

Determination of CMC and interfacial properties of anionic (SDS) and cationic (CPB) surfactants in aqueous solutions

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ABSTRACT

The concentration at which a surfactant forms a micelle called the critical micelle concentration CMC. Therefore, micellar aggregates formation causes significant changes on surfactant physical properties, such as conductivity and surface tension. Here, the self-association and CMC of the anionic surfactant, sodium dodecyl sulfate (SDS), and the cationic surfactant, cetylpyridinium bromide (CPB) have been investigated. Electric conductivity and surface tension techniques have been employed to reveal the surfactant CMC in aqueous solutions. The measurements have been accomplished on a range of concentrations at different temperatures. Obtained data were used to evaluate several parameters, including maximum surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}), surface pressure at CMC (π_{cmc}) and critical packing parameter (CPP). As the temperature increases the onset micellization tends to take place at higher concentrations due to dehydration of surfactant hydrophilic head groups. Thus, the CMC for each surfactant increases with increasing the system temperature. Surface parameters Γ_{max} and A_{min} elucidate comparatively less availability of SDS molecules at the air-water interface, and CPB is more surface active than that of SDS.

KEYWORDS: Critical micelle concentration, maximum surface excess concentration, minimum area per molecule, surface pressure at CMC, critical packing parameter, SDS, CPB .

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I. INTRODUCTION

Surfactants are amphiphilic molecules with polar head groups, which could be cationic, anionic, nonionic and zwitterionic, and hydrophobic tails, that also likely to be hydrogenated or fluorinated, linear or branched. Particularly, anionic surfactants dissociate in water to form amphiphilic anion, and a cation. The cation generally is an alkaline metal (Na^+ , K^+) or a quaternary ammonium. In addition, anionic surfactants are the most commonly used in surface chemistry. For instance, salts of alkyl benzene sulfonic acid, fatty acids, lauryl sulphate, di-alkyl sulfosuccinate, lignosulfonates have been widely used in surfactant applications. One of the most common anionic surfactant is sodium dodecyl sulphate (SDS), ($\text{Na}^+ \text{OSO}_3 \text{C}_{12}\text{H}_{25}$) which is significantly used for their detergent properties. One end of the molecule is charged and therefore has affinity for water, and the other end is non-polar and soluble in fat/oil. However, cationic surfactants are dissociated in water into an amphiphilic cation and anion. This class mostly corresponds to nitrogen compounds such as fatty amine salt and quaternary ammoniums attached to one or several long chain of the alkyl group. The synthesis of such surfactants needs a high pressure hydrogenation reaction, which makes these surfactants are more expensive than anionic type. Moreover, the evaluation of the cationic surfactant properties is achieved in terms of studying critical micelle concentration, aggregation number, sphere-to-rod transition, and thermodynamic quantities. These properties are reflected from surfactant ions including various contributions of hydrophobic tail with hydrophilic group and from counter ion species.²

In a self-association process most surfactants aggregate to form liquid micellar structures. The structures usually are small, approximately spherical, highly dynamic compositions³. The process is highly dependent on the surfactant concentration. Beyond a specific concentration the micellization process takes place. This concentration is called the critical micelle concentration and denoted as CMC. The nature of the

surfactant self-association is studied through investigating the variation of the critical micelle concentration CMC against the chemical and physical parameters¹.

Contrastingly, the CMC values are usually determined from the sudden change of a physical property such as the surface tension, in a range of surfactant concentrations. However, different methods of studying the surfactant behaviour provide some differences in CMC values for the same surfactant. These methods include conductivity, surface tension, viscosity, density, light scattering...etc⁴. On the other hand, many factors affect the micellization process, one example is the molecular structure of the surfactant monomer, which is represented by the influences of the hydrophobic volume, head group area, and chain length. Other factors involve solvents, temperature, pressure, additive, ionic strength, and the presence of other co-solute^{1,5}.

Specifically, the micellization of ionic and amphoteric surfactants is influenced by temperature due to the change in the interaction between head groups and hydrophobic tails. For ionic surfactants, micellization is affected by temperature in two ways as hydrophobic tail and head group interactions change with temperature^{6,7}. Increasing the temperature causes dehydration of both hydrophilic and hydrophobic parts of the surfactant. These two dehydration processes work against each other. Accordingly, dehydration of hydrophilic parts resulting from increasing the temperature, causes repulsion between charged ionic head groups of surfactants and leads to increase the CMC. However, the dehydration of hydrophobic parts leads to support micellization because it causes disruption of the structured water surrounding the hydrophobic group. This participates in increasing the entropy of the system and decreasing the CMC. These two opposite effects define whether CMC increase or decrease over a specific temperature range⁸.

