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Original Article

Biodegradability of single and mixed surfactant formulations

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Abstract

Even though detergent surfactants are mandated to be biodegradable, the environmental fate of these surfactants when mixed together in bodies of water is still not established. The study aimed to determine the biodegradability of NaLAS/CTAB surfactant combinations by measuring the amount of evolved CO_2 which was measured using the OECD 301b procedure. The 90/10 and 10/90 NaLAS/CTAB systems showed a decline in biodegradation behaviors which were recorded as 55.88% and 40.12% biodegradation, respectively, after a 28-day monitoring period. Conductivity results revealed changes in the availability of ions in the system. An inflection point was observed at a CTAB concentration of 700 ppm. The highest turbidity was noted at a NaLAS/CTAB molar ratio of 1.39:1 which indicated the formation of insoluble catanionic salts in the system. Conductivity and turbidity testing revealed the formation of anionic-cationic structures such as micelles and ion-ion complexes. These structures may alter the natural degradation mechanism of microorganisms, thus leading to the slower rate of biodegradation or incomplete degradation of the surfactants.

Keywords: surfactant biodegradation, surfactant combinations, waste water treatment

1. Introduction

The biodegradation of organic substances ensures that the environment does not accumulate with organic contaminants. Defined as the breakdown of organic compounds through the action of microorganisms, it is an important mechanism for the irreversible removal of aquatic and terrestrial contaminants (Mishra & Tyagi, 2006).

Surfactants have high environmental importance because of their large production volume. Of the 2260 kg of surfactant demand in 2005, 55.5% ended up in household applications such as soaps and detergents (Qin, Zhang, Kang, & Zhao, 2005). The presence of surfactants in water systems has led to the noted deterioration of the organoleptic properties of water. Furthermore, undesirable effects of surfactants in wastewater include the reduction in the concentration of dissolved oxygen because of foam formation and concomitant destruction of flora and fauna on the surface of water brought about by enhanced eutrophication (Qin *et al.*, 2005).

The formation of foams and suds in water systems and the consequent negative effects on the organisms prompted the preference for biodegradable surfactants over their non-biodegradable counterparts. Microbes cannot breakdown branched alkylbenzene sulfonates which led to their replacement using straight-chained linear alkylbenzene sulfonates (Qin *et al.*, 2005). The formulation of fabric softening composition with faster biodegradation resulted in the production of quaternary ammonium salts containing ester groups. These “esterquats” have been tested to have rapid and complete biodegradation alongside their improved softening properties (Mishra & Tyagi, 2006; Qin *et al.*, 2005).

Over the years, different surfactants have undergone internationally recognized screening and simulation tests to determine their biodegradation behavior (Garcia, Campos,

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Marsal, & Ribosa, 2009). However, existing literature on the biodegradability of surfactants is limited to reports of biodegradability behavior of a single surfactant system. Tests were conducted to determine whether a particular surfactant would be biodegradable given a certain concentration in the environment.

In reality, commercial compounding is done to obtain better effects among surfactants. Surfactants are mixed with other surfactants to achieve synergistic gains. Because of the more pronounced interfacial properties of mixed surfactant systems, these have been preferentially used to improve detergency, emulsification, and wettability (Homendra & Devi, 2006; Raghavan, Fritz, & Kaler, 2002). For example, complexes of different types of anionic, nonionic, and cationic surfactants have been used in fabric softener and liquid detergent formulations. Aside from these, builders and copolymers are likewise added to these mixed systems to further improve their detergency property. However, complex structures formed from compounding may affect their biodegradability behavior. These complex structures also find their way into sewage which further complicates their biodegradation. The formation of stable structures like admicelles and micelles can interfere in the capacity of microorganisms to biodegrade these compounds.

In this light, the purpose of this study was to determine the biodegradation of surfactants and mixed surfactant systems in surface water. The study used sodium linear alkylbenzene sulfonate (NaLAS), which is a common anionic surfactant, and hexadecetyltrimethylammonium bromide (CTAB), which is a cationic surfactant. An aerobic biodegradation screening test was conducted to measure the amount of evolved CO_2 from the systems after a 28-day monitoring period. The results were used to determine whether the surfactant systems were readily biodegradable under the set conditions. The presence of anionic-cationic structures in the systems was also determined using a conductivity test.

