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Synergy effect for performance of anionic SDS/ADS mixtures with amphoteric and nonionic surfactants

Hongche Noh · Taeho Kang · Ji Soo Ryu · Si Yeon Kim · Seong-Geun Oh†

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

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Abstract : Detergency and surface active properties of mixed anionic surfactants with amphoteric and nonionic were investigated. Sodium dodecyl sulfate (SDS) and ammonium dodecyl sulfate (ADS) as anionic surfactants and cocamidopropyl betaine (CAPB) as an amphoteric surfactant were used. Nonionic surfactants, which are butyl glucoside (BG), octyl glucoside (OG), decyl glucoside (DG), lauryl dimethylamine oxide (AO) and saponin were also used. To study the synergy effects of mixed SDS/ADS anionic surfactant systems, amphoteric and nonionic surfactants were added into the mixed anionic surfactants. Investigated properties of surfactant mixtures were critical micelle concentration (CMC), surface tension (γ), wettability. In addition, based on these properties, detergency of each sample was examined. Surfactant mixtures are anionics (SDS/ADS), anionic/amphoteric/nonionic (SDS/ADS/CAPB/ saponin), and anionic/nonionic (SDS/ADS/BG/ saponin, SDS/ADS/OG/saponin, SDS/ADS/ DG/saponin, and SDS/ADS/AO/saponin). With the addition of amphoteric and nonionic to mixed anionic surfactants, CMC and γ were decreased. Addition of CAPB, which is amphoteric, showed the best property at CMC and γ. Furthermore, as the chain length of hydrocarbon in alkyl glucosides was increased, the CMC and γ were enhanced. However, the wettability did not exactly match up with CMC and γ. The surfactant mixture, which contained DG, showed the best performance at wetting time. Detergency was measured at various temperatures (15 °C, 30 °C, 50 °C). The cleaning performance was enhanced by increasing washing temperature. Moreover, detergency was influenced by not only CMC and γ but also wettability. Although CMC and γ were not minimum at surfactant mixture that included DG, the best cleaning performance showed in that sample.

Keywords : Anionic surfactants; Detergent formulation; Surface activity; Wetting

1. Introduction

Numerous industries and markets use millions of surfactants. These surfactants are applied to chemical synthesis, emulsification, cleaning, dispersion and shape control of materials such as metal oxides and polymers [1]. In addition, surfactant molecules have hydrophilic and hydrophobic groups, which generally consist of polar molecules called as head group such as sulfate and carboxylic, and hydrocarbon chain in surfactant molecules called as tail, respectively. This is known as

†Corresponding author
(E-mail: seongoh@hanyang.ac.kr)

amphipathic structures [2]. Because of the feature of molecules, they show peculiar phenomenon when dissolved in solvent. If the solvents have polar property like water, the tail group is heading to air and head group is heading to water on the surface of solvent. As the surface of surfactants solution is saturated, they made spheres called as micelles in order to be thermodynamically stable. Furthermore, upon the adjustment of surfactant concentration, it is possible to make various forms of micelles such as cylindrical, lamellar and hexagonal [3].

Therefore, surfactants adsorbed to the interface in diluted solution reduce the surface tension. Surfactants are classified as anionic, cationic, amphoteric, and nonionic depending on the type of charges of hydrophilic group in water. Generally, most natural surfaces are negatively charged. Hence, if the hydrophilic part of surfactants is cationic, the adsorption of surfactant is enhanced. However, ionic surfactants, particularly cationic, are found to be toxic and irritable to skin. Nonionic such as alkyl glucoside and zwitterion like cocamidopropyl betaines are known to be mild [2, 4].

The surfactant is used in everyday life, and the cleaning for pollutant that is adhering to skin, hair and cloth is important. "Washing" has been widely used for a long time as a main function of surfactants. This is used for wet cleaning in aqueous solution. Sodium dodecyl sulfate (SDS) is used in many personal care products such as shampoo and cleanser. Although the SDS has a little irritation for skin, it has good properties of detergency and foaming ability [2].