In addition, studying and enhancing interfacial properties of surfactants contribute in developing the surfactant applications such as in cleaning, surface functionalization, foaming and emulsification. Studying the surface pressure, which is a measure of the ability of the surfactant to reduce the surface tension in water, associates to understand the intermolecular forces between surfactant molecules at the interface. Moreover, it provides valuable information about how surfactants pack together⁹. Furthermore, the critical packing parameter hypothesis emphasizes the significance of the surfactant headgroup in anticipating the shape and size of equilibrium aggregates. Basically, micelles with packing parameters in the range of (0-0.33), (0.33-0.5) and (0.5-1) have spherical, cylindrical, and lamellar shapes respectively¹⁰.

Using different methods in order to study a surfactant, may permit to secure complementary and comparative outcomes. Usually, electrical conductivity and surface tension measurements are used for this purpose due to the simple procedure that both techniques have. This paper exemplifies using those techniques to study SDS as anionic surfactant and CPB as cationic surfactant individually in aqueous solutions. The study focuses on the determination of CMC values and measuring their surface parameters such as obtaining maximum surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}), surface pressure at CMC (π_{cmc}) and critical packing parameter (CPP).

II. EXPERIMENTAL METHODS

Sodium dodecyl sulfate SDS (Mol.wt 288.38 g/mol), and cetylpyridinium bromide (CPB) (402.47g/mol) were obtained from (BDH chemicals Ltd, England) with purity of 99%. Further purification has been accomplished by crystallizing both surfactants, SDS in ethanol and CPB in acetone. Next, CPB has been washed with diethylether and then dried. The conductivity of water, which was used as a solvent for all solutions, is $1.14 \times 10^{-6} \text{ Scm}^{-1}$ at 298.15K. To prepare a stock solution of SDS with a concentration of 50mM, 3.605g of SDS was dissolved in 250ml of distilled water. To prepare a stock solution of CPB with a concentration of 10mM, 0.4025g CPB was dissolved in 100ml of distilled water. Then magnetic stirring was carried out for 30 minutes before the use. The surfactant stock solution has been diluted to prepare a series of concentrations for each surfactant. SDS concentrations ranged from 0.05mM to 20mM, and the range of CPB concentrations were between 0.05mM to 1.6mM.

Conductivity measurements were carried out with a TDS conductivity meter (Jenway 4510,UK, having a cell constant (0.7475cm^{-1})). The conductivity cell and vessel used for the measurements were properly cleaned and the meter was standardized before use. The cell constant was determined by calibration with 0.1M of KCl solution. The conductivity of pure water as a solvent was subtracted from the conductometer value of the determined solution in each experiment. Final conductance value recorded is an average of at least 3 measurements. The uncertainty in the conductance measurements was within $\pm 0.5\%$.

The surface tension of all samples was measured using kruss tensiometer K6 (a large measuring range of 1 to 90 mN/m), DuNouys, Germany/ with platinum-iridium ring (diameter:18.7 mm, thickness: 0.37 mm). Temperature was controlled with water circulating system WBT12 (Wedingen, Germany) with an accuracy of $\pm 0.2\text{K}$. Final surface tension value recorded is an average of at least 3 measurements.

III. RESULTS AND DISCUSSIONS

The critical micelle concentration for SDS and CPB has been estimated for each surfactant individually via studying its electrical conductivity and surface tension over a range of concentrations. The surface tension measurements have also been carried out to evaluate the surface parameters of surfactants.

3.1. Conductivity measurements

The conductivity measurements have been employed on a range of SDS and CPB concentrations at different temperatures. The concentrations were selected to be above and below the literature CMCs for each surfactant.

The specific electrical conductivity has been calculated using equation 1¹¹ and then illustrated against the concentration for each surfactant.

$$\kappa_s = \left[\frac{1}{R_{soln}} - \frac{1}{R_{water}} \right] \frac{L}{A} \dots\dots\dots(1)$$

κ_s is the specific conductivity. $\frac{1}{R_{soln}}$ and $\frac{1}{R_{water}}$ are the conductance of the surfactant solution and water at a particular temperature respectively. L is length (cm), A is cross-sectional area (cm²), $\frac{L}{A}$ is the cell constant in cm⁻¹.

