Original Article

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Physicochemical properties and detergency of special electrolytic-reduction ion water

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SUMMARY The detergency of special electrolytic-reduction ion water (S-100) was evaluated in comparison with typical synthetic surfactants. Furthermore, to examine the cleaning mechanism of S-100, various physicochemical characteristics of S-100 were measured and a comprehensive evaluation of cleaning was performed. S-100 (10%) had a detergency comparable to that of various surfactants, such as sodium dodecyl sulfate and sodium dodecyl benzene sulfonate, which are generally blended or mixed in residential detergents. In addition, concentrated aqueous solutions of 10% or more of S-100 showed stronger detergency. The cleaning mechanism of S-100 is mainly attributed to the effect of surface tension reduction due to dissolved hydrogen or hydrogen nanobubbles in S-100, and the alkalinity generated by electrolysis charged the surface of the dirt or adherend, resulting in a peeling effect.

Keywords Detergency, electrolyzed deoxidized and ionized water, soiled fabric, hydrogen nano-bubble, CMC

1. Introduction

Surfactants have a high detergency against oil stains and are essential for daily use as the main component of detergents for homes, tableware and laundry. However, since there are many opportunities for contact with living bodies, many skin and mucosal disorders caused by surfactants have been reported (*1*). In the health hazard hospital monitor report related to household goods from the Ministry of Health, Labour and Welfare, many skin or mucous membrane disorders due to detergents have been published. Furthermore, environmental pollution of rivers and seawater by detergents, as well as toxicity to fish (*2*), are well-known issues.

Electro-reduced water is a strong alkaline and has extremely strong reducing power that can be obtained in the cathode chamber when electrolytically diluting a solution. Electrolyzed water has a high concentration of dissolved hydrogen (*3*), and is used for cleaning by exfoliation (*4*), deodorization, sterilization and dust prevention, as well as rust and antiseptic effects by antioxidant action. Utilizing these characteristics, it is now industrially used as a surface cleaning solution for cutting and precision equipment.

The effectiveness of washing using electrolytically reduced water has been investigated by comparing the detergency with other aqueous solutions (*5*). It has also been reported that special electrolytic reduced water has an emulsifying effect (*6*), and it is possible to prepare a medical emulsion that can be emulsified without using a surfactant. The reported effects of applying electrolytically reduced water to living bodies include antimicrobial properties (*7*), improvement effect on skin injury (*8,9*), protecting DNA from oxidative damage (*10*), anti-diabetic effects (*11*) and antitumor effects (*12*). In contrast, few adverse events have been reported to date.

Specially reduced electrolytic water (S-100) is manufactured using a method that differs from the conventional electrolytic reduced water method. The general production method of electrolyzed reduced water is purified by the flow of tap water → soft water → electrolyte → electrolysis, but the production method of S-100 is purified by the flow of tap water → pure water → deaeration → electrolyte → "electrolysis at high voltage" → "stabilization tank". In general, electrolyzed reduced water uses sodium chloride, fatty acid sodium, potassium chloride or fatty acid potassium as the electrolyte, whereas S-100 utilizes multiple electrolytes originating from natural seawater and minerals.

As mentioned earlier, S-100 as a cleaning agent generally contains properties that are safe for the living body and has little impact on the environment. However, there have been no published studies comparing the cleaning action of S-100 with synthetic surfactants commonly used as residential detergents. In this study, the detergency of S-100 was evaluated in comparison with typical synthetic surfactants. Furthermore, to investigate the cleaning mechanism of S-100, various physicochemical characteristics of S-100 were measured and a comprehensive evaluation of cleaning was performed.

2. Materials and Methods

2.1. Materials

Special electrolytic-reduction ion water (product name S-100) was provided by A. I. System Products Corp. (Aichi, Japan). Sodium dodecyl sulfate (SDoS) was purchased from FUJIFILM Wako Pure Chemicals Co., Ltd. (Osaka, Japan). Sodium dodecyl benzene sulfonate (DBS) and Sodium 1-decane sulfonate (SDeS) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All other reagents were special grade.

Contaminated cloth for measuring detergency was standard artificially contaminated cloth EMPA 101 (Fabric type: cotton, dirt component: carbon black/olive oil) purchased from Nippon Shizai Co., Ltd. (Osaka, Japan).

2.2. Methods

2.2.1. Preparation of sample solution

S-100 stock solution was used as 100% sample solution, and S-100 stock solution was diluted with purified water to prepare aqueous solutions of various concentrations (10, 30, 50 and 80%). Three different anionic surfactants of SDoS, DBS and SDeS were used as comparative controls. Each surfactant was prepared as an aqueous solution with various concentrations (0.1, 0.5, 1.0 and 1.5%).

