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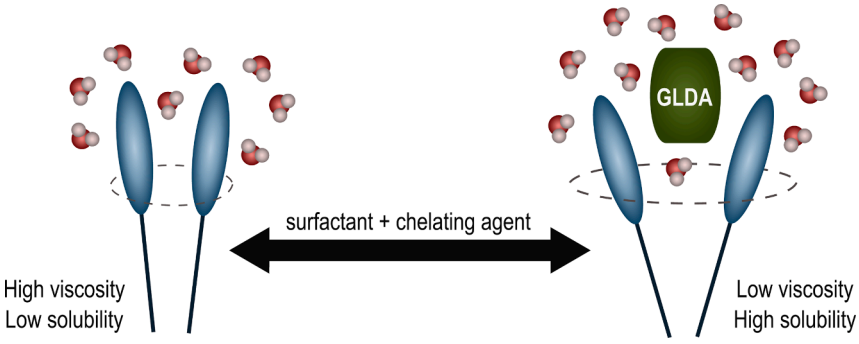
Regular Article

The role of chelating agent in the self-assembly of amphoteric surfactants

Josmary Velásquez [a,b], Lars Evenäs [b], Romain Bordes [b,*]

[a] Nouryon Surface Chemistry AB, Stenungsund, Sweden
[b] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden

GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Limited research has been conducted on the influence of chelating agents on the self-assembly process in surfactant solutions. The traditional approach assumes the chelating agent only interferes as a salting-out ion, therefore promoting surfactant separation. However, the opposite behavior has been observed for iminodipropionate based surfactants, in which the presence of chelating agents of the aminopolycarboxylate type increases solubility of nonionic ethoxylated surfactants in mixed micellar systems. Specific interaction between chelating agents-surfactants can be an important parameter in the self-assembly processes.

Experiments: Physicochemical properties of solutions containing amphoteric surfactant and tetrasodium glutamatediacetate have been investigated. Macroscopic properties, such as viscosity and cloud point, were evaluated in the presence of a non-water-soluble alkyl ethoxylated surfactant. Interactions between amphoteric surfactant and chelating agent were monitored by NMR spectroscopy, including ^{13}C chemical shift and lineshape analysis as well as ^{1}H diffusometry.

Findings: The study reveals that there is an interaction between the head group of the surfactant and the chelating agent forming oligomeric surfactant analogues with larger hydrophilic moieties, which results in smaller, more spherical micelles. The combined interactions provide possibilities for tuning the aggregation behavior of systems containing surfactants and chelating agents, and with that, the macroscopic properties of the system.

* Corresponding author.
E-mail address: bordes@chalmers.se (R. Bordes).

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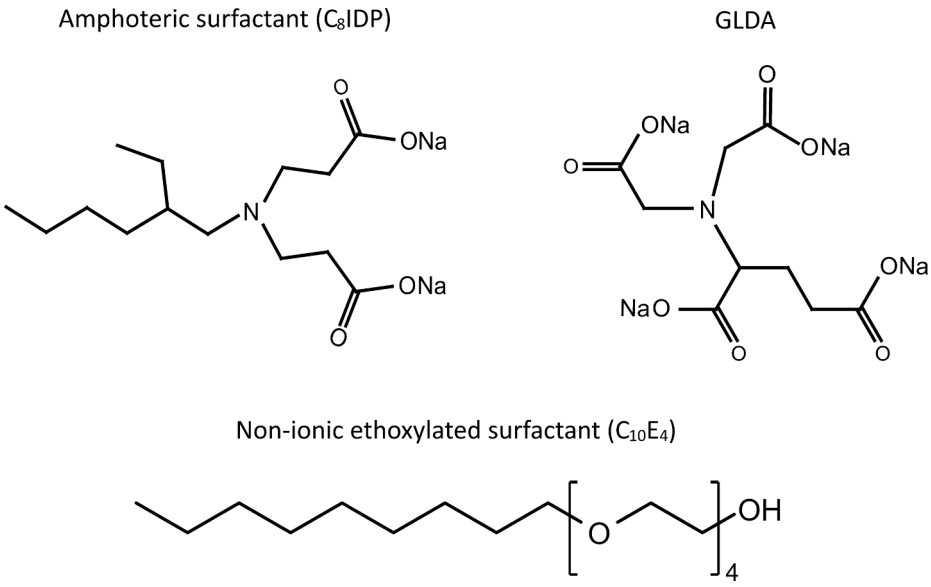

Fig. 1. The amphoteric surfactant, 2-ethylhexyliminodipropionate (C_8IDP), the chelating agent, tetrasodium glutamatediacetate (GLDA), and the nonionic ethoxylated surfactant, ethoxylalated decyl alcohol ($C_{10}E_4$).

1. Introduction

In a large number of applications, chelating agents are combined with surfactants with the aim of maintaining the surfactants' solubility and therefore the surface properties that are often decreased by the presence of polyvalent cations. Chelating agents allow the sequestration of polyvalent cations naturally present in hard water, which are detrimental to the activity of the surfactant. For instance, in cleaning, these cations adsorb onto negatively charged substrates and soil, reducing electrostatic repulsion, and increasing redeposition. Furthermore, they promote the precipitation of anionic surfactants.

Among the various chelating agents in use, aminopolycarboxylates stand out as they are good metal chelators.[1] The first complexing agent of this type industrially manufactured was nitrilotriacetic acid (NTA) in 1936, followed by ethylenediaminetetraacetic acid (EDTA) in 1939. These became widely used only after 1967, following the ban of tripolyphosphates in some countries [2]. Twenty years later, their industrial application was questioned because of their ecological impact, but also due to their toxicity and limited biodegradability, respectively [3]. The development, of more environmentally acceptable alternatives, led to the introduction of two chelating agents in the 1990s that have become more frequent in studies related to cleaning applications, methylglycinediacetic acid (MGDA) and tetrasodium glutamatediacetate (GLDA). The latter is derived from glutamic acid and is readily biodegradable [2].

One common issue observed with the introduction of chelating agents in formulation made of a combination of nonionic and ionic surfactants is the salting out of the nonionic surfactant in solution. The salting out results in micellar growth, leading to precipitation as a result of the predominance of hydrophobic interactions [4]. The salting out effect caused by the chelating agents is explained by their strong hydration and water structuring capacity. However, the understanding of the detailed interactions between the chelating agents and the surfactants remains limited and only a few studies have suggested that chelating agents and ionic surfactants may interact, thus strongly influencing the self-assembly process. For instance, chelating agents of the aminopolycarboxylate type have been studied by Zhao *et al.* [5]. They evaluated the influence of EDTA on gemini cationic surfactants and reported that these molecules form oligomeric surfactant analogues. These complexes self-assemble at a concentration lower than the CMC of the pure gemini surfactant. The formation of the oligomeric surfactants was attributed to intermolecular electrostatic binding in aqueous solution between the carboxylate groups of EDTA and the ammonium in the surfactant. On the other hand, Soontravanich *et al.* [6] found a synergistic behavior on the solubility of soap scum at high pH using a mixture of amine oxide-based surfactant with EDTA. The solubility was found to be several orders of magnitude higher than that in chelate-free systems. Moreover, it was concluded that the increased dissolution of soap scum was a consequence of the formation of mixed micelles between stearate anions and the surfactant, which are promoted by EDTA and the chelated Ca^{2+} ions in the system.