The study aimed to determine the biodegradability of single surfactants and anionic-cationic surfactant systems by measuring the amount of CO_2 evolved through a period of 28 days. The results were compared to assess the possible effects of mixed surfactants on the biodegradation of individual surfactants. The mixed surfactant system was then analyzed using conductivity testing to determine a possible change in the structures formed within the system.

2. Materials and Methods

2.1 Materials

Linear alkylbenzene sulfonate (LAS) and CTAB are presently among the commonly used surfactants for detergents. The LAS molecule contains an aromatic ring sulfonated at the para position and attached to a linear alkyl chain at any position except the terminal carbons. The linear alkyl carbon chain typically has 10 to 14 carbon atoms, with the approximate mole ratio that varies regionally with weighted averages of 11.7–11.8. The alkyl chains are predominantly linear, ranging from 87% to 98%. Commercial LAS consists of more than 20 individual components (OECD SIDS, 2005). Hexadecyltrimethylammonium bromide (CTAB) is a bacterial, cationic detergent, which can be neutralized by soaps and anionic detergents such as sodium dodecyl sulfate (SDS). Trimethylammonium bromide compounds form insoluble complexes with SDS (Sigma Aldrich). CTAB has a reported critical micelle concentration (cmc) of 0.92 to 1.0 mM in water. CTAB is biodegradable in aerobic conditions with about 97% biodegradation in several hours under the shaking flask method (Qin *et al.,* 2005).

The anionic surfactant linear alkylbenzenesulphonic acid (LABSA), with 96% active matter, was purchased from Chemline Scientific and manufactured by Sigma-Alrich. The cationic surfactant hexadecetyltrimethylammonium bromide (CTAB) with 99% purity was likewise obtained from Chemline Scientific. The analytical grade reagents potassium dihydrogen orthophosphate, dipotassium hydrogen orthophosphate, disodium hydrogen orthophosphate dehydrate, ammonium chloride, calcium chloride, magnesium sulphate heptahydrate, and iron (III) chloride hexahydrate were obtained from the stockroom of the Department of Chemistry, Ateneo de Manila University.

2.2 Aerobic biodegradation screening test

The study employed the Organization for Economic Co-operation and Development (OECD) 301b procedure to test the biodegradation of the sample in aerobic conditions. This procedure measures the amount of carbon dioxide (CO_2) evolved from the surfactant system. During the biodegradation of surfactants, their alkyl chains are degraded by microorganisms to produce CO_2 through ω- and β-oxidation.

This test involved the aeration of a measured volume of inoculated mineral medium in diffuse light. Degradation is determined through the measurement of produced CO_2 over 28 days. Barium hydroxide was used to trap the evolved CO_2 and is measured by titration of the residual hydroxide. This is made possible by the reaction of barium hydroxide to the evolved CO_2 resulting to the formation of barium carbonate and water. Barium carbonate appears as white, insoluble powder in the flask. The reaction proceeds through the following equation:

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

The amount of CO_2 produced from the test substance, after having been corrected from the CO_2 derived from the blank inoculum, is expressed as a percentage of theoretical CO_2 yield.

2.2.1 Preparation of the inoculums and samples

The inoculums used for this study were surface water samples taken from the Marikina River. Sample collection was assisted by the Laguna Lake Development Authority. The river water was stored and aerated in the laboratory in diffuse light for 5 days. Preconditioning of the inoculums in the experimental conditions improves the precision of the test method by reducing blank values.

Commercial NaLAS was not available for this study, thus LABSA was neutralized using analytical grade sodium hydroxide to obtain the anionic surfactant NaLAS. To prepare 45% NaLAS, 29.45 grams of NaOH were dissolved in 150 mL of distilled water. One hundred and eighty grams of distilled water were added to 250 grams of 96% LABSA in a beaker while submerged in an ice bath. The NaOH solution was gradually added into the LABSA. The mixture was stirred continuously until it became a viscous brownish paste.

Four surfactant systems were prepared: 100% NaLAS, 90% NaLAS/10% CTAB, 10% NaLAS/90% CTAB, and 100% CTAB. All flasks had a total surfactant concentration of 500 ppm. NaLAS (100%) was prepared by dissolving 1.111 grams of 45% NaLAS in 1 L of distilled water. A solution of 90% NaLAS/10% CTAB was prepared by dissolving 1 gram 45% of NaLAS and 0.05 grams of CTAB in 1 L of distilled water. A solution of 10% NaLAS/90% CTAB was prepared by dissolving 0.111 grams of 45% NaLAS and 0.45 grams of CTAB in 1 L of distilled water. A solution of 100% CTAB was prepared by dissolving 0.5 grams CTAB in 1 L of distilled water.

