Gamma_{NP,\infty}\) is the maximum coverage of NPs at the toluene-water interface, and \(K_{NP}\) describes the interactions between NPs within the interface.
Table S5-3. Fitted parameter for fitting the adsorption isotherms of NPs alone adsorption at toluene-water interfaces using Eqn. (5.10).

<table>
<thead>
<tr>
<th>pH</th>
<th>r&lt;sub&gt;NP&lt;/sub&gt; (nm)</th>
<th>a&lt;sub&gt;L,NP&lt;/sub&gt; (#/mL)</th>
<th>K&lt;sub&gt;NP&lt;/sub&gt;</th>
<th>Γ&lt;sub&gt;NP,∞&lt;/sub&gt; (#/nm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>η&lt;sub&gt;NP,∞&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0</td>
<td>3.5</td>
<td>1.5×10&lt;sup&gt;12&lt;/sup&gt;</td>
<td>0</td>
<td>0.022</td>
<td>0.85</td>
</tr>
<tr>
<td>11.7</td>
<td>3.5</td>
<td>3.0×10&lt;sup&gt;12&lt;/sup&gt;</td>
<td>0</td>
<td>0.018</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>2.7×10&lt;sup&gt;12&lt;/sup&gt;</td>
<td>-1.8</td>
<td>0.008</td>
<td>0.95</td>
</tr>
</tbody>
</table>

5.6.3 NPs zeta potential and surface charge density

Zeta potential is measured using DLS with disposable folded capillary cuvettes (1006C, Malvern Instruments). The Debye-Hückel equation is used to calculate the zeta potential from the mobility. Based on the measurements, the surface charge density (σ) of the NPs is estimated, using the equation given by<sup>32</sup>:

\[
\sigma = \frac{\varepsilon_0 \varepsilon_r kT}{e z} \kappa \left[ 2 \sinh \left( 0.5 \Psi_s \right) + \frac{4}{\kappa \tau} \tanh \left( 0.25 \Psi_s \right) \right],
\]

(5.11)

where \(\varepsilon_0\) is the permittivity constant, \(\varepsilon\) is the permittivity of aqueous solution, \(e\) is element charge, \(z\) is valency, \(\kappa\) is Debye length, given by \(\kappa = \left( \frac{\varepsilon_0 \varepsilon_r kT}{\sum c_i z_i^2 e^2} \right)^{-0.5}\), \(c_i\) is concentration of species \(i\), and \(\Psi_s\) is given by \(\Psi_s = ze \psi_s / kT\), where \(\psi_s\) is the zeta potential (used to approximate surface potential) of NPs. The measurements of the zeta potential and the corresponding estimate of the surface charge density is listed in Table S5-4. It is obvious that the change in zeta potential is small, especially comparing to the variance of the measurements, and the same trend can be observed from the corresponding surface charge density.
Table S5-4. Zeta potential of 5 nm NPs measured with DLS and the corresponding surface charge density calculated using Eqn. (5.11).

<table>
<thead>
<tr>
<th>pH</th>
<th>[TPeA(^-)] / mM</th>
<th>Zeta potential / mV</th>
<th>Surface charge density / C·m(^-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0</td>
<td>0</td>
<td>-51.7 ± 4.2</td>
<td>-0.0192</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-42.6 ± 5.6</td>
<td>-0.0156</td>
</tr>
<tr>
<td>11.7</td>
<td>0</td>
<td>-52.5 ± 7.7</td>
<td>-0.0195</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-41.8 ± 5.7</td>
<td>-0.0153</td>
</tr>
</tbody>
</table>

5.6.4 Fitting adsorption isotherms to Frumkin model

The adsorption isotherms of NPs alone at low concentration were fit to the single component Frumkin adsorption isotherm (described by Eqns. (5.3)-(5.4) in the main text) using MATLAB 2015b by minimizing the distance between each of the data points and the theoretical curve, that is, to minimize the following Eqn. (5.12):

\[
 d = \frac{1}{m} \sum_{i=1}^{m} (X_i - \bar{X}_i) \ ,
\]  

(5.12)

where \(X_i\) is the experimental data of NPs bulk number density, and \(\bar{X}_i\) is the theoretical predicted value using Eqn. (5.3) in main text. Here the fitting parameters for adsorption isotherms are \(a_{L,NP}\), and \(K_{NP}\).

5.6.5 Pure interface (toluene-5 mM KOH solution) interfacial tension

The pure interfacial tension is measured with pendant drop shape analysis with 5 mM KOH solution – toluene interface, as shown below:
5.6.6 *Fitting binary pressure isotherms to binary Frumkin model*

The binary (NPs and TPeA$^+$ ions) pressure isotherms as a function of NPs bulk number density are fit to the binary Frumkin model combined with the area reduction model described by Eqns. (5.6)-(5.9) in the main text. Since the parameters describing single component systems (NPs and ions respectively) are obtained independently, here the only fitting parameter is $K_{NP-I}$. However, since we did not measure the ion surface density directly, we also need to extract the ion surface concentration during the fitting. We do a least square error fitting as well use MATLAB 2015b, note here at each set of data ($C_{NP}$, $\Pi_{Total}$), we treat ion surface coverage as unknown, thus we can obtain the $K_{NP-I}$ that minimizes the distance between experimental measurements and theoretical estimations, shown below:

*Figure S5-2.* Dynamic interfacial tension of toluene-5 mM KOH solution using pendant drop shape analysis.
\[ D = \frac{1}{m} \sum_{i=1}^{m} \left( X_i - \bar{X}_i \right), \]  

(5.13)

where \( X_i \) is the experimental data of NPs bulk number density, and \( \bar{X}_i \) is the theoretical predicted value using Eqn. (5.7) in main text, \( Y_i \) is the total pressure measured and \( \bar{Y}_i \) is the theoretical predicted value using Eqn. (5.9) in main text, \( Z_i \) is the TPeA\(^+\) concentration is the bulk aqueous phase, and \( \bar{Z}_i \) is the theoretical predicted value using Eqn. (5.8) in main text.

### 5.6.7 Ion surface coverage based on fluid area

The ion surface coverage obtained directly is based on the total interfacial area. However, it has been shown that adsorption of NPs at the interface would replace interfacial area, thus would directly causing desorption of ions while still possible to maintain the same equilibrium of ions with the bulk phase. Here we compare the ion surface coverage based on the actual fluid area, \( \Gamma'' \) (considering the replacement of interfacial area by NP adsorption), which can be related to the coverage based on total area, \( \Gamma \), by:

\[ \Gamma' = \Gamma \cdot \frac{1}{1 - \eta_{NP}}. \]  

(5.14)

In Figure S5-3, the two coverages are compared (solid symbols are for \( \Gamma'' \), and open symbols are for \( \Gamma \)). It is obvious that when considering the fact that NP adsorption replaces interfacial area, and thus would desorb ions, the equilibrium of ion between interface and the bulk phase is still shifted, yet with less so.
Figure S5-3. (A) TPeA$^+$ surface coverage as 5 nm NPs number densities increases in 5 mM TPeAOH solution (black hollow circles) and in 0.01 mM TPeAOH solution (red hollow triangles), based on the total area ($A_{Total}$), while the solid symbols with the same color coding correspond the coverage based on fluid area ($A_{Fluid}$). (B) TPeA$^+$ surface coverage during 5 nm NPs adsorption to the interface in 5 mM TPeAOH solution (black hollow circles) and in 0.01 mM TPeAOH solution (red hollow triangles), based on the total area ($A_{Total}$), while the solid symbols with the same color coding correspond the coverage based on fluid area ($A_{Fluid}$). Lines are to guide the eye.

5.6.8 Applying the binary model to other systems

In addition to the experimental system discussed in the main text, this binary model can also be extended to describe competitive adsorption at different pH and with different NP sizes. Here we use the fitting parameters listed in Table 5-1 and Table 5-4 in the main text to predict the EOS of 5 nm NP adsorption in pH 11.0 solution (pink circles), as well
as 10 nm NPs in pH 11.7 solutions (yellow diamonds) (Figure S5-4). Good agreement is reached between measurements and theoretical predictions. We also reach the same conclusions that ions are desorbing as NPs adsorb to the interface (ion equilibrium shifted). Comparing between two different pH (black circles and pink circles), it is obvious that at lower pH, ions desorb at lower NP concentration, likely due to less attraction between ions and the interface at lower pH (Figure 5-4 in main text). Also, as larger NPs adsorb to the interface, more ions desorb, due to a greater change in interfacial area.
Figure S5-4. EOSs (A) and adsorption isotherms (B) of 5 nm NPs in 5 mM TPeAOH solutions at pH 11.0 (pink solid circles) and pH 11.7 (black solid circles), and 10 nm NPs in 5 mM TPeAOH solution at pH 11.7 (yellow diamonds), and the corresponding TPeA$^+$ surface coverage (C) as the NPs adsorbing to the interface obtained from fitting the pressure isotherms to Eqns. (5.6)-(5.9) in the main text. Dashed lines are fitting to the competitive adsorption model.
6 Dynamic Interfacial Tension of NPs

6.1 Overview

We report here modeling of the adsorption dynamics for both single component (NP only) and binary (NP + surfactant) mixture using Ward-Tordai model incorporated with Gibbs adsorption isotherm and wetting EOS.