2.2.2. Detergency test

Each sample solution (25 mL) was placed in a sample bottle, immersed in a contaminated cloth (EMPA 101) cut to 1.5 × 1.5 cm, attached to a shaker and shaken at 185 rpm for 30 minutes. The contaminated cloth was taken out and rinsed with purified water for 5 minutes × 2 times. After which, the reflectance of the contaminated fabric was measured before and after shaking using a compact color and whiteness meter (Color Mater NW-11, Nippon Denshoku Industries Co., Ltd., Tokyo, Japan). The cleaning efficiency was calculated using the following formula. First, the amount of dirt was calculated from the reflectance using the Kubelka-Munk formula (I):

$$K/S = (1 - R)^2/2R \quad \text{(I)}$$

(K = Absorbance coefficient, S = Light scattering coefficient, R = Surface reflectance)

Furthermore, the soil removal rate (%) (II) was calculated using the following equation:

$$\text{Dirt removal rate (\%)} = \frac{\text{contaminated cloth K/S - cleaning cloth K/S}}{\text{contaminated cloth K/S - Clean cloth K/S}} \times 100 \quad \text{(II)}$$

2.2.3. Evaluation of various physicochemical properties

The surface tension of each sample solution was measured by the ring method using a Du Noüy surface tension meter. The oxidation-reduction potential (ORP) of various sample solutions was measured using HORIBA ORP electrodes. The pH of each sample solution was measured using a HORIBA pH electrode. Both measurements were performed at room temperature (25 ± 1°C).

3. Results

3.1. Cleaning efficiency of S-100 and various synthetic surfactants

The concentration of each surfactant was set to 0.1, 0.5, 1.0 and 1.5% with reference to the critical micelle concentration (CMC) of each component. In addition, S-100 was tested in aqueous solutions with concentrations of 50% and 100% for confirming concentration dependence, as well as 10%, which is a concentration used industrially as a cleaning agent. The cleaning efficiency of 10% S-100 aqueous solution was about 90% of the cleaning efficiency of 0.1% SDoS or 0.1% DBS aqueous solution (Figure 1); it also showed higher cleaning efficiency than 0.1-0.5% SDeS aqueous solution. Furthermore, in order to investigate the concentration dependence of S-100 cleaning efficiency in more detail, a test to determine the cleaning efficiency for 30% and 80% concentrations was also conducted in addition to the 10, 50 and 100% aqueous solutions (Figure 2). The cleaning efficiency of S-100 increased in a concentration-dependent manner.

3.2. pH of S-100 and various synthetic surfactants at various concentrations

The pH of the S-100 stock solution (100%) was 12.3 and the pH of the 50% and 10% aqueous solutions were 12.0 and 11.3, respectively (Figure 3). In contrast, various synthetic surfactants were almost neutral at pH 5.5-7.0, irrespective of concentration.

3.3. Surface tension of S-100 and various synthetic surfactants

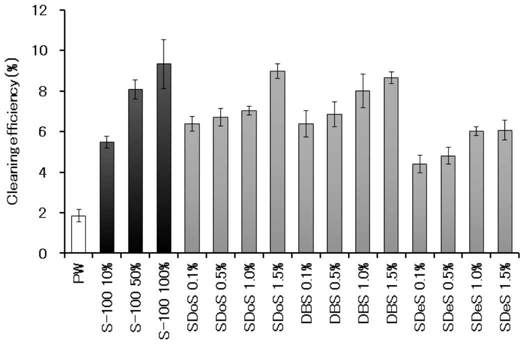

Figure 1. Cleaning efficiency of S-100 and various synthetic surfactants. (*n* = 5, mean ± S.D.). PW: purified water.

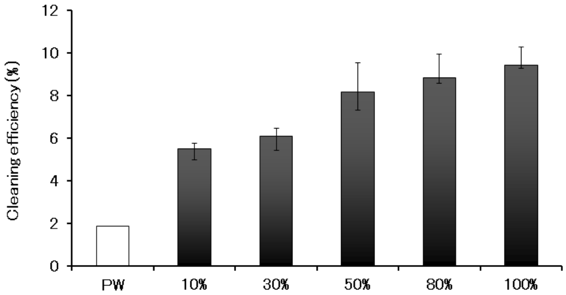

Figure 2. Cleaning efficiency of S-100 at various concentrations. (*n* = 5, mean ± S.D.). PW: purified water.

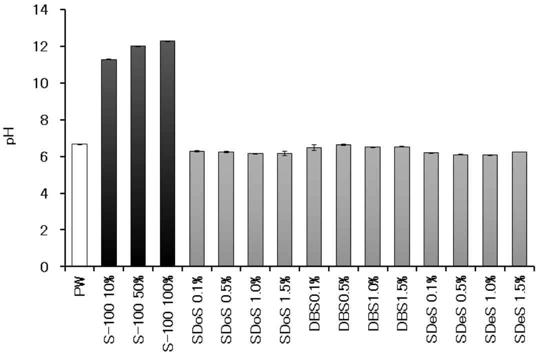

Figure 3. pH of S-100 and various synthetic surfactants at various concentrations. (*n* = 5, mean ± S.D.). PW: purified water.

