From surface tension to molecular distribution: modelling surfactant adsorption at the air-water interface

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▪ Abstract

Surfactants are centrally important in many scientific and engineering fields and are used for many purposes such as foaming agents and detergents. However, many challenges remain in providing a comprehensive understanding of their behaviour. Here, we provide a brief historical overview of the study of surfactant adsorption at the air-water interface, followed by a discussion of some recent advances in this area from our group. The main focus is on incorporating an accurate description of the adsorption layer thickness of surfactant at the air-water interface. Surfactants have wide distribution at the air-water interface, which can have a significant effect on important properties, such as surface excess, surface tension, and surface potential. We have developed a modified Poisson–Boltzmann (MPB) model to describe this effect, which we outline here. We also address the remaining challenges and future research directions in this area. We believe that experimental techniques, modelling, and simulation should be combined to form a holistic picture of surfactant adsorption at the air-water interface.

▪ Introduction

Surfactants are amphiphilic molecules which tend to self-concentrate in the interfacial region and lower the surface tension of the system. This is because they have a polar headgroup and a non-polar alkyl chain which gives them affinity to the interface and result in positive adsorption.¹ Surfactants are widely used for many applications including cleaning, dispersion, emulsification, and foaming, and are particularly crucial for the mining industry.² They modify the hydrophobicity of mineral particles and stabilize the froth during the flotation process, which is essential for the enrichment of valuable minerals such as copper, zinc, and lithium.² Controlling the flotation process relies on the precise prediction of the
underlying properties, such as film stability, which is mainly determined by the adsorption of surfactant. Therefore, a better understanding of surfactant adsorption is crucial to mining and a wide variety of industries.

Many advanced techniques were applied to study the adsorption of surfactants including well-known tensiometry and electrokinetic measurements. However the surface excess and surface potential measured by different methods can vary substantially. Mathematical models describing the adsorption of ionic surfactants were first developed by Davies and then improved by Borwankar and Wasan. Later, this model has been extended to include the counterion binding effect. Recently, several adsorption models (including some from our work) have managed to account for more realistic adsorption layers by either placing multiple surfactant adsorption layers or directly including different energy terms into the modified Poisson-Boltzmann (MPB) equation. For non-ionic surfactant, several studies have considered the possible effects of the molecular area at the interface and the partially charged headgroup, which extends the theory beyond simple Langmuir and Frumkin adsorption models. However, model predictions of surface excess and surface potential are still not in quantitative agreement with experimental results. This is probably because the adsorption layers assumed by adsorption models differ significantly from the actual structures at the air/water interface. Molecular dynamics (MD) simulation results generally agree well with the experiment, especially for the density distribution of surfactant headgroup and alkyl chain. However, MD cannot address the counterion distribution effectively and can predict the opposite trend to experiment and modelling for the counterion affinity with the surfactant headgroup. Therefore, the understanding of surfactant adsorption is far from being complete.

In this article, we mainly focus on reviewing our recent work regarding surfactant adsorption at the air-water interface. We provide a brief review of the classical theories of surfactant adsorption and highlight their drawbacks. Classical approaches assume very thin adsorption layers which are not consistent with experimental results. This structural discrepancy makes surface excess and surface potential predictions unreliable. Therefore we provide experimental evidence of the thick adsorption layers and the under-monolayer adsorption. Some of our work also shows that non-ionic surfactants cannot be well-described by classical theories. We highlight the effectiveness of our new adsorption model for surfactant adsorption at the air-water interface as it incorporates realistic adsorption layer thickness and gives more precise surface potential predictions than classical theories.
We extend this model to account for the ion-specific effect and disjoining pressure of thin liquid film.\textsuperscript{40} Similar model was also used to calculate the surface tension of the surfactant-salt mixture at very low concentration, which is closely related to the Jones-Ray effect.\textsuperscript{19} We show that MD is a useful tool to quantify the surfactant adsorption. However, MD with classical forcefields may not represent the behaviours of surfactant precisely.\textsuperscript{41-43} In this case, quantum mechanical (QM) calculations could potentially be applied to improve the MD predictions.\textsuperscript{43-45} We would like to point out that effectivity all of the models depend on the accuracy of data available only from experiments and simulations because mathematical models were calibrated using experimental and simulation data. However, adsorption models can explain direct measurements and identify the underlying mechanisms which is important for many applications. Therefore, it is necessary to combine all techniques to picture of surfactant adsorption at the air-water interface as no approach is perfect. Thus, experimental methods, modelling and simulation need to work together.

\section*{Historical studies about surfactant adsorption at the air-water interface}

For many classical adsorption models, the surfactant is assumed to form a uniform layer without any actual thickness at the air-water interface.\textsuperscript{15-18} This assumption was also applied for the widely used Frumkin adsorption model, which combines the Frumkin isotherm with the Gibbs equation. The Frumkin isotherm assumes that the interface has certain sites for adsorption, and the adsorbed molecules do not move when bonded to the surface. Also, the lateral interaction between adsorbed surfactants was considered. The Gibbs equation relates the change of surface excess and concentration with the change of surface tension in an effective way.\textsuperscript{1} The Frumkin model contains the following two equations describing the change of surface excess and surface tension according to surfactant concentration.\textsuperscript{46} For more details about the assumptions and derivation of adsorption models, please refer to our previous publication.\textsuperscript{37}

\begin{equation}
K_c = \frac{\Gamma}{\Gamma_\infty - \Gamma} \exp \left( -2\beta \frac{\Gamma}{\Gamma_\infty} \right)
\end{equation}

\begin{equation}
\gamma - \gamma_0 = RT \Gamma_\infty \left[ \ln \left( \frac{\Gamma_\infty - \Gamma}{\Gamma_\infty} \right) + \beta \left( \frac{\Gamma}{\Gamma_\infty} \right)^2 \right]
\end{equation}

where $K$ is the equilibrium constant, $\Gamma$ is the surface excess, $c$ is the concentration of surfactant, $\Gamma_\infty$ is the maximum value for surface excess, and $\beta$ is the intermolecular interaction coefficient (it is not the symbol for $1/k_B T$ in this article). The $\gamma_0$ is the surface
tension of water; $\gamma$ is the surface tension calculated by the model. Two constants are gas constant $R$ and temperature $T$. In this article, the molar concentration is used instead of the activity because the surfactant concentration is quite low in most conditions. Note $K$, $\Gamma_\infty$, and $\beta$ are three adjustable variables. If the intermolecular interaction coefficient is insignificant, the Frumkin model is reduced to the Langmuir adsorption model, which has only two adjustable parameters ($K$ and $\Gamma_\infty$). Frumkin and Langmuir’s models are sometimes referred to as lattice models because the adsorption sites are assumed to be fixed. Some researchers claim that surfactants at the air-water interface can be better described with 2D gas models which are derived from the van der Waals equation for a real gas.\textsuperscript{32, 47} The corresponding models are also named van der Waals adsorption model (for surfactant). This model has the same set of parameters as the Frumkin model. Therefore, this adsorption model reduces to the Volmer model if the lateral interaction for the surfactant is ignorable ($\beta = 0$). Although van der Waals and Volmer models give similar predicted surface tension\textsuperscript{17, 47} to Frumkin, and Langmuir models, they are not very widely used compared to the latter two models.