6.2 Introduction

Adsorption of particles or nanoparticles (NPs) decreases the interfacial tension of a fluid interface and leads to the stabilization of foams and emulsions.\textsuperscript{4, 7, 163} Particle-laden fluid interfaces have also received attention for their applications in catalysis,\textsuperscript{164-165} sensing,\textsuperscript{166-167} and optics.\textsuperscript{68, 168} As a particle adsorbs, oil-water interfacial area is replaced by particle-fluid interfaces. This area replacement causes a decrease of the free energy of the interface, $\Delta E$, (per particle) given by Eqn. (6.1):\textsuperscript{47}

$$\Delta E = -\pi r_N^2 \gamma_{OW} \left(1 \pm \cos \theta_{OW}\right)^2,$$

where $r_N$ is the radius of the NP, $\gamma_{OW}$ is the oil-water interfacial tension, and $\theta_{OW}$ is the contact angle formed by the NP at the oil-water interface.
The decrease in interfacial tension (IFT) caused by the adsorption of a species to a fluid interface is a macroscopic mechanical response that is easily accessible experimentally. For surfactants, the IFT can be employed in conjunction with the Gibbs adsorption isotherm to determine the adsorbed amount when equilibrium is established between the bulk and the interface.\textsuperscript{169} In the case of particle adsorption, steady-state IFT measurements have been employed to test the applicability of Eqn. (6.1).\textsuperscript{46, 113} Similarly, dynamic IFT measurements allow for the characterization of mass transfer and adsorption processes. In the case of surfactants, analysis and interpretation of dynamic IFT measurements have been employed to explain induction times,\textsuperscript{170-171} extract energy barrier,\textsuperscript{172-173} study interfacial phase transitions during adsorption,\textsuperscript{170, 174} and to validate adsorption isotherms and surface equations of state.\textsuperscript{169} However, unlike surfactants, there are no validated models for the diffusion-limited adsorption of particles to fluid interfaces. Despite the importance of particle-laden interfaces, the dynamic of their adsorption to fluid interfaces and its impact on interfacial tension remains poorly understood.\textsuperscript{108, 122} For example, Colosqui \textit{et al.}\textsuperscript{175} has shown that the particle surface heterogeneities may result in physical aging and jamming, giving rise to unexpected long relaxation.

Understanding how particle adsorption influences dynamic IFT has proven to be challenging. Due to their relatively larger sizes compared to surfactants, particles have a smaller diffusivity that slow adsorption and, as a result, dynamic IFT measurements are more susceptible to convection. In addition, the large adsorption energy given by Eqn. (6.1) often makes the adsorption process irreversible, rendering data interpretation more challenging.\textsuperscript{49, 108} Moreover, there is evidence that in some instances adsorbed particles form multilayers or even aggregates at the interface.\textsuperscript{176-177} Finally, there has been limited
characterization of equilibrium particle adsorption at oil-water interfaces.\textsuperscript{112, 178} In particular, adsorption isotherms and EOS are necessary to model the dynamic interfacial tension, and those are often lacking for particle adsorption to fluid interfaces. Despite these challenges, efforts to model the dynamic IFT have clearly demonstrated that the diffusion-limited adsorption of particles is quantitatively different from that of surfactants.\textsuperscript{27, 108, 120} In particular, corrections from the asymptotic behaviors for the dynamic of surfactant adsorption\textsuperscript{179} are necessary to obtain the particle diffusivity. Bizmark \textit{et al.}\textsuperscript{108} corrected for particle wetting (Eqn. (6.1)) and showed good agreement for the short-time diffusion-limited adsorption limit, as described by the Ward-Tordai equations.

Previously, we reported on the reversible adsorption of 5 nm and 10 nm gold nanoparticles functionalized with ion-pair ligands (Figure 6-1 left panel).\textsuperscript{32, 112} Based on pressure and adsorption isotherms, we constructed the equation of state (EOS) for the particles at the oil-water interface. We showed that the adsorption isotherm was well-described by the Frumkin isotherm, while the surface pressure measured in the EOS had two contributions: one originating from the wetting of the NPs to the oil-water interface and the other from the surface activity of the NPs at the oil-water interface. We showed that the contribution from surface activity on the surface pressure was much weaker compared to that of wetting, and in many cases could safely be neglected. However, the dynamics of the diffusion-limited NP adsorption to the oil-water interface was not characterized and compared to a mass transfer model, such as the Ward-Tordai equations used for surfactant adsorption.

Here we show that the Ward-Tordai equations can fully describe the dynamic IFT for 5 nm and 10 nm ion-pair NPs at the water-toluene interface. We show that the Ward-
Tordai equations, when combined with the equilibrium model developed previously, lead to good agreement between data and experiments for the whole adsorption process. The comparison between experiments and the model is achieved without relying on any additional fitting parameters. We also observe deviations between the model and experiments at high surface coverage that could be signature of other kinetic limitations. Finally, we also show that our model can effectively capture the competitive adsorption between NPs and a surfactant for the oil-water interface. To the best of the authors’ knowledge, the data presented here is the first direct test of a measurement and model for the diffusion-limited adsorption of NP to the oil-water interface.

**Figure 6-1.** Schematic of adsorption dynamics illustrating the two primary steps governing the mass transfer to the interface: 1) the adsorption (black up arrow) and desorption (black down arrow) between the sub-surface region and the interface, as well as 2) the diffusion (red arrows) from bulk phase to the sub-surface. The processes are shown for single components (NPs, left panel, and TPeA\(^+\) ion, middle panel) and for a binary mixture (NPs-TPeA mixture, right panel).
Diffusion-limited adsorption model

Ward-Tordai model

The adsorption process in the Ward-Tordai model (Eqn. (6.2)), originally developed for surfactant adsorption to a clean interface is governed by two primary steps: 1) the diffusion of the species from the bulk phase to the sub-surface, followed by 2) the adsorption from the sub-surface region onto the interface, as illustrated in Figure 6-1. In the case of diffusion-limited adsorption, it is assumed that instantaneous equilibrium is established between the surface excess at the interface ($\Gamma_i$) and the concentration in the sub-surface region ($c_i$). Thus the rate of adsorption is limited by the diffusion from bulk phase to the sub-surface region, which can be described by Fick’s law. The solution of the Ward-Tordai model (Eqn. (6.2)) has been employed to capture the diffusion-limited adsorption of various surfactants and macromolecules. Due to near-spherical shape in pendant drop measurements, we rely on the formulation of Lin et al. in spherical coordinates given by:

$$\Gamma_i(t) = \sqrt{\frac{D_i}{\pi}} \left\{ 2C_i \sqrt{t} - \int_0^t \frac{c_i(\tau)}{\sqrt{t-\tau}} d\tau \right\} + \frac{D_i}{r_D} \left\{ C_i t - \int_0^t c_i(\tau) d\tau \right\}, \quad (6.2)$$

where $i$ is the surface active species (NPs for example), $C_i$ is the bulk concentration of the adsorbing species, $r_D$ is the radius of the pendent droplet. $D_i$ is the diffusivity of the adsorbing species, which can be estimated using Stokes-Einstein equation:

$$D_{i-SE} = \frac{kT}{6\pi \mu r_i}, \quad (6.3)$$

where $D_{i-SE}$ specifically refers to the diffusivity predicted using Eqn. (6.3), $k$ is the Boltzmann constant, $T$ is temperature, $\mu$ is the fluid viscosity, and $r_i$ is the radius of the surface active species, here referring to NP for example (Figure 6-1).
Single component adsorption

In diffusion-limited adsorption, instantaneous equilibrium is established between the sub-surface and the interface. The time-dependent surface coverage ($\Gamma_i(t)$) can be related to the sub-surface concentration ($c_i(t)$) through an adsorption isotherm. Here we employ the Frumkin adsorption isotherm, which incorporates non-ideal interactions between adsorbed species within the interface\textsuperscript{41,51}, and describes well the adsorption of the NPs investigated here\textsuperscript{41} as well as surfactants at oil-water interfaces, and is given by:

$$c_i(t) = a_{L,i} \frac{\theta_i(t)}{1-\theta_i(t)} \exp\left[K_i \theta_i(t)\right], \quad (6.4)$$

where $i$ is the adsorbed species (NPs for example), $\theta_i(t) = \Gamma_i(t)/\Gamma_{i,\infty}$ is the transient relative coverage of the surface-active species $i$ at the interface at time $t$, and $\Gamma_{i,\infty}$ is the maximum surface excess of $i$. The affinity between the surface active species and the interface is captured by the dissociation constant, $a_{L,i}$, while the parameter $K_i$ accounts for the interactions between the species $i$ within the interface relative to the thermal energy, $kT$,\textsuperscript{42} where a positive value represents net repulsion, and a negative value represents attractive interactions.\textsuperscript{43}

The integration of the Ward-Tordai equation combined with the Frumkin adsorption isotherm (Eqns. (6.2)-(6.4)) results in dynamic surface excess, which is not easily accessible experimentally. Therefore, an EOS is necessary to relate the surface excess to a measurable dynamic IFT. The corresponding Frumkin EOS, that is thermodynamically consistent with the Frumkin adsorption isotherm following the Gibbs adsorption criteria,\textsuperscript{1} dictates the contribution from surface activity of NPs ($\Pi_{Sd}$), to be\textsuperscript{41,51}:

$$\Pi_{Sd} = -kT \Gamma_{i,\infty} \left[\ln(1-\theta_i) - 0.5K_i \theta_i^2\right]. \quad (6.5)$$
The thermodynamic parameters (parameters in Eqns. (6.4)-(6.5)) associated with description of equilibrium adsorption behavior can be obtained via fitting to equilibrium data (pressure isotherm or adsorption isotherm).\textsuperscript{112}

\textit{Wetting EOS for NP adsorption}

Measured surface pressures caused by NP adsorption are often much larger than those predicted by the Frumkin EOS.\textsuperscript{112-113, 120} The main contribution to the surface pressure is that of the wetting of the NPs at the liquid-liquid interface, as fluid-fluid area is replaced by particle-fluid area.\textsuperscript{47} Du \textit{et al.} proposed that the surface pressure ($\Pi_{NP}$) originating from this area replacement process is given by\textsuperscript{46}:

$$\Pi_{NP} = |\Delta E| \times \Gamma_{NP},$$

(6.6)

where $\Gamma_{NP}$ is the surface coverage of NP at oil-water interface, and $\Delta E$ is the adsorption energy of a single NP given by Eqn. (6.1).

