

Contamination in Sodium Dodecyl Sulfate Solutions: Insights from the Measurements of Surface Tension and Surface Rheology

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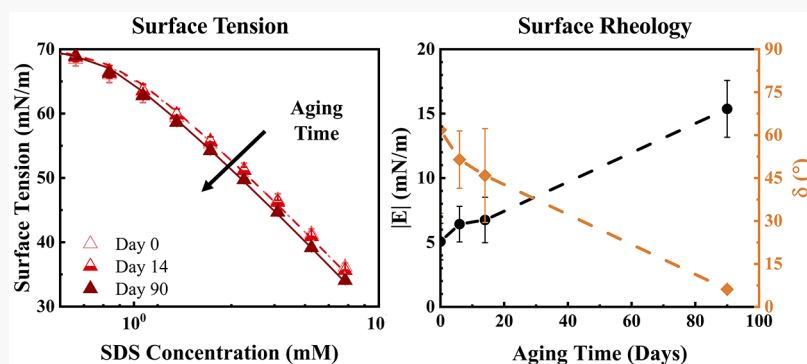
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ABSTRACT: The presence of contamination in sodium dodecyl sulfate (SDS) solutions in the form of dodecanol (LOH) is known to drastically affect the resulting interfacial properties such as surface tension (SFT) and rheology. Dodecanol molecules, which are the product of SDS hydrolysis and are inherently present in SDS solutions, have higher surface activity compared to SDS because they are less soluble in water. A characteristic dip in the SFT isotherm is an indicator of the dodecanol contamination in the sample. The presence of an electrolyte in the solution impacts the surface activity of SDS and its critical micelle concentration, and could yield SFT isotherms that closely match those obtained for pure SDS samples. The interpretation of the isotherms in such cases could thus lead to misinterpretation of the surface purity. In this work, we have examined the SFT isotherms for SDS solutions in both the absence and presence of electrolyte. We have fitted the isotherms to three different thermodynamic adsorption models to estimate the amount of dodecanol present in the sample. We have applied the estimated values for the LOH content in a two-component rheological model to predict the viscoelasticity of such surfactant-laden surfaces. We have compared these results with the experimentally measured interfacial rheological properties. Our findings demonstrate that the presence of impurities can be captured under dynamic expansion and contractions, even for solutions containing background electrolyte.

INTRODUCTION

Surfactants are surface active molecules that are central to various industrial and technological applications such as emulsion and foam stabilization, drug delivery, coatings, and detergency.^{1–5} When present at interfaces, these molecules are responsible for decreasing the excess free energy of the interface. Changes in the excess free energy of the interface are quantified through surface tension (SFT) measurements.³ The surface activity of surfactant molecules is related to their amphiphilic nature, which is determined by the balance between the hydrophilic head group and the hydrophobic tail contribution, often referred to as the hydrophilic/lipophilic balance (HLB).^{3,6} For example, a head group that possesses a higher polarity is able to compensate for the lack of affinity from a longer hydrocarbon tail when considering water-soluble surfactants.⁷

One of the most commonly used surfactants is sodium dodecyl sulfate (SDS), which is an anionic surfactant with a critical micelle concentration (CMC) of 8.2 mM at 25 °C in

the absence of electrolytes.⁸ Its HLB is estimated to be 40, which characterizes it as a highly water-soluble surfactant.⁶ SDS is synthesized by sulfating the long-chain alcohol, *n*-dodecanol, also known as lauryl alcohol (LOH), which is considered a contaminant in SDS samples.⁹ As stated by Mysels,¹⁰ impurities that have similar surface activity to SDS (by weight percent) do not impact the SFT readings. However, LOH exhibits a higher surface activity compared to SDS due to its lower solubility in water, which is attributed to the relatively lower polarity of its head group. As LOH does not form micelles by itself, it is not considered a surfactant species and

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does not have an HLB value attributed to it. However, for means of comparison, utilizing the method developed by Davies,¹¹ one can estimate the HLB of a dodecanol molecule to be ~ 3 . Therefore, even trace amounts of LOH present in the solution can affect the behavior of the solution and resulting experimental measurements.¹² For instance, in a 6 mM SDS solution (99.98 mol %) contaminated with 0.02 mol % LOH, the dodecanol molecules occupy more than 80% of the total surface coverage, which yields an additional 20 mN/m reduction in SFT.¹³ The isotherm is therefore shifted to lower values compared to that obtained for a purified SDS sample. The amplified reduction in SFT, contributed by LOH molecules, will continue to persist as the SDS concentration is increased. This effect can be attributed to an increase in the bulk concentration of LOH molecules present in the sample until the CMC of the SDS solution is reached.¹⁰ Once SDS micelles are formed, contaminant LOH molecules can be solubilized in the micelles.¹⁴ As a result, increasing the SDS concentration past the CMC results in SFT readings that are closer to the values for pure SDS samples.¹⁴ A characteristic dip in the SFT isotherm around the CMC value is thus an indicator for the presence of LOH in the sample.¹⁵ It is important to mention that the presence of LOH molecules at the interface is not as consequential if the non-polar phase is oil. As LOH is highly soluble in organic phases, it does not accumulate at the interface.¹⁶

Adsorption of SDS molecules onto the interface is strongly impacted by the presence of electrolyte in the solution. The air/water interface carries a negative electrostatic potential compared to the bulk due to the ordered water molecules at the interface and/or preferential adsorption of anions (e.g., hydroxyl group from the dissociation of water¹⁷). The net surface charge at the air/water surface becomes less negative in presence of the electrolyte, promoting SDS adsorption.^{18,19} Additionally, the presence of ions in solution increases the surface activity of SDS molecules by decreasing the electrostatic repulsion between the anionic head groups.²⁰ Reduced electrostatic repulsion between the SDS head groups at higher electrolyte concentrations facilitates micelle formation and leads to lower CMC values and higher aggregation number in SDS micelles.^{21,22}

To remove LOH from SDS solutions, several purification methods have been developed. Among these methods, foaming the sub-micellar solution,^{10,23,24} passing the solution through an adsorption column,²⁵ successive compression and aspiration of the surface,²⁶ and repeated recrystallization of the solution with alcohol (e.g., reagent alcohol or ethanol) and water^{10,23,27,28} have been utilized, individually or in series, to achieve a higher degree of purity. However, even after laborious work of purifying the sample, contamination could still remain a problem as SDS molecules hydrolyze back to LOH after the purified solution begins to age with the rate of hydrolysis depending on the concentration of both SDS and LOH molecules, temperature, and pH of the solution.^{10,12,29}

Few methods have been proposed since the 1980s, mostly relying on the direct measurement of fluid properties, to quantify the amount of LOH present in the solution. To our knowledge, Czichocki and co-workers^{30,31} were the first to determine the amount of LOH in SDS samples based on both high-performance liquid chromatography (HPLC) method and later SFT measurements.³¹ The HPLC method was shown to be sensitive to the alcohol chain length and could distinguish between different alcohols present in the solution.