Fitting the surface tensions of polyglycol ethers with the Frumkin model gives a negative intermolecular interaction coefficient, meaning the adsorption of polyglycol ether molecules was inhibited by the increase of surface excess.\textsuperscript{48-49} However, the coefficient $\beta$ was caused by the lateral interaction of alkyl chain molecules which can only be positive according to its physical meaning. Reorientation models were developed to solve this problem.\textsuperscript{26-27} This type of models assumes two different adsorption states for one surfactant: the surfactant molecules occupy the large surface area at the interface when the concentration is low, but they tend to occupy smaller surface areas at high concentration. This type of models gives good prediction for non-ionic surfactants such as polyglycol ethers, n-alcohols, and even surfactant mixtures.\textsuperscript{50-51} The reorientation models were extended further to incorporate the effect of surfactant aggregation at higher concentrations, based on the concept that n-aggregates occupies the same partial surface area as a single molecule.\textsuperscript{52-53} This type of models gives better prediction for the surface tension of decanol and sodium dodecyl sulfate (SDS) than the Frumkin model. However, they predict a much larger surface area for surfactant molecules than the realistic values.\textsuperscript{52} One potential solution is the two-state adsorption model which assigns different adsorption equations for low and high surface excess conditions. However, the transition between the two states is achieved via an empirical transition function.\textsuperscript{54-56} There is no universal adsorption model suitable for even the non-ionic surfactants.
The situation for ionic surfactants is more complicated: the adsorption of ionized surfactants creates a charged adsorption layer which attracts counterions with the opposite charge. Therefore, the counterion also has a positive contribution to surface tension reduction, according to the Gibbs equation. Note that all models (including classical ones and our model) discussed in this article rely on the Gibbs equation to link the surface excess to surface tension. Although some recent studies pointed out the contribution of different ion species to surface tension could be far more complicated,\textsuperscript{57} it is difficult to capture this effect with simplified mathematical models. Early works of Davies, Borwankar, and Wasan combined the Grahame equation with Langmuir and Frumkin model and derived adsorption models for ionic surfactants.\textsuperscript{14-15} Borwankar and Wasan’s model (BW model) can predict the surface tension of SDS in different salt concentrations. However, for each salt concentration, it requires a different equilibrium constant $K$ and maximum surface excess $\Gamma_\infty$.\textsuperscript{15, 17, 58} Several counterion adsorption models were developed to highlight the contribution of counterions.\textsuperscript{15-18} This type of models usually has two equilibrium constants ($K_1$ for surfactant and $K_2$ for counterion respectively), which can be applied to all salt concentrations. Table 1 summarises several typical models for ionic surfactants. In table 1, $\Gamma_1$ and $\Gamma_2$ denote the surface excess of surfactant ions and counterions, $\Gamma_\infty$ is the maximum surface excess and $F$ is the Faraday constant. Generally, $z_1$ describes the valence of surfactants (which is usually $\pm 1$). $c_{1s}$ and $c_{2s}$ denote the ion surfactant and counterion concentrations at the beginning of the diffuse layer, which can be calculated from bulk concentration, $c_1$ and $c_2$, using the Boltzmann equation. Coions do not appear in the adsorption layer because of strong electrostatic repulsion. The surface excess of surfactant is a function of surface potential $\psi_s$ as predicted by the modified Frumkin isotherm:

$$Kc_1 = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1 - \Gamma_2} \exp \left( - 2\beta \frac{z_1 F \psi_s}{\Gamma_\infty RT} \right)$$  \hspace{1cm} (3)

Note in the case of the Stern isotherm of counterion adsorption considered in Table 1, $\Gamma_2$ should not appear in the equation since counterions do not penetrate the adsorption layer as assumed by this model.\textsuperscript{17} This isotherm was named by the author of ref\textsuperscript{17} because it focuses on the counterion occupancy of the Stern layer (also see ref\textsuperscript{1} for a detailed explanation about the Stern layer and different adsorption layer structure). It is also worth mentioning that the surface charge in the following table indicates the total electric charge of surfactants and counterions at the interface.
Table 1. Surface charge equations derived from the surfactant and counterion adsorption isotherms.

<table>
<thead>
<tr>
<th>Surface charge</th>
<th>Counterion adsorption</th>
<th>Adsorption structure</th>
<th>Isotherm model**</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma = z_1 F \Gamma_1 - z_2 F \Gamma_2$</td>
<td>$\Gamma_2 = \Gamma_1 \frac{K_z c_{2s}}{K_1 + K_z c_{2s}}$</td>
<td><img src="image" alt="Stern" /></td>
<td>Stern</td>
</tr>
<tr>
<td>$\sigma = z_1 F \Gamma_1 - z_2 F \Gamma_2$</td>
<td>$\Gamma_2 = (\Gamma_\infty - \Gamma_1) \frac{K_z c_{2s}}{1 + K_z c_{2s}}$</td>
<td><img src="image" alt="Two-layer" /></td>
<td>Two-layer</td>
</tr>
<tr>
<td>$\sigma = z_1 F \Gamma_1$</td>
<td>$\Gamma_2 = \Gamma_1 K_z c_{2s}$</td>
<td><img src="image" alt="Three-layer" /></td>
<td>Three-layer</td>
</tr>
<tr>
<td>$\sigma = z_1 F \Gamma_1$</td>
<td>$\Gamma_2 = 0$</td>
<td><img src="image" alt="No counterion adsorption" /></td>
<td>No counterion adsorption</td>
</tr>
</tbody>
</table>

*Area between two dashed lines denotes the adsorption layer. The structure is shown for anionic surfactant, but the models are applicable for any surfactant.

**The no counterion adsorption model shows no interaction between the surfactant ions and counterions. For the Stern model, the counterions enhance the adsorption of surfactant ions but do not exist in the adsorption layer. The two-layer model and three-layer model consider the penetration and partial dehydration of the counterions, respectively, and those counterions form adsorption layers with surfactants.

Counterion adsorption models can be easily extended to incorporate the effect of different counterions: the ion-specific effect for surfactant can be captured with a slightly different equilibrium constant of counterions. All counterion models have been used to study the ion-specific effect, and they effectively predict the surface tension of surfactants with different monovalent counterions. Some models assume the adsorption energy was caused by the ion-pair formation between headgroup and counterions, while some believe it was from the counterion affinity to the air/water interface. Although adsorption models work well with the surface tension prediction, they may not fully capture the underlying physic of surfactant at the air-water interface.
Problems of classical theories in comparison with experiments