We suggested previously that the measured surface pressure originates from both the surface activity (Eqn. (6.5)) and wetting (Eqn. (6.6)) of the NPs, and validated this hypothesis through measurements of equilibrium pressure and adsorption isotherms.\textsuperscript{115} We proposed that the two contributions could be treated as additive. As a result, the transient reduction in interfacial tension when incorporating these contributions will be given by:

$$\gamma(t) = \gamma_{OW} - \Pi_{SA}(t) - \Pi_{NP}(t).$$

(6.7)

Therefore, prediction for the dynamic IFT due to diffusion-limited adsorption of NPs to an oil-water interface can be obtained by solving Eqns. (6.2)-(6.7). Note here that this approach is different from surfactant adsorption, where surface activity is the only contribution to the measured IFT.
**Binary adsorption**

We also extend the model to the case of competitive adsorption between NPs and surfactants. Thus, a binary Frumkin model\textsuperscript{156} is employed to describe the adsorption isotherms for the two species (NPs and surfactant), which includes the interactions between individual species ($K_{NP}$, $K_i$) and between different species (i.e., NP-ion interactions, $K_{NP,i}$). The corresponding isotherms that captures the instantaneous equilibrium between surface coverage ($\Gamma_i(t)$) and sub-surface concentration ($c_i(t)$) of the two species are given by\textsuperscript{54,156}:

\begin{equation}
    c_i(t) = a_{L,i} \frac{\theta_i(t)}{1 - \theta_i(t) - \theta_{NP}(t)} \exp\left[ K_i \theta_i(t) + K_{NP-i} \theta_{NP}(t) \right], \quad (6.8)
\end{equation}

\begin{equation}
    c_{NP}(t) = a_{L,NP} \frac{\theta_{NP}(t)}{1 - \theta_{NP}(t) - \theta_i(t)} \exp\left[ K_{NP} \theta_{NP}(t) + K_{NP-i} \theta_i(t) \right]. \quad (6.9)
\end{equation}

The corresponding binary EOS related to the binary Frumkin adsorption isotherms is:\textsuperscript{54,156}

\begin{equation}
    \Pi_{Bin} = -kT \Gamma_w \left[ \ln(1 - \theta_i - \theta_{NP}) - 0.5 K_i \theta_i^2 - 0.5 K_{NP} \theta_{NP}^2 - K_{NP-i} \theta_i \theta_{NP} \right], \quad (6.10)
\end{equation}

where $\Gamma_w = (\Gamma_i + \Gamma_{NP})/(\theta_i + \theta_{NP})$ is the total surface coverage, allowing for different maximum coverage for each of the individual components.\textsuperscript{156}

Similar to our approach for NP adsorption, we propose that two contributions (surface activity and wetting of the interface) cause a reduction of the interfacial tension. By adding the two contributions, the instantaneous reduction of the IFT is:

\begin{equation}
    \gamma(t) = \gamma_{OW} - \Pi_{Bin}(t) - \Pi_{NP}(t). \quad (6.11)
\end{equation}
Thus the diffusion-limited adsorption in the case of competitive adsorption is obtained by solving the Ward-Tordai equation (Eqns. (6.2)-(6.3)) along with the proposed binary NP-TPeA\(^+\) mixture adsorption (Eqns. (6.8)-(6.11)) to give predictions of dynamic IFT.

6.3 Materials and Methods

6.3.1 Reagents and chemicals.

All reagents and chemicals are used as received. Potassium hydroxide (KOH, 99.9%), pellets, potassium chloride (KCl, 99.9%), 16-mercaptohexadecanoic acid (MHA, 99%), gold chloride hydrate (HAuCl\(_4\), >49% Au), sodium borohydride (NaBH\(_4\), >96%), tetrapientsylammonium chloride (TPeACl, 99%), tetrapientsylammonium hydroxide (TPeAOH, 20wt% 1 M aqueous solution) are purchased from Sigma-Aldrich. Sulfuric acid (H\(_2\)SO\(_4\), 95.0 to 98.0 w/w %), hydrogen peroxide (H\(_2\)O\(_2\), 30.0 to 32.0%), 2-propanol (> 99.9%), toluene (> 99.8%), NaCl salt disk, and RBS 35 Detergent Concentrate are purchased from Fisher Scientific. Deionized water (DIW, 18.2 M\(\Omega\cdot\text{cm}\)) is obtained from a Milli-Q Gradient system. All glassware, unless otherwise noted, are thoroughly cleaned with piranha solution (4:1 H\(_2\)SO\(_4\):H\(_2\)O\(_2\)), rinsed with DIW and dried overnight in air prior to use. Synthesis, purification, and characterization of ion-pair NPs are reported in our previous work\(^{112}\) All experiments are performed at 295 K.

6.3.2 Solution conditions used to disperse NPs for all experiments.

Throughout the experiments, the ionic strength of all aqueous solutions is maintained constant at 5 mM. The pH of the aqueous phase is adjusted by mixing different ratios of 5 mM KOH/KCl, or different ratios of 5 mM TPeAOH/TPeACl. The TPeA\(^+\) ion concentration at a fixed aqueous pH is adjusted by mixing different ratios of pH11.0
KOH/KCl solutions and pH11.0 TPeAOH/TPeACl solutions, or mixing different ratios of pH11.7 KOH and pH11.7 TPeAOH solutions.

6.3.3 Dynamic interfacial tension measurements.

Dynamic interfacial tension measurements are conducted using the pendant drop method. A toluene drop is formed in aqueous solutions of dispersed NPs. The IFT is monitored as soon as the drop is formed and for over 15,000 s for the 5 nm NPs, and more than 50,000 s for the 10 nm NPs. All the measurements and fits of the drop shapes to the Young-Laplace equation are performed with a FTA 125 apparatus and software (First Ten Angstroms). Prior to the measurements the glass cuvette, glass syringe (2.5 mL, Model 1002 TLL SYR, Hamilton), stainless steel J-needle (20 Gauge, 304SS hub, Cadence), as well as the tubing (Fisher scientific Co.) are sonicated in 1% v/v dilute RBS solution and rinsed thoroughly with deionized water. The glass syringe, stainless steel J-needle, and the tubing were dried with N2 and stored in toluene overnight while the glass cuvettes are stored in deionized water. Right before the measurements the cuvette is rinsed thoroughly with the gold NPs solution and the needle and tubing with toluene. All connections are sealed with Teflon tape (Fisher Scientific) first and then Parafilm (Parafilm M).

6.3.3 Numerical algorithm.

The Ward-Tordai equation is solved numerically following the exact procedure reported by Li et al.\textsuperscript{180}. In short, we use the trapezium rule of numerical integration, while the accuracy of the root finding procedure is ensured by bisection method. A step size of 1 sec is used in our numerical scheme. An error of $1 \times 10^{-10}$ #/nm$^2$ is allowed during the root finding scheme. A constraints is also set during the root finding so that the coverage is not allowed to exceed the maximum coverage of the species.
6.4 Results and Discussions

6.4.1 NP adsorption dynamics

We characterized the adsorption of ion-pair NPs at the oil-water interface using pendant drop measurements to test the diffusion-limited adsorption model. The dynamic interfacial tension is obtained during the adsorption of NPs from the aqueous phase and shown in Figure 6-2. We measured the dynamic IFT during the adsorption of 5 nm NPs from an aqueous solution at pH 11.0 and at pH 11.7. We also repeated the measurements with 10 nm NPs from an aqueous solution at a pH of 11.7. For all three cases, we varied the bulk concentrations of NPs in the aqueous phase to access equilibrium area fractions that span the full range in the measured EOS (shown in the bottom panel of Figure 6-2). For clarity we separated the dynamic IFT data leading to area fraction < 0.3 from those leading to higher area fractions in Figure 6-2. We observe that the IFT decreases faster, and equilibrium IFT is lower as the NP bulk concentration increases, consistent with reported behavior of dynamic IFT for NPs (and surfactants) at the oil-water interface.\textsuperscript{95,108,178}