The HPLC results were complementary to the surface tension readings, which cannot differentiate between varying alcohol chain lengths. A criterion for surface chemical contaminations, under equilibrium and non-equilibrium conditions, and based on surface tension shifts, was derived by Lunkenheimer and Miller et al.³² as a means to check the purity of the system via SFT measurements. Therefore, the criterion is not based on the bulk concentration of the contaminant, but it is based on its impact on the surface. Thus, it relies on the sensitivity and accuracy of the instrument used to measure the SFT values. Vollhardt and Czichocki³³ studied the effect of different isomeric alcohol molecules co-adsorption with SDS. When comparing the reduced SFT in contaminated SDS solutions with that of the purified solutions, it was found that increasing the contaminant concentration leads to an increase in the SFT difference, where 0.1 wt % of contamination yields a 15 mN/m difference from the pure SDS surface tension value. A more rigorous approach based on a thermodynamic adsorption model was developed by Kralchevsky et al.¹³ to determine the amount of dodecanol contamination in the sample. Further information on this thermodynamic model will be provided in the Materials and Methods section.

When considering the use of SFT readings to trace the presence of contamination in SDS solutions, several techniques are available for SFT measurements, such as the Wilhelmy plate (WP), the drop weight, and the bubble shape tensiometry methods. The use of different surface geometries (e.g., planar in the Wilhelmy plate vs spherical in the bubble shape tensiometry) can impact the adsorption dynamics by potentially hindering the adsorption of less concentrated species to the interface.³⁴ Not only the geometry but also differences in aging time for surfaces to reach equilibrium with the bulk phase can be a crucial consideration.³⁵ If one compares the SFT measurements using a pendant liquid droplet in air with that of a rising air bubble (RB) in the solution, besides the higher area per volume ratio (A/V) for the drop geometry, the surfactant adsorption will also be impacted by the concavity of the interface itself.³⁵ A low concentration of contaminants can also be an issue when comparing two different methods; depending on the method's A/V , the initial bulk concentration could be considerably depleted, influencing the equilibrium state of the system.³⁵ This effect has been illustrated by Addison and Hutchinson,²⁷ where the drop weight method (performed at different rates) and the WP method were used to measure the surface tension of SDS solutions. The slower the rate of formation of the drop on the drop-weight method, the more time was allowed for the adsorption of contaminant molecules, and the closer the surface tension was to the SFT readings obtained from the stationary (planar) surface of the WP method. All these factors impact readings of both thermodynamic (surface tension) and dynamic (surface dilational rheology) measurements using the drop geometry.

Dynamics of interfaces can be examined in two modes: shear rheology (i.e., interfacial response to shear deformation at a constant area) and dilational rheology (i.e., interfacial response to variations in the interfacial area while conserving the shape). A number of methods have been developed for probing the response of interfaces to shear such as the magnetic needle,^{36–38} interfacial disk/bicone,³⁹ double-wall-ring,⁴⁰ and microrheology.^{41–43} For example, Poskanzer and Goodrich⁴⁴ studied the effect of dodecanol addition on the surface viscosity of SDS solutions and found that a synergism between

the two molecules greatly increased the surface viscosity (up to a factor of 5). Surface dilational rheology can be probed using techniques such as capillary waves, a Langmuir trough with oscillating barriers, and oscillating drop/bubble,^{45–48} the latter two are the focus of this paper.

The surface dilational rheology of LOH-contaminated SDS solutions was studied by Wantke et al. using the oscillating bubble method with frequencies ranging from 1 to 500 Hz.⁴⁹ To model their experimental results, the one-component rheology model was used due to the relatively constant concentration of LOH molecules at the surface during oscillations. It was shown that pure LOH surfaces exhibit a completely elastic response, whereas pure SDS samples present a strong viscoelastic behavior, with mixtures showing intermediary properties. It should be pointed out that the sample labeled as “pure-SDS” in these experiments exhibited a small dip in the SFT isotherm, which points to some degree of contamination. These results were later utilized by Aksenenko et al.⁵⁰ as input to their two-component rheology model. However, even with the more robust approach compared to ref 49, their model was only able to qualitatively fit the experimental data from the previous work done by Wantke et al.⁴⁹

When considering the effect of background electrolyte, Fainerman et al.⁵¹ measured the dynamic surface tension and the surface rheology of SDS solutions with hardness salts such as CaCl_2 and MgCl_2 present in the solution. It was found that the presence of hardness salts results in a higher viscoelastic modulus when compared to solutions with NaCl as the electrolyte. This behavior was attributed to the formation of $\text{Ca}(\text{DS})_2$ and $\text{Mg}(\text{DS})_2$ complexes that are more surface active than SDS. Moreover, the rate of hydrolysis was much higher for the SDS solutions in the presence of the divalent salts. The dynamic surface tension results were used to estimate the concentration of dodecanol in these solutions via the generalized Frumkin model.⁵²

This paper aims to better understand the relationship between dilational rheological measurements and the models developed for mixed surfactant solutions. We compare the results obtained from the interfacial rheological measurements with the values predicted by different thermodynamic adsorption models. In addition, we investigate the effect of electrolyte on the results obtained for both unpurified and recrystallized samples. Findings of these studies provide valuable insights on more complex interfacial systems in which the interfacial activity of SDS molecules under dynamic conditions is of interest.

MATERIALS AND METHODS

Recrystallization. SDS was acquired from Sigma-Aldrich (purity >99%). The samples of SDS solutions investigated in this work were used as received (labeled as unpurified throughout the text) or recrystallized to remove the LOH. The recrystallization process involves dissolving 25 g of SDS powder in 100 mL of milliQ ultra-pure water (18.2 M Ω -cm), heating the solution to 30 °C, and stirring until SDS molecules are solubilized. The solution is then cooled for 48 h at 5 °C. The precipitates are vacuum filtered and resolubilized in 200 mL of ethyl alcohol (Fisher Scientific) with a similar procedure of heating and stirring. The solution is once again refrigerated at 5 °C for 24 h and then vacuum filtered and rinsed with ethyl alcohol. The crystals are further dried under vacuum for at least 72 h. For measurements with background electrolyte, we utilized 10 mM sodium chloride (NaCl) solutions (Fisher Chemical). The CMC values for unpurified and recrystallized samples were obtained by

carrying out surface tension measurements on solutions at various surfactant concentrations and plotting the SFT readings as a function of the logarithm of surfactant concentration. To examine the aging of the solution, we monitored a recrystallized sample, prepared at 40 mM of SDS and kept at room temperature, for a period of 90 days. This concentration was chosen to increase the rate of hydrolysis based on the work done by ref 29. Surface tension and surface rheology measurements, details of which are provided below, were carried out on this sample on days 0, 6, 14, and 90 of aging.