In this paper, SDS and ammonium dodecyl sulfate (ADS) were used as anionic surfactants. ADS has ammonium as counter ion. Compared to SDS, ADS shows the lower Krafft point and CMC, because the binding energy between surfactant molecule and counter ion of Na^+ is lower than NH_4^+ [5]. To increase the surface active properties like surface tension, CMC, and wettability, nonionic surfactants which are butyl glucoside (BG), octyl glucoside (OG), decyl glucoside (DG), and lauryl dimethylamine oxide (AO) and amphoteric surfactant which is cocamidopropyl betaine (CAPB) were used. The reason why using these surfactants is because the alky glucosides which are called as sugar surfactants is less sensitive to temperature changes than other nonionic surfactants of ethylene oxide. In addition, they are less irritant to the skin because they are synthesized by mild reactants, which are corn starch glucose with a fatty alcohol [6-9]. Furthermore, they are used as cosurfactants which have a good compatibility with all other surfactant types and show synergy effect with anionic surfactants. The CAPB also has good features. It is not affected by water hardness and generates foam well with excellent stability, which are important for commercial products [4].

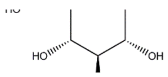
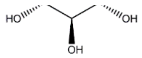
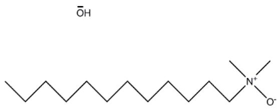
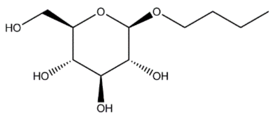
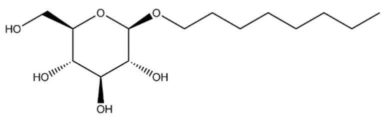
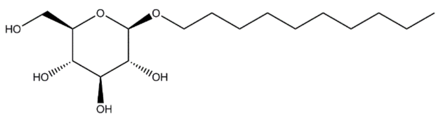
Surfactant mixtures were formulated to investigate the synergy effects of parameter, which are surface tension, CMC, and wettability. Cleaning performance also measured for each sample. The detergency were measured using plates which were deposited with contaminants of soil or oil in previous many other reports. However, this washing process lakes of reality because the cleaning occurred only on the surface of plate [10, 11]. Therefore, we immersed the cotton discs into the contaminated solution and measured detergency. Furthermore, the relationship between detergency and surface tension, CMC and wettability was analyzed.

2. Materials and methods

2.1. Materials

All surfactants except for saponin were commercial grades supplied from industrial company. Table 1 shows that types, nomenclatures, chemical structures and

Table 1. Types, nomenclature, chemical structure, and molecular weight of surfactants

Types and nomenclature	Chemical structure	Molecular Weight (g/mol)
Anionic		
Sodium dodecyl sulfate (SDS)		288.4
Ammonium dodecyl sulfate (ADS)		283.4
Amphoteric		
Cocamidopropyl betaine (CAPB)		342.5
Nonionic		
Butyl glucoside (BG)		236.3
Octyl glucoside (OG)		292.4
Decyl glucoside (DG)		320.4
Lauryl dimethylamine oxide (AO)		229.4

molecular weights of the surfactants used in this work. The anionic surfactants of sodium dodecyl sulfate (SDS) (30 wt.%, MICOLIN S430) and ammonium dodecyl sulfate (ADS) (26 wt.%, MICOLIN A526) were supplied by Miwon Company, Korea. Amphoteric and nonionic surfactants which are cocamidopropyl betaine (CAPB) (30 wt.%, ELOTANT BT100), butyl glucoside (BG) (50 wt.%, ELOTANT Milcoside 410N), octyl glucoside (OG) (65 wt.%, ELOTANT Milcoside 430N), decyl glucoside (DG) (54 wt.%, ELOTANT Milcoside 440N) and lauryl dimethylamine oxide (AO) (32 wt.%, ELOTANT AO32) were provided by LG Household & Health Care Company, Korea. Saponin was purchased from Junsei Chemical.