We fit the measured adsorption isotherm to the Frumkin isotherm (Eqn. (6.4)) to obtain the equilibrium parameters \((a_{L,NP}, K_{NP}, \Gamma_{NP,\infty})\). These parameters are listed in Table 1, are discussed in our prior work\textsuperscript{115}, and the adsorption isotherms are shown in Figure S6-1. The equilibrium parameters are incorporated in the Ward-Tordai model (Eqn. (6.2)) to obtain the time-dependent surface coverage of the NPs, \(\Gamma_{NP}(t)\). The diffusivities of the NPs calculated from the Stokes-Einstein equation (Eqn. (6.3)) are \(8.6 \times 10^{-11}\) m\(^2\)/s and \(4.3 \times 10^{-11}\) m\(^2\)/s for the 5 nm and 10 nm NPs, respectively. Finally, the wetting EOS for the NPs (Eqn. (6.6)) is necessary to compute the dynamic interfacial tension, and we use a core radius with an additional 1 nm for \(r_{NP}\) to account for the surface functional groups.\textsuperscript{112}
corresponding measured EOS is shown in the bottom row of Figure 6-2, where the red solid lines represent the wetting EOS (Eqn. (6.6)). As discussed previously, the data deviates from the predictions of Eqn. (6.6) at higher coverage. We suspect that these deviations are due to polydispersity, where the average NP radius contributing to the equilibrium pressure is smaller at higher coverage. The insets in the EOS show the effective radii corresponding to each equilibrium pressure, which is obtained from

\[ r_{\text{eff}} = r_{\text{NP}} \sqrt{\Pi_{\text{NP}} \gamma_{\text{OW}} \eta_{\text{NP}}} \]. When fitting the dynamic IFT we use the effective radii obtained from the EOS for all concentrations.
Figure 6-2. Dynamic interfacial tension of (A,B) 5 nm NPs in pH 11.0 solution with NP concentrations of $3.5 \times 10^{10}$ /mL (black), $1.2 \times 10^{11}$ /mL (red), $3.5 \times 10^{11}$ /mL (green), $5.5 \times 10^{11}$ /mL (blue), and $1.5 \times 10^{12}$ /mL (pink); (D,E) 5 nm NP in pH 11.7 solution with NP concentrations of $4.7 \times 10^{11}$ /mL (black), $6.4 \times 10^{11}$ /mL (red), $8.5 \times 10^{11}$ /mL (green), $1.2 \times 10^{12}$ /mL (blue), and $5.6 \times 10^{12}$ /mL (pink); and (G,H) 10 nm NP in pH 11.7 solution, with NP concentrations of $6.3 \times 10^{10}$ /mL (black), $1.2 \times 10^{11}$ /mL (red), $3.7 \times 10^{11}$ /mL (green), $8.0 \times 10^{11}$ /mL (blue), $9.0 \times 10^{12}$ /mL (pink). For the first two row, the solid lines are predictions from Eqns. (6.2)-(6.7), with parameters listed in Table 6-1, and dashed lines are with the diffusivity as an adjustable parameter. The measured EOS for the NPs are shown for (C) 5 nm NPs at pH 11.0 (F) 5 nm NPs at pH 11.7, and (I) 10 nm NP at pH 11.7. The color of the data points in (C), (F), and (I) corresponds to each dynamic interfacial
tension data shown in the upper panels. Insets of (C), (F), and (I) are the calculated size based on Eqn. (6.6). For all measurements the ionic strength is 5 mM.

**Table 6-1.** Parameters for the Frumkin adsorption isotherm (Eqn. (6.4)). The relationship between the area fraction of the NPs, $\eta_{NP}$, and their surface excess, $\Gamma_{NP}$, is $\eta_{NP} = \Gamma_{NP} A_{NP}$, and $A_{NP} = \pi r_{NP}^2$.

<table>
<thead>
<tr>
<th>pH</th>
<th>$r_{NP}$ (nm)</th>
<th>$a_{L,NP}$ (#/mL)</th>
<th>$K_{NP}$</th>
<th>$\Gamma_{NP,\infty}$ (#/nm$^2$)</th>
<th>$\eta_{NP,\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0</td>
<td>3.5</td>
<td>$1.6 \times 10^{12}$</td>
<td>0</td>
<td>0.022</td>
<td>0.85</td>
</tr>
<tr>
<td>11.7</td>
<td>3.5</td>
<td>$3.1 \times 10^{12}$</td>
<td>-0.3</td>
<td>0.018</td>
<td>0.71</td>
</tr>
<tr>
<td>6.0</td>
<td>2.7 $\times 10^{12}$</td>
<td>-1.6</td>
<td>0.008</td>
<td>0.95</td>
<td></td>
</tr>
</tbody>
</table>

The measured dynamic IFT is well-described with the proposed model, as shown from the solid lines of Figure 6-2. Note that no fitting parameters are used when comparing the dynamic IFT to the model. In general, the model captures well the diffusion-limited dynamics and equilibration time for area fraction lower than ~0.3. The agreement between the data and the model demonstrates that the treatment for NP adsorption is different from that of surfactant due to the presence of the wetting EOS. In fact, relying solely on the Frumkin adsorption isotherm and its associated EOS (ignoring the wetting contribution) would not lead to a measurable decrease in IFT, see the blue line in Figure 6-3. To the best of our knowledge, this is the first report of using the Ward-Tordai model to describe the full dynamic interfacial tension of NP adsorption onto a liquid-liquid interface. The main distinction with the case of surfactants is the incorporation of a wetting EOS.

We cannot rule out that some amount of convection might be present in our measurements. In particular, short-time data in Figure 6-2 shows a slightly faster decrease
in the IFT than what we expect. If we allow the diffusivity of the NPs to vary we see that a slight increase leads to a better agreement between the experiments and the model (see the dashed line in Figure 6-3 for the 5 nm and 10 nm NPs). Through an extensive parameter space exploration (shown in Figure S6-2 and Figure S6-3), we find that using diffusivity as a fitting parameter \(D_{\text{eff}}\), rather than directly applying the predicted value from Stokes-Einstein model is the only effective way to better capture the dynamic interfacial tension during the adsorption period \(i.e., \) around 100 sec to 1000 sec). The fits using the diffusivity as an adjustable parameter are also shown in Figure 6-2, and the corresponding values for the diffusivities are shown in Figure S6-4.

We predict shorter equilibration time than what is measured experimentally when we increase the bulk NP concentration and reach higher area fractions (middle row in Figure 6-2). Polydispersity of the NPs should also be considered as another possible explanation for a faster adsorption. Schwenke et al.\textsuperscript{27} also showed that when polydispersity of the bulk dispersion increases, faster adsorption could be observed compared to less polydispersed bulk dispersion, although similar equilibrium coverage could be reached, likely due to the replacement of small NPs by large NPs at longer times.\textsuperscript{30} In terms of a slow equilibration time, Schwenke et al.\textsuperscript{27} also showed that local ordering processes directly affect the adsorption at high surface coverage, which slows down the adsorption and thus the decrease in interfacial tension. Kaz et al.\textsuperscript{181} also observed an extremely slow relaxation time for single micron-sized particle. In addition, recent experiments by Huerre et al.\textsuperscript{182} indicate that re-organization within the interface happens during the late stage of adsorption. Finally, Bizmark proposed that an adsorption barrier might be present at later stages of the adsorption process, when the particles have reached a high coverage\textsuperscript{108}.  

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Figure 6-3. Effect of using the diffusivity as an adjustable parameter in Eqn. (6.2) for (A) 5 nm NP with concentration of $3.5 \times 10^{11}$ /mL in 5mM pH 11.0 and for (B) 10 nm NP with concentration of $3.7 \times 10^{11}$ /mL, both in pH 11.7 solutions. The solid lines are predictions using the Stokes-Einstein equation, while the dashed lines are predictions using the diffusivity as an adjustable parameter, with a diffusivity 2.5 fold larger. The blue dashed lines is the dynamic IFT predicted by using Frumkin EOS (Eqn. (6.5)) without the wetting EOS.

### 6.4.2 Competitive adsorption of NP-ion mixture

We test if the proposed dynamic model can be extended to study the diffusion-limited competitive adsorption between the NPs and a surface active species (here the TPeA$^+$ which is also present as a ligand on the NPs). Introducing a surface active species allows us to modulate the surface pressure contributions captured by the Frumkin EOS (Eqn. (6.10)) so that it is no longer negligible. We first characterize the dynamic IFT for the adsorption of TPeA$^+$ to the oil-water interface in the absence of NPs (Figure 6-4). The
dynamic IFT measurements are performed in solutions with a total ionic strength of 5 mM, and at pH 11.0 and pH 11.7. A radius of 0.5 nm is assumed for the TPeA\(^+\) ion\(^{61}\) yielding a diffusivity of 4.3×10\(^{-10}\) m\(^2\)/s using Eqn. (6.3). The thermodynamic parameters obtained from the equilibrium pressure isotherm are listed in Table 6-2 (the equilibrium data is also shown in Figure S6-5). We find that the dynamic IFT is well-described by the Ward-Tordai model. Here we adjust the diffusivity slightly from \(D_{SE}\) (Figure 6-4C). We observe that the diffusivity of TPeA\(^+\) decreases slightly as the bulk concentration of TPeA\(^+\) increases, likely due to existence of adsorption energy barrier as surface coverage increases.\(^{173}\) Similar results have been reported for the adsorption of surfactants.\(^{172-173}\)

Table 6-2. Parameters for the TPeA\(^+\) adsorption at pH 11.0 and pH 11.7 obtained from fitting equilibrium pressure isotherms to Frumkin model, Eqns. (6.4)-(6.5).

