

Formulation of Critical Micellar Concentration of Non- Phosphate Detergents by Surface Tension Measurement

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ABSTRACT

Non-phosphate builders which are environmentally friendly are required for use in detergent formulation to replace the sodium tri-poly phosphate (STPP). Phosphates are excellent fertilizer for algae, bacteria, and other flora and fauna in rivers, lakes and oceans, making them bloom at very rapid rates. This exhausts the oxygen supply both in the surface and in the bottom layers of water bodies, and leading the death of fishes. Sodium metasilicate a non-phosphate builder from Lokoja Quartzite was used to formulate a non-phosphate biodegradable synthetic detergent using 25%, 50% and 75% sodium hydroxide concentrations. The critical micellar concentration (CMC) of a non-phosphate detergent was determined via measurement of surface tension. This method is rapid, reliable and cheap compared to the fluorescence polarization method which required a sophisticated materials such as 1,6-diphenyl-1,3,5-hexatriene as fluorescence probe. The detergents formulated with 75% and 50% sodium hydroxide concentrations have CMC values of 8.6685 mM and 6.9348 mM respectively. From this study, a non phosphate builder synthesized from Lokoja Quartzite has potential of protecting aquatic animals when compared with the conventional STPP currently used in our detergent formulation. Also, the simple and economical approach for determination of detergent's CMC has demonstrated its potentials. These values agree well with the literature value ranges between 7 to 10 mM.

Keywords: Detergent; CMC; Surfactants; Non-phosphate; 1,6-diphenyl-1,3,5-hexatriene

INTRODUCTION

A detergent is a surfactant or a mixture of surfactants having cleaning property in dilute solutions. Detergent, when dissolved in water, gives it the ability to remove dirt from surfaces such as the human skin, textiles and other solids (Yunusa et al., 2009a). Detergents are commonly available as powders or concentrated solutions (Keshwani et al., 2015). They are classified into three groups namely Anionic, Cationic and Non-anionic or zwitterionic detergents, depending on the electrical charge of the surfactants (Yangxin et al., 2008).

The most important property of a detergent is its critical micellar concentration (CMC) (Tschapek et al., 2015). CMC can be defined as the concentration of the detergent in a given solvent at or above which detergent molecules, cluster to form micelles (Gregory et al; 2002). Micelles are spherical groupings of 40 to 100 molecules in which all hydrophobic ends point toward the centre and all hydrophilic ends stick out in the surrounding water. Removal of dirt is facilitated by the ability of the detergent molecules to form these micelles (Gregory et al., 2002). Also, below this CMC, detergent

molecules are present as monomers and thus are not able to emulsify and solubilize oil and grease (dirt) (Campbell, 2008). Above the CMC the concentration of free (monomeric) detergent molecules does not further increase, because addition of more detergent results in the formation of micelles as illustrated in Figure 1 (Held, 2014).

Three of the most popular methods used to determine CMC are surface tension, light scattering and dye solubilization (Held, 2014). Surface tension decreases with the detergent concentration and reaches a minimum around the CMC value. Light scattering as well as the solubility of a hydrophobic dye increase with detergent concentration (Thomas et al., 2006). The points of inflection on a graph obtained by plotting any of the three parameters against the detergent concentration correspond to the CMC of the detergent (Held, 2014).

Detergent surfactant Sodium dodecyl sulfate (SDS), $\text{NaOSO-3C}_{12}\text{H}_{25}$ is known as amphiphilic surfactant because it possesses both hydrophobic and hydrophilic properties. When SDS is dissolved in distilled water it ionizes in the aqueous solution to form Na^+ and $\text{-OSO-3C}_{12}\text{H}_{25}$ ions and these ions exist as

solvated monomer instead of micelle due to low SDS concentration (Yangxin *et al.*, 2008). The number of monomers increases as the concentration of the detergent in the solution increases (Tschapek *et al.*, 2015). Self-dissociation of SDS into micelle is strongly cooperative and occurs at the defined concentration called critical micelle concentration (Gregory *et al.*, 2002). Below CMC, the amphiphile dissolves as monomers. Once the concentration is beyond CMC, the monomers concentration remains unchanged while the micelle concentration increases (Keshwani *et al.*, 2015)

Quartzite is a metamorphic rock consisting largely or entirely of quartz. Most quartzites are formed by metamorphism of sandstone. But some have developed by metasomatic introduction of quartz, often accompanied by

other chemical elements, for example, metals and sulphur (ore quartzite) (Gutti, 1999).