Mineral medium stock solutions were also prepared: A) 8.50 grams of KH_2PO_4, 21.75 grams of K_2HPO_4, 33.4 grams of $Na_2HPO_4 \cdot 2H_2O$, and 0.5 grams of NH_4Cl were dissolved in 1 L of distilled water; B) 27.5 grams of anhydrous $CaCl_2$ was dissolved in 1 L of distilled water; C) 22.5 grams of $MgSO_4 \cdot 7H_2O$ was dissolved in 1 L of distilled water; and D) 0.25 grams of $FeCl_3 \cdot 6H_2O$ was dissolved in 1 L of distilled water. To prepare the mineral medium, 45 mL of stock A was mixed with 4 L of distilled water and then 4.5 mL of stock solutions B, C, and D were added to the solution. Distilled water was added to prepare a 4.5 L solution.

A stock solution of HCL (the titrant) was standardized using 0.1 M NaOH as a primary standard. Potassium hydrogen phthalate (0.1225 grams) was dissolved in 20 mL of distilled water. This solution was titrated to ascertain the concentration of the NaOH solution. NaOH (0.1 M) was then used to titrate 20 mL of HCl. The end point was reached with 22.6 mL 0.1 M NaOH reading a concentration of 0.113 M HCl solution. The $Ba(OH)_2$ solution, which served as the CO_2 absorber, was also standardized using the 0.113 M HCl solution. In the end, 5 L of 0.113 M HCl and 0.0986 M $Ba(OH)_2$ stock solution were prepared for the experiment.

2.2.2 Preparation of the flasks

Four flasks containing the surfactant combinations were prepared. For each flask, 480 mL of mineral medium and the surfactant combinations were mixed. The flasks were inoculated to give a final volume of 1 L. A fifth flask was prepared without the surfactant system to serve as the inoculum control. The flasks were connected to the aerators and set at 100 mL/min using rubber tubes. The flasks were stored in the laboratory in diffuse light. For each flask, 3 absorption bottles were connected. Each absorption bottle contained 20 mL 0.0986 M $Ba(OH)_2$ solution. Each container was fitted with a serum bottle closure. Three runs were done simultaneously.

2.2.3 Evolved CO_2 measurement

OECD 301b recommends that the analysis of CO_2 be done every second or third day during the first 10 days and at least every fifth day until the end of the 28-day period. This is to identify the 10-day window where substances are expected to reach the pass level of 60% biodegradation to be considered readily biodegradable. Therefore, the CO_2 measurements were conducted 12 times in the 28-day period on days 1, 2, 3, 5, 7, 9, 11, 13, 17, 21, 25, and 28. During the measurement days, the $Ba(OH)_2$ absorber closest to the flask was disconnected and titrated using the 0.113 M HCl solution using phenolphthalein as the indicator. The remaining absorbers were then moved one place closer to the flask and a new absorber was placed containing 20 mL of 0.0986 M $Ba(OH)_2$ at the far end of the series.

The weight of CO_2 evolved in each absorber was calculated using Equation 1:

$$weight\ of\ CO_2 = \frac{0.113 \frac{mole}{1000mL} \times (35mL - mL\ HCl\ titrated) \times 44 \frac{gram}{mole}}{2} \tag{1}$$

where 0.113 is the molarity of HCl used, 35 is the amount in mL of 0.113 M HCl needed to titrate 20 mL 0.0986 M $Ba(OH)_2$, 44 is the molecular weight of CO_2, and 2 is the number of mmol of HCl needed for the titration of the remaining $Ba(OH)_2$.

The CO_2 recorded from the blank was deducted from the CO_2 readings of the other flasks. The % degradation was computed using Equation 2:

$$\%\ degradation = \frac{CO_2\ produced}{theoretical\ CO_2\ yield} \tag{2}$$

The theoretical CO_2 yield for 100% NaLAS, 90% NaLAS/ 10% CTAB, 10% NaLAS/90% CTAB, and 100% CTAB were 0.758 grams, 0.7786 grams, 0.9448 grams, and 0.966 grams, respectively.

