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Effect of Glycerol and NaCl on the Krafft point of SDS using Surface tension- pendant drop method.

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The effect of glycerol and sodium chloride (NaCl) on the phase behaviour of sodium dodecyl sulfate (SDS) near the Krafft point was studied by surface tension analysis using the pendant drop method. The critical micelle concentration (CMC) and Krafft Temperature (T_K) of SDS in water:glycerol mixtures, across the full composition range, and in NaCl solutions within 0.025-0.2M were obtained to determine the Krafft point. The addition of glycerol was found to initially decrease the CMC as well as T_K until approximately 20 wt%, above which the CMC increased rapidly (up to 35 mM) and T_K increased linearly to ~31°C. The SDS Krafft point thus shifts to higher temperatures and SDS content in the presence of glycerol, which is interpreted as a result of the reduction in solvent polarity which opposes micellization. By contrast, the addition of NaCl causes the CMC to decrease rapidly, down to approximately 1mM SDS at 0.2 M NaCl, while T_K remains within the 14-16°C range. The Krafft point of SDS in NaCl is thus shifted towards lower SDS concentration, in agreement with the shift of the SDS liquid crystalline phases to low surfactant content, in the presence of salt. Our results establish a competent route for tuning the Krafft point of model surfactant SDS by adjusting solvent quality and salt content.

Introduction

Surfactant micellization in organic solvent mixtures and the effect of electrolytes on surfactant aggregation has been studied for many years. The interest in surfactant chemistry is due to its significance in a wide range of industries such as pharmaceuticals, agrochemicals, oil extraction, food industry, detergent and cosmetic products.[1] The influence of polar organic solvents and electrolytes on surfactant micellization has important practical considerations; cosmetics, cleaning and pharmaceutical formulations contain co-solvents such as glycerol, ethylene glycol and ethanol to improve the sensory feel, solubility of actives and lower freezing points and sodium chloride as thickening agent.[1]

Surfactants have an amphiphilic chemical structure and therefore behave and interact in liquid solutions in a particular manner, self-assembling to form specific aggregates from micelles to liquid crystals, depending on the surfactant concentration and solvent properties.[2, 3] Inter and intra molecular interactions between the hydrophobic tails, between hydrophilic head groups and between the tails/head groups and solvent mixtures, determines the nature of these aggregates.[3, 4] These molecular interactions determine the solubility, Critical Micelle Concentration (CMC) and Krafft temperature (T_k) of surfactants in various systems and therefore are effected by factors such as temperature, pressure, pH, c0-surfactants type- ionic charge, solvent properties and the presence of electrolytes. [5, 6]

The self-assembly aggregation of amphiphiles in water is governed by the combined insolubility of the hydrophobic tails and the electrostatic and/or steric repulsion of the hydrophilic head groups.[4, 6] Environmental conditions, including the addition of solvent or a salt, can alter the balance between these competing terms and hence effect micellization of surfactants. Previous studies investigating surfactant micellization in organic solvents with physical properties similar to water, have reported that the polar solvents require three characteristics to favour surfactant aggregation; high cohesive energy, high dielectric constant and high hydrogen bonding ability.[7-10]

Glycerol has similar properties to water and is a good hydrogen bonding agent.[11] As glycerol is added to water, a hydrogen bonded network is formed between them, exhibiting a low cohesive energy and solvent polarity (compared to water) and increased viscosity.[8, 10, 11] The solubility of ionic surfactants such as Sodium dodecyl sulfate (SDS) in water is due to the hydrogen bonding interaction between the water molecules and the hydrophilic headgroup ($SO4^-$) and the high insolubility of hydrophobic tail ($C_{12}H_{25}$) in the highly polar solvent and the hydrophobic attraction between the tails.[6] With the addition of glycerol, the hydrogen bonding

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interaction between the headgroup and water is disrupted and the hydrophobic attraction between the tails is altered. Also the repulsion effect between the headgroups is less due to the low polarity.[7, 8, 12] Therefore self-assembly is less favourable in glycerol and other organic solvents. It has also been widely reported that the aggregate size of surfactant can either increase or decrease depending on the type of surfactant and the organic solvents, impacting its phase transitions.[13 14]