The geological relations and the shape of quartzite bodies serve to distinguish between them. The metasomatic quartzites are often found as contact products of intrusive bodies (Ibrahim, 1995).

The transition from sandstone to quartzite is gradational (Yunusa *et al.*, 2009a). All stages of relic elastic structures are encountered. Some sandstones are soon completely metamorphosed (Barth, 2012). Others are very resistant and in many highly metamorphic quartzite of the Precambrian, there are relic structures still to be observed (Gutti; 1999). Pure sandstone yields pure quartzite. Impure sandstone yields a variety of quartzite types (Gutti, 1999).

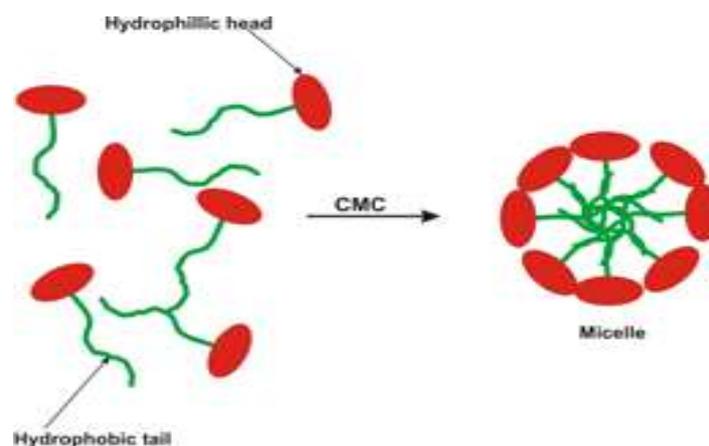


Figure 1: Schematic drawing of Micelle formation (Held, 2014).

MATERIALS AND METHODS

Materials

The Materials used included non-phosphate builder detergent prepared from Lokoja Quartzite, deionized water, the frame which consisted of a copper wire, cotton thread as shown in Figure 2a, with the upper thread and the wire labelled ABC and DEF with the shape indicated in Figure 2b, retort stand, ruler and a beaker.

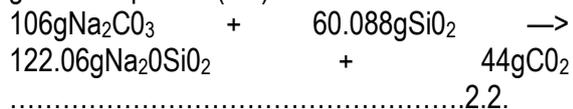
Preparation of a non-phosphate Builder from Lokoja Quartzite

Quartzites were collected from Zagon Daji, a locality of about five kilometers from Lokoja town in Kogi State, Nigeria. The raw quartzite were washed to remove the dust and other dirt on it. The washed quartzite were crushed into 37.5mm mesh using a Jaw Crusher BBI 70992 Shanghai Joyal Machinery Co., Ltd. The crushed quartzite was heated in Electric furnace Nabertherm GmbH, Germany at 800°C for 6 hours. This was to make cracks in the quartzite. It also breaks the complex formation, like metal ore attached to it. The calcined quartzite was ground into fine powder, using grinding machine (SIEBTCHNIK GmbH,

Germany). The finely ground quartzite was sieved through 75, 150 and 300µm mesh sieves. The 75, 150 and 300µm mesh sieved quartzite (SiO₂) and dense form of soda (Na₂CO₃) were weighed into ratio 1:1 according to equation 2.1 and mixed properly according to (James, 1992).



The mass proportions between the reactants is given in equation (2.2)



The weighed mixtures were placed into an LH 120/14 electric furnace Nabertherm GmbH, Germany and was fired at 1000°C, 1050°C and 1100°C for 10, 20 and 30 minutes for quartzite particle sizes of 75µm, 150µm and 300µm respectively.

