Potential of some surfactant mixtures for production of eco-friendly detergents used in seawater

Le Duy Khanh, Nguyen Thi Nhung, Nguyen Le Tu Quynh, Nguyen Khanh Hoang Viet*

Institute of New Technology, Academy of Military Science and Technology.
*Corresponding author: hoangviet1015@gmail.com
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ABSTRACT

Mixtures of surfactants are the most important ingredients which are combined to improve the application properties of liquid detergent. In this study, we evaluated the biological, chemical, and physical properties of various mixtures of anionic, non-ionic, and amphoteric surfactants. The results showed that the SAM5 formulation, consisting of SLES/AOS/CAPB and APG (70:15:5:10, w/w/w/w), was the highest cleaning effective in removing petroleum oily residues in seawater (94.78%). Among six formulations, SAM5 presented the best performance with highly foaming volume (335 mL), good foam stability (95.52%), and low surface tension (24.17 mN/m), readily biodegradable, and corrosion resistance ability. SAM5 formulation is used for further research and application in manufacturing a new liquid detergent used in seawater to remove petrolium oily residues.

Keywords: Surfactant; Environmentally friendly; Seawater; Detergent.

1. INTRODUCTION

Liquid detergent is often a complex mixture involving many different ingredients that chemically and physically interact with each other to improve cleaning performance. In general, the most important ingredients in detergent are surfactant agents. They are amphiphilic molecules which have both hydrophobic and hydrophilic properties [1]. Depending on the polarity of the headgroups, surfactants are classified into four groups: anionic, cationic, nonionic, and amphoteric [2]. Each group has its advantages and disadvantages and different cleaning abilities, therefore, a commercial detergent often contains a mixture of various surfactant groups. The concentration of surfactants in cleaning products comprises from 15% to 40% of total ingredients. [3].

Among four types of surfactants, anionic are used with greater volume than another group due to their good performance and low cost of manufacture [2]. However, its efficacy is decreased in hard or cold water, which leads to the need for the addition of other surfactants that can provide overall benefits and advantages [2]. A number of studies have reported the addition of amphoteric and nonionic to anionic surfactants that provide a mixture with excellent cleaning ability, such as increasing foamability, foam stability, and cleaning performance in freshwater [3-6]. Nevertheless, these studies have only concentrated in freshwater conditions and studies in seawater conditions are still limited.

Nowadays, a modern detergent product is not only reflected in high cleaning ability but also needs the other properties such as being environmentally friendly. That property is expressed through biodegradability, which is the ability of microorganisms in soil or water to degrade the surfactants [3]. Biodegradability as well is important for evaluating the quality and consumer perception of detergent products. Hence, organic surfactants are often selected to manufacture detergents in consideration of economic and environmental factors [7]. Additionally, in seawater, where many ions play a role in electrochemical corrosion, the corrosion resistance properties of the detergents should also be considered [8].

In this study, experiments were conducted to evaluate the bio-physicochemical properties of various mixtures of anionic, nonionic, and amphoteric surfactants in seawater. The goal of this study is to find the potential surfactant mixture which can be applied to make an effective cleaning detergent in seawater.

2. MATERIALS AND METHODS

2.1. Materials

All commercial surfactants were purchased from the companies and used without any further treatment, including *anionic surfactants:* Sodium lauryl ether sulfate (SLES) (C_{12} – C_{14} (2EO) with 70% active substance, BASF, Thailand), Alpha olefin sulphonate (AOS) (C_{14} - C_{16} with 90% active substance, Guangzhou Yiming Chemical Materials, China); *zwitterionic surfactants:* Cocamidopropyl betaine (CAPB) (30% active substance, Cognis Oleochemicals, Malaysia); and *nonionic surfactants:*Alkyl polyglycoside (APG) (C_{12} – C_{14}, with 50% active substance, Cognis Oleochemicals, Malaysia); Cocamide DEA (CDEA) (85% active substance, Hunka Trading, Malaysia).