Electrolytes however have the opposite impact on the micellization behaviour of ionic surfactants. As the concentration of surfactants is increased above the CMC, the micelles start to elongate into rod-like and worm-like structures.[14, 15] Electrolytes have a synergetic effect on growth of surfactant micelles. For SDS, addition of electrolytes, e.g. sodium salts reduces the repulsion effect between the headgroups, as the increased concentration of Na^+ counterion bridges the gap between the $SO4^-$ headgroups, favouring micellization and therefore decreases the CMC.[16 17, 18] The T_K has been reported to either remain fairly constant or slightly increase with the addition of small levels of salt.[19-21] This could be explained as the salt addition also causes micellar growth and increases the SDS aggregate size due to the salting out effect, changing the packing parameter and requiring slightly higher temperatures to form aggreagates.[22-24] As salt is added, the headgroup area (a_0) decreases, whereas the hydrocarbon volume (V) to hydrocarbon chain length (l_c) ratio remains constant, causing an increase in the packing parameter (PP = $V/ a_0 + l_c$) and hence changing the micelle size/structure[17, 24]. The characteristics of the counterion- its size/ shape and ionic strength and its concentration all impacts micelle formation and growth.[17, 18] Many studies have shown that the transition from spherical micelles (just above the CMC) to rod-like micelles is dependent on temperature, surfactant concentration and salt concentration.[15, 17, 25, 26] A number of studies involving SDS have reported that the addition of sodium chloride (NaCl) between 0.4-0.5M induces rapid micellar growth near ~70mM surfactant concentration at 40°C, suggesting this to be the point of transition.[15, 23, 27, 28]

Considerable work has been carried out trying to understand the phase behaviour of surfactants including SDS, an anionic surfactant and the effect of these various factors previously mentioned[9, 12, 17, 18, 29-33] however, limited work has been done so far to understand completely the effect of electrolytes and organic solvents on the Krafft point and solubility boundary, i.e. the transformation of hydrated crystals into micelles and vice versa. This investigation is an essential step towards determining the effect of glycerol and sodium chloride (NaCl) on the precipitation or solubility boundary of SDS in water. The focus of this article is on the effect of glycerol and NaCl on the CMC and T_K of SDS in water using the surface tension, pendant drop based method. These findings will facilitate future investigations in studying the precipitation of surfactants in more complex formulations. Glycerol was chosen as a cosolvent as it is the most widely used organic solvent across many applications (cosmetics, pharmaceuticals, detergents) as it is water soluble, non-hazardous and a clear viscous liquid.[11, 34] Previous studies have looked at the effect of glycerol and other polar solvents such as ethylene glycol and formamide on SDS micellization[7, 12, 13, 34-36] however, either the concentration range of these polar solvents and in particular for glycerol is limited (up to 60%) or the SDS concentration range is restricted. Again many studies have been carried looking at the effect of electrolytes and in particular NaCl on SDS micellization and aggregation,[17, 18, 22, 25, 35] but these studies mostly use conductivity method, therefore using the pendant drop method to determine CMC and T_K of SDS is novel.

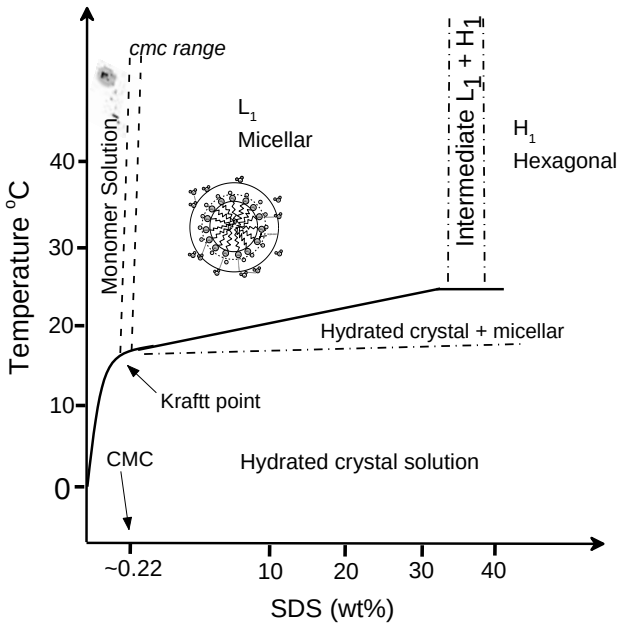


Fig. 1 Schematic Phase diagram of SDS/water, showing the different phases at low temperature and low surfactant concentration, with the solubility boundary and Krafft point- (adapted from Hamley I.W, 2007 p.210).