Surface Tension Measurements. The surface tension measurements were carried out using two techniques: WP and optical tensiometry. The WP (DCAT 25 from DataPhysics) was used to measure the surface tension isotherms of solutions with different purity levels and with no added salt and in 10 mM NaCl solutions. In the WP method, a platinum plate hanging from a high precision balance is lowered until it contacts the air/solution surface. The change in the measured force when the plate contacts the water surface is used to calculate the surface tension acting on the plate. In the drop shape tensiometer (Biolin Scientific), surface tension measurements were carried out using a RB suspended in the SDS solutions. The Attension Theta software fits the shape of the bubble to the Young–Laplace equation, which balances surface tension and gravitational forces. As it takes more time for surface tension equilibration,³⁵ the RB method can be used to probe the dynamic surface tension of a system by allowing the bubble age in the solution while monitoring its shape.

Utilizing the WP method, we characterized the CMC values of the samples following the procedure in ref 53. In the absence of electrolyte, the CMC values are measured to be 6.7 and 7.5 mM SDS for unpurified and recrystallized SDS solutions, respectively. In 10 mM NaCl solutions, the CMC values are decreased to 3.5 and 5.5 mM SDS for unpurified and recrystallized SDS solutions, respectively.

Thermodynamic Modeling. We utilized three thermodynamic models for the fitting of the adsorption isotherms: the Frumkin model, the van der Waals model, and a model developed by Kralchevsky et al.¹³ The latter builds on the van der Waals adsorption model to include the electrostatic contribution to the free energy of the system. The surface tension isotherms experimentally obtained for the SDS samples, via the WP technique, were used as an input to each adsorption model. For the sake of simplicity, we show the adsorption isotherm equations for a one-component system. The reader can find the equations derived for a two-component system in the [Supporting Information](#).

The Frumkin isotherm model assumes a localized adsorption as follows⁵⁴

$$Kc = \frac{\omega\Gamma}{1 - \omega\Gamma} \exp\left(-\frac{2\beta\Gamma}{k_B T}\right) \quad (1)$$

or

$$Kc = \frac{\theta}{1 - \theta} \exp(-2\alpha\theta) \quad (2)$$

where K is the adsorption constant, k_B is the Boltzmann constant, T is the absolute temperature, c is the bulk surfactant concentration, Γ is the surfactant adsorption at the interface, and ω is the minimum molecular area at the interface. Parameter β is the interaction parameter, usually attributed to the tail–tail van der Waals interactions.¹³ Parameter α is the dimensionless interaction parameter, $\alpha = \beta/\omega k_B T$, and $\theta = \omega\Gamma$ is the surface coverage for the surfactant adsorbed to the surface. The equation of state can then be written for one-component systems as follows

$$\pi = -\frac{k_B T}{\omega_0} \ln(1 - \omega\Gamma) - \beta\Gamma^2 \quad (3)$$

or

$$\pi = -\frac{k_B T}{\omega_0} [\ln(1 - \theta) + \alpha\theta^2] \quad (4)$$

where π is the surface pressure, defined as the air/water surface tension minus the surface tension in the presence of the surfactant molecules ($\pi = \gamma_w - \gamma$). The excluded molar area has been shown to be dependent on the surface pressure of the system by the following expression:^{54–56}

$$\omega = \omega_0(1 - \epsilon\pi\theta) \quad (5)$$

where ω_0 is the excluded area at zero surface pressure and ϵ is the intrinsic compressibility coefficient, which can be interpreted as the change in the tilt angle of the molecule tail upon an increase in the surface pressure or surface compression.⁵⁵

The van der Waals adsorption model is similar to the Frumkin model, but assumes a non-localized adsorption.⁵⁷ The equations can be written as follows

$$Kc = \frac{\omega\Gamma}{1 - \omega\Gamma} \exp\left(\frac{\omega\Gamma}{1 - \omega\Gamma} - \frac{2\beta\Gamma}{k_B T}\right) \quad (6)$$

or

$$Kc = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta} - 2\alpha\theta\right) \quad (7)$$

$$\pi = \frac{k_B T \Gamma}{1 - \omega\Gamma} - \beta\Gamma^2 \quad (8)$$

or

$$\pi = \frac{k_B T}{\omega_0} \left[\frac{\theta}{(1 - \theta)} - \alpha\theta^2 \right] \quad (9)$$

where the notation used in eqs 1–5 applies here. To model the experimentally measured isotherms, the adsorption constant (K), the interaction parameters (α or β), the excluded area at zero surface pressure (ω_0), and the compressibility coefficient (ϵ) of each individual species must be known. For two-component systems, one must also consider the intermolecular parameters (ω_{12} and α_{12}). By varying the initial guess on the amount of contaminant in the bulk, one can find the LOH concentration that gives the best fit to the measured surface tension isotherm. For both unpurified and recrystallized isotherms, one can vary the initial guess for the molar fraction of dodecanol and solve the two-component equations (provided in the Supporting Information) by changing the surface coverages (θ_1 and θ_2) until the sum of squared differences between each experimental point and the value calculated by the adsorption model are minimized.

The Kralchevsky model utilizes eqs 6–9 and solves for the free energy of the surface accounting for electrostatic interactions present in the system with the Gouy equation.^{58,59} By taking advantage of the pre-determined values for α and ω for each surfactant, Kralchevsky et al. were able to develop an algorithm with only the molar fraction of LOH as an adjustable parameter.¹³ Briefly, the intermolecular parameters (α_{12} and ω_{12}) were first calculated (see the Supporting Information). Next, a guess was made for the molar fraction value of LOH, followed by guesses on the surface adsorption concentrations Γ_1 and Γ_2 . The adsorption isotherm was solved for the LOH adsorption to determine the optimum values of Γ_2 for the given values of Γ_1 . Next, the dimensionless surface potential was calculated based on the Gouy equation to implicitly solve for Γ_1 . Finally, the surface tension was calculated from the obtained variables and compared to the experimental data. By changing the molar fraction of LOH, one can find the best fit for the measured surface tension isotherm. After its determination, the molar fraction of dodecanol can be used to quantify important parameters of the surface, such as adsorption quantities, surface potential, and the Gibbs elasticity. The authors used previous data from ref 60 to validate their model.