2.3 Characterization

2.3.1 Conductivity testing

Conductance measurements were carried out using a digital conductivity meter (Oakton Conductivity Wand) with a sensitivity of 0.1% and a dipping type conductivity cell with a platinum electrode cell constant of 1.0. All measurements were made at ambient temperature (25 °C). Conductivity testing of the surfactant systems was done at dilute concentration from 100 ppm to 1000 ppm. Two sets of dilute solutions were prepared. For the first set, the NaLAS concentration was made constant at 500 ppm. This was prepared by dissolving 1.11 grams of 45% NaLAS in 1 L of distilled water. A stock solution of 1000 ppm CTAB was also prepared by dissolving 1 g of CTAB in 1 L of distilled water. From this, dilutions from 100 ppm to 900 ppm in 100 ppm intervals were prepared. An equal volume of each surfactant solution was added to make a volume of 100 mL for each testing. After measuring the conductivity of the 10 mixtures, the CTAB concentration was made constant at 500 ppm. The NaLAS concentration was varied from 100 ppm to 1000 ppm. The conductivity readings were plotted to identify possible deflection points to indicate changes in the ion behaviors in the solutions.

2.3.2 Ultraviolet-visible (UV-Vis) spectroscopy

Absorbance measurements were performed in a

Shimadzu 1800 double beam spectrophotometer using 10-mm path length quartz cuvettes which were available at the Angeles University Foundation. The diluted concentrations prepared for the UV-Vis testing were the same samples used for the conductivity testing. Each sample was tested at the wavelength range of 200–600 nm. The turbidity test was performed by absorption at 470 nm. The absorbance results were plotted against the concentrations of the samples from 100 ppm to 1000 ppm.

3. Results and Discussion

3.1 Biodegradation profiles of the surfactant systems

The aerobic biodegradability of the surfactant systems were assessed using the CO_2 evolution test (OECD 301b). A compound is considered readily biodegradable if the biodegradation level exceeds 60% within 28 days. It is assumed that such compounds will rapidly and completely biodegrade under aerobic conditions. The biodegradation curve shows the increasing amount of evolved CO_2 from the flasks because of the degradation of the test substance. Upon reaching 10% degradation a ‘10-day window’ commences and rapid biodegradation is expected with the microorganisms having adapted to the test material. At this point, the ‘10-day window’ can be identified which is the period where 60% biodegradation must be achieved for the substance to be considered readily biodegradable. In any case, the 10-day window must end before the 28-day monitoring period. The curve ends with a plateau indicating a decrease in the evolved CO_2 from the flask.

Low values from the screening test do not necessarily mean that the test substance is not biodegradable under environmental conditions. It simply indicates that more work is necessary to establish its biodegradability. Likewise, if the plot does not plateau by 28 days, the test substance may not be considered readily biodegradable. The theoretical amount of 100% biodegradation is not expected in this method as some of the carbon becomes part of the biomass of the microorganisms. Figure 1 shows the rate of biodegradation of the four surfactant systems.

Figure 1 shows the % biodegradation of the surfactant systems throughout the 28-day monitoring period. As expected, none of the systems achieved 100% biodegradation. The amount of CO_2 measured through titration was subtracted from the CO_2 reading from the control (flask without the test materials) and compared with the theoretical CO_2 yield for each of the surfactant systems. There was an increasing amount of evolved CO_2 from day 1 to day 15 with a plateau appearing from day 17 to day 28. There was an apparent similarity with the biodegradation curves of the four surfactant systems because of the presence of similar alkyl chains from the surfactants. It is from these alkyl chains that CO_2 evolves from the systems.

At 28 days, the NaLAS reached 81.79% biodegradation, while CTAB recorded 61.12% biodegradation. Since they passed 60% biodegradation, these surfactant systems are considered readily biodegradable in nature. This conforms to the existing literature (Scott & Jones, 2000) that stated that both NaLAS and CTAB were biodegradable under aerobic conditions. CTAB apparently takes longer to biodegrade compared to NaLAS because it has longer alkyl chains. Biodegradation starts from one end of the alkyl chain, thus the longer the chain is, the longer time it takes for all carbon links to be broken.

The mixed surfactant systems reached 55.88% biodegradation for the 90% NaLAS/10% CTAB and 40.12% for the 10% NaLAS/90% CTAB. The latter system recorded a lower biodegradation rate because of the higher concentration of CTAB in the system. While these systems did not achieve the pass level for the screening test, these mixed surfactant systems cannot be classified as non-biodegradable in nature. The results imply that the systems are not readily biodegradable and require further simulation tests to fully describe their biodegradation behavior.