Unreliable prediction of properties of the air-water interfaces

Classical adsorption models were widely used to fit the experimental surface tension data to extract the property of surfactant (e.g. adjustable parameters $K$, $\beta$, and $\Gamma_\infty$). In this way, the surface properties such as the surface excess and surface potential can be obtained.\textsuperscript{15-18} However, many classical adsorption models are not mathematically stable: similar fitting quality can be achieved using different sets of adjustable parameters\textsuperscript{37}. More specifically, several combinations of $K$, $\beta$, and $\Gamma_\infty$ will result in the same fitting quality, determined by the sum of squares between experimental and predicted surface tension. Therefore, extracting surfactant properties using only surface tension data may not be reliable. We identified that two sources are affecting the extracted parameter reliability of adsorption models: one from the model amplification of experimental error, and another from the process of fitting surface tension data to extract adjustable parameters. To investigate those problems quantitatively, we define the local instability as the change of model output divided by the change of model input. It indicates how adjustable parameters changes according to a small perturbation of experimental data, which should be small for a stable adsorption model. We also define the global instability as how difficult to find the best-fit parameters from the global minimal at the cost function hyperspace. Briefly, if a function has a single minimum, its instability is zero. This value is small for systems having clustered minima and large for those with scattered minima. The detailed approaches were discussed in our previous work.\textsuperscript{37}

Figure 1A shows two types of instabilities calculated from some typical adsorption models.\textsuperscript{27, 50-51} The Frumkin type of models have much higher instability than Langmuir type of models. Langmuir adsorption model always has zero function instability because its cost function has a single minimum. It is difficult to get consistent adjustable parameters by fitting the surface tension data with Frumkin type models because of the scattered minima. Figure 1B shows that although Frumkin type of models usually gives better fitting quality, their best-fit adjustable parameters may not be realistic because of their poor stability. We emphasize that having more adjustable parameters decreases the stability of the system, which should be avoided in model development. However, except for a few attempts to reduce the number of adjustable parameters,\textsuperscript{59} its number increases significantly as the adsorption model becomes more complex. For example, there are eight parameters in the adsorption model accounting for counterion and specific-ion effect.\textsuperscript{22} This is probably because having more adjustable parameters increases the fitting quality and many researchers are in favour of this feature
instead of parameter reliability. We want to point out that good fitting quality does not guarantee that a model is suitable as high instability would invalidate the extracted parameters.

Figure 1. Parameter instabilities of several adsorption models (A). Surface tensions of polyglycol ethers predicted by Langmuir and Frumkin models (B). Reprinted with permission from ref. 37. Copyright 2018 Elsevier.

The surface tension data has limited information, and it cannot support complicated adsorption models with too many parameters. The model instability can be reduced by combing surface tension data with additional information, determined by simulations or experiments. For example, the equilibrium constant and the maximum surface excess can be determined experimentally. Also, Monte Carlo (MC) simulation can be used to calculate the surface areas of molecules such as polyglycol ethers and SDS. Molecular dynamics (MD) was also used to quantify the surfactant adsorption. Those methods significantly reduced the number of adjustable parameters which would increase model stability. It is worth mentioning that sum-frequency generation spectroscopy (SFG) can be used to determine the orientation angle of surfactant molecules. It may seem straightforward that the classical curve fitting method can be combined with additional techniques to reveal the mystery of surfactant adsorption. However, those techniques produce very different results, and there is no way to determine which result is more realistic. This is another complex problem which will be discussed in the next section.

Disagreement between experiments and modelling: the real adsorption layer is thick

It is a well-known issue that the surface excess and surface potential determined by different techniques are not comparable with each other. Also, different adsorption models do not give the same prediction for those two surface properties despite all of them effectively predict the surface tension drop according to surfactant concentration.
Figure 2A shows the surface excesses of SDS measured by experimental techniques and predicted by several adsorption models\textsuperscript{16-18} from Table 1. The surface excess derived from tensiometry agrees with model predictions but significantly lower than that measured by neutron reflection (NR) and radiotracer (RT) techniques.\textsuperscript{10} Figure 2B shows the experimental and model-predicted surface potential for SDS. Note the surface potential determined by different techniques are not quantitatively comparable so that we plotted the highest and lowest potential from the literature.\textsuperscript{71-72} Although experimental surface potential gradually increases with concentration, adsorption models predict nearly constant values.

\textbf{Figure 2.} Compare the surface excess of SDS from different model predictions\textsuperscript{16-18} and experimental results\textsuperscript{10, 73} (A). Compare the surface potential from different model predictions\textsuperscript{16-18} and experimental results\textsuperscript{71-72} (B). Reprinted with permission from ref. 11. Copyright 2019 Elsevier.

The mismatch of surface properties between experimental results and model predictions is likely to be caused by the oversimplification of an actual adsorption layer structure. Soluble surfactants, especially ionic surfactants such as SDS, form thick adsorption layers at the air-water interface which cannot be sufficiently represented by infinitely thin layers assumed by adsorption models. The existence of a thick adsorption layer was proved by many experimental and simulation results such as NR,\textsuperscript{33, 74-78} X-ray reflectivity,\textsuperscript{79-82} neutral impact collision ion scattering spectroscopy (NICISS),\textsuperscript{83-89} SFG,\textsuperscript{38-39, 69} and MD.\textsuperscript{90-94} As the adsorption layer is a few nanometres thick, there could be a surfactant depleting region or under-monolayer adsorption underneath the first adsorption layer.\textsuperscript{38, 95} Although those changes in surfactant concentration cannot be detected by measurement techniques because of their limited probing depth, they still contribute to the surface tension drop.\textsuperscript{1} While the surface excess derived from the surface tension represents the whole system, the surface
excess determined from RT and NR may only come from the first adsorption layer, and therefore their values should be different.

Similar explanations can be applied to the surface potential discrepancy, and the oversimplification of the actual adsorption layer structure brings about more troubles here. The thin layer assumption was widely used to convert experimentally measured values to surface potential. This applies to different techniques such as electrokinetic, vibrating plate, ionization, and non-linear spectroscopy. Converting measured results to surface potential values based on a realistic concentration profile is challenging. The electrokinetic methods detect the surface potential of a dynamic system, and the surfactant may not reach the adsorption equilibrium under this condition. For the vibrating plate and ionization electrode, the contribution of the molecular polarizability to the potential drop is significant but difficult to eliminate. This is partly because the orientation of surfactant molecules varies according to bulk concentration. SFG or SHG (second harmonic generation) provides relative surface potential instead of absolute values, and organic molecules and water molecules can contribute significant additional signals. Also, the surface potential discrepancy could be caused by the variation of the measurement depth of each experimental technique. It is obvious that the surface potential strongly depends on the distance from the interface, but measurement techniques may not measure this value at the same point. The surface potentials predicted by adsorption models are only comparable with experimental results if they have similar distances to the air-water interface. It requires that the position of the slipping plane in the electrokinetic approach overlaps with the beginning of the diffuse layer in adsorption models, which is unlikely to be true. And this problem is shared with other experimental techniques, which will be further discussed in this article.