Figures 1 and 2 represent the specific electrical conductivity values of SDS and CPB solutions versus the concentrations at a range of temperatures (20°C - 45°C) respectively. It is well known that the conductivity of both premicellar and postmicellar regions is linearly correlated to the surfactant concentration¹². Based on Kohlrausch's Law of independent mobility of ions, ionic surfactants below CMC behave as strong electrolytes and dissociate completely into its ions^{13,14}. However, above CMC, the dissociation becomes weaker as micelles are partially ionized¹³. Accordingly, in figures 1 and 2, a linear increase of conductivity was observed with increasing the surfactant concentration for both surfactants up to the CMC. Further, the slope in the premicellar region is greater than that in the postmicellar region in both cases. The CMC values have been estimated from the intersection point of each curve, and are listed in table 1.

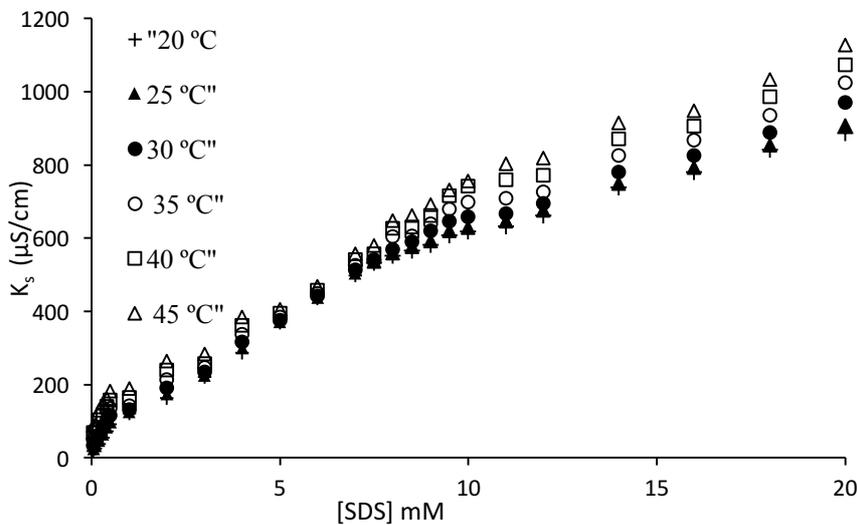


Figure 1. The variation of specific conductivity of SDS aqueous solutions with the concentration at different temperatures.

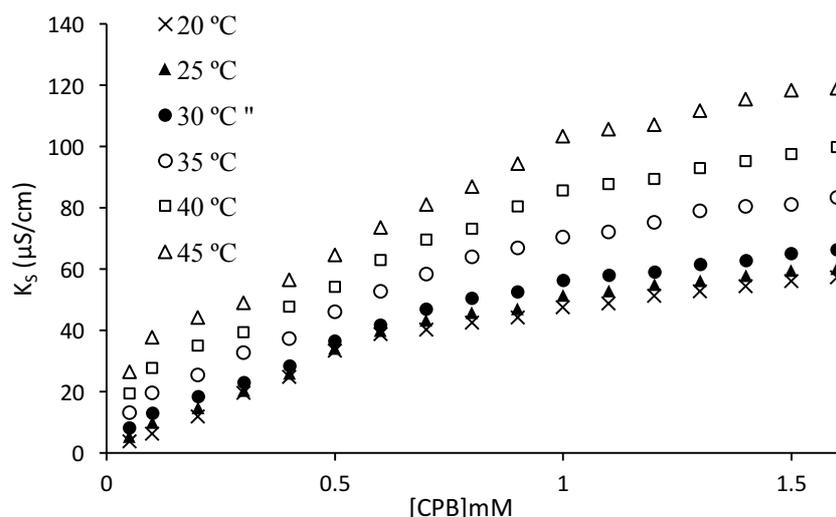


Figure 2. The variation of specific conductivity of CPB aqueous solutions with the concentration at different temperatures.