Surface Rheology Measurements. The interfacial rheology of RBs suspended in SDS solutions (unpurified, recrystallized, and aged recrystallized) were measured using the Attension Theta optical tensiometer (Biolin Scientific). For unpurified and recrystallized samples, the rheology measurements were performed in a

concentration range of 1–10 mM SDS, with both no NaCl and 10 mM NaCl. For the aged recrystallized samples, measurements were done only at 5 mM SDS concentration. The surface rheology was probed using rising bubbles ($\sim 6 \mu\text{L}$) generated on an inverted needle (Biolin Scientific, 14 gauge). The concentration of SDS was varied by incrementally increasing the bulk surfactant concentration for the same bubble under study. The amount of solution required to increase the concentration by 1 mM was added using an automatic pipette (Eppendorf, 20 μL) in 10-step increments, separated by 2 min intervals, to avoid large perturbations to the system. Once the desired bulk concentration was reached, the bubble was aged until the surface tension reading was stable. The bubble volume was then oscillated at a small amplitude, corresponding to small oscillations in the surface area within the linear viscoelastic regime (area variation of less than 3%), and at a frequency of 1 Hz, which is within the reliable frequency limit for the oscillating bubble tensiometry.⁶¹

Rheological Modeling. To model the surface dilational rheology, we based our calculations on the work done by Aksenenko et al.⁵⁰ The dilational surface viscoelastic modulus (E) can be defined as follows⁶²

$$E(i\Omega) = \frac{d\gamma}{d(\ln A)} e^{i\delta} \quad (10)$$

where γ is the surface tension, A is the available interfacial area, Ω is the angular frequency of oscillations, and δ is the phase shift of the resulting surface tension in response to the applied oscillations in the available surface area. The surface viscoelastic modulus can be further divided into real (E') and imaginary (E'') parts, which correspond to the elastic and viscous contributions, respectively. Assuming that a diffusion-controlled exchange of surfactant molecules between the adsorption layer and adjacent bulk solution is the governing relaxation process in the system, the resulting surface rheology of a one-component solution is as follows^{63,64}

$$E(i\Omega) = \frac{E_0 \left(\frac{d\Gamma}{dc} \sqrt{\frac{i\Omega}{D}} \right)}{\left(1 + \frac{d\Gamma}{dc} \sqrt{\frac{i\Omega}{D}} \right)} = E_0 \frac{1 + \zeta + i\zeta}{1 + 2\zeta + 2\zeta^2} \quad (11)$$

$$E_0 = \frac{d\pi}{d(\ln \Gamma)} = - \frac{d\gamma_{eq}}{d(\ln \Gamma)} \quad (12)$$

$$\zeta = \left(\frac{\Omega_D}{\Omega} \right)^{1/2} \quad (13)$$

$$\Omega_D = \frac{D \left(\frac{dc}{d\Gamma} \right)^2}{2} \quad (14)$$

where E_0 is the Gibbs elasticity (i.e., the limiting elasticity at low frequencies), γ_{eq} is the equilibrium surface tension as a function of the surfactant adsorption (Γ), ζ is the dimensionless ratio between the time scale of the experiment and that of the diffusion process, Ω_D is the characteristic diffusion frequency, and D is the surfactant's bulk diffusivity. A description of the equations used for the two-component mixture is provided in the Supporting Information. A more in-depth discussion on the surface rheology of surfactant systems can be found elsewhere.⁴⁸

Using the relationship between Γ and c , obtained from the fitting of SFT isotherms to thermodynamic adsorption models, one can apply the surface rheology equations to estimate the complex modulus (eq 10) of a surface populated with one type of surfactant or a binary mixture of surfactant species. From the resulting information, the real and imaginary contributions to the complex dilational modulus can be calculated.

Estimation of Depletion Effects. The depletion effects were calculated based on the work done by Alvarez et al.,³⁵ which describes how the depleted bulk concentration is a function of the area available for adsorption (A), the volume of the solution (V), the bulk concentration of surfactants (c_i), their surface adsorption at the

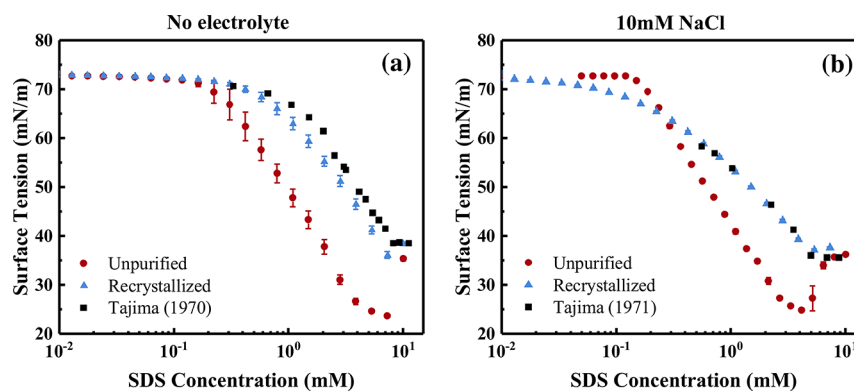


Figure 1. Surface tension isotherms of unpurified (red circles) and recrystallized (blue triangles) SDS solutions with (a) no background electrolyte and (b) 10 mM NaCl. Comparison is also provided with reference data (black squares) from Tajima on the following: (a) pure SDS solutions with no electrolyte⁶⁵ and (b) pure SDS solutions with 10 mM electrolyte.⁶⁶ Some error bars are not visible because they are smaller than the symbol size. Data adapted from refs 65 and 66 are provided with permission from the Bulletin of the Chemical Society of Japan.

maximum packing arrangement (Γ_{∞}), and their adsorption constant (K). By applying eq 15, one is able to calculate the effective depleted concentration of a surfactant species (c_{eff}) as follows

$$\frac{c_{\text{eff}}}{c_i} = \frac{1}{2} \left(1 - \vartheta - \frac{\vartheta}{f} \right) + \frac{1}{2} \sqrt{\left(1 - \vartheta - \frac{\vartheta}{f} \right)^2 + 4 \frac{\vartheta}{f}} \quad (15)$$

where $f = \Gamma_{\infty} A / K V$ is the ratio of the minimum bulk concentration needed to populate the interface at maximum packing to the adsorption constant K , and $\vartheta = \Gamma_{\infty} A / c_i V$ is the maximum fractional potential mass lost to the interface.

The time necessary for equilibration is dependent mostly on the depletion depth (h_p) associated with the adsorption. For a planar surface adjacent to a semi-infinite surfactant solution, h_p can be defined as follows

$$h_p = \frac{\Gamma}{C_{\infty}} \quad (16)$$

The timescale for diffusion in this system is then given by $\tau_D = h^2 / D$, where D is the bulk diffusion constant of a surfactant molecule in the solvent, and $h = h_p$ for the planar case. This is a good approximation for methods such as the WP. However, for surfaces with an associated curvature, h must be corrected to account for the deviation from a planar geometry (see the Supporting Information). A more in depth discussion can be found in ref 35. The before mentioned equations (eqs 15 and 16) were used to estimate time scales and appropriate geometries for our experiments in order to maximize the impact from LOH molecules.