Additional adsorption layer of surfactant under the first layer proved by SFG studies

Our work provides further evidence that soluble surfactants have significant adsorption underneath the first adsorption layer. Figure 3B shows that the normalized SFG intensity of methyl isobutyl carbinol (MIBC) in water does not change after 20 mM under two polarisation combinations, while the surface tension decreases significantly after this concentration. This observation cannot be explained by classical adsorption theories as the surface excess determined from SFG results does not agree with that from the surface tension. The SFG intensity is proportional to the surface excess when both the SSP and PPP (the symbol S and P indicates the polarized light direction for SFG, IR and VIS beam) signals do
not change so that the monolayer saturation is reached at 20 mM. However, the surface excess derived from surface tension data using Gibbs isotherm continues increasing beyond that point. We explain this by introducing an additional surfactant adsorption layer. At high concentration, even the surface monolayer is already saturated, the under-monolayer region still provides adsorption sites for MIBC molecules.\textsuperscript{38, 68} The under-monolayer region is not detectable by SFG because this technique is highly interfacial specific. However, surfactant molecules adsorbed in this region still contribute to the total surface excess as observed by the surface tension drop. This finding echoes with a series of work from Shibata et al.\textsuperscript{111-113} They also showed that several experimental observations could not be explained by classical adsorption theories and assume some surfactant molecules can have positive adsorption at the under-monolayer region instead of right at the interface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The measured foamability of pentanol, MIBC, and hexanol solutions versus concentration (A). The vertical lines show the monolayer saturation determined by SFG. The foamability drops sharply after the vertical line regardless of the surfactant type, showing that sub-monolayer adsorption significantly reduces the film stability. The surface tension data and normalized SFG signal intensity according to the concentration of MIBC in water (B). The surface tension continues decreasing after the monolayer saturation, so that surfactant molecules are likely adsorbed under the first adsorption layer higher than that concentration. Reprinted with permission from ref. 38-39. Copyright 2016 PCCP Owner Societies (A). Copyright 2017 American Chemical Society (B).}
\end{figure}

Although the surface tension of the surfactant does not show the point of monolayer saturation and subsequent sub-monolayer adsorption, dynamic properties of the fluid surface such as surface elasticity and foam stability are very sensitive to this point.\textsuperscript{39} Figure 3A shows the foamability (measured as the foam volume under constant airflow rate) of several typical surface-active alcohols. The foamability increases with the surfactant concentration until it reached the monolayer saturation, then it drops sharply. Note the point of monolayer
saturation for each surfactant was determined by SFG experiments (indicated by the constant signal intensity, as shown in Figure 3B). This means the film becomes increasingly unstable with the sub-monolayer adsorption. The initial increase of the surface elasticity was believed to be caused by stabilizing Marangoni effect, which grows with surface coverage and reaches its maximum at monolayer saturation. However, the under-monolayer adsorption weakens the Marangoni effect by the fast supplying of surfactant molecules from the second adsorption layer. At high surfactant concentration, the expansion of thin-film will not cause considerable local surface tension gradient because of the ultra-fast transfer of the surfactant molecules from the under-monolayer. This process significantly weakens the Marangoni effect and decreases the surface elasticity, and consequently, the liquid film containing under-monolayer surfactants becomes unstable.

We developed an adsorption model to quantify the under-monolayer adsorption. In this model, the ionic surfactant SDS has a primary adsorption layer at the air-water interface, and a secondary adsorption layer underneath the interface, immersing into the water phase. This model extends the two-layer model in Table 1 into four layers, including counterion adsorption layers for each surfactant adsorption layer. Briefly, the additional layer facilitates the adsorption of both surfactant and counterions and consequently reduces the surface tension more effectively. This model explains why the adsorption of SDS at the oil-water interface is lower than that at the air-water interface, while the oil phase has higher hydrophilicity than air. This is because SDS immerse deeper into the water phase at the air-water interface. The significant immersion of the surfactant brings adjacent molecules into close contact, which results in high surface excess, despite its lower adsorption energy compared to the oil-water interface. According to this model, the immersion degree of SDS at the oil-water interface is around 70% less, and the consequent strong lateral repulsion between the sulfate headgroups results in 30% less adsorption compared to the air-water condition. This model shows that ionic surfactants tend to have a wide density distribution at the air-water interface, which is incompatible with the thin layer assumption of classical theories.

**Partially charged non-ionic surfactant discovered by the ionic electrode**

As indicated by the brief review in section 2 that several models for surface potential at the air/liquid interface have been proposed. The concept of charged layers was believed only applicable for ionic surfactants. However, the potential difference (ΔV) measured for non-ionic surfactants using the vibrating plate, and ionization method
revealed that they can be partially charged. Therefore, we need an appropriate model to describe the adsorption of non-ionic surfactant molecules and electrolytes at the interface. Note the potential difference measured by the vibrating plate, and ionization method is the sum of weighted surface excess (always positive) and the surface potential (can be positive or negative). If non-ionic surfactants carry no charge, all of them will react the same to electrolyte solution since there is no surface potential. However, 1-hexanol and MIBC show opposite behaviour to the common electrolyte NaCl as shown in Figure 4, and we developed a partial charge model to explain this phenomenon. In electrolyte solutions, the headgroup of the alcohols is assumed to possess an effective partial charge, $\alpha$, which is thermodynamically balanced by the net charge of enhanced electrolytes within the interfacial region. In this model, $\alpha$ is a fitting parameter determining the enhancement of either cations or anions at the interface. If $\alpha$ is positive, there will be more cations adsorbing to the interface compared to the negative counterparts, and vice versa.

![Figure 4](image)

**Figure 4.** Compare the potential difference (between the electrode in the air and the electrode in the bulk solution) of MIBC (A) and 1-hexanol (B) with and without salt added. The potential difference between those two surfactants reacts differently to the increase of NaCl concentration. This is because MIBC and 1-hexanol carry opposite partial charges. In both cases, increasing NaCl concentration would reduce the surface potential. However, for MIBC, it reduces a positive surface potential, and the potential difference will be lower with 2 M NaCl. For 1-hexanol, it reduces a negative surface potential, and the potential difference will be higher with 2 M NaCl. Reprinted with permission from ref. 28-29. Copyright 2012-2013 American Chemical Society.

The partial charge model successfully described the potential difference of two widely used non-ionic surfactants (1-hexanol and MIBC) with different NaCl concentrations as shown in Figure 4. Interestingly, increasing the concentration of NaCl increased the potential
difference of 1-hexanol, yet decreased that of MIBC regardless of surfactant concentration\textsuperscript{28}. The best-fit value of $\alpha$ showed the opposite behaviour of 1-hexanol and MIBC at the air/brine interface. While adsorbed MIBC promoted the presence of cations ($\alpha > 0$), the presence of anions was enhanced by adsorbed 1-hexanol ($\alpha < 0$). This finding is contradictory to classical adsorption models, in which the molecular structure of surfactants has not been accounted for\textsuperscript{37, 115}, and therefore the difference in ion attraction of these two isomers cannot be quantified. We explained that the straight chain of 1-hexanol molecules was unable to alter the anion enhancement of NaCl at the air/pure water interface as witnessed in literature\textsuperscript{116-117}. Whereas, the hydrocarbon branches of MIBC molecules reduced the interfacial space and hence prevented the penetration of anions into the interfacial layer.