2.2. Surface tension and critical micelle concentration (CMC) measurements

Surface tension and CMC of surfactant mixtures were examined by surface tensiometer (K10ST, KRÜSS, Germany). The solutions were diluted with deionized water (Milli-Q Plus system). The range of concentration was from 0.1 to 100 mb (mmol/kg). They are determined by ring method and the temperature was adjusted to 25 °C by digital precision refrigerated bath (WCR-P22, Wised, Korea)

2.3. Wettability test

Wettability was investigated by measuring the time when cotton discs (W-TNV-30, DIN53901/ISO 8022, Test fabrics, Korea), called Draves skein, start to sink. This method is a kind of Draves test. Concentration of all samples is 5 mb and the temperature was fixed to 23 °C. The test method is as follows. The 100 ml of surfactant mixtures was filled into graduated cylinder. Then the cotton discs were dropped onto the surfactants mixtures. As time goes, the cotton slowly wetted by surfactant mixture solutions. Finally, the cotton was fully wetted and start to skink to the bottom of cylinder. The time when the cotton start to fall into bottom was measured as wetting time.

2.4. Detergency test

Raw materials of surfactants are very highly concentrated, therefore it is hard to recognize the difference in detergency between the samples. Hence, all surfactant mixtures were diluted to 0.01 b and test was conducted at 15 °C, 30 °C, and 50 °C. The cleaning performance was measured by the following order and the scheme for this was shown in Fig. 1. First, contaminated solution which consists of 20 g of oleic acid (90 wt.%, Sigma, Korea), 6 g of palmitic acid (Kanto, Japan), and 0.1 g of Oil red O (DAEJUNG) in 100g of chloroform (99.5 wt%, DAEJUNG, Korea) were prepared. Then, cotton disks were put into the solution at 30 °C and they took out from the solution and dried about 60 min at 25 °C. After that, the contaminated cottons were cleaned by 100 mL of surfactants solution or D. I. water at various temperatures with stirring at 350 rpm in thermostatic water bath. After 20 minutes cleaning, the washed cottons were taken out from the detergent solution then dried 60 min at 25 °C. To measure how much contaminates remained on the cottons, the washed cottons were dropped into 40 g of tetrachloroethylene (99.5 wt.%, DAEJUNG, Korea) and stirred at 350 rpm for 60 min at 25 °C. After the contaminant was extracted by tetrachloroethylene, the solutions were analyzed by UV-vis spectroscopy (Agilent 8453, Agilent Technology, USA).

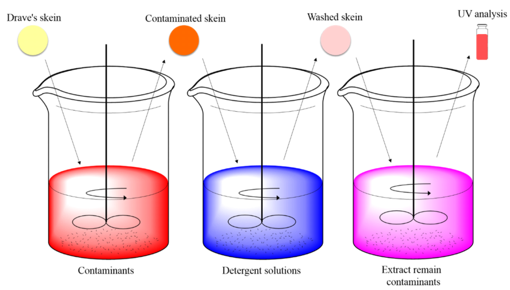


Fig. 1. Process of cleaning performance for various samples.

3. Results and discussion

3.1. Surface tension and critical micelle concentration (CMC) of surfactant mixtures

Surface tension and CMC are very important factors to surfactants. The CMC value was examined by surface tension. CMC is a concentration when the micelles start to form. Surface tension is determined how many surfactant molecules are absorbed on the surface of solution. As the surfactants were put into the solvent, they firstly absorbed onto the surface of the solvent. If they are absorbed and saturate at the surface, the surfactants formed micelles in solvent. Measured on the surface of surfactant solution, surface tension shows constant value after the micelles are formed. Hence, the CMC was determined by the surface tension when the surface tensions initiate to remain constant [3].

Six samples of surfactant mixtures and their mixing ratio, CMC and surface tension that over CMC were summarized in Table 2. Surface tension was found to be 28.4 dyne/cm by means of SDS/ADS mixture (sample 1). All surfactant mixtures, except sample number 3, have lower or similar surface tension compared to sample number 1. Anionic with amphoteric and nonionic surfactants take advantage of surface tension and CMC against the samples, which only composed of anionic surfactants. Fig. 3 (a) shows the scheme for the surfactant

Table 2. Property of surfactant mixtures: ratio, critical micelle concentration, surface tension, wetting time and detergency