The fired samples were removed from the crucibles and crushed, then sieved into 1.2mm. After crushing and sieving of the fired samples, they were analyzed. Two methods used for the analysis of soluble silicate were gravimetric for silica (SiO₂) and atomic absorption spectrophotometer, (AAS) Shimadzu Corporation LTD, Japan, for determining sodium oxide (Na₂O) (Yunusa et al., 2009b).

Formulation of Non-Phosphate Biodegradable Detergent.

This step involved dissolving 50g, 75g and 25g of sodium hydroxide pellets separately in 50ml of distilled water and made up to 100ml in order to get 50%, 75% and 25% respectively, the solution was stirred continuously to ensure complete dissolution of NaOH pellets. Each of the prepared sodium hydroxides (NaOH) was used to neutralize the linear alkyl benzene sulfonate (LABS) to form a neutral detergent paste. The process was controlled by monitoring the pH value using Kent 7020 pH meter, UK.

The solid additives such as sodium metasilicate, carboxyl methyl cellulose (CMC),

colour etc were mixed in 50wt. %, 20wt. %, and 10wt. % respectively. This was then mixed with 10 wt. % of water to form slurry. The slurry was then mixed with the neutral detergent paste. The resulting mixture was stirred using a 73-660 mechanical stirrer Silverson Machines LTD, England to prevent formation of lumps. The resulting detergent was dried in an open air with the assistance of a ceiling fan. The dried detergent was then sieved through a 1.2 mm sieve size into powder. Lemon perfume was added to the powder detergent produced to improve the appearance and to make the washed clothes smell nicely.

Determination of CMC of a non-phosphate detergent

The CMC of a non-phosphate detergent was determined employing a method of measuring a surface tension of the detergent solution in form of a film as outlined by Konyehi, (2008)

0.05 g of detergent was dissolved in a 100 ml of deionized water and the solution stirred. Then the frame was carefully lowered into the solution as shown in Figure 2a. Then the frame was withdrawn and allowed to drain and any films appearing between the upper thread and the wire ABC and DEF were punctured, the thread assumed the shape indicated in Figure 2b. Then the measurement of GH, DF and CF were taken with a transparent ruler. The procedure was repeated with weight of 0.00, 0.45, 0.85, 1.02 and 1.20g attached at point E as shown in Figure 2a. This procedure was repeated with detergent concentrations of 0.0005, 0.0010, 0.0015, 0.0020, 0.0025 and 0.0030 ml/g. The values GH and CD for each detergent concentration was measured with a ruler, recorded and graph plotted using the relationship in equation 1. A surface tension was determined from the slope of the graph, for every run, until the surface tension became constant and ceased to decrease with an increase in the concentration of detergent and this point is called critical micelle concentration (CMC).

$$\frac{h^2 - d^2}{d} = \frac{mg}{2\gamma} - 2a \quad (1)$$

Where,

$$AC = DF = 2a \quad (2)$$

$$GH = 2b \quad (3)$$

$$AD = CF = 2h \quad (4)$$

$$\text{slope} = \frac{g}{2\gamma} \quad (5)$$

$\gamma = \text{surface tension, } g = 9.81\text{m/s}^2$

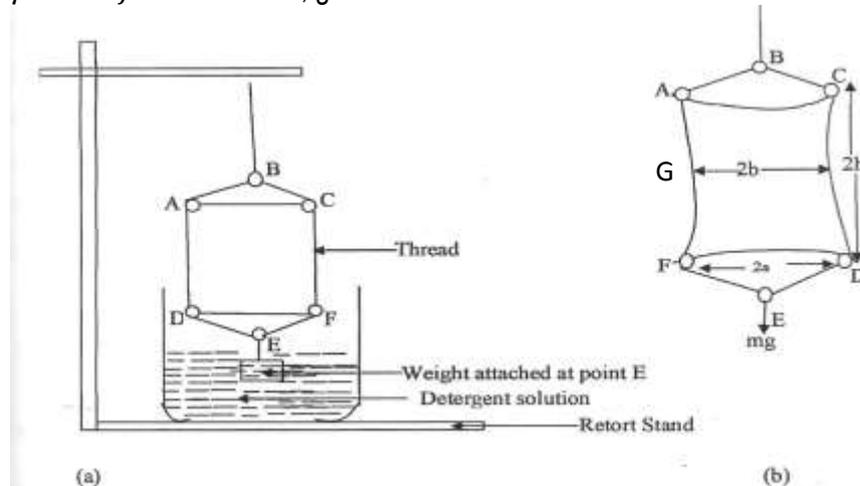


Figure 2: (a) Experimental set-up for surface tension test (b) Graphical representation of the Film formed in the detergent solution