Determined CMC values using specific conductivity are listed in table 1. These values are in reasonable agreement with the literature. Comparing the two CMC values for SDS and CPB, it can be stated that the repulsive interactions of the pyridinium hydrophilic group in CPB are lower than those of the ionic head group in SDS¹⁵. This is resulting in the lower CMC value of CPB at different temperatures comparing to that in SDS solutions.

On the other hand, generally the conductivity of a solution increases with temperature, as the mobility of ions increases¹³. This is compatible with the outcomes of each surfactant in figures 1 and 2. Moreover, the CMC values of SDS have been considered in terms of changing the temperature. CPB surfactant has a similar pattern to that in SDS, so it is not pointed out here. Figure 3 shows the relationship between the CMC values, estimated by the conductivity, of SDS and the temperature. The observed increase of CMCs for SDS with increasing the temperature is strongly associated with the dehydration of surfactant ionic head groups (hydrophilic parts) which leads to a repulsion between these charged SDS groups. Accordingly, at higher temperatures the equilibrium between monomers and micelles in the solution is suggested to be shifted towards monomers^{16,17} which contributes to commence the micelle formation at higher concentrations⁸.

Table.1. The values of CMC/mM estimated from the electrical conductivity measurements of SDS and CPB in aqueous solutions at different temperatures.

Temp/ °C	20	25	30	35	40	45
SDS	7.70	7.90	8.50	9.00	9.70	10.0
Literature	8.14 ^{18,19,20}		9.12	9.26		
CPB	0.60	0.66	0.75	0.80	0.88	0.94
Literature	0.462 ^{21,22,23}		0.641 0.82 ²⁴ 0.78	0.735		

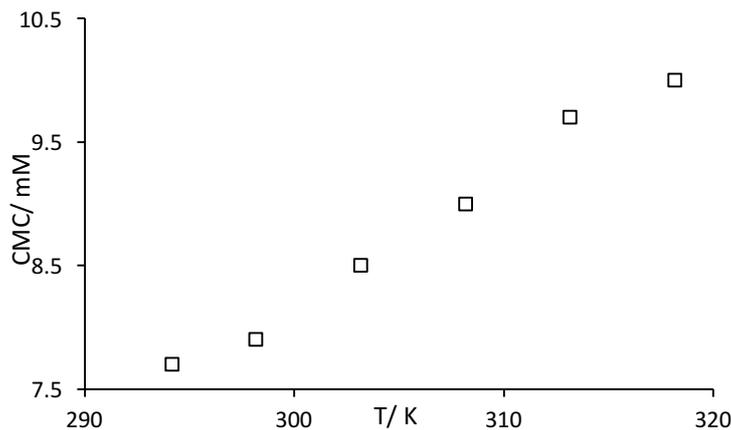


Figure 3. The variation of CMC values of SDS aqueous solutions with the temperatures.

3.2 Surface tension measurements

The variation of surface tension with the concentrations for SDS and CPB aqueous solutions is represented in figures 4 and 5 respectively. The measurements have been accomplished for only two different temperatures 20 °C and 30 °C due to lack of ability of equipping measurements at other studied temperatures. It is clearly that the surface tension sharply decreases with increasing the surfactant concentration for each surfactant up to the CMC beyond which no considerable change was noticed. Micelle formation is denoted by the breaking points which were used to obtain CMC data. That could be explained by the basics of the surface chemistry, which indicates that the surfactant adsorption is sustained until the surface becomes saturated with the surfactant molecules. Subsequently any addition of the surfactant has no influence on the surface tension. Thus, at this point the solution physical properties distinctly change with the variation of the concentration.

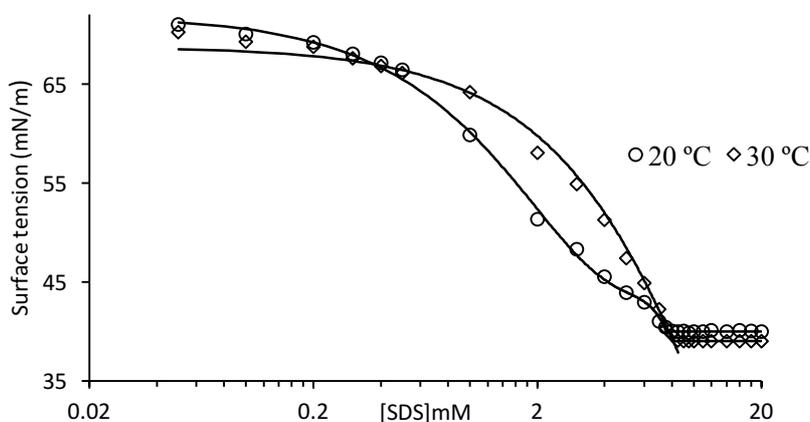


Figure 4. The variation of surface tension of SDS aqueous solutions with the concentration at different temperatures.