MD was employed for elucidating this opposition\textsuperscript{118}. It is worth noting the Gibbs dividing plane could not quantify the ions adsorption revealed by the partial charge model. Then, a newly proposed dividing plane was defined positioned at the positive peak of the dipole order of water molecules, which is governed by adsorbed surfactant molecules. This new dividing plane can verify the relative adsorption of cations and anions at the air/brine interface. Further studies\textsuperscript{119-120} combining the modified partial charge model and molecular dynamics simulation also successfully predicted the potential difference of NaCl and NaI at the air/water interface. The modelled adsorbed concentration of positive and negative ions reflects the opposite experimental results of the potential difference that NaCl increases while NaI decreases the potential difference of the air/water interface. The application of the partial charge model needs to be extended to other non-ionic systems for validation. Particularly, the model should be modified to describe the adsorption of complicated non-ionic surfactants such as polyethylene glycols which are widely utilized in numerous applications. The undermonolayer adsorption which has currently been discovered by SFG measurements should also be accounted for in this model to improve its accuracy, and hence clarify the adsorption and molecular structure of non-ionic surfactants at the interface.

- **The modified Poisson–Boltzmann model based on experimental ion distribution**

  The development of the MPB model for adsorption at the air-water interface

  We mentioned that soluble surfactants form thick adsorption layers at the air-liquid interface, which cannot be simplified by thin adsorption layers assumed by classical approaches\textsuperscript{11}. Therefore, we developed a new adsorption model for ionic surfactants at the air-water interface that incorporates the effect of adsorption layer thickness using a MPB equation. In this model, the surfactant ions have a wide distribution of concentration at the
interface compared with experimentally detected density profiles. This model also gives more accurate surface potential predictions than classical models. Note we only present the case of univalent ionic surfactants with salts for simplicity. The mean-field theory can be used to the air-water interface loaded with the ionic surfactant, and the free energy minimization gives ion distribution according to the Poisson–Boltzmann equation:

$$
\varepsilon_w \varepsilon_0 \frac{d^2 \psi(x)}{dx^2} = -e \sum_i z_i c_i \exp \left[ -\frac{1}{k_B T} (z_i \psi(x) + G_{im}(x) + G_{it}(x)) \right]
$$

where $\varepsilon_w = 80$ is the relative permittivity of water, $\psi(x)$ is the potential as a function of distance $x$, $z_i = \pm 1$ denotes the valency of ion type $i$, and $c_i$ is the bulk concentration of different types of ions. The classical Poisson–Boltzmann (PB) equation contains the electrostatic energy $z_i \psi(x)$, image charge energy (short-range electrostatic repulsion caused by the image charges in the air phase) $G_{im}(x)$ in Wagner form, and the interaction energy $G_{it}(x)$. The interaction energy (represents the overall non-electrostatic interaction between surfactant and the air-water interface) has a Gaussian form as: $G_{it}(x) = -A \exp \left[-(x/d)^2\right]$.

Where $A$ is the amplitude, $x$ is the distance from the interface, $d$ is the decay distance. The parameter $A$ determines how strong the interaction will be, and the $d$ determines the range of the interaction. We use MD to determine the concentration-dependent $d$ value, and then the $A$ can be extracted by fitting the experimental surface tension data. For simplicity, we use the Wagner form of image charge energy and the Gaussian form of interaction energy as they are sufficient to reproduce the experimental density distribution of surfactant. Using more complicated functions does not significantly improve the model prediction and detailed justifications can be found in our previous publications. Solving this equation gives $c_i(x)$ and $\psi(x)$, which are distance-dependent surfactant concentration and electrostatic potential. Integrate the concentration of all ionic species gives the surface excess, and the surface tension can be calculated from this property using the Gibbs equation. This model provides good predictions for experimentally determined surface tension and density profile. Especially, our model prediction quantitatively agrees with NICISS data and it is comparable with X-ray reflectivity results since those two techniques provide similar density profile for surfactants.
We directly compare the ion distribution and surface potential profiles predicted by our model with several classical adsorption models (from Table 1) as shown in Figure 5. Both the ion distribution and surface potential profiles predicted by each model are significantly different. The perpendicular black lines indicate the beginning of the diffuse layer: it starts right at the interface ($x = 0$) for the no counterion adsorption model\textsuperscript{15}, for the three-layer model\textsuperscript{16} this distance was 0.35 nm and for our model, it is $x = d = 2.55$ nm at this concentration. The ion distribution predicted by our model is very similar to experimental and simulation results, but other adsorption models fail to account for this property. In particular, experiments and simulations show that surfactant forms a thick adsorption layer which can only be captured by our model. Our model has a 2.55 nm adsorption layer while the thickness of this layer is zero for classical models, according to the concentration profiles of Figure 5. Also, in classical models, the surfactant concentration jumps from infinity to almost zero at the Gibbs dividing surface indicated by the black line as they assume the Dirac delta function density distribution of the adsorption layer. Consequently, classical models predict much lower surfactant concentration close to the interface (for example, at 2 nm), which contradicts experimental and simulation results.\textsuperscript{8,93}

Figure 5. The potential profile and ion distributions for several adsorption models\textsuperscript{15-16}. The perpendicular black lines indicate the beginning of the diffuse layer. Reprinted with permission from ref. 13. Copyright 2020 American Chemical Society.
The positions of experimental surface potentials being measured\textsuperscript{18, 98, 113, 125}, and the potential profile predicted by adsorption models\textsuperscript{15-16}. The vertical black line indicates the beginning of the diffuse layer of the MPB model. Reprinted with permission from ref. 13. Copyright 2020 American Chemical Society.

The surface potential predicted by our model agrees very well with experimental results determined by vibrating plate/ionisation\textsuperscript{18, 113} and SFG\textsuperscript{125} because we considered a realistic potential profile, as shown in Figure 6. Ionization and vibrating plate likely detected the potential at $x = 0$ and the SFG signal is related to the potential at $x = 2.55$ nm. The slipping plane defined by the electrokinetic measurements should be quite close to the diffuse layer if adsorption equilibrium can be reached. This figure also highlighted the problematic prediction of surface potential by classical models\textsuperscript{15-16}, especially for the diffuse layer potential. Our model shows that this potential should be around -100 mV, but the classical counterion model and classical thin layer model predict -50 mV and -70 mV. Classical models predict much lower surface potential because they ignore the adsorption layer thickness, which inhabitants the potential reduction from the interface. Therefore, we believe this new model is a better alternative for interpreting surface potential measurements than classical models.

The MPB model can incorporate the ion-specific effect for surfactants

The MPB model in the previous section can be extended to account for the ion-specific effect of monovalent cations for ionic surfactant SDS. This model can accurately predict the surface tension of the anionic surfactant SDS in the presence of the monovalent salts LiCl, NaCl, KCl, and CsCl. Also, the model predictions agree very well with SFG and MD results.\textsuperscript{21} SDS behave like a large ion, and it prefers to bind with large counterions so that large counterions enhance the surface adsorption and lower the surface tension the most. The
same equation in our previous work (Eq. 4 in Section 4.1) was used for this model, and the model calibration procedures are similar except for one modification: the Gaussian form of the adsorption energy now applies for both surfactant and counterions. Therefore, we have two adjustable parameters for the amplitude of adsorption energy: $A_1$ for surfactant and $A_2$ for counterions. To reduce the number of adjustable parameters, we use the same $d$ for surfactant ion and counterions. This simplification is reasonable because the counter ion adsorption is mostly caused by binding to the surfactant, as shown in our MD simulation.\(^{21}\)

![Figure 7.](image)

**Figure 7.** The experimental surface tension of 1mM SDS in LiCl, NaCl, KCl and CsCl solution (points) and model predictions using the MPB equation (solid lines) (A). The dashed lines indicate the model prediction without adsorption saturation. The corresponding concentration and potential profiles for LiCl and CsCl, calculated from Eq.4 (B). Reprinted with permission from ref. 21. Copyright 2020 American Chemical Society.