The suppression of the biodegradation of the mixed surfactant systems may be because of the interaction of the surfactants with each other. The interaction of surfactants in mixed systems can alter the physicochemical properties of the system as revealed in the studies conducted by Raghavan *et al.* (2002) and Homendra and Devi (2006). The interaction of the alkyl chains of the oppositely charged headgroups can

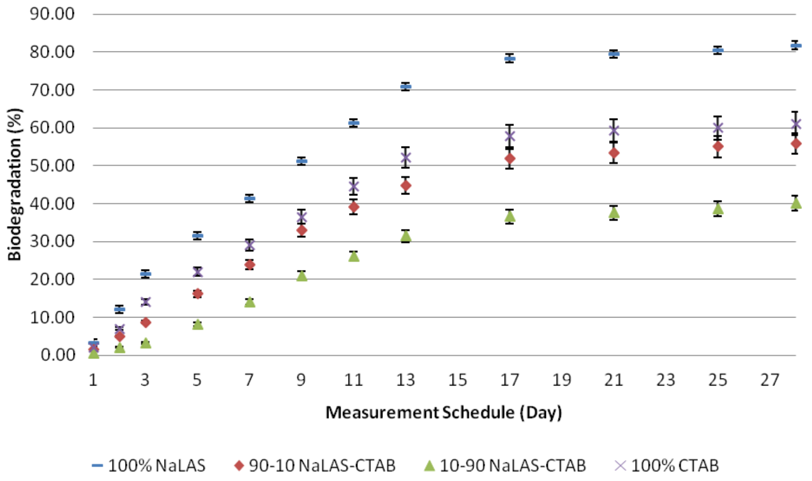

Figure 1. Aerobic biodegradation curves at a total surfactant concentration of 500 ppm.

likewise modify the behavior of the system as reported by Kohler, Raghavan, and Kaler (2000).

3.2 Determination of cationic/anionic structures

3.2.1 Conductivity of the mixed surfactant systems

Conductivity measurements are widely used to characterize ionic surfactants such as NaLAS and CTAB. The change in electrical conductance of aqueous ionic surfactant solutions at the cmc occurs because of the difference in the degree of surfactant ionization below and above the cmc. Below the cmc, surfactant monomers behave as strong electrolytes and above the cmc the micelles are partly ionized (Dominguez, Fernandez, Gonzalez, Iglesias, & Montenegro, 1997). Because of the change in the conductance of the solution, a deflection is observed in the conductance plot which indicates the concentration at which the micelles are formed. Figure 2 shows the conductivity measurements of the NaLAS/ CTAB systems with the NaLAS concentration at 500 ppm.

The specific conductance values at a constant concentration (500 ppm) of NaLAS were obtained by varying the concentration of CTAB from 100 to 1000 ppm. The cmc of NaLAS reported in the literature is 100 ppm (Berna *et al.*, 2007). At a concentration of 500 ppm, which is above the cmc, the micelles and monomers of NaLAS are present in the solution (Dominguez *et al.*, 1997). NaLAS at 500 ppm and 0 ppm of CTAB recorded a conductivity of 735 µS. The addition of 100 ppm of CTAB into the solution caused the conductivity to drop to 414 µS. The monomers of NaLAS present in the solution, which formerly contribute to the conductance of the solution, have formed ion-ion complexes with the cationic CTAB. This resulted in decreased conductivity of the solution. Further addition of CTAB into the solution increased the ion-ion complexes in the system and decreased the amount of free ions. However, the conductivity of the solution increased because of the increased concentration of the surfactants in the system. The continual addition of surfactants caused an increase in the free ions in the system as indicated by the rising slope.

The conductivity of the solution increased linearly with the concentration of the surfactants. An inflection point was seen at 700 ppm. Beyond the inflection point, the slope indicated an increase in the conductivity of the solution, but with an apparent decrease in the increment. The addition of CTAB in the solution resulted in the formation of ion-ion complexes, which reduced the conductivity of the system. The lowering of the conductivity beyond the inflection point indicated the formation of micelles. Micelles can drastically lower the conductivity of the solution because they are only partially ionized (Diaz & Velasquez, 2007).