RESULTS

Surface Tension Isotherms. The surface tension isotherms of the unpurified and recrystallized samples, measured using the WP method, are depicted in Figure 1. A comparison is provided with the reference data from Tajima and coworkers⁶⁵ on pure SDS solution (purified by isotropic mixing with dodecanol in ethanol, followed by extraction with ether to remove the dodecanol), also measured using the WP method and with no background electrolyte present. From Figure 1a, it is noticeable that the SFT measurements obtained for both the unpurified and recrystallized samples are not in agreement with the reference data. This is due to the synergistic effect of SDS and LOH when both present at the surface, which results in a decrease of the SFT to a larger extent compared to a surface solely populated by SDS molecules.⁴⁴ The difference between the measured curve for the recrystallized sample in this study and the reference curve in⁶⁵ hints at the presence of LOH molecules in the solution

even after the recrystallization process. Data obtained for the recrystallized sample displays the characteristic contamination dip in the curve before plateauing at concentrations above CMC.

Next, we moved on to SFT measurements in the presence of electrolyte using 10 mM NaCl solutions, as shown in Figure 1b. For comparison with the data available in the literature, in this case, we used the reference curve provided by Tajima.⁶⁶ Reference 66 measured the SFT with the drop-volume (i.e., drop-weight) method, with a similar pure SDS sample from ref 65, but using 10 mM NaCl solutions. For the present study, the measured SFT curve for recrystallized samples in 10 mM NaCl solutions overlaps with the reference data in ref 66. The higher ionic strength of the solution promotes the adsorption of SDS, which can be explained by the decreased electrostatic repulsion between the negatively charged dodecyl sulfates and the reduction in net negative charge at the air/water surface,¹⁸ thus increasing SDS activity. However, as established from the results in Figure 1a, it should be noted that the recrystallized sample still contains LOH molecules. Therefore, the presence of background electrolyte could mask the presence of dodecanol impurities in the surfactant solution when one is only interpreting the thermodynamic data via the surface tension isotherm.

Depletion Effects in Different Techniques. Determining the appropriate technique for measuring the surface tension of dilute SDS solutions is an important factor. The difference in geometry (i.e., the area-to-volume ratio) between varying techniques makes one method more sensitive to contamination than other. This is because a smaller volume used in a method results in fewer total molecules being present in the bulk in one technique compared to another. For instance, the WP method relies on a large volume with a relatively small area available for adsorption ($A/V \sim 100 \text{ m}^{-1}$), which makes it more sensitive to impurities—usually present in small concentrations—compared to the pendant drop shape tensiometer, which has a larger area-to-volume ratio ($A/V \sim 2000 \text{ m}^{-1}$). This phenomenon is caused by the depletion effect that takes place when highly surface-active molecules, such as LOH, are present in bulk in dilute concentrations and have access to a large area available for adsorption.³⁵ When the amount of molecules on the surface exceeds the amount of molecules in the bulk ($\Gamma \times A > c \times V$), depletion is considered to be significant.³⁵ As explained by Semmler and Kohler,⁶⁷

when depletion effects cannot be neglected, both dynamic and equilibrium surface tension readings differ from systems with an infinite surfactant reservoir. Therefore, one should take depletion into account when the conditions of the application fall into the before mentioned criterion. Table 1 shows the A/V for the three geometries discussed in this work.

Table 1. Values of Area to Volume Ratio (A/V) Calculated for Different Methods Used in the Measurement of the Surface Tension

method	A/V [m^{-1}]
Pendant Drop	1916
Rising Bubble (RB)	110
Wilhelmy Plate (WP)	94

In order to compare the impacts of different geometries, the normalized effective concentration (c_{eff}/c_p , eq 15) of LOH, calculated for the unpurified sample, is provided in Figure 2a. Pendant drop shape tensiometer results are most affected (notice the high A/V value in Table 1), having less than 100% of the initial LOH bulk concentration (c_p , eq 15) over the entire range of SDS concentrations. By analyzing this graph one can infer that both WP and the RB shape tensiometry (overlapping) are less affected by depletion of the contaminant compared to the pendant drop shape tensiometry. This is mostly caused by the higher surfactant reservoir available in both WP and RB methods in contrast to the pendant drop. Therefore, methods with a high A/V value may not be suitable for capturing the impact of contamination's presence in the bulk through surface measurements.

As diffusion to the surface is a key factor in the systems affected by depletion, aging time is also expected to play a role in the results. Figure 2b compares the isotherms obtained for the unpurified sample using the WP method and the RB shape tensiometry. Two major differences can be noticed between these measurements. First, the surface tension measurements in the RB geometry take a longer time to stabilize due to the slow adsorption process.^{34,35} For comparison, the surface tension readings after 30 s and 3 h are provided as a function of concentration for the RB measurements. Such slow adsorption is caused both by the A/V of the system and the “quasi-

spherical” shape of the bubble, and the fact that the air/water surface is surrounded by the surfactant solution and adsorption is taking place in a convex surface;³⁵ hence, the time necessary to reach equilibrium is increased as compared to the WP, which has a planar adsorption geometry and a slightly smaller A/V value (see Table 1). In addition, measurements at low surfactant concentrations (below 1 mM of SDS for our samples) indicate that even after 3 h the surface tension readings from the RB measurements do not match those obtained by the WP (Figure 2b). This is possibly due to the slightly larger A/V for the RB, which can affect the equilibrium surface tension at a constant bulk concentration.^{35,67}

Finally, by using eq 16, one can calculate the depletion depth and the diffusion time scale for WP geometry. For the RB geometry, one has to correct h_p to h to account for the curvature.³⁵ Comparing the two geometries, as shown in Figure 2c, it can be seen that the WP requires less time for equilibration than the RB, for both unpurified and recrystallized samples. At lower concentrations of SDS, the number of LOH molecules present in the bulk is small; therefore, the time required for equilibrium is just a function of the geometry. As SDS concentration increases, the unpurified and recrystallized samples start to behave differently due to the different molar fraction of LOH present. There is a peak in the diffusion time scale for LOH molecules in both unpurified and recrystallized samples, which can be explained by the sharp increase in the equilibrium adsorption (Γ) calculated for LOH (see Figure S2a in the Supporting Information). Therefore, there is an increase in demand for LOH molecules from the surface, while the bulk concentration increases at a constant rate. The peak shift in LOH diffusion time scale peak observed between the unpurified and recrystallized samples can also be explained by the different molar fraction in both samples, as shown in Figure S2b, where both adsorption curves for LOH increase sharply at the same bulk LOH concentration. Past this critical point, the diffusion time decreases with the bulk concentration and the surface adsorption does not change drastically.