The experimental and predicted surface tension (using the MPB model) of 1mM SDS in the presence of LiCl, NaCl, KCl, and CsCl was shown in Figure 7A. Adding salts to the surfactant solution decreases the surface tension, and surface tension is strongly counterion-specific: Li$^+$ ion affects the surface tension of SDS the least while Cs$^+$ ion reduces it the most. Our model can predict the surface tension of SDS/salt mixtures. It is straightforward that counterion with higher (more negative) adsorption energy reduces the surface tension of surfactant more effectively. Figure 7B highlights the effect of Li$^+$ ion and the Cs$^+$ ion on the density profile of SDS. The concentration peak of surfactant and counterions in the presence of CsCl is almost 1.5 times higher than that of LiCl, which was caused by the higher adsorption energy of the Cs$^+$ ion. This is the reason why CsCl results in higher surface excess and lower surface tension.\(^{21}\)
Figure 8. The SFG spectra of 1mM SDS at the air/water interface in the presence of LiCl and CsCl, at different salt concentrations. Reprinted with permission from ref. 21. Copyright 2020 American Chemical Society.

The SFG spectra at the air/water interface formed by 1mM SDS in the presence of LiCl and CsCl at different concentrations were shown in Figure 8. Briefly, the height of organic peaks from 2800 cm\(^{-1}\) to 3000 cm\(^{-1}\) is proportional to the number of surfactant at the interface.\(^{108}\) The signals from 3000 cm\(^{-1}\) to 3600 cm\(^{-1}\) were mostly caused by the water molecules ordered by the charged adsorption layer at the interface, which is directly related to the surface potential.\(^{101,105}\) Therefore, in the presence of CsCl the organic peaks are stronger, meaning higher surface excess. The water signals were higher for LiCl, which corresponds to a higher surface potential. Large ions such as Cs\(^{+}\) should have higher concentrations close to the adsorption layer than small ions such as Li\(^{+}\) and the concentration of counterions follows the order of Cs\(^{+}\)>K\(^{+}\)>Na\(^{+}\)>Li\(^{+}\). Our SFG results agree very well with our model prediction. Using the additional experimental technique, we validate our ion-specific model for SDS. We would like to mention that the model validation step is generally missing in several previous studies for surfactant adsorption.\(^{15-17,20,22}\)

**MPB model for the thin liquid film: precise disjoining pressure predictions of foam films**

We found that the MPB model gives a much better prediction of the disjoining pressure for the thin liquid film compare to classical models.\(^{40}\) The disjoining pressure is the pressure difference between the film surface and the bulk, which significantly affects the film stability. As we discussed in previous sections that soluble surfactants have wide density distributions at the air-water interface, and this concept applies to foam film systems too. A thick adsorption layer will increase the electrostatic potential inside the film and lead to higher disjoining pressure. Classical theories ignored this fact and predicted unphysical electrostatic potential profiles, which underestimate the disjoining pressure. Our MPB model gives an
accurate prediction of the disjoining pressure over a wide surfactant concentration range because we considered the realistic thickness for the adsorption layer. In this work, the same equation was used to calculate the surface excess and surface potential. However, the model calibration requires density distribution and surface excess information for a specific surfactant. In this work we only focus on SDS and we will not extend the discussion for non-ionic systems involving complex non-DLVO forces. The disjoining pressure can be calculated by the following equation according to the DLVO theory: the first term stands for the repulsion caused by adsorbed charged species and the second term stands for the van der Waals attraction between two air bodies separated by the thin film.

\[
\Pi(H) = k_B T \sum c_i \left[ \exp\left( -\frac{z_i e \psi_{H/2}}{k_B T} \right) - 1 \right] - \frac{A_H}{6\pi H^3} \left( 1 - \frac{H}{2} \frac{dA_H}{dH} \right) \tag{5}
\]

where \(k_B\) is the Boltzmann’s constant, \(T\) is the temperature, \(c_i\) is the number per unit volume of ions of type \(i\) in the bulk solution far from the interface, \(\psi_{H/2}\) is the electrostatic potential at the middle plane of the film, \(e\) is the electron charge and \(z_i = \pm 1\) denotes the valency of ion type \(i\). The Hamaker constant \(A_H\) decreases with film width \(H\) and is further reduced by the presence of the surfactant adsorption layer due to the retardation effect. The disjoining pressure is straightforward to calculate from Eq.5 when the MPB equation (Eq.4) is solved as the electrostatic potential at the middle plane of the film is part of the distance-dependent potential obtainable from the MPB equation.

**Figure 9.** The disjoining pressure as predicted by different approaches for the thin liquid film formed by 7mM SDS and 0.5 mM NaCl (A). The potential profile as predicted by our model and classical approaches according to the distance from the interface (B). The vertical dashed lines indicate the beginning of the diffuse layers. The electric potentials given in the legend are the electrostatic potential according to the distance to the surface. The surface potential
and the midplane potential can be obtained at 0 nm and 5 nm, respectively. Reprinted with permission from ref. 40. Copyright 2020 American Chemical Society.

Figure 9A shows that our model agrees with the experimental results,\textsuperscript{130} while classical approaches fail to predict the experimental disjoining pressure. Note the further increase of the surface potential beyond -200 mV has a negligible effect on the predicted disjoining pressure as predicted by the PB equation.\textsuperscript{1} Therefore, the measured disjoining pressure will always be higher than predictions using classical approaches, no matter how high the surface potential. This is because classical models do not have realistic electrostatic potential profiles, as shown in Figure 9B. All classical approaches have a lower middle plane potential $\psi_H$ (at 5 nm) compared to our model, which means lower predicted disjoining pressure according to Eq.5. The value of the surface potential has only a limited effect: even the classical model starts with a -200mV potential, it gets lower than our model after 2 nm from the interface. This is because our model considers a thicker adsorption layer which enables a slower potential reduction. All classical approaches assume very thin adsorption layers (1.1 nm),\textsuperscript{131-133} compare to our model (2.63 nm).

**Figure 10.** The Disjoining pressure prediction assuming different adsorption layer thicknesses for the thin liquid film formed by 7mM SDS and 0.5 mM NaCl (A). The disjoining pressure was calculated by Eq.5 with different adsorption layer thicknesses. The surface excess was kept constant. The model prediction of the electrostatic potential according to distance under different adsorption layer thicknesses (B). The potential profile was calculated by Eq.4. Reprinted with permission from ref. 40. Copyright 2020 American Chemical Society.