RESULTS AND DISCUSSION

Table 3.1 presents the chemical compositions of the produced sodium metasilicate at 1000°C, while Table 3.2 gives the comparison of chemical compositions of the standard sodium metasilicate to that of the produced sodium metasilicate at 1050°C and 1100°C at various particle sizes and different times of samples firing. Ratios of oxides of silica to sodium are as well presented. Samples with a quartzite particle size of 75µm when fired at 1000°C for 10, 20 and 30 minutes, fused and solidified immediately after it was removed from the furnace. It was bluish in colour. The bluish colour was due to the presence of element such as copper (Cu) in the quartzite and other impurities. Ordinarily, it should be either whitish or colourless (Yunusa et al; 2009b).

The analyzed standard sodium metasilicate is made up of 21.3wt.% SiO₂ and 23.9wt.% Na₂O (Table 3.2). James (1992) reported the following values for three forms of sodium metasilicate: the sodium metasilicate pentahydrate; 29.3wt%. Na₂O and 26.4wt.% SiO₂, anhydrous sodium metasilicate, 51wt% Na₂O wt.% and 47.1 wt.% SiO₂, sodium metasilicate nonahydrate 22-23wt.% Na₂O and 19- 21wt.SiO₂.

When the values obtained for the three forms of sodium metasilicate were compared with the results obtained in Table 3.1 for all process conditions, it can be seen that sodium metasilicate cannot be produced under these conditions. At 1050°C and 75µm particle size for 10, 20, 30 minutes the samples fused and solidified with bluish colour.

When the standard and literature values of SiO₂ and Na₂O weight compositions were compared with the results in Table 3.2, it can be seen that only sample fired at 1050°C for 20 minutes produced sodium metasilicate nonahydrate for particles of 75µm and 150µm and samples fired at 1050°C for 30 minutes sodium silicate anhydrous glasses were formed because James, 1992 reported the values to be 33wt.% Na₂O and 66wt.% SiO₂. While samples fired at 1100°C for all particle sizes produced sodium metasilicate because the results agree with James, 1992 for sodium metasilicate nonahydrate.

Figures 3a, b and c. shows that there was a steep change of the slope of the graph as detergent concentration increases until concentration of detergent was reached when the slope of the plot remains unchanged which demonstrates that the molecular micelles start to form. As shown by the plots in Figures 3a, b

and c as the concentration of the detergent increases the slope of the graph also increases until the slope remains unchanged as concentration of detergent further increases. Figure 3a is a plot for 25% based NaOH formulated detergent, while Figures 3b and 3c are for 50% and 75% NaOH based formulated detergent at different concentration of the detergents respectively. From the plots, the detergent concentrations at which the slope of the graphs remained unchanged were 0.0025 g/ml, 0.0020 g/ml and 0.0015 g/ml for 75%, 50%, 25% based NaOH formulated detergents respectively and the corresponding slope value has about 12.03 cm/g. The CMC's values were found to be 8.6685 mM, 6.9348 mM and 5.2011 mM for 75%, 50% and 25% based NaOH formulated detergent respectively.