The solubility boundary of SDS in water in a wide range of SDS concentration is well established.[6, 14, 37] In water, SDS is mostly in a hydrated crystalline phase (C) at temperatures below 16°C. At low SDS concentration, less than 30%, as the temperature approaches 16°C, the SDS hydrated crystals transition into micellar phase (L1).[3, 37] An adapted schematic phase diagram of SDS in water is shown in Figure 1, with the solid curve representing the solubility boundary (15-17°C) and showing the main transition points/ phases which can be effected by organic solvents and electrolytes. The CMC- surfactant concentration (narrow) range at which micelles begin to form, and the T_K - the temperature above which the micelles form for SDS is well established of SDS in water to be between 6.9mM to 8.3mM and 16-17°C respectively.[3, 6] The CMCs of surfactants are important to determine as they hugely influence the composition of surfactant containing formulations. The T_K is an important parameter as below this temperature the surfactant is not fully soluble and remains in a

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hydrated crystalline form.[6, 20] Therefore this temperature is critical for the surfactant/ surfactant solution to carry out its properties e.g. emulsification and foaming. For ionic surfactants micellization is thermodynamically favoured above the T_K where the surfactant becomes fully soluble.[20, 21] The critical solubility point at which the CMC curves and T_K intersect is known as the krafft point.[6, 19] Determining the effect of glycerol on the krafft point would not only benefit achieving the desired activity of SDS in organic solvents, but also allow us to map out the SDS phase boundary in various water-glycerol mixtures.

Surface tension was measured to determine the CMC and T_K of SDS in the various water-glycerol mixtures and NaCl solutions. This was done using the pendant drop method. The method involves suspending a fluid droplet from a blunt needle in air, allowing the droplet to be deformed by gravity, forming a pendant drop.[38] An image of the droplet is acquired and through a computational method the Young-Laplace equation (equation 2) is fitted to the imaged droplet shape. This determines the interfacial tension between the fluid and air based on the droplet shape/curvature (radius), taking into account the gravitational pull, fluid density, drop size and viscosity.[38-40]

Surface tension analysis and in particular the pendant drop method was used rather than other techniques to determine the CMC, as high levels of glycerol were employed. Reportedly, CMC determination in high glycerol mixtures has proven difficult, e.g. when using conductivity method, due to the high viscosity and poor conductivity of glycerol mixtures.[7]

Experimental Section

Materials

Sodium dodecyl sulfate (99%), glycerol (>99.5%) and sodium chloride (>99%) were purchased from Sigma Aldrich and used as received, since analytical grades. Solutions were prepared by mass. Purity of the SDS sample was tested by determining its CMC in water using surface tension measurements, and corroborated with published CMC values.

Methods

Surface tension measurement - Surface tension analysis was carried out using the pendant drop method 38 by Krüss EasyDrop Standard- Drop Shape Analysis (DSA1) v 1.92. This instrument has a sensitivity of ± 0.1 mN/m.

Procedure - 1% SDS Stock solutions were prepared for all the solvent mixtures, which were diluted down to the required level. All samples were tested 2 hours after being prepared. A drop of the solution was dispensed under gravity using a blunt end metal needle and the drop image acquired using a digital camera after allowing the droplet profile to equilibrate for 5 seconds. DSA1 v1.92 software was used, to fit the Young-Laplace equation[38] (1) to the drop shape

$$\Delta P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (1)$$

where ΔP is the pressure difference across the interface, r_1 and r_2 are the principal radii of curvature, the yielding γ is surface tension. The experiment was performed at 23 ±1 °C and an average of ten drops was taken for each solution. Drop volumes were kept within 0.5µl for each set of mixtures. DI water (Milli-Q) was used for calibration.

Krafft temperature measurement- The T_K was determined using the surface tension analysis as explained above, over a range of temperatures using a glass cuvette chamber SC30. The pendant drop was suspended inside a hollow cuvette and temperature was controlled using a water bath. The temperature was measured with a precision of ±0.1°C and the measurements were carried out in 1°C increments.

Procedure - All samples were prepared and stored below 4°C and used within 48 hours. The SDS concentration for each mixture was taken from the CMC determined in the experiment above. The temperature of the bulk sample was kept at the required measurement temperature before being taken for the surface tension analysis. Each drop was suspended in the cuvette for 5mins to equilibrate the temperature and the droplet profile. 10 measurements were carried out for each sample and the surface tension was determined using the procedure mentioned above. The TK was taken as the temperature where the surface tension vs temperature curve showed a significant change in the slope.

Results and discussion

Surface tension analysis and CMC determination

All CMCs were determined from the surface tension measurements using the point of intersection method, where the surface tension was plotted against surfactant concentration and the curve above and below the CMC are extrapolated. This method has proven to determine the CMC with good accuracy.[41]

The CMC value determined for SDS in water was 8.0± 0.17mM (0.23% SDS) which is within the widely reported CMC range of 6.9-8.3mM.[6, 42, 43] This data also acted as a method validation as the surface tension and CMC values obtained from these methods were in good agreement with published values.[42] To determine the CMC, Figure 2a shows the change in surface tension as a function of SDS concentration in various water-glycerol mixtures (0-100% glycerol). In the absence of SDS, as the glycerol level is increased in the water-glycerol mixtures, the surface tension is also decreased.