Figure 10A shows the predicted disjoining pressure with different adsorption layer thicknesses. In this case, the adsorption amount (surface excess $\Gamma$) of surfactant is kept constant by changing the parameter $A$ (amplitude of the interaction energy) in the subsequent
equation of Eq. 4. Overestimation and underestimation of the adsorption layer thickness will result in overestimation and underestimation of the disjoining pressure, respectively. This is because a thicker adsorption layer leads to a lower potential at \( x = 0 \) while higher potential at \( x = H/2 \) and vice versa, as shown in Figure 10B. Form Eq.5, a higher potential at the middle plane will produce higher disjoining pressure. These results explain why the thick adsorption layer would increase the disjoining pressure. This work shows that a realistic adsorption layer structure must be considered to make an effective disjoining pressure prediction, and it is crucial to incorporate a realistic adsorption layer thickness into an understanding of thin liquid film behaviour.

**The Jones-Ray effect explained by the MPB model**

The MPB model can also be used to explain the Jones-Ray effect, i.e. the small surface tension minimum at a low salt concentration of a few mMs.\(^{19}\) There are several explanations proposed for the Jones-Ray effect, yet those theories are far from perfect. We believe that the Jones-Ray effect could be caused by the existence of trace amounts of ionic surfactant impurities in “pure water” and we have shown this with experimental surface tension measurements and modelling.\(^{19,23-24}\) We also demonstrate that the low concentrations of the surfactant necessary to create the Jones-Ray effect are too small to be detected.\(^{19}\) This work suggests that the purity standards for water may be inadequate, and that background impurities are a continuing concern. To demonstrate this effect, we used the MPB equation as described by Eq.4, but with a Heaviside step function for the adsorption energy for both the surfactant and counterions. In other words, a 0.5 nm wide square well. This simplification is reasonable as the surface concentration for surfactant and ions are extremely low, which means that non-electrostatic between the solutes can be neglected.

**Figure 11.** Experimental and predicted surface tension difference (compare to pure water) for NaCl in pure water and surfactant solution (decylammonium hydrochloride, DAH) (A). Surface potentials calculated with the Poisson-Boltzmann equation as a function of salt and
surfactant concentration (B). Reprinted with permission from ref. 19. Copyright 2018 AIP Publishing.

Figure 11A shows that intentionally adding surfactant can reproduce the same pattern as the Jones-Ray effect: The Jones-Ray-like behaviour consists of an initial drop in surface tension followed by an increase at higher salt concentrations. The red points are data from the original Jones-Ray experiments using distilled water. The minima originally observed by Jones and Ray are too small to be resolved at this scale. This result demonstrates that the Jones-Ray effect can be predictably controlled to enhance the magnitude of this effect. The good agreement demonstrates that the theory is accurately capturing a real physical mechanism. We also compare the fitted surface tension changes for some ions with the experimentally measured values of Jones and Ray. The details of the fitted parameters are shown in our work and the Jones-Ray effect for various ions can be reproduced by our model with no higher than 0.1µM ionic surfactant as the impurity.

The mechanism of this effect is clear from Figure 11B, which plots the electrostatic surface potential for the case of 0M, 0.002M, and 0.2M of NaCl with and without 0.1 µM of the surfactant. The surfactant impurities create a very long-range electrostatic potential which extends far into bulk due to the large Debye length at low concentrations. This potential is much larger than the potential created by the salt ions adsorbing on their own to the interface and is the driving force that attracts the added cations to the air-water interface at very low concentrations. At higher salt concentration, this potential is screened and significantly reduced in size consistent with the fact that the Jones-Ray effect is only observed at very low concentrations. One objection to the notion that surface contamination could be the explanation for the Jones-Ray effect is that these contaminants should be observable using surface-sensitive spectroscopic measurements. However, in this work, we also demonstrate that there are no observable signal differences in the CH stretch region between DI water and decylammonium chloride in 0.1 µM, even with salt addition (which increases the surfactant adsorption and amplifies the signal). This shows that surface-sensitive spectroscopy is not sensitive enough to resolve the presence of the surfactant at such low concentrations. Therefore, surfactant impurity adsorption is a plausible mechanism causing the Jones-Ray effect.
- Molecular simulations reveal more details about surfactant adsorption

Using MD to quantify film thickness and ion-specific effect

MD simulation provides essential information for modelling, which is not obtainable in other ways, such as the thickness of the adsorption layer. Although advanced techniques such as NR and NICISS can determine this property, they only work reliably at high surfactant concentrations.\(^7-^8\) We also use MD to quantify the film structure, especially the distribution width of the surfactant. As far as we know, there is no experimental evidence on the exact value of the adsorption layer thickness for liquid films thicker than 10 nm.\(^137-138\) Our MPB models in previous sections incorporate the effect of adsorption layer thickness extracted from molecular dynamics simulation. Also, we rely on MD to study the physical mechanism of ion-specific effect on surfactant. Most experimental techniques are rather macroscopic, which shows differences in surface tension, surface excess and surface potential without explanation. Modelling can only attribute those differences to the general counterion adsorption energy, which could be caused by various origins such as counterion interactions with surfactant headgroup, alkyl chain groups or with air/water interface. We performed simulations to determine which effect contributes the most.

Figure 12A shows a significant change in the distribution of surfactant headgroup at the interface according to the surface concentration. In particular, the distribution becomes wider as the surface concentration increases, corresponding to a thicker adsorption layer.\(^40\) At high surface concentration, the interface will be crowded, and surfactant molecules tend to push each other into the water phase, resulting in a thicker layer of surfactant.\(^20\) This suggests that the adsorption layer thickness is not constant, and it needs to be considered as a variable dependent on the surface concentration in our model. The distribution of surfactant from our simulation agree well with NR results (only available for high concentration).\(^139-141\) Our simulations also show that the distribution of surfactant and counterions does not change significantly with the thickness of the water layer in between them.\(^40\) Therefore, this surface concentration-dependent layer thickness applies to both single air-water interface and thin liquid film cases. The density profiles in Figure 12B show that large ions such as Cs\(^+\) tend to have higher concentrations near the adsorption layer.\(^21\) Also, the distance between the peak of surfactant headgroup and counterion is shorter for large ions, which follows the order of Li\(^+\)\(\to\)Na\(^+\)\(\to\)K\(^+\)\(\to\)Cs\(^+\), which is consistent with classical adoption theories.\(^22,\, 47\)
Figure 12. The snapshots at 10 ns of the adsorption layer and the density profile of surfactant headgroup derived from the MD simulations for SDS at different surface concentrations (A). The density profiles produced by simulation (B). Solid lines indicate the concentration of surfactant headgroup and dashed lines indicate the concentration of counterions. Note we use the same number of surfactants for all counterion cases, which yields the same surfactant concentration. This limitation of MD was discussed in the last section. Reprinted with permission from ref. 21 and 40. Copyright 2020 American Chemical Society.