Seawater was obtained from Ha Long Bay (Vietnam) with a salinity of $31^{o}/_{oo}$, and petroleum oil residue was taken from the Motor shop. Other chemicals also were obtained from companies that include NH_4Cl, K_2HPO_4, KCl, $MgSO_4$, $FeSO_4$ (Sigma-Aldrich, USA), and Sea Safe Boat Wash (Star Brite, USA).

2.2. Preparing of the mixture and contaminated plate

The total surfactant concentration was 20% (w/w) in the stock solution. The mixture was diluted in deionized water and mixed as described in table 1, then pH of the mixture was adjusted with NaOH (1M).

Table 1. *The mixtures of surfactant formulations.*

Formulation	Mixture of surfactant	Ratio (w/w)
SAM1	SLES/AOS	80:20
SAM2	SLES/AOS/CAPB	70:15:15
SAM3	SLES/AOS/APG	70:15:15
SAM4	SLES/AOS/CDEA	70:15:15
SAM5	SLES/AOS/CAPB/APG	70:15:5:10
SAM6	SLES/AOS/CAPB/CDEA	70:15:5:10

The contaminated steel plate was prepared by coating the petroleum oily residues on one side of the steel plate (100 x 50 x 0.5 mm), then the plate was dried at room temperature for 4 hours.

2.3. Foam formation and stability

Foam formation and stability were conducted at the Department of Molecular Biotechnology Lab, which measured following the method as described in 64 TCN 108:1998 standard [9].

2.4. Detergency performance

For washing, all testing stock solutions were diluted to 1% with seawater at 25 ^oC. The contaminated steel plate was weighed and dipped in a 500 mL beaker containing 400 mL washing solution. Then the beaker was stirred at 400 rpm for 15 min by a stirring machine, followed by a step that the plate was taken out to dryness at room temperature for 4 hours and weighed again. The experiment was performed at Department of Molecular Biotechnology Lab. The detergency performance was calculated by the formula [10]:

$$\textbf{Detergency performance}\ (\%) = \frac{m_o - m_s}{m_o}$$

where: m_o: Weight of steel plate before washing; m_s: Weight of steel plate after washing.

2.5. Surface tension

The surface tension of surfactant mixtures was measured by a surface tensiometer (TSD DAC 300) at 25 ^oC in seawater, following the method of ASTM D1331 standard [11]. The experiment was conducted at the Center for Research and Technology Transfer.

2.6. Testing of biodegradability

Testing of biodegradability of liquid surfactant mixtures in an aqueous medium was primarily established according to the TCVN 6001-2:2008 standard method known as the biochemical oxygen demand after n days [12]. Biochemical oxygen demand was measured every 5 days during the analyzed time of 25 days. The experiment was performed at the Department of Molecular Biotechnology Lab.

2.7. Corrosion rate

The corrosion rate of surfactant mixtures on steel electrodes was determined by linear polarization following ASTM G5-14 standard in an Autolab PGSTAT 302 Potentiostat/Galvanostat – Institute of Chemistry and Material [13]. The scanning range of -0,1 to 0,1 V vs. OCP. Obtained Tafel curves were treated by NOVA software (version 2.1.5) to calculate the corrosion rate. The measurements were conducted in a 100 mL electrochemical cell composed of three electrodes, with Ag/AgCl as a reference and platinum as an auxiliary electrode. The used electrolyte was 1% of stock solution or commercial product in deionized water. The result was calculated following the corrosion rate of steel per year (mm/year).

2.8. Statistical analysis

The data of experiments were assessed with a one-way analysis of variance (ANOVA) using SPSS ver 23.0 (SPSS Inc. Chicago, IL, USA). Significant differences among each sample were evaluated with Fisher's least significant difference test. The corrosion rate was analyzed by student t-test. A p-value ≤ 0.05 was considered to be statistically significant.