Sample number	Type of surfactant mixture	Ratio (b/b)	CMC (mb)	γ (dyne/cm)	Wetting time (s)
Anionic					
1	SDS/ADS	50:50	8.89	28.4	22
Anionic/amphoteric/nonionic					
2	SDS/ADS/CAPB/Saponin	40:40:15:5	4.91	25.1	21
Anionic/nonionic					
3	SDS/ADS/BG/Saponin	40:40:15:5	8.87	28.9	64
4	SDS/ADS/OG/Saponin	40:40:15:5	8.08	28.5	21
5	SDS/ADS/DG/Saponin	40:40:15:5	6.01	28.4	14
6	SDS/ADS/AO/Saponin	40:40:15:5	12.4	25.6	21

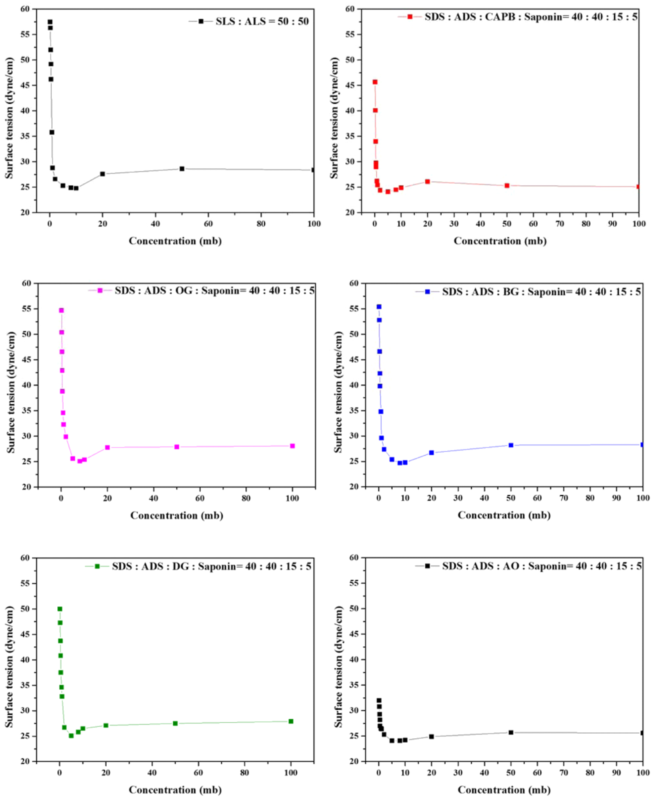


Fig. 2. Surface tension versus concentration for each surfactant mixture at 25 °C.

absorption on the surface. Anionic surfactants have negatively charged hydrophilic group called as head group. The head groups with same electric charges repel each other, so that the amount of absorption on the surface is reduced. On the other hand, addition of nonionic or amphoteric surfactant makes increase for quantity of absorbed surfactants on the surface because the repulsion of head groups is decreased. The surface tension was further decreased by this reason. Moreover, the CMC is also decreased due to the similar reason. Fig 3 (b) shows formulations of micelle. The repulsive energy between polar groups from the anionic surfactants is decreased in mixed surfactants [11, 12].

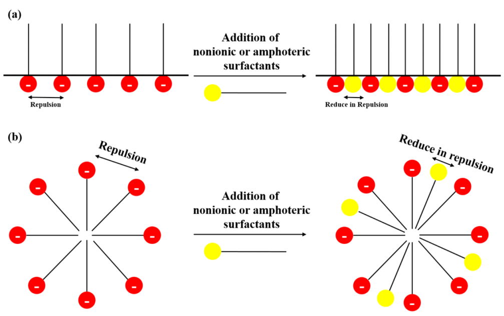


Fig. 3. Scheme for synergy effect of (a) surface absorption (b) micelle formulation on anionic surfactants and addition of nonionic surfactants

Sample 2 and 6, which contain cocamidopropyl betaine (CAPB) and lauryl dimethylamine oxide (AO) showed the good surface tension. SDS, ADS, and CAPB shows week acid (pH 6~7). CAPB has bifunctional groups, which are both cationic and anionic property. In acidic atmosphere, CAPB acts as cation [13]. Therefore, the charge interaction between anionic and cationic is dramatically reduced and it influences to surface tension and CMC [14].