In a similar spirit, studies between amino acids and surfactants have also shed light on specific interactions and their consequences on self-assembly. Yan *et al.* [7] not only observed a decrease in CMC as previously mentioned for the EDTA-surfactant system, but also the aggregation number of cationic surfactants in presence of amino acids decreased, suggesting that micelle formation is facilitated when these small molecules are present. Chauhan and Sharma [8] proposed that the presence of amino acids in surfactant solutions may affect and reduce the hydration shell around the alkyl chain of the surfactant, due to interactions between the head group of the surfactant and the amino acids. Similar observations were made by Kandpal *et al.* [9] when studying a system containing anionic surfactant and glycine. The research noted that this interaction occurs at low concentrations of surfactant and reaches a saturation point. The subsequent addition of surfactant leads to a regular micellization process in presence of additives.

Such interactions have been well reported in the literature [10,11,12] the common denominator in most cases being the presence of two species in aqueous solution, a surfactant with an ammonium-based head group and an amino acid.

In this work, we hypothesize that interactions between nitrogen-containing surfactants and chelating agent can be advantageously used to prevent potential salting out effects, and even promote the solubilization of hydrophobic nonionic surfactants. The capacity for solubilizing hydrophobic surfactants becomes relevant in highly concentrated systems as those used in diverse industrial applications, where concentrations are often well above the CMC.

The system selected includes therefore a nitrogen-containing surfactant, based on iminodipropionate (IDP), a nonionic ethoxylated surfactant ($C_{10}E_4$) with a cloud point below room temperature, and tetrasodium glutamatediacetate (GLDA) as chelating agent (Fig. 1). The concentration range includes systems below the CMC, where

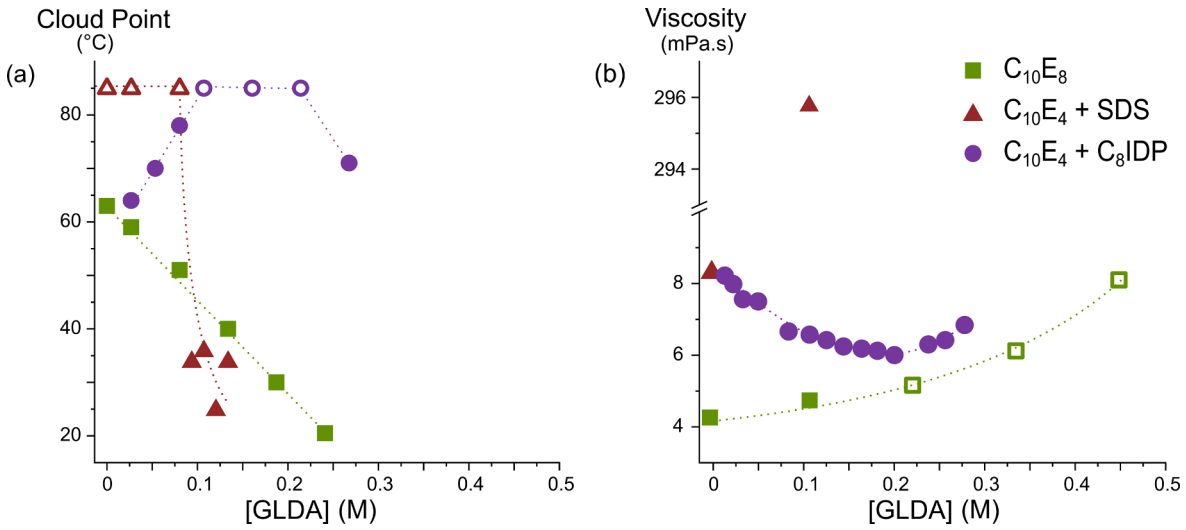

Fig. 2. Evolution of (a) cloud point and (b) viscosity as GLDA concentration increases. Non-filled symbols are used to represent systems with a cloud point higher than 85 °C in (a) and viscosity values measured on systems below their cloud point in (b). The dotted lines are included as a guide to the eye.

interactions between species can be more easily monitored, up to concentrations well above the CMC, where the macroscopic changes become clearer.

The details of the interactions between C_8IDP and GLDA, were investigated using NMR techniques, including ^{13}C chemical shift and lineshape analysis as well as ^{1}H diffusometry.

The carbon nucleus was selected for chemical shift and lineshape analysis in this study for several reasons. The aggregation behavior of surfactants is detectable with higher resolution for (heavier) nuclei with wide chemical shift range [13,14]. Atoms with more electrons tend to have larger shielding and, hence, a larger chemical shift range. They also show a stronger solvent effect, meaning that larger changes in chemical shift are observed due to changes in the microenvironment. But more importantly, there are several almost chemically equivalent moieties in both molecules yielding to fewer resolved ^{1}H NMR signals, while ^{13}C NMR generates distinctly resolved signals for a larger number of atoms in both molecules allowing the evaluation of changes in the chemical microenvironment in more detail.

2. Experimental methods

2.1. Materials

Ethoxylated decyl alcohol with 4 and 8 ethoxylated groups (referred to as $C_{10}E_4$ and $C_{10}E_8$ respectively), 2-ethylhexyliminodipropionate (C_8IDP), sodium cocopropylenediamine tripropionate, tetrasodium glutamatediacetate (GLDA), and methylglycinediacetic acid (MGDA) were supplied by Nouryon. sodium dodecyl sulfate (SDS), ≥97 % purity, and ammonium citrate tribasic (NH4 citrate), ≥97 % purity, were purchased from Sigma Aldrich. All chemicals were used as received.

Milli-Q water was used with a resistivity of ≥ 18.2 MΩ·cm at 25 °C and a total organic carbon content below 400 ppb.

2.2. Formulation preparation

The formulations for cloud point and viscosity measurements were prepared by adding 6 % w/w nonionic surfactant to water, along with a solubilizer. The amount of solubilizer was chosen to ensure that most of the cloud point values fell between room temperature and 85 °C. The concentration of C_8IDP and SDS used was 6 % w/w, while for sodium cocopropylenediamine tripropionate the concentration used was 2 % w/w. Several systems were prepared with different concentrations of chelating agent, varying from 0 to 20 % w/w. The pH was not adjusted.

2.3. Cloud point

The solution was added to a glass test tube containing a thermometer. The test tube was placed in a water bath and heated gently to complete turbidity. The sample was allowed to cool down slowly while stirring with the thermometer until a clear solution was visually observed. The temperature at which the system clarifies was recorded as the cloud point for the given system.