<table>
<thead>
<tr>
<th>pH</th>
<th>(a_{L,I}) (mM)</th>
<th>(K_I)</th>
<th>(\Gamma_{I,\infty}) (#/nm(^2))</th>
<th>(\eta_{I,\infty})</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0</td>
<td>1.0×10(^{-6})</td>
<td>6.0</td>
<td>0.204</td>
<td>0.160</td>
</tr>
<tr>
<td>11.7</td>
<td>2.5×10(^{-7})</td>
<td>6.6</td>
<td>0.207</td>
<td>0.163</td>
</tr>
</tbody>
</table>

Dynamic IFT measurements for binary mixtures of NPs and TPeA\(^+\) are shown in Figure 6-5. Here the TPeA\(^+\) bulk concentration is maintained at 0.01 mM, while NP bulk concentration is varied across 2 orders of magnitude. Because we characterized the dynamic IFT for the single components (Figure 6-2 and Figure 6-4), all the equilibrium adsorption parameters for the single components are available (listed in Table 6-1 and Table 6-2). For the binary mixture, an additional parameter is necessary to account for the NP-TPeA\(^+\) interactions within the interface in the binary Frumkin model (Eqns. (6.8)-(6.10)). In our previous work,\(^{115}\) we obtained the equilibrium EOS and found that the best fit for the interaction parameter in the binary Frumkin equations was \(K_{NP,I} = -7\), making all
equilibrium parameters available to predict the dynamic IFT for the case of competitive adsorption. To compare with the experimental data, we use diffusivities calculated from Stokes-Einstein equation for each species. The predicted dynamic IFT are shown as the solid lines in Figure 6-5 A and C. The lines are obtained by solving the Ward-Tordai equation for two species simultaneously, along with the binary Frumkin adsorption isotherm as well as the binary Frumkin EOS and the wetting EOS for the NPs. We highlight the fact that lines in Figure 6-5 are obtained without adjustable parameters. As shown, the predictions agree relatively well with the data and the observed equilibration time for NP area fractions up to ~0.1 (Figure 6-5A). Similar to what we observe for the pure NPs, we find that at high NP bulk concentration, a shorter equilibration time is predicted compared to the experimental data, where slower dynamic is observed.
Figure 6-4. Dynamic IFT of TPeA$^+$ ions in 5 mM solutions at (A) pH 11.0 with TPeA$^+$ concentrations of $2.5 \times 10^{-4}$ mM (black), $1.25 \times 10^{-3}$ mM (red), $2.5 \times 10^{-3}$ mM (green), $5 \times 10^{-3}$ mM (yellow), $1.25 \times 10^{-2}$ mM (blue), and at (B) pH 11.7 with TPeA$^+$ concentrations of $1.25 \times 10^{-4}$ mM (black), $2.5 \times 10^{-4}$ mM (red), $1.25 \times 10^{-3}$ mM (green), $2.5 \times 10^{-3}$ mM (yellow), $1 \times 10^{-2}$ mM (blue). Solid lines are fitting to Ward-Tordai model (Eqn. (6.2)) combined with Frumkin model (Eqns. (6.4)-(6.5)). The corresponding diffusivity used is shown in (C) with corresponding colored circle representing diffusivity at pH 11.0 and corresponding colored squares representing diffusivity at pH 11.7.
**Figure 6-5.** Dynamic IFT of mixtures of 0.01 mM TPeA\(^+\) and NP with concentrations of 7.2×10\(^{11}\) /mL (green square, A), and 3.5×10\(^{13}\) /mL (pink square, C) in pH 11.7 solutions. Solid lines in (A) and (C) are predictions from the Ward-Tordai model (Eqn. (6.2)) combined with binary Frumkin model (Eqns. (6.8)-(6.10)) and wetting EOS (Eqn. (6.6)). Relative coverage of the TPeA\(^+\) ion (solid lines) and the NPs (dashed lines) with NP bulk concentration of 7.2×10\(^{11}\) /mL (green dashed line, B), and 3.5×10\(^{13}\) /mL (pink dashed line, D) respectively are obtained from solving Ward-Tordai model (Eqn. (6.2)) for NP and TPeA\(^+\) simultaneously. Vertical dashed lines show the induction time estimated for TPeA\(^+\) and for the NPs.

In Figure 6-5A, an initially sharp decrease (< 100 s) of the predicted IFT (solid lines) can be attributed to the diffusion of the smaller TPeA\(^+\) ions to the interface. For single component adsorption, the adsorption time scale can be estimated by \(\tau_{in} = (\Gamma_i / C_i)^2 / D_i\), \(^{183}\) which gives us an adsorption time scale for TPeA\(^+\) to be around 30 s, and for NPs at the two different concentrations shown to be around 5000 s and 500 s respectively (Figure
6-5 B and D). In the case of competitive adsorption, the time necessary for the initial decrease of the interfacial tension is close, but slightly longer than 30s, which suggests that the adsorption dynamics of the surface active ions is slowed down when NPs are present in the solution. This effect is even more pronounced as the NP bulk concentration increases. This prolonged induction time with addition of a second species has been observed in the dynamics of binary adsorption of hydroxypropylmethylcelulose and octanesulfonic acid sodium salt mixture as well. Moreover, it is consistent with our previous work on the competition between NP and TPeA\(^+\) ion for the interface. A few parameters could be adjusted to improve the agreement with the experimental data. However, the coverage of TPeA\(^+\) within the interface is extremely close to its maximum coverage, making it numerically challenging to perform a parametric study.

Based on the dynamic model proposed and its agreement with experimental data we can highlight how the individual thermodynamic parameters \((a_{L,NP}, K_{NP, \infty}, a_{L,I}, K_{I, \infty}, K_{NP-I})\) affect the instantaneous and equilibrium surface excess of the NPs at the interface (Figure 6-6). First, consider the differences in the dynamic surface excess between the two pHs for the adsorption of 5 nm NPs (cyan solid line for 5 nm NP dispersed in pH 11.0 solution and green long dashed line for 5 nm NP dispersed in pH 11.7 solution in Figure 6-6). The only significant difference between the two curves is the smaller dissociation constant for the particles in a pH11.0 solution (the particles have the same size, therefore the same diffusivity). We see that initially the coverage is identical, but as the adsorption process proceeds the NPs in pH 11.0 have a higher surface excess than the NPs in pH 11.7. Then, a comparison between the 5 nm and 10 nm in pH 11.7 illustrates the case where the dissociation constant is similar, but the diffusivity for the smaller particles is larger. As a
result, we see that initially the small NPs adsorb to the interface faster, but over time a higher area fraction is obtained for the larger NPs. Finally, competitive adsorption due to the presence of a surfactant leads to a lower NP coverage at all times, even if the dissociation constant and diffusivity for the NPs remain the same (green and black line in Figure 6-6).

**Figure 6-6.** Evolution of the surface coverage for 5 nm NPs at pH11.0 solution (cyan solid line), 5 nm NP at pH11.7 solution (green long dashed line), 10 nm NP at pH11.7 solution (blue medium dashed line), 5 nm NP in the presence of 0.01 mM TPeA$^+$ (black short dashed line) at a bulk concentration of $7.5\times10^{11}$/mL.

### 6.5 Conclusion

We measured dynamic interfacial tension of NPs, TPeA$^+$ ions, and NP-TPeA$^+$ ion mixtures at toluene-water interface. We obtain predictions for dynamic interfacial tension of the three different systems based on the Ward-Tordai model, the Frumkin adsorption isotherm, and the addition of a wetting contribution for the NPs. We demonstrate that the
Ward-Tordai model can be employed to describe the diffusion-limited adsorption of NPs to a fluid interface. Good agreement is reached at low NP bulk concentrations, where some deviations are observed at high NP bulk concentration. We suspect that deviations are likely due to convection or polydispersity of the NPs causing an apparent faster adsorption after the induction period. Slower dynamics at the late stages of adsorption could arise due to NP re-arrangement within the interface or the existence of energy barriers when interfacial coverage is high. This proposed method of modeling the dynamic adsorption reduces the complexity of analyzing short term and long term asymptotic behaviors by only necessitating one diffusivity. In addition deviations from this simple model open the door to quantify other more complex effects occurring at the interface such as polydispersity or relaxation. The model in this work demonstrates the relative roles of mechanisms that reduce interfacial tension for adsorption of NPs and NP-surfactant mixtures (as well as indicating the need for more complex models at high coverages). Finally, the modeling approach reported in this work was extended to describe binary competitive adsorption of NP-surfactant mixtures.

6.6 Supporting Information

6.6.1 Adsorption isotherms of NPs

The adsorption isotherms of ion-pair NPs are measured with UV-Vis spectroscopy (shown in Figure S6-1). Details of the experimental protocol are discussed in our previous work. The Frumkin model (Eqn. (6.4)) is used to fit the data.
**Figure S6-1.** Adsorption isotherms of 5 nm NPs in 5 mM KOH solutions at pH 11.0 (cyan dotted circles) and pH 11.7 (green squares), as well as 10 nm NPs in 5 mM pH 11.7 KOH solution (blue triangles). Dashed lines are best fits to the Frumkin adsorption isotherm (Eqn. (6.4)) with fitting parameters listed in Table 6-1.