3. RESULTS AND DISCUSSION

3.1. Foaming and foam stability

In the present study, we constructed some formulations based on the previous study about the ratio between anionic, amphoteric, and nonionic surfactants, which showed high detergency performance in freshwater [3, 4, 12]. According to the results, all mixtures showed good solubility and formed foam voluminously in seawater (figure 1A). Among them, the foam formed by SAM1 formulation was at the lowest volume and decreased rapidly after 5 mins. Notably, when an anionic surfactant mixture dissolved into seawater, the solution was clear**,** and there was no coalescence. Some studies confirmed that the addition of AOS to SLES can enhance the tolerance of the mixture in an environment containing a high concentration of sodium ions [13, 14]. On the other hand, the best foaming volume and foam stability were obtained from the SAM5 formulation with the presence of both APG and CAPB.

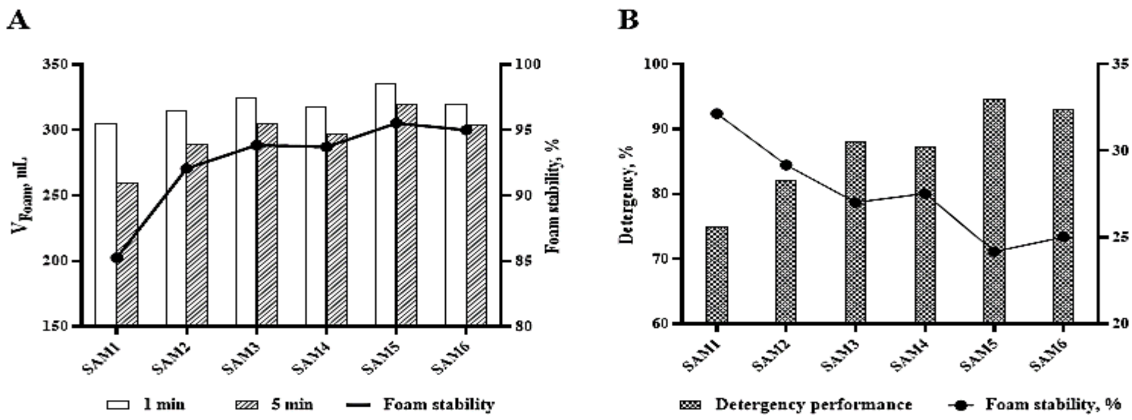

Figure 1. *Foam formation and stability (A), the detergency performance, and surface tension of six mixtures (B) in seawater. Data are from three independent triplicates and presented as mean.*

3.2. Detergency performance

Most detergent products use a combination of various surfactants to balance their performance [15]. In the present study, six formulations were subjected to test detergency performance and measured surface tension (ɣ) in seawater, and the results are presented in figure 1B. In general, detergency performance and surface tension tended to be disproportionate to each other, and the mixtures gave better detergency performance than single surfactants with the same total concentration. The best cleaning performance (94.78%) was obtained with the SAM5 formulation, which gave the lowest surface tension (24.17 mN/m). Together with that SAM6 also exhibited high detergency (93.68%), and the surface tension was recorded at ɣ = 25.02 mN/m. In contrast, the SAM1, a mixture of anionic surfactants, induced surface tension at the highest value (32.15 mN/m), while its cleaning efficiency was the lowest compared to that of the other formulations.

The cleaning performance of surfactant mixtures can be attributed to the interaction of hydrophilic and hydrophobic groups. Therefore, the combination of anionic, amphoteric, and nonionic surfactants can give a synergistic effect that leads to enhancing detergency and a significant reduction in surface tension. Moreover, nonionic and amphoteric surfactants are not sensitive in seawater environments, and they have high specificity with oily residues [5, 16]. In the study reported by D.T. Ngo, the solution of the mixture of APG with other surfactants could remove up to 97,6% oily petroleum residues on the steel plate when washing in freshwater [10].