Figure 3 shows the conductivity of the solutions with a constant CTAB concentration (500 ppm) mixed with varying concentrations of NaLAS. CTAB has a cmc at 365 ppm (Scott & Jones, 2000). Thus, at 500 ppm, the micelles of CTAB were already present in the system. Because the concentration is above the known cmc for CTAB, monomers were also found in the system which accounted for the conductivity reading of the solution. The addition of NaLAS (100 ppm) initiated the formation of ion-ion complexes similar to that in Figure 2. However, the inflection point for this combination was noted at a lower concentration as opposed to a set concentration of NaLAS (500 ppm). The cmc of the mixed surfactant systems was observed between the cmc of the individual surfactants. This may be attributed to the difference in the length of alkyl chains of the individual surfactants. Since the NaLAS had a greater concentration (500 ppm) and a lower cmc (100 ppm), the inflection point appeared at a lower concentration (Tanhaei *et al.*, 2013). Similar to the results reflected in Figure 2, micelles are suggested to form beyond the inflection point which indicated the lower conductivity of the solution.

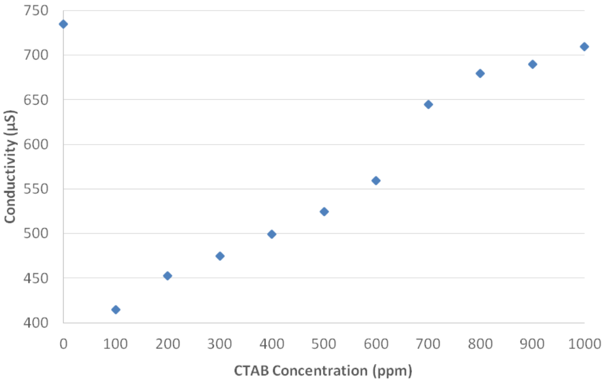

Figure 2. Conductivity of a NaLAS/CTAB system at a constant concentration of 500 ppm of NaLAS.

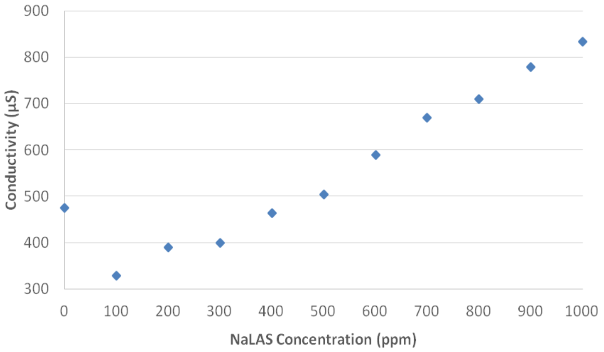

Figure 3. Conductivity of a NaLAS/CTAB system at a constant concentration of 500 ppm of CTAB.

3.2.2 Absorbance of mixed surfactant systems

Turbidity testing was carried out to verify the presence of insoluble catanionic salts formed by the ion-ion complexes in the systems. This was done by testing the diluted samples (100 ppm–1000 ppm CTAB at a constant 500 ppm of NaLAS) under UV-Vis spectroscopy at 470 nm. The absorbance readings of the samples at 470 nm were taken and plotted against the concentrations gleaned from Figure 4.

From 100 ppm to 600 ppm, the systems remained transparent indicated by the low absorbance of the systems. The gradually increasing absorbance from these concentrations was possibly due to the increasing amount of suspended particulates, which may account for the insoluble catanionic salts or ion-ion complexes. These insoluble salts are formed by the interaction of the anionic and cationic headgroups (Raghavan *et al.*, 2002).

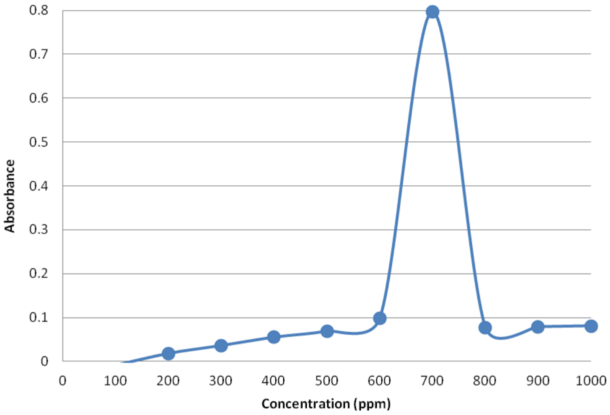

Figure 4. Plot of absorbance versus various concentrations of CTAB at a constant concentration of 500 ppm of NaLAS.