### 6.6.2 Effects of all parameters on fitting dynamics of NP adsorption

The role of the different parameters on the dynamic data is shown Figure S6-2 and Figure S6-3 for the adsorption of 5 nm NP dispersed in pH 11.0 solution and 10 nm NP dispersed in pH 11.7 solution. The corresponding parameters are listed in Table S6-1 and Table S6-2 respectively.
Figure S6-2. Fitting dynamics of adsorption of 5 nm $3.5 \times 10^{11}$ /mL NPs dispersed in 5 mM pH 11.0 KOH solution, with the corresponding fitting parameters shown in Table S6-1.

Table S6-1. Parameters of fitting the dynamics of adsorption of 5 nm $3.3 \times 10^{11}$ /mL NPs dispersed in 5 mM pH 11.0 KOH solution, with the highlighted parameters adjusted compared to the original parameters.

<table>
<thead>
<tr>
<th>#</th>
<th>$r_{NP}$ (nm)</th>
<th>$a_{L,NP}$ (#/mL)</th>
<th>$K_{NP}$</th>
<th>$\eta_{NP,\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>3.5</td>
<td>$1.6 \times 10^{12}$</td>
<td>0</td>
<td>0.85</td>
</tr>
<tr>
<td>1</td>
<td>3.5</td>
<td>$1.6 \times 10^{12}$</td>
<td>1</td>
<td>0.85</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>$1.6 \times 10^{12}$</td>
<td>-1</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>$0.5 \times 10^{12}$</td>
<td>0</td>
<td>0.85</td>
</tr>
<tr>
<td>4</td>
<td>3.5</td>
<td>$2.5 \times 10^{12}$</td>
<td>0</td>
<td>0.85</td>
</tr>
<tr>
<td>5</td>
<td>$2.5$</td>
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<td>0</td>
<td>0.85</td>
</tr>
<tr>
<td>6</td>
<td>$5.5$</td>
<td>$1.6 \times 10^{12}$</td>
<td>0</td>
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</tbody>
</table>
Figure S6-3. Fitting dynamics of adsorption of 10 nm 3.7×10^{11} /mL NPs dispersed in pH 11.7 5 mM KOH solution, with the corresponding fitting parameters shown in Table S6-2.

Table S6-2. Parameters of fitting the dynamics of adsorption of 10 nm 3.7×10^{11} /mL NPs dispersed in pH 11.7 5 mM KOH solution, with the highlighted parameters adjusted compared to the original parameters.

<table>
<thead>
<tr>
<th>#</th>
<th>$r_{NP}$ (nm)</th>
<th>$a_{L,NP}$ (#/mL)</th>
<th>$K_{NP}$</th>
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<tbody>
<tr>
<td>Original</td>
<td>6.0</td>
<td>2.7×10^{12}</td>
<td>-1.6</td>
<td>0.95</td>
</tr>
<tr>
<td>1</td>
<td>6.0</td>
<td>2.7×10^{12}</td>
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<td>0.95</td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>2.7×10^{12}</td>
<td>0</td>
<td>0.95</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>3.5×10^{12}</td>
<td>-1.6</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>1.5×10^{12}</td>
<td>-1.6</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
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</tr>
<tr>
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<td>-1.6</td>
<td>0.95</td>
</tr>
</tbody>
</table>

6.6.3 Diffusivity used to obtain better predictions

Diffusivity is allowed to vary in order to obtain better predictions for NP adsorption dynamics shown in dashed lines in Figure 2 in the main text. The diffusivity used compared to the Stokes-Einstein diffusivity is shown below.
**Figure S6-4.** Value of the diffusivity ($D_{\text{eff}}$) used as a fitting parameter to predict dynamic IFT in Figure 6-2 for 5 nm NP dispersed in 5 mM KOH solutions at pH 11.0 (circles), 5 nm NP dispersed in 5 mM KOH solutions at pH 11.7 (squares), and 10 nm NP dispersed in 5 mM KOH solutions at pH 11.7 (diamonds).

### 6.6.4 Pressure isotherms of TPeA$^+$ adsorption

The pressure isotherms of TPeA$^+$ in solution with total ionic strength of 5 mM solution at pH 11.0 and pH 11.7 are shown in Figure S6-5. The lines represents fits to the equilibrium pressure isotherms, with parameters listed in Table 6-2.\textsuperscript{41}
**Figure S6-5.** Surface pressure of TPeA$^+$ ions in 5 mM, pH11.0 solution (pink triangles) and pH11.7 solution (black circles). The lines are the corresponding fits using Frumkin model described by Eqns. (6.4)-(6.5). The fitting parameters are listed in Table 6-2. Inset is the predicted EOS for TPeA$^+$ for the same conditions using Eqn. (6.5) in the main text also with parameters listed in Table 6-2.
7 General Description of Diffusion-Limited Nanoparticle Adsorption Dynamics at Fluid Interfaces

7.1 Overview

This chapter shows the general applicability of the dynamic model describing diffusion-limited nanoparticle adsorption dynamics at fluid interfaces.

7.2 Introduction

Dynamic interfacial tension (IFT) measurements allow for the characterization of mass transfer and adsorption processes.\textsuperscript{49} In the case of surfactants, analysis and interpretation of dynamic IFT measurements have been employed to explain induction times,\textsuperscript{170-171} extract energy barrier,\textsuperscript{172-173} study interfacial phase transitions during adsorption,\textsuperscript{170,174} and to validate adsorption isotherms and surface equations of state (EOS).\textsuperscript{169} However, unlike surfactants, there are no validated models for the diffusion-limited adsorption of particles to fluid interfaces. Despite the importance of particle-laden interface, the dynamic process remain poorly understood. Challenges of understanding the NP adsorption dynamics
include limited characterization of equilibrium adsorption, as well as its effect on the surface pressure.\textsuperscript{112,178}

Previously we have developed a dynamic model that combines Ward-Tordai model with Gibbs adsorption isotherm (\textit{i.e.}, Langmuir isotherm, Frumkin isotherm, \textit{etc.}) and wetting EOS for NP (Eqns. (7.4)-(7.5)).\textsuperscript{185} It has been shown that the model is capable of predicting dynamic IFT for the 5 nm and 10 nm ion pair gold NP adsorption at toluene-water interface. We have shown good agreement between the measurements and predictions from the model, especially at low NP concentrations. We observed deviation at high concentration, which is likely due to kinetic limitations or existence of energy barrier.\textsuperscript{27,175}

Here we show that we can apply the same model to more general experimental systems. We used data from prior literature reports with a wide range of NP size and materials,\textsuperscript{17,108,113,178} including Fe$_3$O$_4$ NP capped with polymer shell,\textsuperscript{178} ethyl cellulose (EC) NP,\textsuperscript{108} silica NP grafted with polymers,\textsuperscript{17} and partially hydrophobic silica NP.\textsuperscript{113} We extract the reported adsorption dynamics at different fluid interfaces. We demonstrate that thermodynamic parameters obtained from modeling pressure isotherm could be incorporate into the dynamic model, providing good agreements without needing for further fitting parameters.

7.3 Diffusion-limited adsorption model

Ward-Tordai model\textsuperscript{49,55}, which is often used to describe diffusion-limited adsorption behavior of surfactants\textsuperscript{51-52} and macromolecules\textsuperscript{53-54}, is employed here to capture the
diffusion-limited adsorption of NPs. Due to near-spherical shape in pendant drop measurements, we rely on the formulation of Lin et al. in spherical coordinates given by:\textsuperscript{55}

$$
\Gamma(t) = \sqrt{\frac{D}{\pi}} \left\{ 2C \sqrt{t} - \int_0^t \frac{c(\tau)}{\sqrt{t-\tau}} d\tau \right\} + \frac{D}{r_D} \left\{ Ct - \int_0^t c(\tau) d\tau \right\} .
$$

(7.1)

where $C$ is the bulk concentration of NPs, and $c$ is the sub-surface concentration of NPs, $r_D$ is the radius of the pendent droplet. $D$ is the diffusivity of NP, which can be estimated using Stokes-Einstein equation:\textsuperscript{56}

$$
D_{se} = \frac{kT}{6\pi\mu r} .
$$

(7.2)

where $k$ is the Boltzmann constant, $T$ is temperature, $\mu$ is the fluid viscosity, and $r$ is the radius of NP.

In diffusion-limited adsorption, instantaneous equilibrium is established between the sub-surface and the interface. The time-dependent surface coverage ($\Gamma(t)$) can be related to the sub-surface concentration ($c(t)$) through an adsorption isotherm. Here we employ the Frumkin adsorption isotherm, which incorporates non-ideal interactions between adsorbed species within the interface\textsuperscript{41,51}, and describes well the adsorption of the NPs investigated here\textsuperscript{41} as well as surfactants at oil-water interfaces, and is given by\textsuperscript{41}:

$$
C = a_L \frac{\Gamma}{\Gamma_{\infty} - \Gamma} \exp \left( K_{NP} \frac{\Gamma}{\Gamma_{\infty}} \right) ,
$$

(7.3)

where $\Gamma_{\infty}$ is the maximum surface excess of NP, the affinity between NP and the interface is captured by the dissociation constant, $a_L$, while the parameter $K_{NP}$ accounts for the interactions between NPs within the interface relative to the thermal energy, $kT$\textsuperscript{42}. A positive value of $K_{NP}$ represents net repulsion between NPs within the interface, and a
negative value represents attractive interactions.\textsuperscript{43} When $K_{NP} = 0$, the Frumkin adsorption isotherm is reduced to Langmuir adsorption isotherm.