Given the practical difficulties and increased margin of error present when measuring the cloud point in the vicinity of the boiling point of water, the cloud point measurements were not taken above 80 °C.

2.4. Viscosity

The dynamic viscosity was measured using a LV DV1 Digital Viscometer from Brookfield Ametek. The experimental conditions used were a sample size of 100 ml, spindle LV-01 and a rotating speed of 100 rpm.

2.5. NMR spectroscopy

All NMR measurements were carried out using a 400 MHz Varian VNMRS spectrometer operating at 25 ± 0.1 °C. Each 5 mm NMR tube contained a sealed glass capillary with deuterated methanol (99.6 % purity, Fisher Scientific), which served both as ^{2}H locking solvent and a ^{13}C chemical shift reference.

The ^{13}C chemical shift, δ, for the NMR signals of surfactant solutions at various concentrations, was determined in absence and presence of the chelating agent. The MeOD signal was calibrated to 49 ppm.

The bipolar pulsed-field gradient stimulated echo (DBPPSTE) sequence was used on the ^{1}H nucleus to acquire self-diffusion coefficients. In the experiments, the gradient time, the diffusion time, the variable gradient strength, and the number of gradient steps in the variable array were adjusted, depending on the composition of the sample, to achieve the desired signal attenuation.

3. Results and discussion

The systems at high concentration were used to evaluate the changes in cloud point and viscosity, and to compare against non-nitrogen-based surfactant-chelate systems. Since the cloud point is a characteristic feature of polyoxyethylene-based surfactants, a surfactant of this type is included in this part of the study. The systems with concentrations below

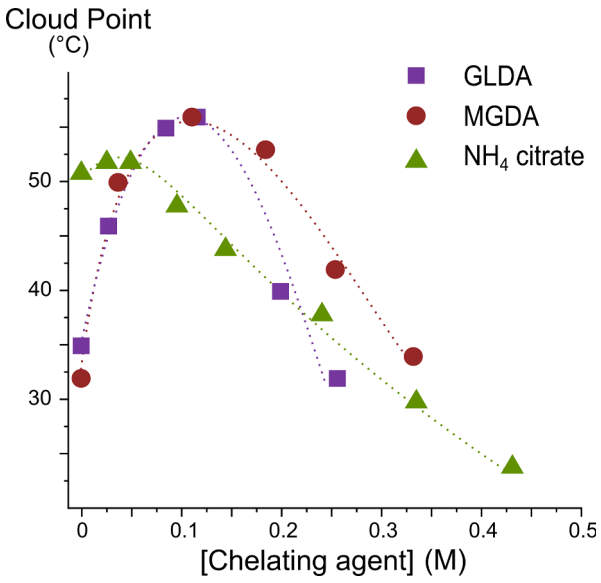

Fig. 3. Evolution of the cloud point as GLDA concentration increases. The dotted lines are included as a guide to the eye.

or close to the CMC were used to study intermolecular interactions.

3.1. *Effect of GLDA on the cloud point and viscosity of surfactant solutions*

Fig. 2 shows the evolution of the cloud point and viscosity of mixed surfactant systems upon the addition of GLDA. When a soluble nonionic ethoxylated surfactant is used ($C_{10}E_8$ in this study) a reduction in cloud point and an increase in viscosity are observed as the concentration of GLDA is increased. This is expected considering that the chelating agent induces salting out. GLDA depletes the water molecules available to hydrate the surfactant head group, resulting in lower solubility of the nonionic surfactant in water and consequently lower cloud point temperatures. The lower solubility also induces an increase of viscosity, due to micellar growth [15].

To evaluate the sensitivity of different solubilizers to the presence of GLDA, a non-water-soluble nonionic surfactant, $C_{10}E_4$, was used. The amphoteric surfactant (C_8IDP) or SDS were used as solubilizers.

As expected, the anionic surfactant SDS provides a high cloud point at low concentration of GLDA, but the increase of concentration of GLDA induces a sharp reduction of the cloud point above 0.1 M GLDA, while the viscosity steeply rises with GLDA concentration. These results are in agreement with the expected behavior of ionic surfactants; the addition of electrolytes results in screening the repulsive head-to-head