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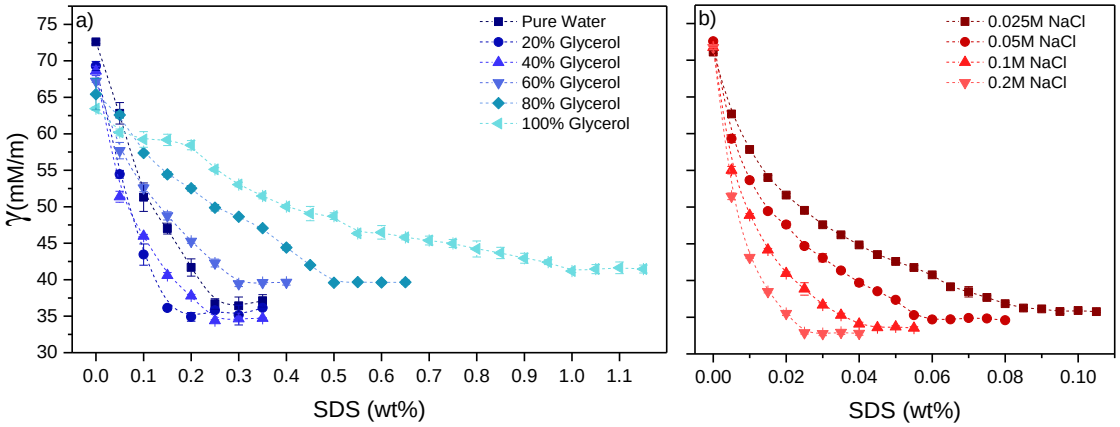


Fig. 2- Surface tension of SDS aqueous solution as a function of SDS concentration at 23°C in (a) 0 to 100% glycerol (b) NaCl solutions.

This is because pure glycerol has a surface tension of ~63.4 mN/m at 20°C and DI water is ~72.7 mN/m. The change in surface tension for SDS in NaCl solutions is shown in figure 2d. In these plots the change in the minimal surface tension across various water-glycerol mixtures and NaCl solutions can be seen clearly.

Effect of glycerol – Figure 3a shows the CMC values obtained here along with literature CMC values using different methods. To our knowledge, the CMC of SDS has not been previously determined in more than 60% glycerol. From our study it can be seen that the CMC initially decreases slightly and reaches a minimum at 20% glycerol, after which it starts to increase back to the original CMC ~8.0mM between 40% and 50% glycerol. Beyond 50% glycerol the CMC increases dramatically reaching ~34.7mM SDS concentration at 100% glycerol. The same trend was observed, in up to 50% glycerol, by Dai and Tam using an isothermal titration calorimetric (ITC) method.[8] Conductivity has also been used to determine the CMC of SDS in up to 60% glycerol.[7] However this conductivity method did not observe a minimum in the CMC at 20% glycerol, but rather a more plateau response and saw an increase after 20% to 60% glycerol. The data from both of these studies are also plotted in figure 3a. The ITC method is in very good agreement with our surface tension analysis, whereas the conductivity methods reported slightly higher CMC values, but a similar trend overall.

The initial drop in CMC in up to 20% glycerol can be explained by the effect that solvent polarity has on micellization previously mentioned. As a small level of glycerol is added to water, the cohesive energy and dielectric constant remain fairly high and the solvent polarity is hardly changed.[11] However due to glycerol containing three OH groups, it forms strong hydrogen bonded networks with water molecules and the SO_4^- headgroups, therefore the electrostatic repulsion between the headgroups is reduced, favoring micellization hence CMC decreases.[7, 8] As the glycerol content is increased further (over 20%), the water structure is disrupted, the cohesive energy and dielectric constant are reduced, decreasing the solvent polarity.[8, 10] It has also been reported that the hydrogen bonding ability of water molecules weakens with increasing glycerol content[44]. This causes the solubility of the hydrophobic tails to increase slightly and the electrostatic repulsion between the headgroups is also increased, which opposes micellization and the CMC increases.[6-8, 34] At high levels of glycerol (70-100%), small amounts of water is dissolved into the glycerol and the solvent polarity is significantly reduced from 78.5 in DI water to 40.1 in pure glycerol at 25°C.[11] The hydrocarbon tails become more soluble and as the dielectric constant is lowered further the headgroup repulsion effect becomes significantly high, therefore a higher concentration of SDS is required to form micelles.[7, 8, 12]

This behaviour is supported by a previous study, where the effect of another similar organic solvent on the CMC of SDS was investigated, showing the same trend.[35] Up to 80% ethylene glycol was used and the CMC was measured using surface tension and conductivity. Both methods gave very similar results, with a small decrease in CMC from 0 to 20% ethylene glycol, after which the CMC increased dramatically up to ~70mM SDS concentration at 80% ethylene glycol. The greater increase in CMC of SDS in ethylene glycol compared to glycerol can be explained by the differences in dielectric constant, hydrogen bonding ability and viscosity of the two solvents.[8, 11] Ethylene glycol is less polar and less viscous than glycerol, therefore it opposes micellization more. Also ethylene glycol contains two OH groups compared to three OH groups in glycerol, therefore the hydrogen bonded network is weaker in ethylene glycol in comparison and hence the electrostatic repulsion effect is much higher, opposing micellization.