Measured surface pressures caused by NP adsorption are often much larger than those predicted by the Frumkin EOS.\textsuperscript{112-113, 120} It has been found that the main contribution to the surface pressure is that of the wetting of the NPs at the liquid-liquid interface, as fluid-fluid area is replaced by particle-fluid area.\textsuperscript{47} Du \textit{et al.} proposed that the surface pressure ($\Pi_{NP}$) originating from this area replacement process is given by\textsuperscript{46}:

$$\Pi_{NP} = |\Delta E| \times \Gamma_{NP},$$

(7.4)

where $\Gamma_{NP}$ is the surface coverage of NP, and $\Delta E$ is the adsorption isotherm, given by\textsuperscript{47}:

$$\Delta E = -\pi r_{NP}^2 \gamma_{OW} (1 - |\cos \theta_{OW}|)^2,$$

(7.5)

where $\gamma_{OW}$ is the pure oil (air)-water interfacial tension, $\theta_{OW}$ is the contact angle at the interface.

Therefore, the transient reduction in interfacial tension when incorporating the wetting EOS is given by:

$$\gamma(t) = \gamma_{OW} - \Pi(t).$$

(7.6)

Thus, prediction for the dynamic IFT due to diffusion-limited adsorption of NPs to an oil-water interface can be obtained by solving Eqns. (7.1)-(7.6).

### 7.4 Results and Discussions

To better explain the mechanism of this model, Figure 7-1 illustrates the procedures to apply this model. First of all, the equilibrium IFT and the surface pressure (Eqn. (7.6)) can
be extracted from the steady-state of dynamic measurement (red region in left panel of Figure 7-1). Assuming that bulk NP concentration is constant throughout measurement, the pressure isotherm can be obtained combining equilibrium surface pressure and bulk concentration. Surface excess of NP can be related to surface pressure via wetting EOS (Eqns. (7.4)-(7.5)). Note that we ignore the contribution from surface activity since it is less than 0.5 mN/m for NPs larger than 1 nm. As a result, adsorption isotherm (if not applicable experimentally) could be interpreted from pressure isotherm, which could then be modeled using Frumkin adsorption isotherm (Eqn. (7.3)). Note that assumptions associated with Frumkin adsorption isotherm is the equilibrium between NPs at the interface and NPs in the bulk phase, while for Ward-Tordai model, assumption is made that the type of adsorption to be diffusion limited adsorption. Thermodynamic parameters \((a_L, \Gamma_\infty, K_{NP})\) could be obtained via modeling of equilibrium data, therefore, prediction of NP adsorption dynamics can be made by solving Eqns. (7.1)-(7.6).

**Figure 7-1.** Schematic of fitting NP adsorption dynamics at fluid interfaces. The input information is from literature reports, including: radius of NP \((r_{NP})\), clean oil-water interfacial tension \((\gamma_{OW})\), and NP contact angle at oil-water interface \((\theta_{OW})\), listed in Table 7-1 as well as dynamic measurements data at each bulk concentration, \(C\). Equilibrium pressure isotherm obtained from dynamic data together with other input information and
Eqns. (7.4)-(7.5), can result in adsorption isotherm. Fitting to adsorption isotherm using Eqn. (7.3) assuming Gibbs monolayer adsorption and equilibrium between bulk phase and the interface, yields thermodynamic parameters describing equilibrium adsorption (Table 7-2). With Eqns. (7.1)-(7.6) and all parameters listed in Table 7-1 and Table 7-2, as well as the assumptions of diffusion-limited adsorption, fitting to the dynamic IFT can be achieved.

The direct information extracted from literature reports are shown in Table 7-1, including the radius of NP ($r_{NP}$), and the corresponding diffusivity ($D_{SE}$) estimated using Stokes-Einstein model (Eqn. (7.2)), the contact angle of NP at fluid-interface ($\theta_{DF}$), the IFT of the clean interface ($\gamma_{DF}$), as well as the adsorption energy ($\Delta E$) predicted with Eqn. (7.5). Note that if contact angle is not reported, then 90° is assumed to simplify the problem. Table 7-2 lists the thermodynamic parameters ($a_L, \Gamma_\infty, K_{NP}$) obtained from modelling the Frumkin adsorption isotherms using Eqn. (7.3).

Therefore, predictions of the dynamic IFT (Figure 7-2) can be obtained by solving for Eqns. (7.1)-(7.6), with the parameters needed listed in Table 7-1 and Table 7-2. We show comparison to prior literature reports of four different NPs, including ion-pair gold NPs, EC NP, silica NP grafted with polymers, and magnetic Fe$_3$O$_4$ particle capped with catechol-terminated random copolymer brushes and partially hydrophobic silica. In general, good agreements are observed. Induction time as well as equilibration time are mostly well captured. Yet details are worth discussing from case to case.

First of all, it is obvious that equilibrium isotherms fitting quality greatly affects the predictions of dynamic IFT. Although fittings of equilibrium isotherms shows good agreement, small deviations in equilibrium fitting could result in large deviations in
dynamic IFT fittings. Specifically, shown in panel D\textsuperscript{178} of Figure 7-2, Frumkin adsorption isotherm (solid lines) captures the equilibrium isotherms well, yet it propagates into larger deviations in the prediction of dynamic IFT. In addition to fitting quality of equilibrium data, other source of experimental noise could also result in deviations with theoretical predictions. For example, since NPs are relatively larger compared to surfactants, the diffusivity is smaller, leading to slower dynamics that are more susceptible to convection. Like in our own case with 5 nm ion-pair gold NPs, we discussed the possible reasons for deviation, including possible convection during experimental measurements. Also polydispersity could give rise to an apparent faster adsorption\textsuperscript{27,185}. Moreover, in some cases with high bulk concentrations, early or faster acquisition time is needed since IFT decreases too fast to be captured.

After ruling out the possible source of error as discussed above, than deviations may indicate intriguing mechanisms that is not considered in our proposed model. More specifically, we assume diffusion-limited adsorption, which buried with it the assumption that instantaneous equilibrium between the interface and sub-surface should be maintained. Thus deviation (after ruling out experimental noise) from such predictions will suggest encouraging mechanisms occurred during adsorption dynamics, such as reaction-limited adsorption, kinetic barrier at high surface coverage.\textsuperscript{172-173} Figure 7-2 panel B\textsuperscript{108} depicts excellent agreements between predictions and measurements except for the first concentration (0.1 g/L, black points and lines). Yet deviations are observed at longer times, indicating complicated adsorption behavior compared to the simple diffusion-limited adsorption, possibly due to existence of kinetic barrier,\textsuperscript{108} NP re-orientation or re-organization at the interface.\textsuperscript{182}
To summarize, the dynamic model demonstrate the capability of predicting diffusion-limited adsorption behavior, producing good agreements especially considering no fitting parameters used. Deviations from the predictions, if not due to experimental noise, could indicate possible mechanisms that are not considered in our model, but worth further investigation.

**Figure 7-2.** Reported dynamic IFT from (A) Hua et al. using 5 nm ion-pair gold NP adsorption at toluene-water interface, (B) Bizmark et al. with 42 nm EC NP adsorption at air-water interface, (C) Alvarez et al. using 91.4 nm silica NPs with polymer coating adsorption at xylene-water interface, and (D) Stefaniu et al. using 8 nm Fe₃O₄ NP with polymer coating adsorption at air-water interface. Symbols in top row are extracted dynamic IFT. Curves are predictions using the dynamic adsorption model (Eqns. (7.1)-(7.6)). Bottom rows: fitting to Frumkin adsorption isotherm (solid lines, Eqn. (7.3)), and fitting to pressure isotherm with wetting EOS (Eqns. (7.4)-(7.5)), with parameters listed in Table 7-1 and Table 7-2.
Table 7-1. Parameters describing the experimental system obtained from literature reports.

<table>
<thead>
<tr>
<th></th>
<th>Ion-pair gold NP</th>
<th>EC NP</th>
<th>Polymer coated silica</th>
<th>Magnetic NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{NP} / \text{nm}$</td>
<td>3.5</td>
<td>21.0</td>
<td>45.7</td>
<td>8.0</td>
</tr>
<tr>
<td>$D_{SE} / \text{m}^2 \text{s}^{-1}$</td>
<td>$8.6 \times 10^{-11}$</td>
<td>$1.0 \times 10^{-11}$</td>
<td>$4.7 \times 10^{-12}$</td>
<td>$6.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>$\gamma_{OW} / \text{mNm}^{-1}$</td>
<td>35.8</td>
<td>72.8</td>
<td>37.9</td>
<td>72.8</td>
</tr>
<tr>
<td>$\theta_{OW} /^\circ$</td>
<td>90</td>
<td>73.7</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$</td>
<td>\Delta E</td>
<td>/ kT$</td>
<td>$1.7 \times 10^3$</td>
<td>$1.3 \times 10^4$</td>
</tr>
</tbody>
</table>

Table 7-2. Thermodynamic parameters obtained from fitting Frumkin adsorption isotherm (Eqn. (7.3)). Note maximum area fraction is defined as: $\eta_\infty = \Gamma_\infty \times \pi r_{NP}^2$.