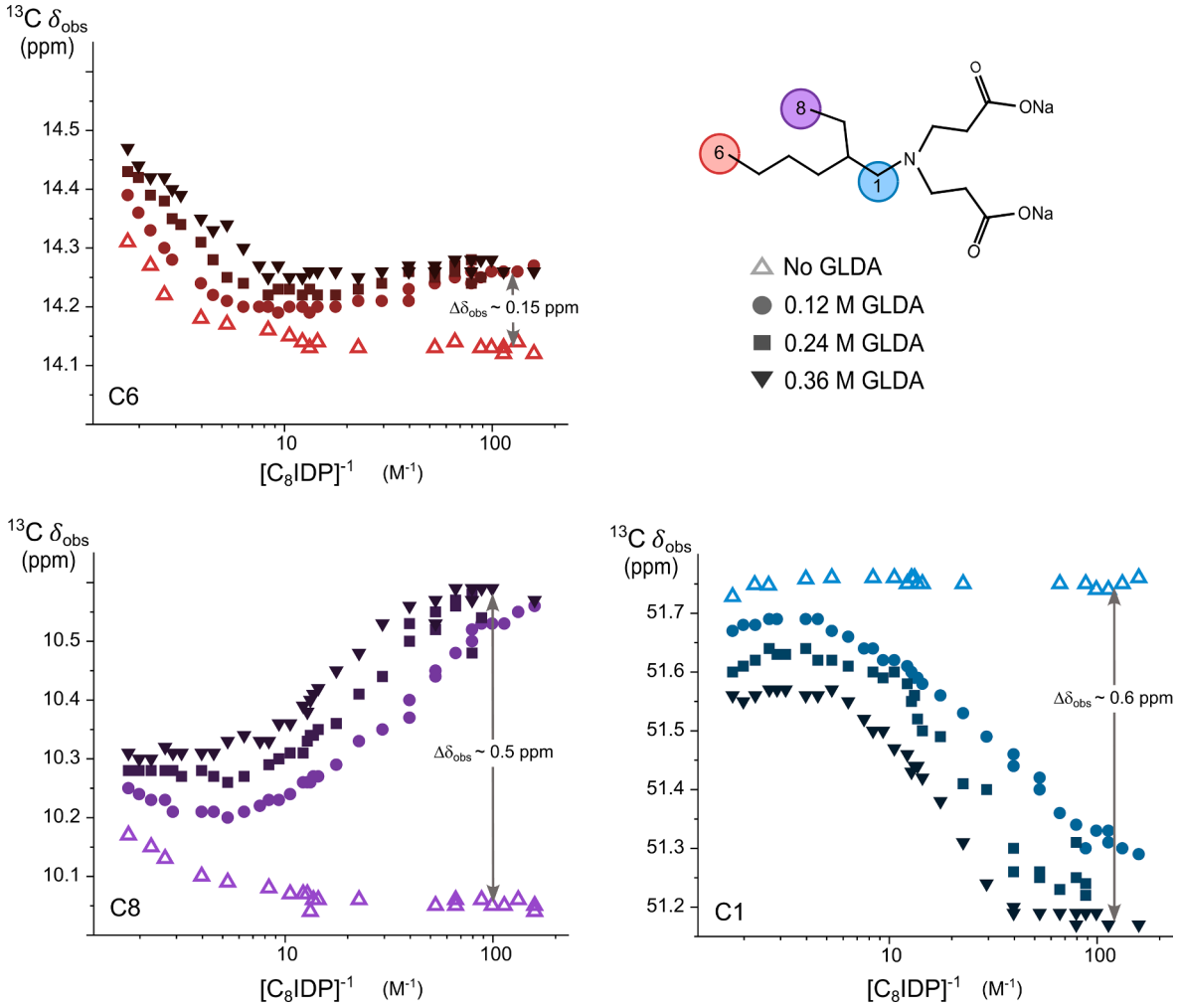

Fig. 4. Observed chemical shift as a function of the reciprocal concentration of amphoteric surfactant (C_8IDP) in the system without additive and in systems of different GLDA concentrations; 0.12 M, 0.24 M and 0.36 M (increased darkness as GLDA concentration increases). Each plot corresponds to a different signal for carbon atoms forming part of the lipophilic chain, color-coded as indicated in the molecule. Note that the x-axis is represented in terms of the reciprocal surfactant concentration. Consequently, surfactant concentration increases from right to left along the axis.

electrostatic interactions [16], promoting micellar growth [17], decreasing their solubility in water, and increasing viscosity [18].

The behavior of the nonionic is, however, very different when the amphoteric surfactant is used as solubilizer. An increase in cloud point that reaches its maximum in the range of 0.1–0.25 M GLDA takes place, followed by a decrease at higher concentrations (above 0.3 M). In terms of viscosity, a clear minimum is observed for the same concentration range of the chelating agent. The increased solubility and reduced viscosity correspond to a behavior opposite to the regular salting out effect observed with ionic surfactants.

Amphoteric surfactants are pH sensitive and GLDA increases both the ionic strength and the pH of the system, therefore one possible claim is that the observed effect on the cloud point could be attributed to the ionic strength and pH. However, in systems at the same pH and ionic strength, a difference of more than 20 °C in the cloud point is observed (data in supporting information), clearly indicating that the increased solubility is driven by a different phenomenon.

To evaluate the extent to which these results could be extrapolated into other systems, the cloud points of different polycarboxylic acid based chelating agents were evaluated in systems solubilized by a different amphoteric surfactant, sodium cocopropylenediamine tripropionate. These results are presented in Fig. 3. In all the cases, the shape of the curve resembles that of the previously shown system containing C_8IDP, $C_{10}E_4$ and GLDA.

Since viscosity increases with micellar size [15], while a decrease takes place for the cloud point [19], a reduction in micellar size when the chelating agent is added to a surfactant solution stabilized by an amphoteric surfactant can be suggested. Morphological changes of surfactant aggregates in water are often described by the Critical Packing Parameter (CPP), a model able to predict the structure and properties of aqueous mixtures of surfactants by considering surfactant geometry [15,20]. This concept has demonstrated its reliability in various scenarios, including mixture of surfactants [21], surfactant and additives [22], and when considering the hydration shell as a part of the head group [23].

A reduction of micellar size in the system stabilized by amphoteric surfactant could be explained by an increase of area occupied by the hydrophilic head group of the surfactant, which could be a consequence of the formation of a complex between the chelating agent and the surfactant head group. Therefore, the critical packing parameter decreases promoting the formation of smaller, more spherical micelles.

3.2. Effect of GLDA on the aggregation behavior of an amphoteric surfactant

Fundamental NMR chemical shift analysis of micellar systems relies on the fact that the chemical environment around a surfactant molecule is expected to be quite different if the molecule exists as a free unimer surrounded by water molecules or as part of micelles surrounded by other surfactant molecules.

The observed chemical shift of the resonance peak can be expressed as a population average of the states of free unimer and micellized surfactant. Fast exchange kinetics between these states, compared to the time scale of NMR detection, is the reason for the averaged observed chemical shift. According to the pseudophase transition model [24], this can be expressed as:

$$\delta_{obs} = \left(\frac{C_{uni}}{C_T}\right)\delta_{uni} + \left(\frac{C_{mic}}{C_T}\right)\delta_{mic} \quad (1)$$

where δ_{uni} and δ_{mic} represent the chemical shifts related to the free unimers and surfactants in the micelles, respectively; C_{uni} and C_{mic} are the free surfactant concentration and the concentration of surfactant in the micelles, respectively; and $C_T = C_{uni} + C_{mic}$ is the total surfactant concentration.

Fig. 4 shows the chemical shift variation for three carbon atoms in the amphoteric surfactant molecule as its concentration increases in the absence (unfilled data) and presence (filled data) of GLDA. The system without GLDA is discussed first.

The observed chemical shift for the terminal carbon atoms in the surfactant molecule (C6 and C8 in Fig. 4) as a function of the reciprocal surfactant concentration follows Eq. (1), which is the expected trend for surfactant solutions [25]. At low concentrations the chemical shift remains constant as surfactant concentration increases ($C_{mic} = 0$; $C_T = C_{uni}$) which corresponds to the chemical shift of surfactant molecules dissolved as unimers. At higher surfactant concentration, the chemical shift moves downfield, suggesting that the environment around the methyl group is changing due to micellization.

The chemical shift of the carbon atom belonging to the methylene group in the vicinity of the nitrogen, C1, is also reported in Fig. 4. This carbon atom is close to the head group of the surfactant. The main observation from this data is that the chemical shift does not change significantly with the concentration of surfactant. Only a small decrease in the observed chemical shift can be seen when passing from unimers in solution into micelles. This steady behavior correlates with a microenvironment that does not change even after the surfactant aggregation takes place. In other words, there is no change in polarity of the microenvironment, which is expected for carbon atoms at the micelle surface [26].

The variation in the chemical shift at increased concentrations of GLDA (Fig. 4) shows a different pattern compared to the data discussed above.

The addition of a salting-in or salting-out additive should displace the chemical shift to a different value, and the inflection point to a higher or lower concentration, depending on whether the additive promotes or prevents the micellization process. However, the overall response to the reciprocal concentration should remain. A change in the shape of the curve can only be explained by the introduction of another term in eq. (1), considering an interaction between GLDA and the amphoteric surfactant or between GLDA and the micelles. Therefore, the change in the shape of the curve becomes a clear indicator that GLDA is not freely moving in the surfactant solution but interacting with the surfactant in it. Considering the interacting species, Eq. (1) can now be written as:

$$\delta_{obs} = \left(\frac{C_{uni}}{C_T}\right)\delta_{uni} + \left(\frac{C_{uni+GLDA}}{C_T}\right)\delta_{uni+GLDA} + \left(\frac{C_{mic}}{C_T}\right)\delta_{mic} + \left(\frac{C_{mic+GLDA}}{C_T}\right)\delta_{mic+GLDA} \quad (2)$$

where the two new terms, uni + GLDA and mic + GLDA, account for the surfactant interacting with GLDA as a unimer or in the micelle, respectively.