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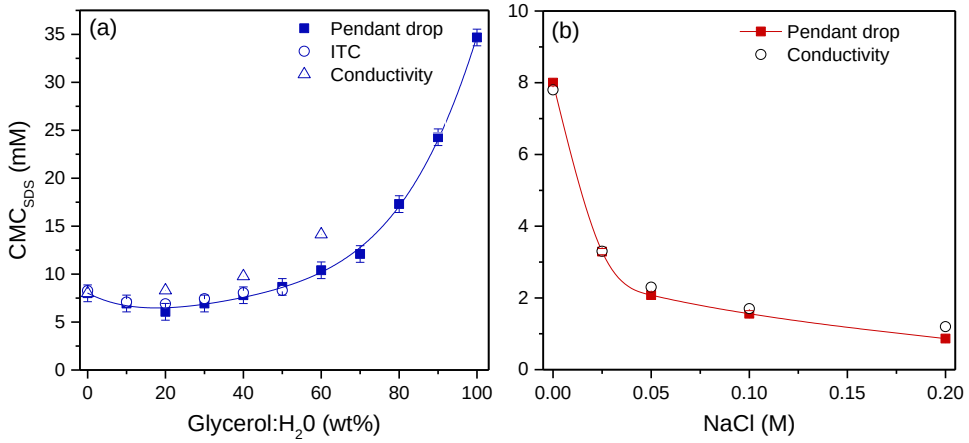


Fig. 3 (a) Effect of glycerol on the CMC of SDS, in water-glycerol mixtures, comparing (■) experimental data at 23°C (pendant drop method) with published values (○) ITC method[8] and (△) Conductivity method[7] at 25°C. (b) Effect of salt on the CMC of SDS in water, comparing (■) experimental data at 23°C (pendant drop method) with published values (○) Conductivity method[17] at 25°C.

Effect of NaCl - A lot of work has been done looking at the effect of salt on SDS aggregation and CMC and it is well established that salts such as NaCl decreases the CMC of SDS in water whilst the aggregation number is increased.[4, 14, 17, 18, 45] Our surface tension measurements and CMC determination for the effect of NaCl on SDS confirmed these findings and further validates our method. Increasing the salt concentration seems to lower the minimum surface tension value slightly for SDS in water as shown in figure 2b. Minimum surface tension for SDS in a 0.025M NaCl solution is ~35.7 ± 0.1 mN/m, whereas for a 0.2M NaCl solution its ~32.8 ± 0.2 mN/m. The low surface tension observed as the NaCl concentration is increased is due to the alteration in the surface layer as more counterions (Na^+) are present and more surfactant molecules are packed at the interface- the Stern layer.[14]

The CMC was determined for all four solutions as shown in Figure 3b. Adding small amounts of NaCl reduces the CMC drastically and increasing the NaCl concentration further decreases the CMC to very low SDS concentration ~0.7mM in a 0.2M NaCl solution. Figure 3b also compares the CMC values obtained from our surface tension- pendent drop method to CMC values from the literature determined using the conductivity method.[17] Both the methods are in very good agreement with each other. As previously explained, reduction in the CMC of SDS in water, on the addition of NaCl is due to the decrease in the repulsion effect between the polar headgroups favouring SDS micellization.[14, 17] The Na^+ counterion from the salt interacts with the SO_4^- headgroup in the stern layer and reduces the electrostatic repulsion between them and therefore a lower SDS concentration is required to form micelles.

Determining Krafft temperature

The T_K were also determined using the point of intersection method, where the surface tension was plotted as a function of temperature and the curve above and below the point of gradient change are extrapolated, shown in Figure 4. The x value at the point of intersection was taken was the T_K. The SDS concentration used for each mixture differed as it was taken from the CMCs determined above.

As the temperature is increased, the surface tension of water and organic solvent is decreased due to the thermal energy lowering the cohesive forces[46]. However the drop in surface tension is very gradual for these solvents. For a temperature increase from 20 to 50°C, surface tension of pure water and 99% glycerol decreases from ~72 to ~68 mN/m[46] and from ~62 to ~61 mN/m[11] respectively. Therefore the change in the surface tension of these mixtures (at their particular CMCs) is due to the SDS aggregation behaviour as a function of temperature.