Comparing these results with the reported values of 7-10mM by Yunusa et al., (2009a) . It can be observed that, 75% and 50% NaOH based formulated detergents with the CMC's values of 8.6685 mM and 6.9348 mM agree with literature values, while 25% based NaOH

formulated detergent with CMC value of 5.2011 mM does not agree with Yunusa et al., (2009a) reported values. From the results it can be seen that 75% NaOH based detergent has a higher value of CMC followed by the 50% NaOH based detergent, while 25% NaOH based detergent has the lowest CMC. This may be due to the fact that both 75% and 50% based detergent samples have a lower concentration of surfactant, hence it required a higher concentration detergent before the formation of micelles. Conversely, the 25% NaOH based detergent had a higher concentration of surfactant and formed micelles at lower concentration of the detergent. From this study, a non-phosphate builder synthesized from Lokoja Quartzite has potential of protecting an aquatic animals when compared with the conventional STPP currently used in our detergent formulation. Also, the simple and economical approach adopted in this work for determination of detergent's CMC has demonstrated its potentials.

Table 3.1: Composition of the fired Samples of sodium metasilicate produced at 1000°C

S/N	Time (min)	Particle Size(μm)	Concentration of Na (mg/L)	SiO ₂ wt. %	Na ₂ O wt. %	SiO ₂ : Na ₂ O Mole ratio
1	10	75	13.9606	25.04	3.74	6.66
	20	75	53.7735	29.61	14.5	2.04
	30	75	58.3629	37.50	15.73	2.38
2	10	150	0.5960	15.24	0.16	95.30
	20	150	24.1063	18.07	6.50	2.78
	30	150	65.1397	29.04	17.56	1.65
3	10	300	0.3807	13.70	0.10	137.0
	20	300	10.6430	24.08	2.87	8.39
	30	300	38.8701	26.06	10.48	2.49

Table 3.2: Composition of the produced and standard sodium metasilicate

S/N	Temp.(°C)	Time (min)	Particle Size (μm)	Concentration of Na (mg/L)	SiO ₂ wt. %	Na ₂ O wt. %	SiO ₂ :Na ₂ O mole ratio
1	1050	20	75	93.3535	23.81	25.16	0.95
2	1050	20	150	80.9586	20.32	21.82	0.93
3	1100	10	75	84.1038	21.10	22.67	0.93
4	1100	10	150	82.6300	20.90	22.30	0.94
5	1100	10	300	81.6910	20.60	22.00	0.94
STANDARD SODIUM METASILICATE							
6	-	-	-	88.9410	21.30	23.90	0.90

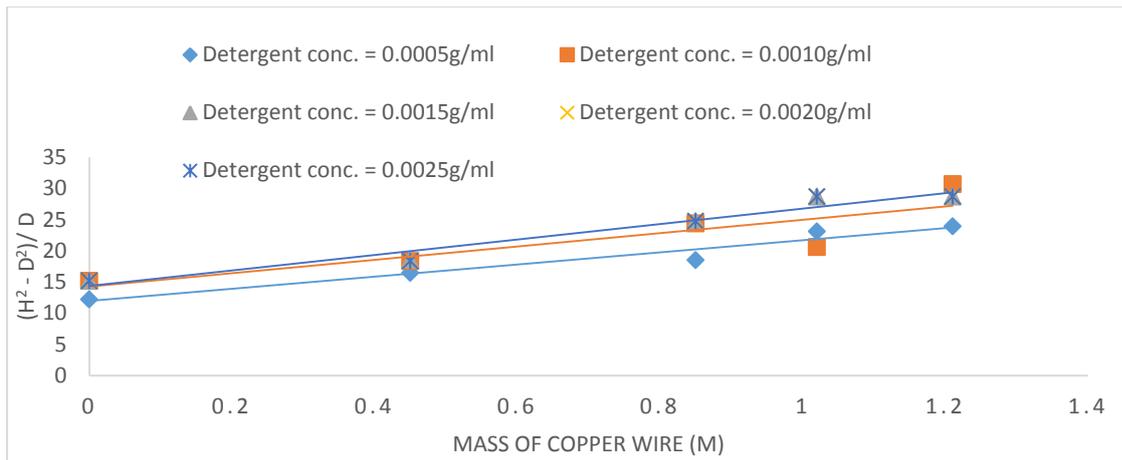


Figure 3a: Determination of CMC's of 25% NaOH based Non-phosphate builder Detergent using different detergent concentrations