The highest turbidity was noted at 700 ppm (1.39:1 NaLAS/CTAB molar ratio). The appearance of precipitates at an equimolar ratio was consistent with the report by Raghavan *et al.* (2002). The formation of catanionic salts is likely to happen because of the strong interaction between the cationic and anionic headgroups and almost equal tail lengths of the surfactants. The tail lengths of NaLAS (n=12) and CTAB (n=16) pack efficiently in the crystalline lattice thereby inducing the formation of a stable precipitation in the solution, hence rendering the system turbid. This is not observed with surfactants with asymmetric tail lengths which show a homogeneous phase throughout a range of compositions. The solution went back to being transparent beyond a concentration of 700 ppm which suggested the presence of homogeneous micellar solutions over the composition range.

3.3 Biodegradability of the surfactant mixed systems

Biodegradation of substances in the environment ensures that organic compounds will not accumulate in the ecosystems. With large volumes of surfactants released into the environment from various sources, biodegradation must be ensured. However, the CO_2 evolution test revealed that the biodegradation profile of surfactants when mixed with other surfactants was suppressed. The 90/10 and 10/90 NaLAS/CTAB were not readily biodegradable compared to their pure surfactant counterparts. Although the screening test did not conclude that the tested surfactant systems were not biodegradable in the environment, the change in the biodegradation profile may pose effects on the water systems. With the absence of water treatment facilities in the Philippines, particularly in residential areas, surfactants are released directly into the sewage systems or bodies of water. As a result, surfactants face an inevitable interaction with other surfactants.

The change in the ionic conductance of the NaLAS/CTAB systems is explained through the formation of various structures such as micelles and ion-ion complexes. The formation of these structures was also verified by the turbidity test showing the formation of homogeneous micellar solutions and insoluble catanionic salts at an equimolar ratio. The ion-ion complexes formed by the strong interaction of the headgroups of the cationic and anionic surfactants were determined through UV-Vis spectroscopy.

While the study takes the biodegradation of the tested systems at extreme surfactant combinations (90/10 and 10/90 NaLAS/CTAB), an apparent suppression of the biodegradation level was identified. This suppression determined that these mixed surfactant systems, relative to the 60% pass level of OECD 301b, are not readily biodegradable in nature. From the characterization tests, at these concentrations, micelles formed in the solution with small amounts of ion-ion complexes. The formation of these structures was possibly the reason for the suppressed biodegradation of the mixed surfactant systems.

Scott and Jones (2000) explained that the structures that surfactants take and form influence their properties as in the case of the branched alkylbenzenesulfonate and linear alkylbenzenesulfonate surfactants. Branched alkylbenzenesulfonates do not biodegrade quickly in the environment because microorganisms cannot breakdown the compounds. The enzymes in microorganisms that are evolved in breaking down hydrocarbons may be incapable of digesting these structures. Instead of taking the ω- and β-oxidation mechanism, branched alkyl surfactants degrade one carbon at a time through α-oxidation which causes these compounds to accumulate in the water system.

Similarly, the formation of micelles and ion-ion complexes in the mixed surfactant systems must have altered the biodegradation behavior of the surfactants leading to their suppressed biodegradation levels.

4. Conclusions

The biodegradation of surfactant systems was suppressed compared to the individual surfactants. The NaLAS/CTAB system tested in this study did not pass the readily biodegradation level based on the screening test conducted. Conductivity testing revealed changes in the free ions available in the system which may be attributed to the formation of catanionic salts and micelles at dilute concentrations. The turbidity test also showed a great increase in absorbance at an equimolar ratio confirming the formation of insoluble catanionic salts.

The researcher concludes that the decline in the biodegradation of the surfactant systems was possibly due to the presence of different structures formed by the interaction of the surfactants at dilute concentrations. These structures may alter the natural degradation mechanism of microorganisms, thus, leading to the slower rate of biodegradation or incomplete degradation of the surfactants.

Therefore, it is recommended that ultimate biodegradation tests be conducted to verify the biodegradability behavior of the mixed surfactant systems under aerobic conditions. Available simulation tests may be conducted to assess the ultimate biodegradation of the mixed surfactant system. Furthermore, biodegradation studies should be conducted for surfactant systems close to the equimolar ratio to verify the effects of the ion-ion complexes on the biodegradation behavior of the surfactants.

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