Determination of the Impurity Content via Thermodynamic Models. Isotherms obtained for both unpurified and recrystallized samples were fitted by the three thermodynamic adsorption models in order to estimate the degree of contamination in the samples. Results achieved from each

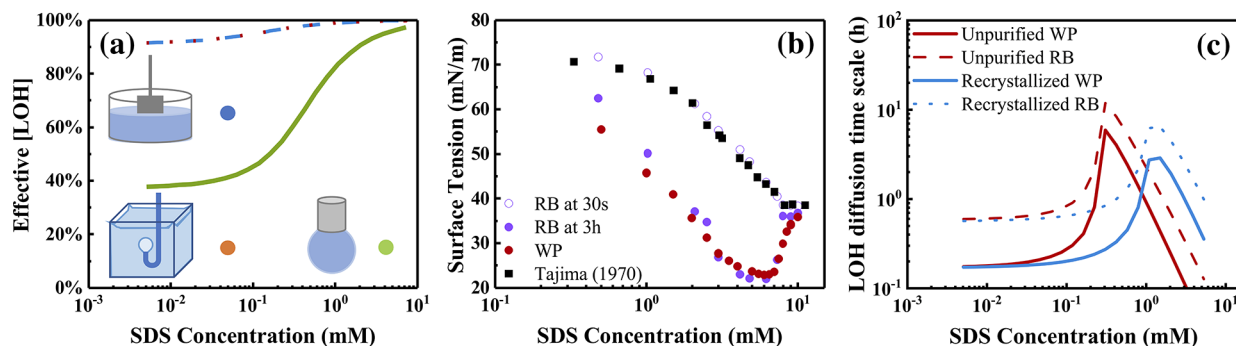


Figure 2. (a) LOH normalized effective concentration for different geometries (blue dashed curve for WP; red dotted curve for RB; and green full curve for pendant drop) at different SDS concentrations. (b) Comparison of the surface tension isotherms for unpurified SDS solutions in the absence of electrolyte measured with the following: (i) the rising bubble shape tensiometer (RB), at two different aging times (open purple circles are 30 s, full purple circles are 3 h), and (ii) the WP method (red circles). The values reported by Tajima for pure SDS solutions (measured by the WP technique) are provided as a reference (black squares).⁶⁵ (c) Calculated diffusion time scales with model given by ref 35 for LOH molecules based on their bulk availability in unpurified (red curves, estimated molar fraction of 0.478 mol %, see next section) and recrystallized (blue curves, molar fraction of 0.104 mol %) for both WP (full) and RB (dashed) geometries.

Table 2. Molar Fraction of Dodecanol (xLOH in Mol %) Obtained from Best Fit of the Experimentally Measured Isotherms, Using WP Method, to Each Thermodynamic Model for Both Unpurified and Recrystallized Samples

Adsorption Model	Unpurified (mol %)	Recrystallized (mol %)
Frumkin	0.435 ± 0.009	0.028 ± 0.003
van der Waals	0.338 ± 0.027	0.044 ± 0.007
Kralchevsky	0.478 ± 0.006	0.104 ± 0.004

model are shown in Table 2. The error related to the LOH molar fraction estimation was calculated, based on the method used in the appendix of ref 13, by relating the minimum standard deviation calculated comparing the fit to the experimental data to the estimated error on the molar fraction value. The Kralchevsky model yielded a higher degree of contamination, which can be attributed to the additional feature of considering the charged air/water surface.

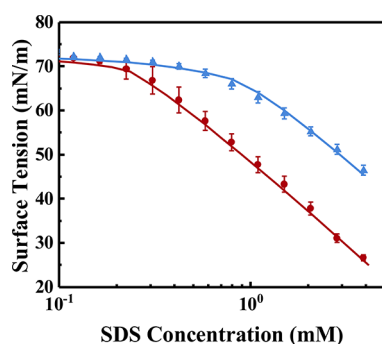


Figure 3. Surface tension isotherms for the unpurified (red circles) and recrystallized (blue triangle) samples fitted to the thermodynamic model developed by Kralchevsky et al.¹³

The fit obtained by the Kralchevsky model for both unpurified and recrystallized samples is shown in Figure 3. The fits obtained using both Frumkin and van der Waals models are shown in Figure S1. As previously discussed in Figure 2a, at lower SDS concentrations, the depletion effect is significant, which could possibly result in a higher surface tension reading. To circumvent the effect of the depletion phenomenon, data obtained for SDS concentrations above 1 mM SDS were used to fit the model. The best fits to the unpurified and recrystallized samples corresponded to LOH

molar fractions of 0.478 and 0.104 mol %, respectively. The order of magnitude of the results agrees with those obtained in the original work by Kralchevsky.¹³

Surface Rheology Measurements. In order to obtain the surface rheology of the adsorbed layer, one can impose oscillations to a bubble surface area, as illustrated in Figure 4a, and track how the surface tension changes with the applied perturbations (eq 10). The surface storage modulus (E') obtained from rheological measurements on a rising bubble suspended in unpurified and recrystallized samples is shown in Figure 4b. Results are provided for solutions in the absence and presence of the electrolyte. The surface viscous modulus (E'') of both unpurified and recrystallized samples is not negligible as depicted in Figure 4c. This implies that the surface layer is populated by a mixture of SDS and LOH molecules because a surface purely covered with LOH molecules would be elastic in nature with a negligible viscous modulus.^{49,50} As expected, due to the higher concentration of LOH molecules in the unpurified solutions, these samples resulted in a higher surface elastic modulus (1 order of magnitude larger) compared to those measured for the recrystallized samples.