In a small and diluted concentration range, the plots in Fig. 4 show a chemical shift that remains constant. The extent of the chemical shift variation compared to the system without GLDA differs depending on the atom monitored, being larger for the carbon atoms close to the head group and smaller for the carbon atoms located in the far end of the lipophilic chain. This is highlighted in Fig. 4 by the arrows showing $\Delta\delta$ values varying from 0.14 ppm to around 0.6 ppm. Both observations indicate that the change in microenvironment differs depending on which carbon atom in the surfactant molecule is being evaluated, suggesting that GLDA is preferentially surrounding the head group of the surfactant, where the changes in chemical shift are greater.

With increased surfactant concentration, a second region emerges, observed at concentrations around 10 and 40 M^{-1}. This region shows different behaviors depending on the carbon atom considered. For the carbon atoms forming part of the terminal methyl groups in the lipophilic chain there is an upfield shift of the signals. The change is significantly sharper for C8 which is closer to the head group of the surfactant compared to C6. On the other hand, the methylene group C1 close to the hydrophilic region of the surfactant shows a downfield

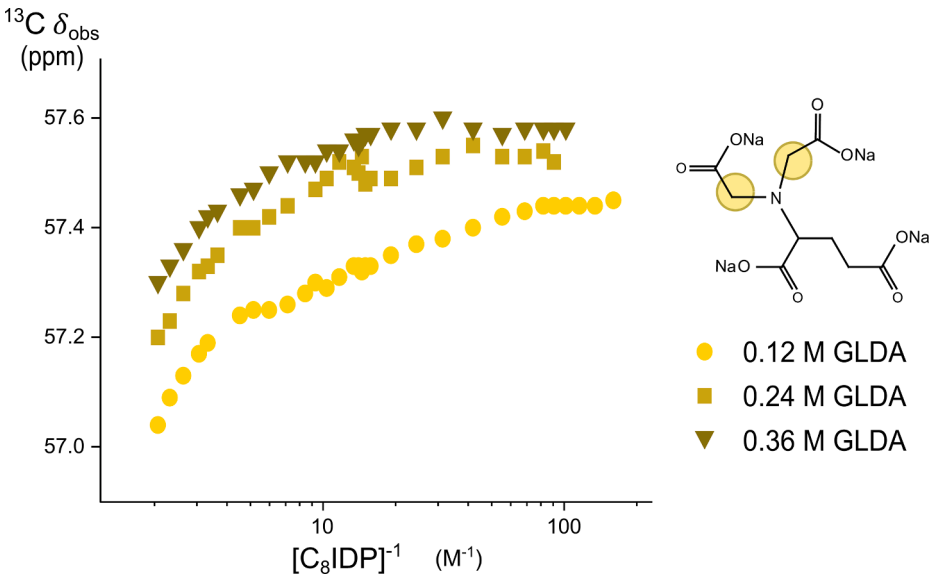

Fig. 5. Observed chemical shift as a function of the reciprocal of the concentration of amphoteric surfactant (C_8IDP) for a carbon atom in GLDA. The data was collected at different GLDA concentrations: 0.12 M, 0.24 M and 0.36 M. Note that the x-axis is represented in terms of the reciprocal surfactant concentration. Consequently, surfactant concentration increases from right to left along the axis.

chemical shift pattern in the same concentration region. In other words, the observed chemical shift is now approaching the chemical shift observed for the system without GLDA.

The change in chemical shift in this region corresponds to an increased concentration of surfactant which is not interacting with GLDA. This leads to an equilibrium that can be described by:

Below CMC:

$[C_8IDP] + [GLDA] \leftrightharpoons [C_8IDP \bullet GLDA]$ *(3)*

Above CMC:

$[C_8IDP] + [micelles] + [GLDA] \leftrightharpoons [C_8IDP \bullet GLDA] + [micelle \bullet GLDA]$ *(4)*.

At even higher concentrations, a third region becomes apparent. The signal for C6, located in the far end of the lipophilic chain, moves to a lower field while it levels off for the atoms closer to the head group (C8 and C1).

For C6 the change in chemical shift due to the interaction with GLDA is small because this atom is far from the head group of the surfactant where the interaction takes place. Therefore, variations in chemical shift due to the complexation between GLDA and the surfactant can be neglected. In terms of Eq. (2), the following simplification can be made $\delta_{uni} \approx \delta_{uni+GLDA}$ and $\delta_{mic} \approx \delta_{mic+GLDA}$. Consequently, at high surfactant concentration, the shape of the curve approximates that of the system without GLDA.

For C1 and C8, the description of the microenvironment is more complex because these atoms are located close to the micelle surface. Therefore, their microenvironment includes the lipophilic core of the micelle, the water molecules hydrating the surfactant's head group, and the neighboring GLDA molecules interacting with the surfactant. The resulting chemical shift is thus a combination of the contributions from all these interactions.

From the GLDA perspective, the observed chemical shift of the resonance peaks can be expressed as:

$$\delta_{obs} = \left(\frac{C_{GLDA_{non\,int}}}{C_{T_{GLDA}}}\right)\delta_{GLDA_{non\,int}} + \left(\frac{C_{GLDA_{int\,uni}}}{C_{T_{GLDA}}}\right)\delta_{GLDA_{int\,uni}} + \left(\frac{C_{GLDA_{int\,mic}}}{C_{T_{GLDA}}}\right)\delta_{GLDA_{int\,mic}} \quad (5)$$

which considers the population average between the non-interacting species ($GLDA_{non\ int}$), and the interacting GLDA molecules with unimers ($GLDA_{int\ uni}$) and micellized surfactant ($GLDA_{int\ mic}$). Here $C_{T_{GLDA}}$ refers to the total GLDA concentration.

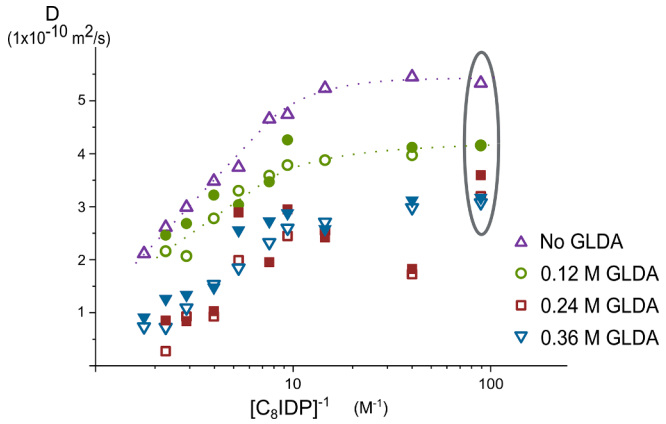

Fig. 6. Self-diffusion coefficient as a function of the reciprocal concentration of amphoteric surfactant (C_8IDP) for the amphoteric surfactant (non-filled data) and the chelating agent (filled data). The data were collected at different GLDA concentrations: 0.12 M, 0.24 M and 0.36 M. The dotted lines are included as a guide to the eye. Note that the x-axis is represented in terms of the reciprocal surfactant concentration. Consequently, the concentration increases from right to left along the axis.