Compared in sample 3 to 5, the difference between them is hydrocarbon length of lipophilic group. As it can be confirmed from chemical structure in Table 1, the hydrophobic chain length of butyl glucoside (BG), octyl glucoside (OG) and decyl glucoside (DG) is four, eight and ten, respectively. Generally, alcohols with 3 to 7 hydrocarbons used as cosurfactants. However, the alcohols, which have short alky chain length (〈5), can easily miscible with water. Besides, BG is more hydrophilic than butanol, thus, it is more miscible in water than butanol and interrupts the formation of micelles. Therefore, the sample 3 showed that not good property of CMC and surface tension compared with sample 1 [5]. The sample 5 showed best performance among the surfactant mixtures, which include alkyl glucoside. DG has longer chain than BG and OG. In general, the surface tension and CMC shows the best when hydrophobic chain length around 10 to 12 [10, 15]. This is because if the chain is too short, the surfactants are simply miscible to water. On the other hand, if the chain is too long, the surfactants cannot form the micelle because they are hardly dissolved in water.

The plots of surface tension versus concentration of samples are shown in Fig. 2. Theoretically, the surface tension increases as the concentration of surfactant decreases. The surface tension measured in this paper, however, is decreased around CMC. Most of raw materials are commercial products, therefore, they have some impurities. For example, alkyl glucosides are derived from fatty alcohol and glucose. SDS and ADS are also synthesized by alcohol, which is lauryl alcohol. The impurities in surfactant, especially, alcohol, cause this phenomenon. They exist in micelles when concentration is over CMC, however, if the concentration is lower than CMC, the micelles are broken and the impurities are absorbed on to the surface of the solution. The surface tension a little decreases around CMC from this reason.

3.2. Wettability test for surfactant mixtures

The wetting time was evaluated for

surfactant mixtures at room temperature (23 °C). Surfactant mixture consisting of SDS/ADS/DG/saponin (sample 5) showed the best wettability (14 sec). Although the surface tension is not improved against consisting of only anionic surfactants, the wetting power was greatly advanced. The cottons are textiles having very large surface area, thus, the rate of wetting of surface is important. In single surfactant solutions, wettability is increased as the alkyl chain length is increased at very low concentration (0.1 wt.%). Furthermore, if there are branched hydrocarbon chain, wettability is improved. Since they have larger molecular area, they can diffuse to surface rapidly. On the other hand, the wetting can be enhanced by decreasing in equilibrium surface tension or increment of solubility for surfactant in water at mixed surfactant solutions system. The mixture with DG showed a low surface tension and DG has a lot of hydroxyl group that can help soluble well in water, hence, the sample 5 showed the lowest wetting time [13, 16-18].

3.3. Cleaning performance test for surfactant mixtures

The detergency of various surfactant mixtures at different temperatures is presented in Fig. 4 and 5. Fig. 4 indicates that the absorption spectra of contaminate, especially oil red. Oil red has the appearance of red powder with maximum absorption at 359 and 518 nm. Detergency was computed by