The impacts of electrolyte's presence in the solution on the resulting surface properties have also been examined for both unpurified and recrystallized samples. As illustrated in Figure 4b, the E' of the unpurified sample is not greatly affected by the addition of 10 mM NaCl at concentrations below the CMC, other than shifting the entire curve to lower SDS concentrations. This indicates that the composition of the surface layer is not very different between the two cases, possibly due to the high degree of dodecanol contamination present in the unpurified sample. In contrast, the addition of electrolyte to the recrystallized solutions resulted in a decrease in E' and an increase in E'' . This can be attributed to the higher surface-activity of SDS molecules in the presence of NaCl in the aqueous phase. While the screening of the electrostatic repulsion between the SDS polar head groups is present in both unpurified and recrystallized samples, the larger contamination present in the former is sufficient to mask this effect. As a result, the addition of salt did not result in a pronounced impact on the surface rheological response of the unpurified solutions. For all samples, there is a significant drop in E' at concentrations above the CMC. This behavior indicates that the surface is populated by both SDS and LOH molecules at concentrations below the CMC, whereas the

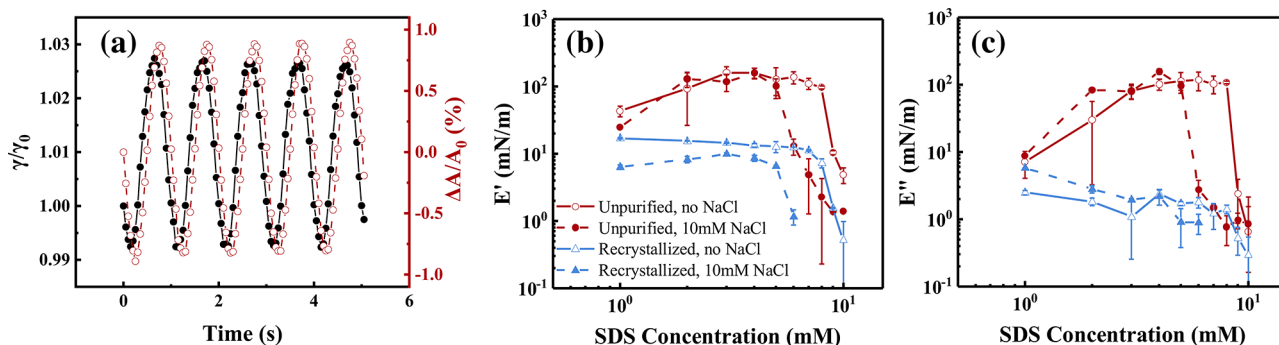


Figure 4. (a) Area oscillations (red open circles) and resulting surface tension readings (black full circles) of a 2 mM unpurified SDS solution at 1 Hz. (b) The elastic modulus (E') and (c) viscous modulus E'' of unpurified (red symbols) and recrystallized (blue symbols) samples. Legend used in (b) applies to (c) as well. Effect of electrolyte is examined using samples with no added salt (open symbols) and in 10 mM NaCl solutions (full symbols). Some error bars are not visible because they are smaller than the symbol size.

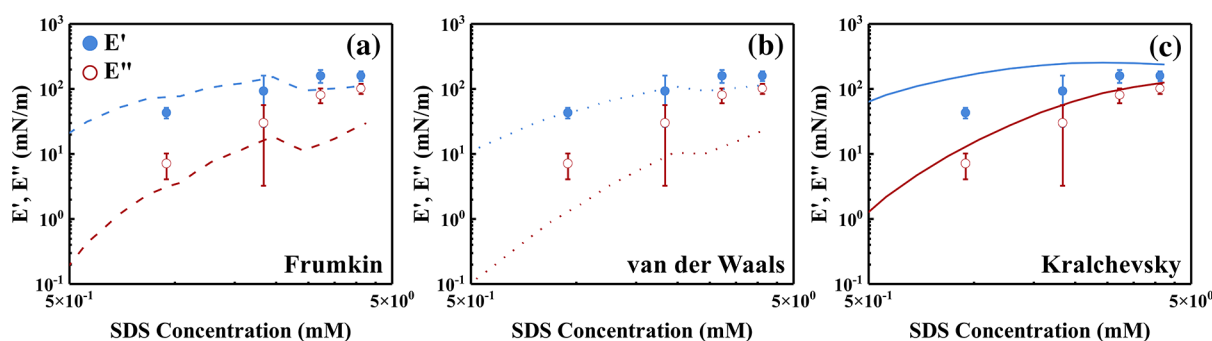


Figure 5. Comparison of the experimentally measured surface rheological properties (elastic modulus, E' , in full blue circles and viscous modulus, E'' , in red open circles) to the predictions obtained from a two-component rheological model. Presented data are for unpurified samples and no electrolyte is added to the solutions. Input to the two-component rheological model is provided from fitting of the surface tension isotherms to (a) Frumkin, (b) van der Waals, and (c) Kralchevsky adsorption models.

solubilization of LOH molecules into SDS micelles at concentrations above CMC dramatically reduces the effective concentration of LOH in the bulk, which drives the adsorbed LOH molecules out of the surface and into the bulk.^{12,14} For the recrystallized samples in 10 mM NaCl, measurements on SDS solutions at concentrations larger than 6 mM SDS (above the CMC of 5.5 mM for this sample) yielded negligible rheological readings.

Surface Rheological Modeling via the Two-Component Model. The composition of the solution (i.e., the amount of LOH and SDS present in the sample), obtained from the fitting of SFT isotherms to thermodynamic models (see Table 2), is used in calculating the resulting surface rheology via a two-component model. The experimentally measured rheological properties (i.e., Figure 4b,c) are compared to results obtained from the two-component model, as illustrated in Figure 5. For the unpurified SDS sample, there is a qualitative agreement between the experimental data and the predicted values. However, using the LOH values obtained from the fits of the SFT isotherms to Frumkin and van der Waals models (Figure S1a,b) as an input for the rheological modeling yields some features in the rheology predictions (see Figure 5a,b) that are not observed in the experimentally measured data and are not expected, as the surface concentration of both molecules is expected to increase monotonically with bulk concentration (for concentrations below the CMC). In comparison, these local minima and maxima are not present in predictions derived from Kralchevsky's model, as shown in Figure 5c. These local maxima and minima present for both Frumkin and van der Waals models are the result of variations in adsorption values (Figure S2c,d) that were obtained from the surface tension fits (Figure S1a,b). In addition, the Kralchevsky model properly predicts the viscous contribution measured experimentally; however, there is a large difference in the predicted versus experimentally measured elastic modulus. This is likely due to both the bulk depletion affecting LOH adsorption (Figure 2c) and the high LOH adsorption value predicted from the adsorption isotherm (Figure S2a).

For the recrystallized sample, a good agreement does not exist between the measured data and the predicted results based on any of the adsorption model inputs, as shown in the Supporting Information (Figure S3). This could be due to depletion effects playing a more prominent role in the recrystallized samples because of the much lower LOH content in these systems. This will affect both the time

necessary to achieve the equilibrium surface tension and the magnitude of it, as discussed earlier.