3.3. Biodegradability of surfactant mixtures

According to the above results, the SAM5 and SAM6 formulations showed the highest detergency performance, and they continue to be studied for biodegradability. The biodegradability of both SAM5 and SAM6 were evaluated through their BOD value in comparison to those of a commercial product. The BOD values were determined in 30 days, and the results were presented in figure 2. Both samples were highly biodegradable, with the BOD value decreasing over time and getting to level 1 (<30 mg/l) according to TCVN 6772 - 2000 standard [17] after 30 days, which was quite similar to the commercial product. This is obvious due to both samples were formulated with anionic (SLES, AOS), amphoteric (CAPB), and nonionic (APG, CDEA) surfactants, which are based on natural products [7, 18-20]. A more detailed comparison between the two formulations regarding the decrease in BOD value clearly showed that SAM5 is more readily biodegradable than SAM6. The present results show that SAM5 is a high potential candidate for further studies.

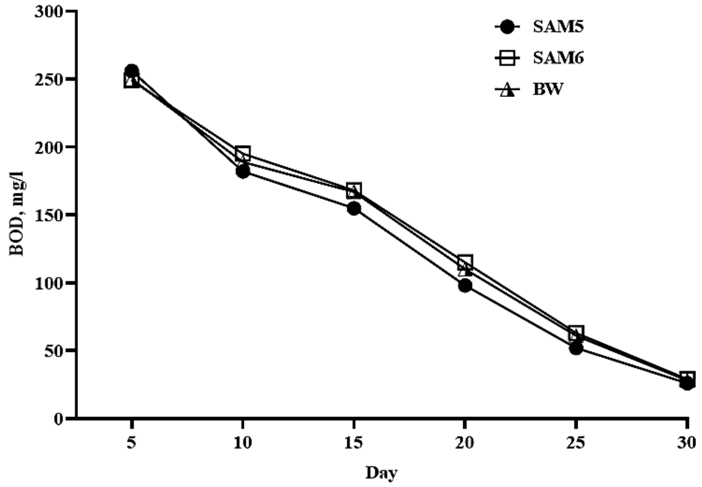

Figure 2. *The decrease of BOD index of three samples after 30 days. BW: Sea Safe Boat Wash. Data are from three independent triplicates and presented as mean.*

3.4. Corrosion resistance

A lot of acidic surfactants can increase the corrosion rate of steel in the environment if they remain on the steel surface [8]. However, if the surfactants have anticorrosion activity, they could provide a barrier between the metal surface and harmful elements, especially in seawater [21]. In the present study, the corrosion rate of SAM5 formulation was measured and compared with that of a commercial detergent product used for washing boats on seawater (figure 3). Formulated by natural ingredients such as CAPB and APG, SAM5 showed relatively low corrosion rates (0.1866 mm/year), nevertheless, which was slightly higher than that of the commercial product (0.1688 mm/year). This is understandable due to commercial products consisting of various detergent builders, and some of them have corrosion-resistant activity [22].

