Molecular modelling as a downstream effort in the discovery of novel anionic sulphate surfactants

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Abstract. Sulphate anionic surfactant is a type of surfactant that is widely used as a cleaning agent. The discovery and development of anionic sulphate surfactant molecule is necessary because it has a huge impact, both in science and economics. Molecular modelling to produce new anionic sulphate surfactant molecules has been carried out. The mathematical equation of the Quantitative Structure-Property Relationship (QSPR) based on Ab Initio has been obtained. Molecules that were candidates for structural modelling and modification were those that have the smallest critical micelle concentration (CMC). The smallest experimental data was C_{16}H_{33}SO_4Na with a CMC value = 0.000579 M. The result of this study was C_{17}H_{35}SO_4Na molecules with a theoretical CMC value of 0.000515 M.

1. Introduction

The population in the world is increasing every year, indirectly it will encourage the use of cleaning materials, namely detergents used for washing clothes, household utensils, transportation and industrial fields for the past 40 years [1]. Detergent contains ingredients that have surface active agent (surfactants). Detergents that are sold freely in the market usually contain 20-40% surfactants, while the rest are chemicals called additives or detergent builders which function to increase the clean power of detergents. Generally, after the use of surfactants, the waste is simply disposed of into the environment. The surfactant content contained in detergents is generally a type of anionic surfactant. Anionic surfactants are a type of surfactant that is non-degradable, so their high use causes environmental pollution [2]. One of the parameters used to determine the performance of the surfactant is the Critical Micelle Concentration (CMC). CMC is the concentration of saturated surfactant in an emulsion or it can also be interpreted as the concentration of surfactant when there is a physical change of two phases that do not mix with each other [3].

There are two ways, classic and modern, to obtain new molecules. The classical method is done in the laboratory using laboratory materials and equipment. The weakness of the classical method is causing environmental pollution, while the modern method is done by using computer technology and software in it. The modern method is known as the computational chemistry approach. The advantage of the computational chemistry approach is that it is environmentally friendly [4].

The computation method used is the ab initio method with a large basis set (6-31G**). The ab initio method was chosen because the results of the calculations obtained have a high degree of accuracy in providing information about the physical properties of a molecule [5]. The computational chemistry approach taken to design new molecules is the analysis Quantitative Structure-Property
Relationship (QSPR). In producing a novel molecular design, it cannot be separated from the experimental data that has been done by previous researchers. Experimental data in the form of physicochemical properties are used to create mathematical equations [6]. Mathematical equations are used to predict the physicochemical properties of new molecules. The aim of this research was to obtain the best QSPR mathematical equation which can be used to find the theoretical CMC value for the needs of the new sulphate group anionic surfactant compound.

2. Methods

2.1. Material and equipment
The tools and materials needed in this research were: One computer with a Core i5 Processor, 2 GB RAM; Hyperchem 8.0 Software; 3-dimensional structural model for anionic sulphate surfactant molecules; Experimental data of CMC value of 26 anionic surfactant molecules, see table 1.

Table 1. The experimental data on the critical micelle concentration (CMC) value of the 26 molecules of anionic sulphate surfactant. Atom H is not included in the structure [7].

| Number | Name of Molecule                  | Log CMC Experiment | Number | Name of Molecule                  | Log CMC Experiment |
|--------|----------------------------------|--------------------|--------|----------------------------------|--------------------|
| 1      | C_{10}SO_{4}Na                   | −3.237             | 14     | C_{4}(C_{4})SO_{4}Na             | −2.013             |
| 2      | C_{12}SO_{4}Na                   | −2.658             | 15     | C_{4}C(C_{4})SO_{4}Na            | −2.171             |
| 3      | C_{12}(C_{2})SO_{4}Na            | −2.658             | 16     | C_{6}C(C_{6})SO_{4}Na            | −2.629             |
| 4      | C_{10}C(C_{4})SO_{4}Na           | −2.469             | 17     | C_{7}(C_{7})SO_{4}Na             | −2.177             |
| 5      | C_{11}SO_{4}Na                   | −1.783             | 18     | C_{15}SO_{4}Na                   | −2.921             |
| 6      | C_{8}SO_{4}Na                    | −1.209             | 19     | C_{7}(C_{7})CSO_{4}Na            | −2.523             |
| 7      | C_{6}C(C_{6})SO_{4}Na            | −1.714             | 20     | C_{10}(C_{5})SO_{4}Na            | −2.269             |
| 8      | C_{10}SO_{4}Na                   | −1.481             | 21     | C_{12}C(C_{5})SO_{4}Na           | −1.081             |
| 9      | C_{6}C(C_{5})SO_{4}Na            | −1.328             | 22     | C_{15}SO_{4}Na                   | −2.367             |
| 10     | C_{2}C(C_{2})SO_{4}Na            | −1.081             | 23     | C_{9}C(C_{9})SO_{4}Na            | −3.027             |
| 11     | C_{6}SO_{4}Na                    | −0.854             | 24     | C_{16}EO_{2}SO_{4}Na             | −1.925             |
| 12     | C_{12}SO_{4}Na                   | −2.066             | 25     | C_{13}C(C_{13})SO_{4}Na          | −2.764             |
| 13     | C_{11}C(C_{2})SO_{4}Na           | −2.187             | 26     | C_{12}EO_{2}SO_{4}Na             | −2.396             |