Aging and Hydrolysis. Over the 90 days period of the aging, surface tension and rheology experiments were performed on a recrystallized SDS solution. The occurrence of the hydrolysis process is expected to increase the overall degree of contamination in the sample.²⁹ Shown in Figure 6a are the surface tension isotherms measured after 0, 14, and 90 days of aging. The measured surface tension isotherms are also fitted to the Kralchevsky thermodynamic model, results of which are provided in Figure 6a as well. The sample's dodecanol quantity, obtained from the thermodynamic model, is tracked as a function of aging time as shown in Figure 6b. As can be seen from this data, there is no appreciable difference between the surface tension measurements from day 0 ($x_{\text{LOH}} = 0.119 \pm 0.004$ mol %) to day 14 ($x_{\text{LOH}} = 0.122 \pm 0.003$ mol %). However, once 90 days have passed, it is possible to notice a downward shift of the surface tension values, corresponding to a larger dodecanol content ($x_{\text{LOH}} = 0.138 \pm 0.003$ mol %). By comparing the isotherms at 5 mM SDS, it can be seen that the surface tension values exhibit a slight decrease due to aging (i.e., 46.5 ± 0.9 mN/m at day 0 and 44.7 ± 0.2 mN/m at 90 days of aging). To capture the effect of aging on the surface rheology, rising bubble shape tensiometry measurements were carried out in parallel on solutions at 5 mM SDS concentration. This concentration was chosen because it is high enough to maximize the adsorption of LOH molecules within a reasonable experimental time necessary (Figure 2c), ~ 1 h, while remaining below the CMC of the solution to prevent the solubilization of the LOH molecules into the SDS micelles. As shown in Figure 6c, the complex modulus (E) of the surface increases with aging time,^{12,51} while the phase angle (δ) exhibits a reduction in magnitude, indicating a more elastic response. This is expected for surfaces with high coverage of LOH molecules, which behave more elastically than SDS populated surfaces.^{49,50} When comparing the values from day 0 to day 90, E increases by a factor of 3 and δ decreases from 62 ± 29 to $6.1 \pm 0.8^\circ$. In agreement with the results obtained from fitting of the isotherms to the thermodynamic models, the surface rheology of the system points to a higher degree of contamination of the aged sample. However, it is noticeable that the increase in the complex modulus and the decrease in the phase angle are more pronounced than the increase in the molar fraction given by the best fit to the thermodynamic model. This highlights the

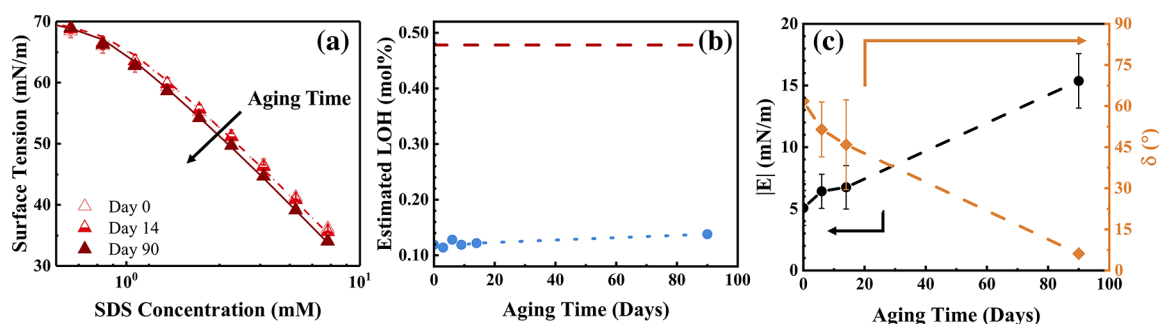


Figure 6. (a) Surface tension isotherm of aged samples for day 0 (empty triangles), 14 (half-filled triangles), and 90 (full triangles), and the corresponding fits from the Kralchevsky adsorption model. (b) Molar fraction of LOH present in a recrystallized SDS sample as a function of the solution aging time (blue circles). The amount of LOH contamination in an unpurified sample is also shown for reference (red dashed line). (c) Surface rheological results obtained for a recrystallized sample at 5 mM SDS as a function of the aging time. The complex modulus is shown in black circles and the phase angle is shown in orange diamonds. Some error bars are not visible because they are smaller than the symbol size.

higher sensitivity obtained when examining the dynamics of the surface in contrast to its equilibrium condition.

CONCLUSIONS

This paper discussed the implications of LOH presence in SDS solutions. In mixed SDS and LOH solutions, even small concentrations of LOH (e.g., below 0.5 mol %) has a strong impact on the surface properties, such as surface tension and surface dilational rheology, which is summarized as follows.

- In contrast with pure SDS solutions, the surface tension of mixed systems can further decrease by 20 mN/m at concentrations close to the CMC. The adsorption models were used to calculate the degree of contamination present in the solution, where a higher contamination was predicted by the Kralchevsky model.
- With regards to the surface rheology, the surface becomes more elastic as the surface concentration of LOH increases in the mixed solution. For instance, the complex modulus increases one order of magnitude as the amount of LOH contamination goes up from 0.1 to 0.5 mol % in the bulk. Fitting of the surface tension isotherms to the three thermodynamic models provided an estimate for the LOH content in the solution; these values were then used as an input to a two-component rheological model. All thermodynamic models yielded surface rheology predictions for the mixed solution that were in fairly good agreement with the experimentally measured data. Nevertheless, the only model able to capture the experimentally measured rheological data, without features that are not physical, was the Kralchevsky model.
- The presence of background electrolyte improves the SDS adsorption and decreases the overall impact of LOH molecules on the readings of surface measurements carried out on the contaminated sample. This was evidenced by the apparent disappearance of the characteristic dip in the surface tension isotherm for the mixed solutions (Figure 1b) and the lower values of elastic modulus for the recrystallized sample in the presence of added electrolyte (Figure 4b). However, the surface rheology of the 10 mM NaCl system probed at concentrations lower than the CMC indicates that traces of impurity are present in the recrystallized samples. This is further confirmed by the decay in the elastic modulus once the CMC is reached, with the LOH

desorbing from the interface and populating the mixed micelles.

- The hydrolysis process that converts SDS molecules back into LOH molecules was examined using a recrystallized sample. Both surface tension and surface dilational rheology were measured during the aging time up to 90 days. The effect of aging on surface tension and surface rheology readings were compared using data at 5 mM SDS. While the surface tension values exhibited a slight decrease due to aging, our results highlight that the surface rheology measurements can capture the increase in LOH content through an increase in the complex modulus and a decrease in the phase angle.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.2c00460>.

Equations for the two-component adsorption models; calculation of the depletion parameters for nonplanar surfaces; fits to the surface tension isotherms using the Frumkin van der Waals adsorption models; surface adsorption curves calculated based on the three thermodynamic models for both unpurified and recrystallized samples in WP and RB geometries; and data on the rheology of the recrystallized sample and the fit from the models (PDF)

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Notes

The authors declare no competing financial interest.

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