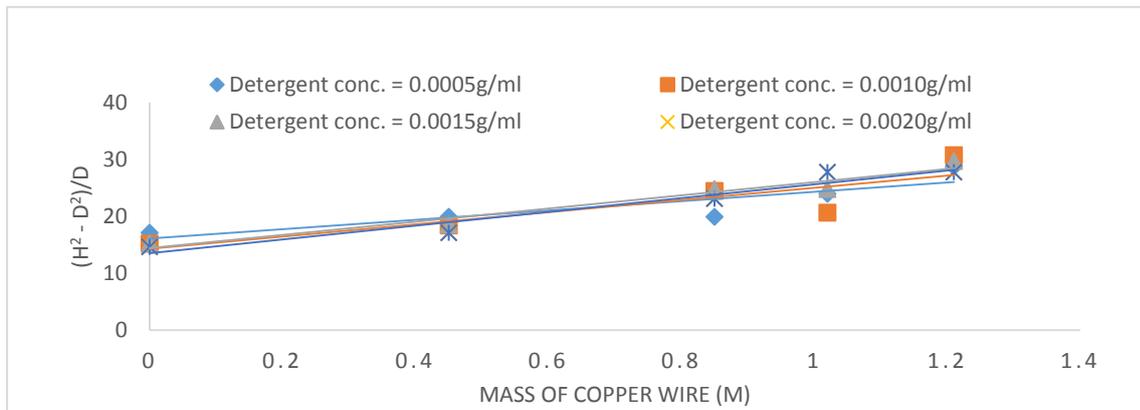


Figure 3b: Determination of CMC's of 50% NaOH based Non-phosphate builder Detergent using different detergent concentrations

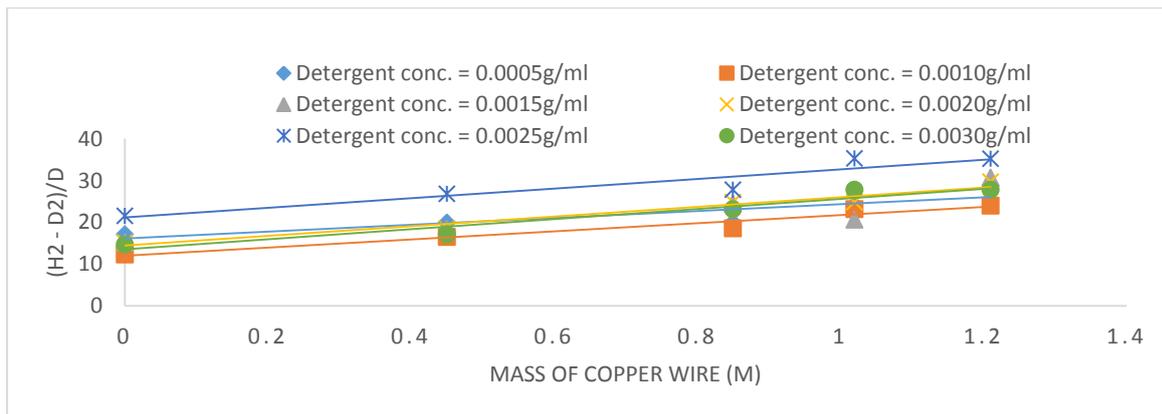


Figure 3c: Determination of CMC's of 75% NaOH based Non-phosphate builder detergent using different detergent concentrations.

CONCLUSION

From the results obtained in this work it can be concluded that the CMC's values of the non-phosphate detergent formulated using 75% and 50% NaOH found to be 8.6685 mM and 6.9348 mM respectively, conform well to that of the literature value of the range (7-10 mM). While that of 25% based NaOH detergent found to be 5.2011 mM does not agree with the values reported by Yunusa et al., (2009). The results also showed that, non-phosphate detergent prepared from Lokoja quartzite meets the requirement of good detergent and can replace phosphate detergent sold currently in the market which causes an eutrophication in our environment. Also, the CMC indicate amount of detergent needed to be used for a particular type of detergent. Hence, the more the CMC value the higher the quantity of detergent required.

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