To investigate the ion-specific effect for surfactant, we plotted the radial distribution function (RDF) between the surfactant headgroup of SDS and the counterions, as well as the RDF between the surfactant headgroup and the first carbon atom of the alkyl chain, which are shown in Figure 13. The RDF describes how density of counterions varies as a function of distance from the reference particle (S atom or the first carbon atom connected to the surfactant headgroup as described in the figure). Therefore, the figure shows that large ions are more likely to be found around the surfactant headgroup than small ions. The direct contact of the Li$^+$ ion is very improbable due to its strong hydration shell so that the binding between this ion and the surfactant headgroup will normally be separated by water molecules.$^{142-143}$ Figure 13 also shows that large ions such as Cs$^+$ have a stronger affinity for the alkyl chain of the surfactant. As part of the alkyl chain was immersed in the water phase, they can come into contact with the counterions.$^{20, 93}$ This alkyl chain-counterion affinity explains why Cs$^+$ pairs with surfactant stronger than K$^+$ ions even though the headgroup-counterion affinity is similar for those two ions. Our MD results explain the underlying origin of ion-specific effect: both the counterion binding to the headgroup and the alkyl chain contribute to this effect.$^{21}$
Figure 13. The RDF between counterions and surfactant headgroup. The RDF between counterions and the first carbon atom of the alkyl chain. Both the counterion-headgroup and counterion-alkyl chain interactions are highly ion-specific. Reprinted with permission from ref. 21. Copyright 2020 American Chemical Society.

Although MD is a useful tool to investigate the surfactant adsorption, its predictions need to be compared with experiments and modelings. Many previous simulations show small ions such as Li\(^+\) have higher concentrations close to the surfactant headgroup than larger ions,\(^{34-36}\) which is exactly the opposite trend of experimental observations.\(^{22, 87, 144}\) We believe that the attraction between the surfactant headgroup and the counterions might be overestimated if default Lennard-Jones parameters are used. We reduce this attraction according to the literature\(^{145-148}\) and reasonable surfactant/counterion interaction is achieved, which agrees with the experimental results. Another problem of MD is that classical forcefields may not sufficiently represent the surfactant behaviour at the air-water interface. Many interactions at the interface require a polarisable model or a QM treatment.\(^{41-43}\) However, simulations with higher levels of theory can only be performed on a limited scale. Therefore, some important properties, such as the bulk concentration and ionic strength, cannot be reproduced correctly. For this reason, QM studies for surfactants are quite rare, and we are working on those issues for a better solution.

Using quantum mechanical calculations to validate MD data

The accurate calculation of ion binding strength with the surfactant molecule in water is essential for predicting the ion-specific variation in the properties of surfactant solutions as the counterion is varied. A reasonable approximation for estimating the ion-surfactant binding is to split the interaction into two parts. Namely, the ion-headgroup interaction and the ion-backbone interaction.\(^{149}\) Unfortunately, however, the more fundamental problem of predicting these interactions is still a significant unsolved scientific challenge in its own right. For example, the activity and osmotic coefficients of salt solutions are determined
predominantly by the strength of ion-ion interactions in water. Yet these properties still cannot be predicted with any reliability from first principles.\textsuperscript{150} And hence systems of equations such as the Pitzer equations with parameters fitted to experiment must be used to describe them.\textsuperscript{151-152} One option is to use these parameters to shed light on ion-surfactant interactions. For example, the pairing strength of alkali ions with the acetate anion should give some indication of the strength of ion binding to surfactant molecules with carboxylate headgroups.\textsuperscript{151} Relying on classical molecular dynamics to resolve this issue is problematic due to the large numbers of parameters in these simulations, which are difficult to reliably fit and can lead to incorrect qualitative trends in some cases as mentioned above.

![Figure 14](image.png)

**Figure 14.** Some of the short-range PMFs (shown as free energy $\beta W$ against distance $r$) predicted by simulation (A). The Coulomb attraction has been removed. Comparison of experimental and theoretical osmotic coefficients (shown as osmotic coefficients $\phi$ against concentration $c$) (B). The theoretical values (dashed lines) are calculated based on simulation. The experimental values (symbols) are determined from ref.\textsuperscript{151} after conversion. Reprinted with permission from ref. \textsuperscript{43}. Copyright 2016 Elsevier.

Fundamentally, these binding strengths are determined by the full QM energies of the ion-surfactant-water system. Hence, high-level QM calculations are in principle necessary for their accurate determination. There are several options for how these calculations can be used. One is to use them to determine the values of the parameters in classical molecular dynamics simulation.\textsuperscript{153} Alternatively, direct QM calculations using a polarisable continuum approximation to treat the background solvent can be used.\textsuperscript{41} Unfortunately, neither of these approaches can be straightforwardly used to make sufficiently accurate predictions. As far as we know, there are very few QM studies about surfactants\textsuperscript{44-45}. In these works, the equilibrium distance (and energy) between surfactant headgroup and counterions were used to determine the relative strength of headgroup-ion interactions. However, the realistic
interaction between surfactant and counterions cannot be sufficiently described by single point energy, especially when implicit solvation is used.

An approach to resolving this problem is emerging from the ongoing improvements in quantum mechanical density functional theory-based simulation of solute-pairing in water. These simulations are approaching the required accuracy where they can reliably predict the strength of solute binding in solution. The information from these simulations can then be used to test and parameterize simpler and computationally cheaper models of ion-ion interactions in water, which can then be used to predict the strength of ion binding for much wider categories of ions. As shown in Figure 14B, the predicted osmotic coefficients of several salts calculated with this approach based on the potential of mean force (PMF) of Figure 14A agree well with experimental results for several salts. A similar approach should be possible for ion-backbone interaction. Once these ion binding strengths can be reliably determined it should be possible to incorporate them into models of surfactant solution properties and make reliable predictions of the ion-specific properties of surfactant systems.

### Conclusion

In summary, we have outlined several recent advances in our understanding of the behaviours of surfactant solutions. We pointed out that classical adsorption models fail to explain experimental surface potential, and this problem cannot be fixed by introducing more model parameters due to the decreasing model stability. A better alternative is to incorporate the adsorption layer thickness into mathematical modelling. We developed the modified Poisson–Boltzmann model which requires parameters determined from simulation and advanced experimental techniques other than tensiometry. This new surfactant adsorption model produces more realistic density and electrostatic potential profiles compared to classical theories. It also effectively explained the previously underestimated disjoining pressure and possibly the surfactant induced Jones-Ray effect. Our work highlighted the importance of the combined use of computational simulation, mathematical modelling, and experiment and we strongly believe this is the desired approach for future research in the field of surfactant adsorption.

We also want to emphasize that each of these approaches on their own has key advantages as well as critical limitations which mean that it is not possible to conclusively understand the properties of surfactant solutions with any of them alone. Molecular dynamics provides unique insight into the molecular scale behaviour of these solutions but many
properties such as surface-bulk equilibria cannot be probed due to the short time scales and many interaction parameters mean quantitative predictions are very challenging. Mathematical modelling, on the other hand, can examine surface-bulk equilibria but these models require many parameters such as the surface thickness and adsorption interaction energies. Normally these energies are fitted to reproduce the experiment they are aimed at explaining, i.e., surface tension data. But by using simulation and experimental results some of these parameters can be determined independently, thereby increasing the confidence and robustness of the obtained results. Experiments are crucial for confirming and testing the predictions of the simulation and modelling but can rarely provide direct unambiguous measurement of important fundamental properties such as ionic distribution profiles. Hence, reliable simulation and modelling are essential for interpreting the meaning and significance of experimental results. We, therefore, believe that future research should focus on closely integrating all three approaches as much as possible to avoid the limitations of individual methods.

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**References**


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