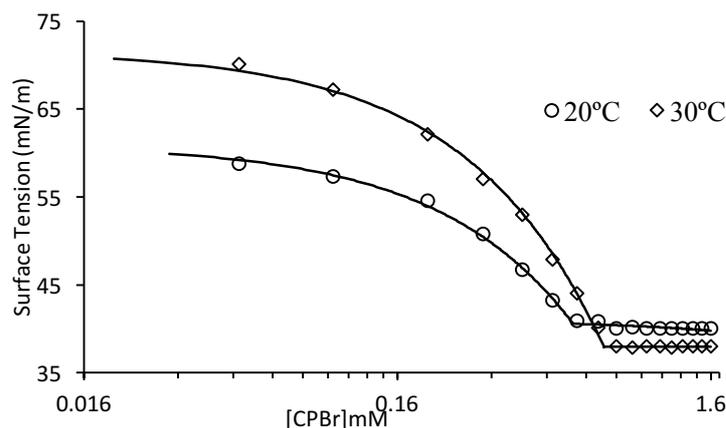


Figure 5. The variation of surface tension of CPB aqueous solutions with the concentration at different temperatures.

The values of CMCs determined by surface tension measurements at two different temperatures (20°C & 30°C) have also been listed in table 2. In spite of the difficulty to find the relationship between the method of CMC determination and its value, CMCs in table 2 are in a good agreement with the CMCs obtained by conductivity method (table 1.)

Over and above that, some interfacial properties of SDS and CPB in aqueous solutions at 20°C and 30°C have been obtained using the surface tension data. The calculations include, maximum surface excess concentration (Γ_{max}), minimum area per molecule (A_{min} /molecule), surface tension at CMC (γ_{cmc}), surface pressure at CMC (Π_{cmc}), and critical packing parameter (CPP) as shown in table 2.

Table 2. Values of the CMC, maximum surface excess concentration, minimum area per molecule, surface tension at CMC, surface pressure at CMC, and packing parameter at 20°C and 30°C for SDS and CPB.

Tempe./°C	CMC/mM γ	$\Gamma_{max} \times 10^6$ mol/ m ²	A_{min} /molecule nm ²	γ_{cmc} mN m ⁻¹	Π_{cmc} mN m ⁻¹	CPP
SDS						
20	7.50	1.95	0.85	40.2	32.0	0.25
30	8.30	2.42	0.69	39.0	33.4	0.31
Literature ²⁵	8.13	2.13	0.78	-	40.9	0.26
CPB						
20	0.58	2.60	0.64	39.9	32.5	0.33
30	0.73	3.57	0.47	37.9	34.7	0.45
Literature ²⁶	0.575	-	0.55	-	-	-
Literature ²	0.8	-	0.41	34.8	-	-

3.3. Maximum surface excess concentration (Γ_{max})

The slope of the plot (γ versus \ln concentration) can be used as a measure of interfacial adsorption efficiency of surfactant, which is denoted by the term of maximum surface excess concentration per unit area

(Γ_{max}). Equation²⁵ 2 has been used for this purpose at 20 °C and 30 °C for both surfactants and obtained data is listed in table 2.

$$\Gamma_{max} = - \frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \ln C} \right) \dots\dots\dots (2)$$

Where, n is the number of adsorbed species at air/solution interface (for ionic surfactants, $n = 2$), $(\partial \gamma / \partial \ln C)$ is the slope of the straight line in the surface tension plot below CMC, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature in absolute scale.

In each surfactant, the trend for changes in the Γ_{max} values is the same as that observed for the CMC changes with temperature. Higher CMC and Γ_{max} values are related to the higher temperature. It is also clear that the higher Γ_{max} values the higher surface activity, thus CPB is more surface active than that of SDS.