Effect of Glycerol - Figure 5 shows that glycerol has a similar effect on T_K as it did for the CMCs. As the glycerol content is increased up to 30%, there is no significant change in the T_K range determined. Beyond 40% glycerol, there is a steady linear increase in T_K up to 100% glycerol from 18 to 31 ±0.5°C. Figure 6a shows a schematic of SDS micellization in high water-low glycerol content, where the water structure is not disrupted and solvent polarity has not changed significantly. This illustrates how the CMC and T_K remain fairly consistent at low glycerol levels. As discussed above, adding glycerol to water beyond 30% starts to decrease the solvent polarity, reducing the cohesive energy and dielectric constant, opposing micellization of SDS.

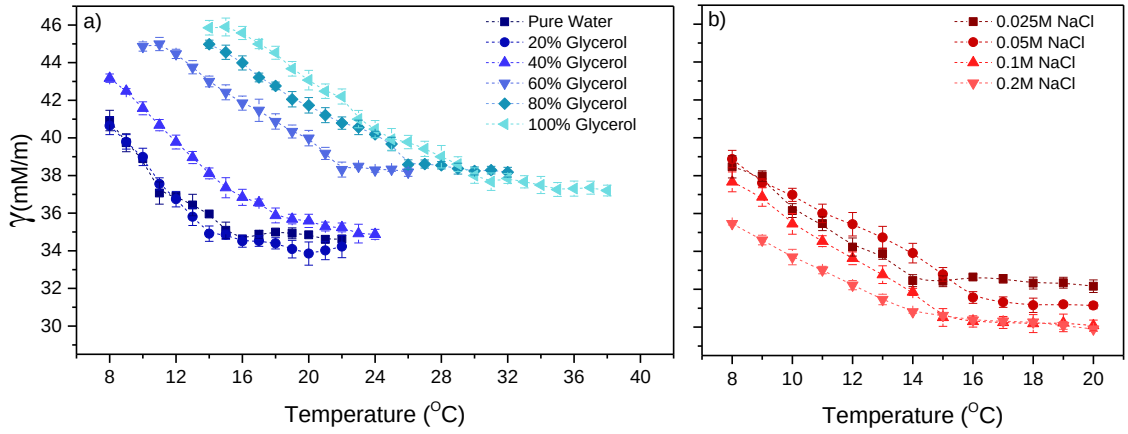


Fig. 4 Surface tension of SDS aqueous solution as a function of temperature at specific CMCs for (a) 0 to 100% glycerol (b) NaCl solutions.

At high glycerol levels, the hydrocarbon tails become more soluble and the electrostatic headgroup repulsion is increased, therefore it is thermodynamically more favourable that the SDS monomers to not aggregate. Therefore, for SDS concentrations at the CMC or just above, higher temperatures are required to thermodynamically favour micelles to form. Increasing the temperature does cause the solvent polarity to decrease, hence opposing micellization, however with increasing glycerol levels, the CMC is also increasing leading to larger ionic strengths, requiring higher temperatures to form micelles.[13] The higher temperature has a more dominating effect on the ionic interaction between the headgroups by weakening the hydrogen bonds and reducing the repulsion effect, hence favouring micellization over decreasing solvent polarity. This SDS micellization in high levels of glycerol is illustrated in figure 6b.

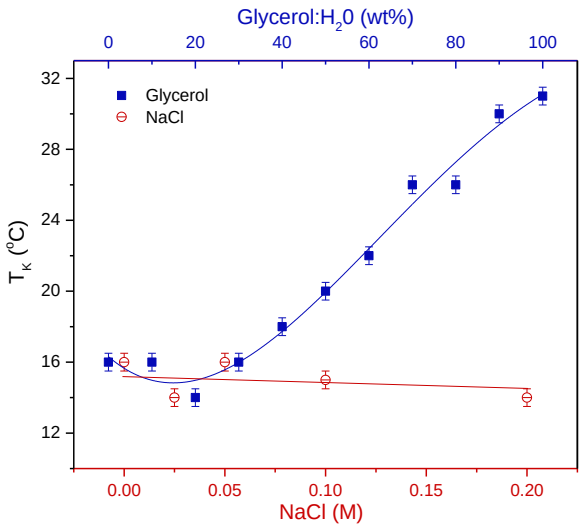


Fig. 5 Effect of glycerol and NaCl on the T_K of SDS, as a function of glycerol concentration (%) top x-axis and NaCl (M) bottom x-axis respectively.