The chemical shift observed as a function of the reciprocal of the surfactant concentration for one of the carbons in the methylene groups of GLDA is presented in Fig. 5 and can be described by three regions. The first region takes place at low surfactant concentration, where the observed chemical shift remains constant. The larger the GLDA concentration is, the more extended this region becomes. At low surfactant concentration, there are no micelles ($C_{GLDA_{int\,mic}} = 0$) and the concentration of GLDA not interacting with surfactant is much larger than the complexes ($C_{GLDA_{int\,uni}} \ll C_{GLDA_{non\,int}}$). As a result, the second and third terms in Eq. (5) can be neglected, resulting in a constant chemical shift that corresponds to the chemical shift of GLDA at the given concentration in the absence of surfactant.

The second region, with a surfactant concentration around 10 and 40 M^{-1}, shows a reduction in the chemical shift. At this surfactant concentration there are no micelles formed, but the concentration of GLDA molecules interacting with surfactant increases and cannot be

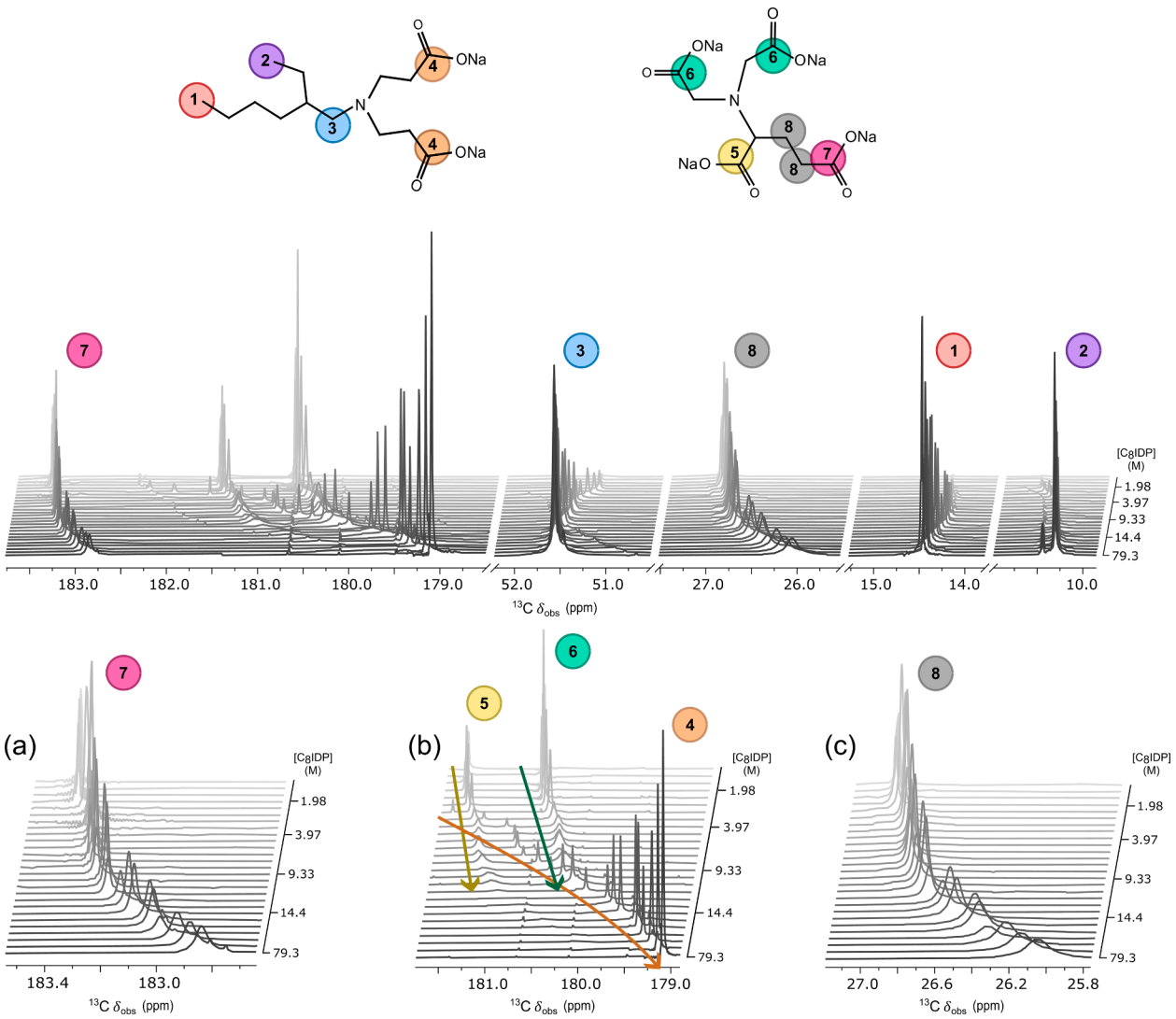

Fig. 7. Evaluated areas of the ^{13}C NMR spectra for the system containing 0.36 M of GLDA at increasing concentrations of amphoteric surfactant. The figures in the bottom part are zoomed-in versions of the spectra at the top.

neglected anymore. Therefore, Eq. (5) can be rewritten as:

$$\delta_{obs} = \left(\frac{C_{GLDA_{non\ int}}}{C_{T_{GLDA}}}\right)\delta_{GLDA_{non\ int}} + \left(\frac{C_{GLDA_{int\ uni}}}{C_{T_{GLDA}}}\right)\delta_{GLDA_{int\ uni}} \quad (6)$$

The increased concentration of interacting species is causing the decrease in chemical shift observed. This second region extends to the concentration value where the aggregation of the amphoteric surfactant starts.

The final region occurs at high surfactant concentrations, displaying a more negative slope. The observed chemical shift at high concentrations reflects contributions from the three possible GLDA species present in the system. This observation indicates that GLDA interacts not only with unimers but also with surfactant molecules, forming micelles.