2.2. Molecular modelling
Molecular modelling begins with depictions on the Hyperchem 8.0 Program canvas. This study also used the molecular structure data of anionic surfactants along with the CMC values obtained from the experimental results. The chemical structure of the anionic sulphate surfactant molecule used in this study was made a two-dimensional (2D) model using the Hyperchem 8.0 device. The model is then equipped with a hydrogen atom on each atom, and is formed into a three-dimensional (3D) structure using the Build menu (Add H and Model Build). The picture of the anionic sulphate surfactant molecule is then saved in .HIN format [8]. The surfactant molecules described were optimized to form the most stable structure.

2.3. CMC calculation
In order to calculate CMC the sulphate anionic surfactant molecule was calculated based on equation (1). The mathematical equations to predict [9] resulting from Ab Initio's Quantitative Structure-Properties Relationship were:
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\[ \lg \text{CMC} = -5.665 + 0.042(BM) - 0.095(\text{Pol}) - 0.012(\text{Vvdw}) - 0.027(\text{MD}) 
+ 1.418(\text{QC1}) - 14.562(\text{QC2}) \]  \hspace{1cm} (1)

The \( \lg \text{CMC} \) is the logarithmic of the CMC, after which it is constant. BM and Pol were molecular weight and polarizability. Then Vvdw and MD were van der Waals volumes and dipole moments. Then QC1 and QC2 were the net charges of atoms C1 (C polar) and C2 (C non polar), see equation (1).

3. Result and discussion

3.1. Molecular modelling of surfactant sulphate group

Anionic surfactants are surfactants whose alkyl portion is attached to an anion. Its hydrophilic nature comes from the ionic head which is usually a sulphate group or a sulfonate group [4]. One of the important properties that can indicate the quality of the surfactant is the value of CMC. CMC is an important property of a surfactant which indicates the critical concentration limit of the surfactant in a solution. Surfactants have good quality if the CMC value is getting smaller.

This study used the sulphate group anionic surfactant in a linear chain. Molecular modelling of sulphate group surfactants was carried out on the Hyperchem 8.0 canvas on the build menu. The modelling of the structure of the sulphate group anionic surfactant on the Hyperchem 8.0 canvas is shown in figure 1. One molecule of the sulphate anionic surfactant was a molecule of Sodium Lauryl Sulphate, \( \text{C}_{17}\text{H}_{35}\text{SO}_4\text{Na} \).

![Figure 1. Molecular modelling of anionic surfactants for the sulphate group, Sodium Lauryl Sulphate, C\(_{17}\)H\(_{35}\)SO\(_4\)Na.](image)

3.2. Geometry optimization and CMC calculation

Geometry optimization is a process of changing the conformation of molecular structures to obtain the lowest energy. Energy optimization can also be said as an energy minimization stage. Optimization of geometry aims to obtain the structure of compounds that are in stable conditions, namely compounds with the lowest potential energy. Optimization of the geometric structure of the sulphate group anionic surfactants was carried out using the Ab Initio method with the basis set is 6-31G** [5].

After the optimization was complete, the \( \text{C}_{17}\text{H}_{35}\text{SO}_4\text{Na} \) molecule was continued by calculating the theoretical CMC value or calculated CMC [10].

\[
\lg \text{CMC} = -5.665 + 0.042(BM) - 0.095(\text{Pol}) - 0.012(\text{Vvdw}) - 0.027(\text{MD}) 
+ 1.418(\text{QC1}) - 14.562(\text{QC2}) \\
= -5.665 + 0.042 \times 358.51 - 0.095 \times 34.18 - 0.012 \times 1180.60 - 0.027 \times 9.485 
+ 1.418 \times 0.10534 - 14.562 \times (-0.332393) \\
= -5.665 + 15.05742 - 3.2471 - 14.1672 - 0.256095 + 0.14937212 + 4.84031 \\
= -3.288 \\
\text{CMC} = 10^{-3.288} \text{ M} = 0.000515 \text{ M}
\]
The theoretical CMC value or the calculation result of the C_{17}H_{35}SO_{4}Na molecule obtained was 0.000515 M and this was actually lower than the C_{16}H_{33}SO_{4}Na molecule which was 0.000579 M.

4. Conclusion
The results of the study concluded that the mathematical equations resulting from the quantitative structure-properties relationship of Ab Initio could be used to predict sulphate anionic surfactants. The theoretical CMC value was C_{17}H_{35}SO_{4}Na of 0.000515 M.

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