Effect of NaCl - The addition of NaCl does not seem to have any significant effect on the T_K of SDS as shown in Fig 5. The T_K remains ~14-16 ±0.5°C as up to 0.2M salt is added, using the pendant drop method. A previous study, using the conductivity method, showed that the T_K of SDS increased slightly from 14.36 to 16.25°C as the level of NaCl was increased from 0 to 0.02M.[21] Although this was carried out at a constant SDS concentration of 0.25M, the results are in good agreement with the temperature range determined from our pendant drop method. The conductivity method seems to give more sensitive T_K readings, whereas in the pendant drop method the changes in surface tension over temperature are very gradual, therefore to determine the T_K, the temperature change needs to be reasonability significant (~2°C). However, both these studies show that the addition of NaCl does not have a significant effect on the T_K at low SDS concentrations (below and around the CMC). An explanation for this is that as the concentration of counterions is increased, the repulsion between the headgroups is reduced, promoting micellization and therefore requiring less thermal energy. However, as explained previously, addition of NaCl increases the packing parameters of SDS and produces larger micelles, requiring slightly higher temperatures to allow micellization with increasing SDS and NaCl concentrations. These two effects of NaCl act together, as illustrated in figure 6c, causing the CMC to decrease whereas the T_K remains fairly consistent around 14-16°C at low SDS concentration.

Pendant Drop Method

The pendant drop method has proven to be extremely valuable for determining the complete effect of glycerol on the CMC, as the traditional conductivity analysis used has been unsuccessful due to the poor conductivity of high levels of glycerol.[7] Even determining CMCs of SDS in NaCl solutions, the pendant drop method was shown to be robust and allowed for a fairly high throughput.

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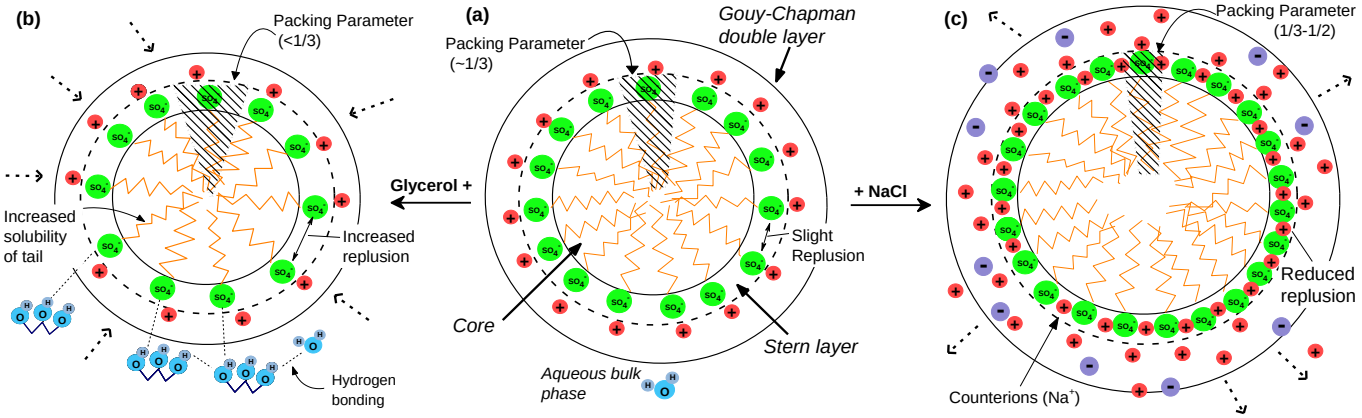


Fig. 6 Schematic showing the SDS micelles in (a) high water- low glycerol content (b) high glycerol level and (c) NaCl solutions.

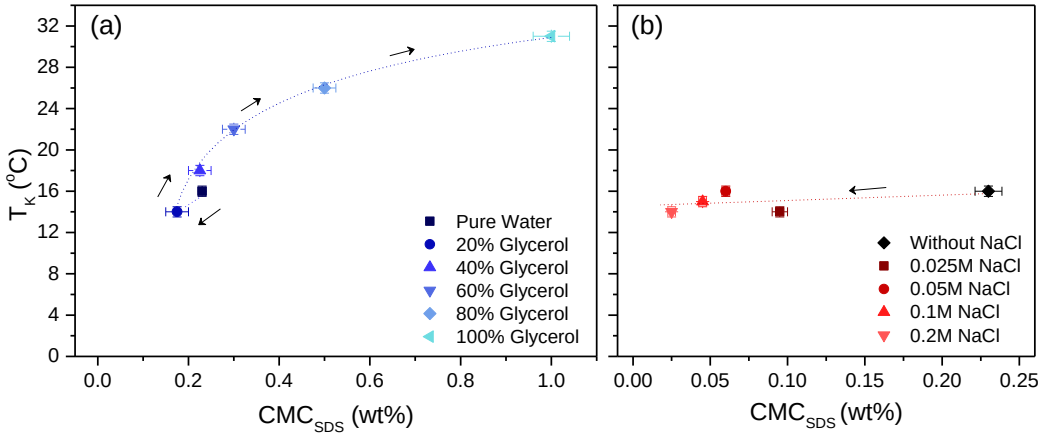


Fig. 7 Effect on the Krafft point of SDS in the presence of (a) Glycerol (b) NaCl solutions.