<table>
<thead>
<tr>
<th></th>
<th>Ion-pair gold NP</th>
<th>EC NP</th>
<th>Polymer coated silica</th>
<th>Magnetic NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_L (# / \text{mL})$</td>
<td>$3.1 \times 10^{12}$</td>
<td>$2.5 \times 10^{12}$</td>
<td>$8.0 \times 10^9$</td>
<td>$5.5 \times 10^{12}$</td>
</tr>
<tr>
<td>$\Gamma_\infty (# / \text{nm}^2)$</td>
<td>$1.8 \times 10^{-3}$</td>
<td>$6.6 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$1.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\eta_\infty$</td>
<td>0.71</td>
<td>0.91</td>
<td>0.75</td>
<td>0.36</td>
</tr>
<tr>
<td>$K_{NP}$</td>
<td>-0.3</td>
<td>-1.5</td>
<td>6</td>
<td>-3.5</td>
</tr>
</tbody>
</table>

To further discuss the effect of fitting quality of equilibrium data, an example is taken using the 8 nm magnetic NP capped with polymer shells. It needs to be pointed out that since polydispersity could potentially affect the apparent adsorption dynamics, as well as the equilibrium value. Here the adsorption energy (Eqn. (7.5)), which is directly associated with the size of NP ($r_{NP}$), is treated as an adjustable parameter ($\Delta E_{\text{eff}}$) to obtain better fitting for the longer time dynamic IFT (Figure 7-3). We also compare the effective adsorption energy with the estimated adsorption energy (bottom of Figure 7-3). First, it can be noted from top of Figure 7-3 that the longer time dynamic IFT is better captured compared to the ones shown in Figure 7-2. The $\Delta E_{\text{eff}}$ is in general, relatively larger at low NP concentration (except for the first concentration), where less NPs are adsorbed at the interface, while at high NP concentration, the overall $\Delta E_{\text{eff}}$ is smaller. This is similar to
what has been observed and discussed in our own system,\textsuperscript{185} where we hypothesize that although small NP adsorb faster (diffuse faster), larger NP will replace small NPs at the interface.\textsuperscript{30} This is more obvious at low NP surface coverage, yet at high surface coverage, likely due to kinetic limitations, that small NPs replacement by large NPs may not be as obvious.\textsuperscript{27}

As has been discussed above, the model we proposed shows general applicability for a wide range of experimental systems undergoing diffusion-limited adsorption. The model avoids the complicated asymptotic analysis and can provide fittings in good agreements with experimental measurements without the need for fitting parameters. After ruling out experimental noise, the deviations from the fitting could suggest interesting adsorption mechanisms that worth further investigation.
Figure 7-3. Effective adsorption energy ($\Delta E_{\text{eff}}$) used as fitting parameters to obtain better predictions at longer times for 8 nm Fe$_3$O$_4$ NP with polymer coating adsorption at air-water interface.\textsuperscript{178}

7.5 Conclusions

We demonstrated that the dynamic model, combining Frumkin adsorption isotherm and wetting EOS, incorporated with Ward-Tordai equation, can be used to describe diffusion-
limited adsorption dynamics of NP with sizes ranging from 5 nm to 500 nm, and with diverse materials and surface chemistries, at fluid interfaces. We employed the steady-state pressure values from dynamic measurements to construct pressure isotherms. The corresponding adsorption isotherms are estimated via wetting EOS. We applied Frumkin adsorption isotherms to capture equilibrium adsorption behavior and to obtain thermodynamic parameters \((a_L, \Gamma_\infty, K_{NP})\), which are incorporated in the dynamic model to make predictions. We observed good agreements between measurements and predictions given no fitting parameters (Figure 7-2). We extended the application of this model to elucidate other kinetic behaviors in addition to diffusion-limited adsorption. Our results highlight general applicability of the dynamic model to be a facile and fast approach to understand kinetic behaviors during NP adsorption at fluid interfaces.
8 Conclusions and Future Work

8.1 Conclusions

The objective and motivation of this thesis is to elucidate the mechanism of particle adsorption at oil-water interface and the corresponding effect on surface pressure.

Chapter 2 describes the background of characterizing and modeling surfactant adsorption, proposed effect of NP adsorption on surface pressure, techniques used in this thesis, as well as the synthesis and characterization of ion-pair gold NPs used throughout this thesis.

Chapter 3 shows the validation the experimental system. The formation of Gibbs monolayers of NPs is characterized, and compared to that of soluble surfactants. Similarities between NPs and surfactants are observed in terms of the adsorption isotherm, and in terms of mechanical reversibility of the adsorbed NPs. The NP adsorption isotherm can be well-described by the Frumkin adsorption isotherm. In contrast the EOS shows strong deviation from the Frumkin description, but better captured by wetting EOS. This chapter is to confirm the model particle employed in the following work.

Chapter 4 demonstrates the thermodynamic consistency of the wetting EOS of NP and the Frumkin EOS that captures the surface activity of adsorbed species. Vigorous derivation of interfacial thermodynamics is shown to explain the difference between NP and surfactants in terms of their effect on the interfacial energy, or surface pressure. This chapter lays the foundation of the future work and modeling in this thesis.

Chapter 5 characterizes the competitive adsorption of NPs and surfactants at the oil-water interface, where both species adsorb reversibly at the interface. The particles are 5 nm and 10 nm gold NPs functionalized with ion-pair ligands, while the surface active
species was tetraklyl ammonium cation (TPeA⁺). EOS of the mixtures at the fluid interface is obtained through independent measurements of the adsorption and pressure isotherms of the NPs. A competitive adsorption model is presented, that takes into account the wetting of the particles at the oil-water interface as well as their surface activity caused by interactions (particle-particle, particle-surfactant, and surfactant-surfactant). This competitive adsorption model elucidates and isolates how the surface pressure arises from a combination of wetting of the NPs to the interface and the surface activity of the adsorbed species. Competitive adsorption enables independent control over both area fraction of NPs and surface pressure at the oil-water interface. The concentration of ions and NPs in the aqueous phase can be used to control both parameters.

Chapter 6 illustrates the models validated in previous Chapter 5, including model for NP adsorption and model for binary mixtures, could be employed to predict dynamic behavior as well. Predictions for dynamic interfacial tension of the three different systems can be obtained based on the Ward-Tordai model, the Frumkin adsorption isotherm, and the addition of a wetting contribution for the NPs. Good agreement is reached at low NP bulk concentrations, where some deviations are observed at high NP bulk concentration, likely due to convection during the measurements. Slower dynamics at the late stages of adsorption could arise due to NP re-arrangement within the interface or the existence of energy barriers when interfacial coverage is high. This proposed method of modeling the dynamic adsorption reduces the complexity of analyzing short term and long term asymptotic behaviors by only necessitating one diffusivity. In addition deviations from this simple model open the door to quantify other more complex effects occurring at the interface such as polydispersity or relaxation. The model demonstrates the relative roles of
mechanisms that reduce interfacial tension for adsorption of NPs and NP-surfactant mixtures (as well as indicating the need for more complex models at high coverages).

Chapter 7 extends the dynamic adsorption model to other experimental systems in the prior literature reports. It is again validated that the proposed model in Chapter 7 can be applied to diffusion-limited particle adsorption dynamics at fluid interfaces, for a wide range of NP size from 5 nm to 500 nm, with different material and surface chemistry, also at different fluid interfaces. Better agreements can be reached at low NP concentrations compared to high NP concentrations, likely due to kinetic limitations.

8.2 Future Work

Current research in this dissertation has made great. The following sections will discuss two possible study directions that open up new avenues for controlling surface coverage and surface properties.

8.2.1 Particle interactions within the interface

Although particle surface activity (interactions within the interface) does not contribute much to surface pressure, understanding the interactions of particle within the interface is essential in terms of particle stability at the interface. For example, adjusting solvent conditions in order to avoid 2D aggregation or jamming is important in maintaining ‘reversibility’ within the interface. One of the approaches to investigate particle-particle interactions is by monitoring the 2D radial distribution, followed by inverse Monte Carlo simulation in order to extract the interaction potential at the interface.
8.2.2 Effect of NP mixtures on surface properties

It has been demonstrated that both wetting and surface activity could contribute to interfacial energy. Moreover, the wetting contribution is independent of particle size, only depending on the actual coverage of the interface. Thus it would be interesting to introduce more approaches to adjust the surface activity while maintaining the surface coverage. For example, by mixing NP with much smaller sized NP (i.e., 1 nm NP), which is capable of introducing surface activity contribution to interfacial properties. Therefore by adjusting the adsorbed amount of small sized NP, as well as the surface chemistry of small NP to control small NP – large NP interaction, one is able to control surface properties while maintaining surface coverage.
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4. **Hua, X.**; Bevan, M. A.; Frechette, J., Thermodynamic Analysis of Nanoparticle Adsorption at Fluid Interfaces, in prep.


12. **Hua, X.**; Zhang, T.; Ren, J.; Zhang, Z.; Ji, Z.; Jiang, X.; Ling, J.; Gu, N., A facile approach to modify polypropylene flakes combining O$_2$-plasma treatment and graft

**Patents**