The self-diffusion coefficient data for C_8IDP (unfilled) and GLDA (filled) are presented in Fig. 6. One important feature is the change in self-diffusion coefficient as a function of GLDA concentration, particularly at the minimum concentration of amphoteric surfactant. This area is highlighted in the figure with an oval. The decrease in self-diffusion coefficients as the concentration of GLDA increases within the highlighted oval is not inversely proportional to the changes in viscosity of the systems. While the viscosity increases steadily in this region with values of 2.8 mPa.s, 3.6 mPa.s, 4.08 mPa.s and 5.04 mPa.s for the systems with 0 M, 0.12 M, 0.24 M and 0.36 M GLDA, respectively, the self-diffusion coefficient decreases significantly with the first addition of GLDA and less pronouncedly as the concentration of GLDA increases further. The pronounced decrease in self-diffusion coefficient does not follow the Stokes-Einstein equation unless the interaction between the surfactant and the chelating agent is considered. The effect of the change in size due to the interactions between both molecules is reinforced by the viscosity changes; therefore, the first addition of GLDA results in a larger change in the self-diffusion coefficient.

Another important observation is that the self-diffusion coefficients for GLDA and the amphoteric surfactant are similar at any surfactant concentration, which supports the hypothesis of the formation of a complex between GLDA and C_8IDP.

Furthermore, the diffusion values decrease with a less pronounced slope for the systems containing GLDA than for the system without GLDA, indicating that the micelles formed in the presence of GLDA have a smaller radius than those in absence of GLDA.

A lineshape analysis of the ^{13}C spectra was used to support the discussion. Fig. 7 presents relevant areas of the spectra for the system containing 0.36 M of GLDA. The surfactant concentration in this figure ranges from diluted, where surfactants are solubilized as unimers, to concentrated, where micelles are present. The main observations are: first, the signals for GLDA around 26.5 and 183 ppm (Fig. 7a and c) change from sharp and narrow to smooth and wide; their intensities also

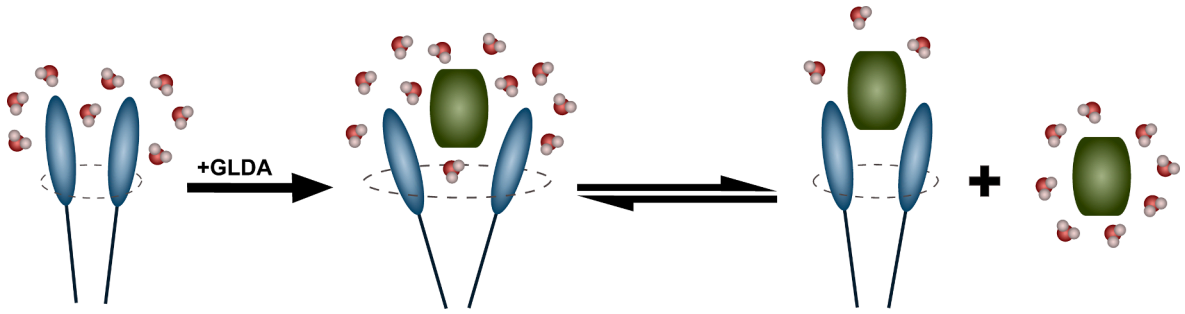

Fig. 8. Illustration of the changes in area of the hydrophilic area of the micelle upon the addition of GLDA.

decrease even when the concentration of GLDA is constant. The broadening of the NMR signals indicates the complex formation.

Secondly, the signal corresponding to the carbonyl groups in the amphoteric surfactant (signal 4 in Fig. 7b) undergoes the most substantial change in chemical shift, with a displacement of approximately 2 ppm. This notable alteration in chemical shift indicates that the interaction predominantly affects the head group of the surfactant molecule.

Finally, the signals attributed to the carbonyl groups of GLDA, with chemical shifts approximately at 180.5 and 181.5 ppm (corresponding to carbons 5 and 6), also exhibit significant broadening, to the extent that these signals vanish completely at surfactant concentrations around 10 M. These signals pertain to the carbonyl groups nearest to the nitrogen atom in the GLDA molecule. This notable broadening, distinct from the broadening observed in the signal of the other carbonyl group (carbon 7), suggests that the nitrogen atom contributes to the interaction between these two molecules.

4. Conclusions

The study focused on understanding the behavior of GLDA, a biodegradable chelating agent, in aqueous systems in the presence of an amphoteric surfactant. While the macroscopic properties showed that GLDA acted as a salting-out ion for anionic and nonionic surfactants, in the presence of amphoteric surfactants, the introduction of GLDA had very different effects. Initially, it increased the solubility of a nonionic surfactant, followed by a salting-out effect after reaching a certain concentration threshold. Through ^{13}C NMR studies and ^{1}H diffusometry, an interaction between GLDA and the hydrophilic head group of the amphoteric surfactant was evidenced, resulting in an equilibrium between interacting and non-interacting species in solution.

Specifically, our findings suggest that at low GLDA concentrations, most GLDA molecules interact with the amphoteric surfactant, both as unimer and as part of the micelles. Since the interaction takes place in the vicinity of the surfactant's head group and GLDA is a hydrophilic molecule, the overall effect is the formation of a complex-like surfactant with a larger head group. Consequently, the micellar critical packing parameter decreases, leading to the formation of smaller, more spherical micelles. In systems containing a water-insoluble nonionic surfactant, the reduced micellar size translates into a decrease in viscosity, and an increase in cloud point values. This also enables the solubilization of larger amounts of nonionic surfactant.

At higher concentrations, once the equilibrium is established, the excess of non-interacting GLDA molecules, i.e., the GLDA molecules free in solution, induces a salting-out effect, causing a decrease in cloud point, and an increase in viscosity. This is illustrated in Fig. 8, which graphically summarizes the effect of adding GLDA to an amphoteric surfactant solution at concentrations above the CMC.

Based on previously reported electrostatic interactions between amino acids and ammonium compounds [7,8,9,10,11], we hypothesized that the similarity in the chemical structures of the chelating agent and the amphoteric surfactant would enable strong intermolecular interactions, resulting in increased hydrophilicity and thereby impacting the macroscopic properties of complex surfactant systems.

Previous researches, including studies on EDTA with cationic [5] or amine-oxide [6] surfactants, has suggested that these surfactants could interact with EDTA, potentially altering both the critical micelle concentration (CMC) and the system's ability to solubilize tertiary components. Nevertheless, the detailed interactions between chelating agents and surfactants are still poorly understood, despite the central role of chelating agents in numerous applications, such as cleaning, oil recovery, and agriculture, among others. Here, we not only described the molecular interactions taking place between chelating agents and amphoteric surfactants, but also correlated these interactions with the macroscopic properties of more complex systems containing a water-insoluble nonionic surfactant.

Overall, these results underscore that by carefully designing a system based on specific interactions between surface-active agents and chelating agents, it is possible to prevent salting-out effects and, conversely, improve the solubility of complex surfactant mixtures. This approach can enhance the performance of the system in practical applications and provide guidelines for formulation design and optimization.

CRediT authorship contribution statement

Josmary Velásquez: Conceptualization, Investigation, Data curation, Writing – original draft, Visualization. **Lars Evenäs:** Writing – review & editing, Supervision. **Romain Bordes:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2024.07.131.