However the determination of T_K using this method was not as efficient/precise as expected. This is mostly due to the effect of temperature on the surface tension of water and other organic solvents, as surface tension is not as responsive to change in temperature as conductivity. Pendant drop analysis was carried out on pure water and glycerol looking at the effect of temperature. There is a very gradual decrease in surface tension of both water and glycerol as the temperature is increased. A significant change in temperature of ~3°C is required to see a noticeable decrease in the surface tension. Therefore the T_K precision for this method is not as good as the conductivity method. However, this pendant drop method still proves to be more effective at studying the effect of glycerol on T_K compared to the conductivity method, although some direct experimental comparison is yet to be done.

Krafft Point

The main purpose of this study was to determine the overall effect of glycerol and NaCl on the SDS phase diagram, particularly at low concentrations. The robust CMC data and the satisfactory T_K data produced from the pendant drop method can both be used together to adeptly show how the Krafft point is affected under these conditions and how the phase diagram may shift. Fig 7a shows the change in Krafft point on the SDS phase diagram as glycerol levels are increased. The Krafft point shifts upwards towards higher T_K and towards higher CMCs with increasing glycerol content. This suggest that the SDS solubility boundary would also shift upwards and the SDS phase transitions/boundary are likely to shift towards the right (higher SDS concentration) as glycerol level is increased. With the addition of NaCl, the Krafft point mainly shifted towards lower SDS concentration but there was no change across the temperature as shown in Fig 7b. This supports previous studies where the addition of NaCl is shown to have no significant effect on the solubility boundary of SDS but shifts the various surfactant phases towards low SDS concentration.[17, 18, 22]

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Conclusions

The micellization behaviour of SDS in various water-glycerol mixtures and NaCl solutions has been investigated using the pendant drop- surface tension analysis. This method proved very efficient for CMC determination and particularly for studying the effect of glycerol on CMC and T_K as glycerol is not well suited to the common conductivity methods. The observations from the CMCs and T_K measurements determined in this investigation can be combined together to examine the effect of organic solvent and ionic strength on the phase behaviour of SDS micelles. It was observed that increasing glycerol content made micellization of SDS less favourable. The CMCs determined through surface tension analysis showed an exponential increase as the level of glycerol was increased beyond 40%. With regards to the solubility boundary, determined through T_K, a gradual linear increase in temperature was seen on the addition of glycerol, after 30%. At high glycerol content, the solvent polarity and cohesive energy are reduced and the water structure is disrupted significantly. This causes the solubility of the hydrophobic tails and the electrostatic repulsion between the headgroups, both to increase, therefore opposing micellization, making the SDS less soluble in glycerol. At low glycerol content (<20%) the solvent properties are not changed significantly therefore SDS micellization occurs similar to as it does in pure water. Hence the Krafft point/solubility boundary of SDS with increasing glycerol levels are shifted towards higher temperatures and higher SDS concentrations on the phase diagram. This suggests that to induce the SDS phase transitions in glycerol, higher temperatures and SDS levels are required.

The effect of NaCl on the micellization behaviour of SDS is consistent with previous studies. The Na^+ counterion from the salt causes the electrostatic repulsion between the headgroups to reduce favouring micellization. Adding NaCl reduced the CMC drastically and we found the SDS concentration at CMC to be ~0.7mM in a 0.2M NaCl solution. As NaCl addition also induces micellar growth due to an increase in the packing parameter and requires higher temperatures for micellization to occur, but this is cancelled out by favourable micellization conditions keeping the T_K ~14-16°C. Therefore the Krafft point of SDS in NaCl only shifts to the left, indicating that the SDS phase transition in NaCl occurs at lower SDS concentrations. This paper determines the effect of NaCl on the CMCs and T_K of SDS using the pendant drop method for the first time, and has shown to produce comparable results. However, the conductivity method was determined to be more precise for T_K measurements, but a direct experimental comparison will be useful particularly involving organic solvents.

While the concentration of SDS studied here is around the CMCs, a variety of SDS concentration are used in both formulated products and research, therefore further investigation is required to determine the effect of glycerol and NaCl on the solubility boundary across a range of SDS concentrations. This will allow us to map out the SDS phase diagrams fully to better understand the effect of organic solvent and ionic strength on surfactant phase behaviour.

Acknowledgements

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