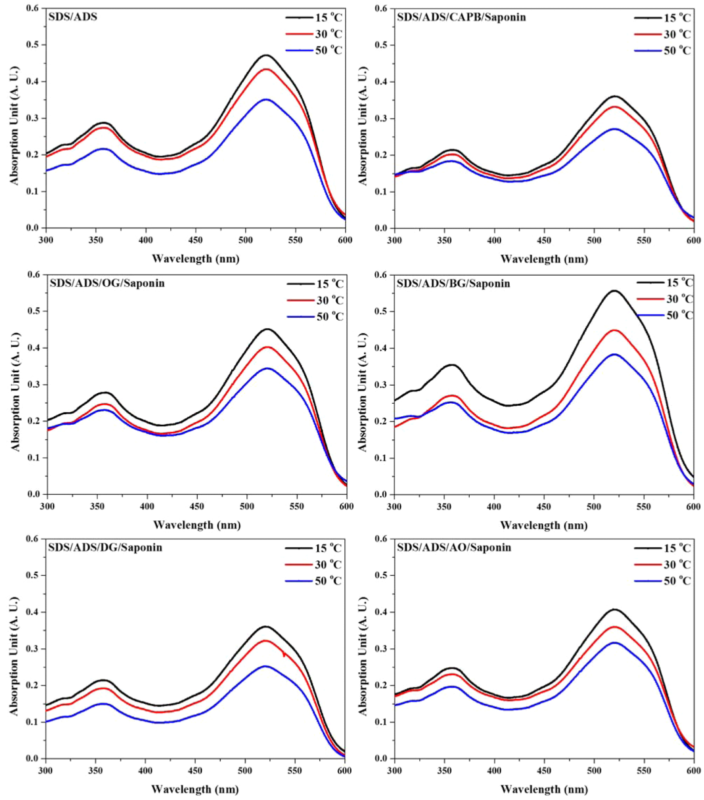


Fig 4. Absorption spectra of contaminants extracted by tetrachloroethylene for formulations at 15 °C, 30°C, and 50°C

absorption peak at 518 nm. It was calculated in the following manner.

$$Detergency = 1 - \frac{A_{sample}}{A_{water}},$$

where A_{sample} and A_{water} are absorption peaks of contaminate at 528 nm from each sample and washed by only water, respectively. The cleaning power of every sample was increased as the temperature rises. This is because the activity of surfactant and the dispersion of pollutant to water were improved. In addition, the CMC was reduced as the temperature was increased. Thermodynamic factors for transfer of surfactant molecules in solution to micelles were predicted from the temperature dependence of CMC. The free energy of transfer could be indicate by

$$\Delta G_{w \to m} = -RT \ln CMC$$

From this expression, △G shows more negative as the temperature increases [19]. Therefore, the detergency was proportional to the temperature.

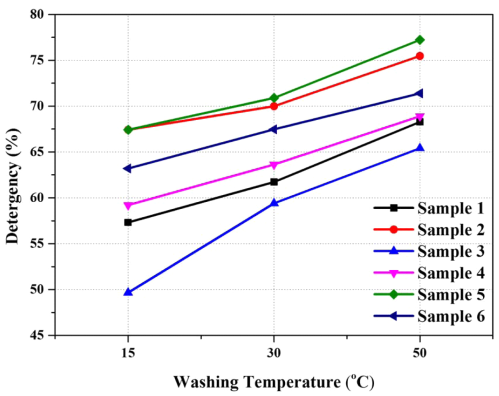


Fig. 5. Detergency performance for various samples at 15 °C, 30°C, and 50°C

The best performance of cleaning is surfactant mixtures with DG (sample 5). For high temperature detergency, the sample 5 showed more than 10 % of the cleaning power compared to sample 5 which showed the lowest performance. Compared to sample 2 and 5, sample 2 suggested a little more enhancement than sample 5. Although sample 2 showed the best at CMC and surface tension, the wettability of it was lower than sample 5. The washing was occurred not only at the surface but also in the cotton. If the surface tension is low, the cleaning power of the surface is good. However, this does not describe the detergency inside of the cotton. Consequently, detergency should be evaluated surface tension and CMC as well as wettability.

4. Conclusions

This paper reports the property and performance of surfactant mixtures which are anionic, anionic/amphoteric/nonionic, and anionic/nonionic. Six numbers of samples were evaluated by surface tension, wetting time, and based on them, detergency was measured. The synergy effect was revealed by adding amphoteric and nonionic surfactant. In mixed SDS/ALS anionic surfactants, addition of different type of surfactants enhanced the surface tension, CMC and wettability. Because of the charge interaction between surfactants, the surface properties of mixtures were enhanced. If the surface tension and CMC were enhanced, the wettability was also improved. However, they are not exactly related to wettability. This is related charge interaction as well as solubility of surfactants. The hydrocarbon chain length is also important factor. When the hydrocarbon chain length is too short, they are easily solubilized in water and it hampers the formation of micelles.

Detergency was influenced not only surface tension but also wettability. In many papers, they explain cleaning performance by using only surface property of surfactants, such as surface tension and CMC. To assess the cleaning power, cotton discs were used and the contaminants were immersed on the surface and in the cotton. Since the surface area of cotton is large, detergency is hard to be explained using only surface property of surfactants. Detergency was evaluated with surface tension as well as wettability.

Acknowledgments

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