3.4. Surface area per molecule (A_{min} , $\text{nm}^2/\text{molecule}$)

The degree of packing and orientation of the adsorbed surfactant molecule compared with its dimensions is usually elucidated by the evaluation of minimum area per molecule at the interface²⁷. Further, Γ_{max} values have been used to calculate the minimum surface area per surfactant molecule at air/water interface, using equation²⁸ 3.

$$A_{min} = \frac{10^{18}}{N_A \Gamma_{max}} \dots\dots\dots (3)$$

Where Γ_{max} (mol m^{-2}) is the surface excess concentration and N_A is the Avogadro's number.

The obtained data for SDS and CPB at 20 °C and 30 °C is listed in table 2. It is clearly that CPB has less A_{min} , implying greater number of CPB monomers at the interface. Since the area per molecule at the interface is fundamentally influenced by the size of head group, it can also be anticipated that a larger area per molecule is attached to the anionic surfactant SDS comparing to CPB at each temperature.

3.5. Surface pressure at CMC (π_{cmc})

Various types of interactions including van der Waals forces, hydrogen bonding, adsorbate-adsorbent interactions and electrostatic interactions, contribute in the surfactant adsorption at the interface. This effectively influences the surface pressure value of a surfactant²⁷. Surface pressure at CMC (π_{cmc}) for SDS and CPB has been estimated using equation²⁷ 4.

$$\pi_{cmc} = \gamma_{water} - \gamma_{cmc} \dots\dots\dots (4)$$

γ_{water} is the surface tension of water (solvent) and γ_{cmc} is the surface tension of surfactant solution at CMC.

3.6. Critical packing parameter (CPP)

The shape of micelles for SDS and CPB has been investigated by studying the critical packing parameter using equation^{29,30} 5. Spherical micelles are predictable when $CPP < 1/3$ ³⁰.

$$CPP = \frac{V}{l_c A_{min}} \dots\dots\dots (5)$$

Where V is the volume of the hydrophobic tail, A_{min} is the area of the area per head group at the air/solution interface., and l_c is the maximum chain length (hydrophobic tail). According to:

$$V = 0.0274 + 0.0269n \dots\dots\dots (6)$$

$$l_c = 0.150 + 0.1265n \dots\dots\dots (7)$$

Where n is the total number of carbon atoms of the hydrophobic tail of the surfactant, V is in cubic nanometer (nm^3) and l_c is in (nm).

The values of packing parameter of SDS and CPB are included in table 2. From the obtained data, SDS micelles are spherical in both temperatures, which is consistent to the literature. Packing parameter for both surfactants increases with increasing the temperature. In SDS, the increase does not affect the shape of the micelle since both values are in the range of spherical structures. In contrast, it is not known whether this increase influences the shape of the CPB micelles based on a temperature change. To conclude, CPB micelles

have different shape from SDS spherical micelles, and more investigations related to the structure of CPB micelles are required.

IV. CONCLUSION

The CMC and interfacial properties of the ionic surfactant SDS and cationic surfactant CPB in aqueous solutions have been investigated by means of conductance and surface tension measurements. The conductivity study has carried out at a range of temperatures, whereas the surface tension technique has been utilized at only 20 °C and 30 °C. The CMCs obtained by both techniques were compatible and consistent to the literature. Surface tension outcomes have been used to investigate many parameters such as the maximum surface excess concentration which has been used further to calculate the minimum surface area per molecule. Other calculated parameters include the surface pressure at the CMC and critical packing parameters which are responsible for understanding the intermolecular forces between surfactant molecules near to the CMC. Furthermore, the micelle shape and size is significantly estimated by investigating the surfactant packing parameter. Collected data for SDS elucidates that obtained interfacial parameters are in agreement with the literature and SDS micelles are spherical as predicted. This was motivating for our team to continue and investigate the thermodynamics of surfactant adsorption at air-water interface, which will be published soon. However, due to lack of sources, some important questions regarding CPB micellar structure and micelle shape and size, were not yet answered. The obtained CPB data indicates that its necessary to do further measurements in order to emphasize what were found here so far, and estimate more information about its micellization process.

Credit author statement

Fatima M .Elarbi :Conceptualization, methodology and data analysis .Zaineb O. Ettarhouni :* Conceptualization ,methodology ,analysis of data, writing - original draft, writing - reviewing and editing . Abdulhakim A .Janger /Methodology .Laila M. Abu-sen /Methodology.

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