References

[1] T.P. Knepper, Synthetic chelating agents and compounds exhibiting complexing properties in the aquatic environment, TrAC - Trends in Analytical Chemistry 22 (10) (2003) 708–724, https://doi.org/10.1016/S0165-9936(03)01008-2.

[2] D. Kołodyńska, "Complexing Agents," in: Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, 2019, pp. 1–26. doi: 10.1002/0471238961.0308051208152301.a01.pub3.

[3] B. Nowack, J.M. VanBriesen, "Chelating Agents in the Environment," 2023. [Online]. Available: https://pubs.acs.org/sharingguidelines.

[4] W. Kunz, P. Lo Nostro, B.W. Ninham, The present state of affairs with Hofmeister effects, in: Current Opinion in Colloid and Interface Science, Aug. 2004, pp. 1–18. doi: 10.1016/j.cocis.2004.05.004.

[5] W. Zhao, et al., Aggregation of a cationic gemini surfactant with a chelating molecule and effects from calcium ions, Langmuir 33 (44) (2017) 12719–12728, https://doi.org/10.1021/acs.langmuir.7b03137.

[6] S. Soontravanich, H.E. Lopez, J.F. Scamehorn, D.A. Sabatini, D.R. Scheuing, Dissolution study of salt of long chain fatty acids (Soap Scum) in surfactant solutions. Part I: Equilibrium dissolution, J Surfactants Deterg 13 (4) (2010) 367–372, https://doi.org/10.1007/s11743-010-1208-5.

[7] Z. Yan, L. Liu, X. Chen, Y. Niu, Physicochemical studies on molecular interactions between small biomolecules and drug benzalkonium chloride at different temperatures T = (293.15–313.15) K, J. Mol. Liq. 274 (2019) 115–124, https://doi.org/10.1016/j.molliq.2018.10.063.

[8] S. Chauhan, K. Sharma, Effect of temperature and additives on the critical micelle concentration and thermodynamics of micelle formation of sodium dodecyl benzene sulfonate and dodecyltrimethylammonium bromide in aqueous solution: A conductometric study, J. Chem. Thermodyn. 71 (2014) 205–211, https://doi.org/10.1016/j.jct.2013.12.019.

[9] N.D. Kandpal, S.K. Joshi, R. Singh, K. Pandey, Thermodynamic parameters of micellization and transfer of amino acid from water to aqueous linear alkyl benzene sulphonate, J. Indian Chem. Soc., Apr. 87 (2010) 487–493.

[10] D. Otzen, "Protein-surfactant interactions: A tale of many states," *Biochimica et Biophysica Acta - Proteins and Proteomics*, vol. 1814, no. 5. Elsevier B.V., pp. 562–591, 2011. doi: 10.1016/j.bbapap.2011.03.003.

[11] N.A. Malik, Surfactant–Amino Acid and Surfactant-Surfactant Interactions in Aqueous Medium: a Review, Appl Biochem Biotechnol 176 (8) (Aug. 2015) 2077–2106, https://doi.org/10.1007/s12010-015-1712-1.

[12] A. P. Singh Raman *et al.*, "A Review on Interactions between Amino Acids and Surfactants as Well as Their Impact on Corrosion Inhibition," *ACS Omega*, vol. 7, no. 51. American Chemical Society, pp. 47471–47489, Dec. 27, 2022. doi: 10.1021/acsomega.2c03629.

[13] B.-O. Persson, T. Drakenberg, B. Lindman, 13C NMR of Micellar Solutions. Micellar Aggregation Number from the Concentration Dependence of the 13C Chemical Shifts [Online].Available: J Phys Chem 83 (23) (1979) 3011–3015 https://pubs.acs.org/sharingguidelines.

[14] B.-O. Persson, T. Drakenberg, B. Lindman, Amphiphile Aggregation Number and Conformation from Carbon-13 Nuclear Magnetic Resonance Chemical Shifts [Online].Available: J Phys Chem 80 (19) (1976) 2124–2125 https://pubs.acs.org/sharingguidelines.

[15] B. Kronberg, K. Holmberg, B. Lindman, Surface chemistry of surfactants and polymers, Wiley (2014), https://doi.org/10.1002/9781118695968.

[16] M.L. Corrin, W.D. Harkins, The Effect of Salts on the Critical Concentration for the Formation of Micelles in Colloidal Electrolytes [Online].Available: J. Am. Chem. Soc. 69 (3) (1947) 683–688 https://pubs.acs.org/sharingguidelines.

[17] M.F. Emerson, A. Holtzer, On the ionic strength dependence of Micelle Number, J. Phys. Chem. 69 (11) (1965) 3718–3721, https://doi.org/10.1021/j100895a010.

[18] J.H. Mu, G.Z. Li, X.L. Jia, H.X. Wang, G.Y. Zhang, Rheological properties and microstructures of anionic micellar solutions in the presence of different inorganic salts, J. Phys. Chem. B 106 (44) (2002) 11685–11693, https://doi.org/10.1021/jp014096a.

[19] K. Shigeta, U. Olsson, H. Kunieda, Correlation between micellar structure and cloud point in long poly(oxyethylene)n oleyl ether systems, Langmuir 17 (16) (2001) 4717–4723, https://doi.org/10.1021/la001260x.

[20] M.J. Rosen, J.T. Kunjappu, Surfactants and Interfacial Phenomena. Wiley, 2012. doi: 10.1002/9781118228920.

[21] I.K. Mkam Tsengam, et al., Transformation of lipid vesicles into micelles by adding nonionic surfactants: elucidating the structural pathway and the intermediate structures, J. Phys. Chem. B 126 (11) (2022) 2208–2216, https://doi.org/10.1021/acs.jpcb.1c09685.

[22] V. Lutz-Bueno, S. Isabettini, F. Walker, S. Kuster, M. Liebi, P. Fischer, Ionic micelles and aromatic additives: A closer look at the molecular packing parameter, PCCP 19 (32) (2017) 21869–21877, https://doi.org/10.1039/c7cp03891g.

[23] K. Mochizuki, The packing parameter of bare surfactant does not necessarily indicate morphological changes, J. Colloid Interface Sci. 631 (Feb. 2023) 17–21, https://doi.org/10.1016/j.jcis.2022.10.163.

[24] H. Wennerström, B. Lindman, Micelles, physical chemistry of surfactant association, Phys. Rep. (Rev. Sect. Phys. Lett.) 52 (1) (1979) 1–86.

[25] X. Cui, S. Mao, M. Liu, H. Yuan, Y. Du, Mechanism of surfactant micelle formation, Langmuir 24 (19) (2008) 10771–10775, https://doi.org/10.1021/la801705y.

[26] N. Muller, H. Simsohn, Investigation of micelle structure by fluorine magnetic resonance [Online].Available: J. Phys. Chem. 75 (7) (1971) 942–945 https://pubs.acs.org/sharingguidelines.