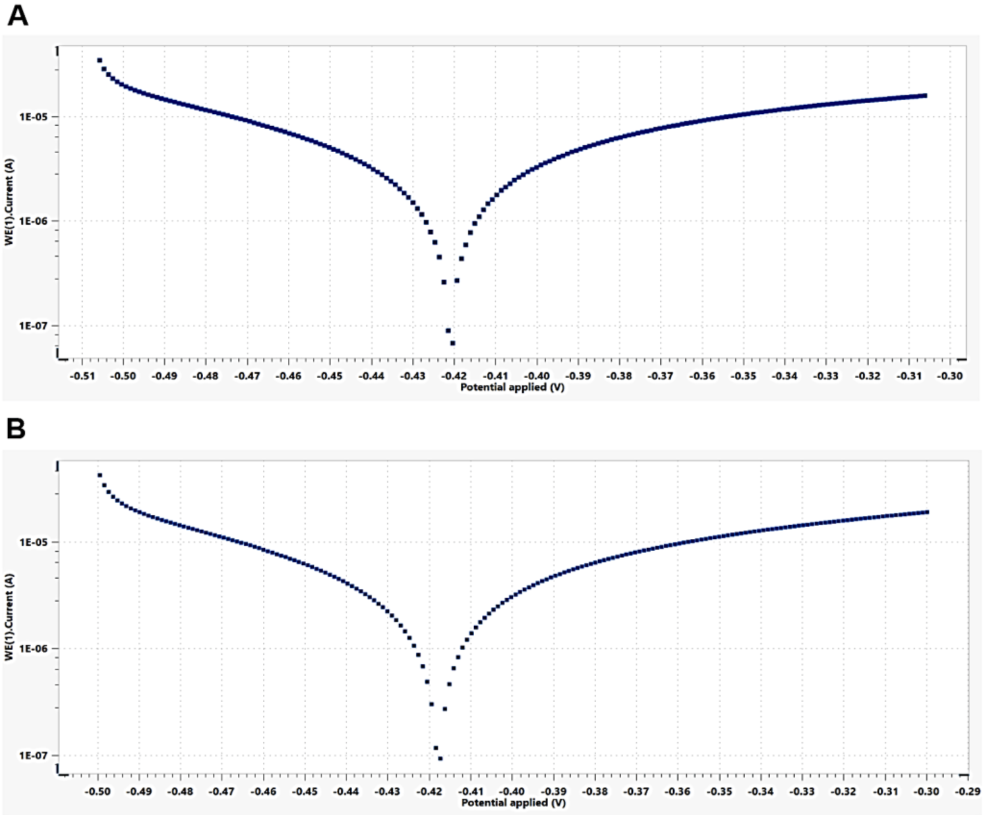

Figure 3. *Curves Tafel (E-logi) of steel CT3 in a solution containing 1% SAM5 (A), and "Safety Sea Boat Wash" (B).*
Data are from three independent triplicates and presented as mean.

4. CONCLUSIONS

In the present study, we evaluated some characteristics of liquid mixtures of anionic, amphoteric, and nonionic surfactants with different ratios. Among six formulations, the combination of SLES, AOS, CAPB, and APG (w/w/w/w = 70:15:5:10 ratio), namely SAM5, shows the best performance and efficacy. Those properties include highly in foaming and foam stability (>95%), excellent cleaning performance (94.78%), being easily biodegradable, and corrosion resistance. These results show that SAM5 formulation has a high potential for practical application to manufacture detergent used in seawater. This is the first report of the evaluation of the combination of three types of surfactants in seawater.

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TÓM TẮT

Tiềm năng của một số hỗn hợp chất hoạt động bề mặt cho việc chế tạo chất tẩy rửa thân thiện môi trường sử dụng trong nước biển

Các chất hoạt động bề mặt là thành phần quan trọng nhất quyết định tới đặc tính, hiệu quả sử dụng của các chất tẩy rửa dạng lỏng. Trong nghiên cứu này, chúng tôi đánh giá một số đặc tính sinh học, hóa học và vật lý của hỗn hợp với tỷ lệ khác nhau của các chất hoạt động bề mặt dạng anion, không ion và lưỡng tính. Kết quả cho thấy công thức SAM5, bao gồm các chất hoạt động bề mặt SLES, AOS, CAPB và APG với tỷ lệ lần lượt là 70:15:5:10 (về khối lượng), có hiệu quả làm sạch cao nhất để loại bỏ cặn dầu hỏa trong nước biển (94,78%). Bên cạnh đó, công thức SAM5 có khả năng tạo bọt cao (335 mL), độ ổn định bọt tốt (95,52%), sức căng bề mặt thấp (24,17 mN/m), dễ phân hủy sinh học và có khả năng chống ăn mòn trên bề mặt kim loại. Qua đó cho thấy tiềm năng của công thức SAM5 để tiếp tục nghiên cứu và ứng dụng vào sản xuất chất tẩy rửa dạng lỏng dùng trong nước biển.

Từ khoá: Chất hoạt động bề mặt; Thân thiện môi trường; Nước mặn; Chất tẩy rửa.