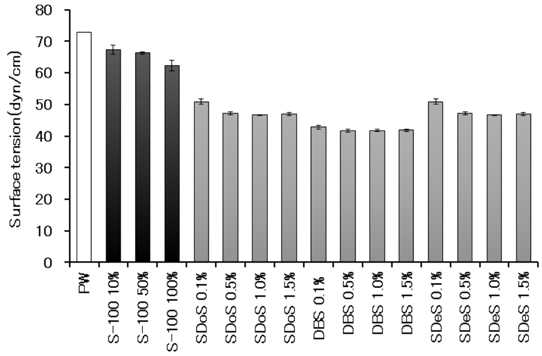

Figure 4. Surface tension of S-100 and various synthetic surfactants. (*n* = 5, mean ± S.D.). PW: purified water.

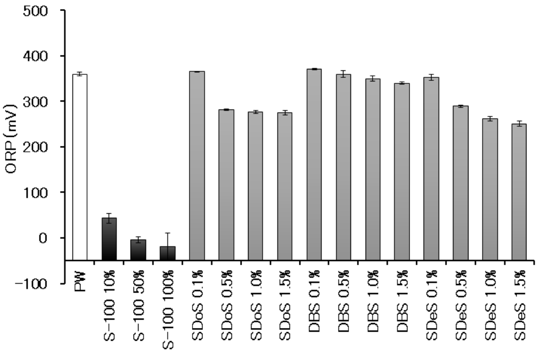

Figure 5. ORP of S-100 and various synthetic surfactants. (*n* = 5, mean ± S.D.). PW: purified water, ORP: oxidation-reduction potential.

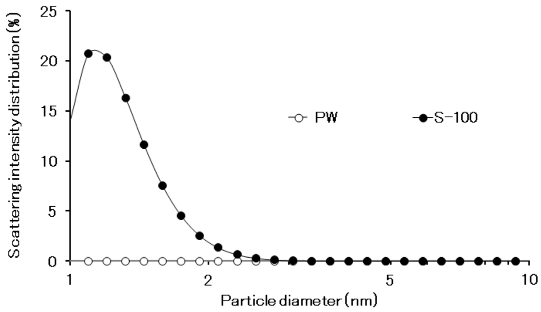

Figure 6. Scattering intensity distribution of hydrogen nanobubbles in S-100 solution and purified water (%). PW: purified water.

The surface tension of the S-100 stock (100%), 50% aqueous and 10% aqueous solutions were 62.3 dyn/cm, 66.3 dyn/cm and 67.4 dyn/cm, respectively. These values were all lower than that of purified water (72.8 dyn/cm) (Figure 4). In contrast, the surface tensions of various synthetic surfactants were in the range of 41.8-50.9 dyn/cm, and all the surfactants showed values lower than that for S-100.

3.4. ORP of S-100 and various synthetic surfactants

The ORP (oxidation-reduction potential) of the S-100 stock (100%), 50% and 10% solutions were -18.9 mV, -4.3 mV and 43.4 mV, respectively, which were significantly lower than that of purified water (360.0 mV) (Figure 5). In contrast, the ORPs of various surfactants were between 250-370 mV, which were similar to or lower than the ORP of purified water.

3.5. Scattering intensity distribution of hydrogen nanobubbles in S-100 solution

The particle size and particle size distribution were measured using the zeta-potential and particle size analyzer system ELSZ-1000ZS (Otsuka Electronics Co., Ltd., Osaka Japan). S-100 was confirmed to contain particles with an average particle size of 1-3 nm (average particle size 1.3 nm) (Figure 6).

Table 1. Names and structural formulas of surfactants used in this study

Surfactant name	Chemical structural formula	MW	CMC (mM)
Sodium dodecyl sulfate (SDoS)	$C_{12}H_{25}OSO_3Na$	288.38	8.2
Sodium dodecyl benzenesulfonate (DBS)	$C_8H_{17}C_6H_4SO_3Na$	348.50	3.5~8.9
Sodium 1-decanesulfonic acid (SDeS)	$C_{10}H_{21}SO_3Na$	244.33	40

CMC (Critical micelle concentration in pure water at 25°C), MW: Molecular weight, CMC: critical micelle concentration, SDoS: Sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$), DBS: Sodium dodecyl (octyl) benzenesulfonate ($C_8H_{17}C_6H_4SO_3Na$), SDeS: Sodium 1-decanesulfonic acid ($C_{10}H_{21}SO_3Na$)

4. Discussion

In order to evaluate the detergency of S-100 special electrolyzed reduced water in comparison with typical synthetic surfactants, the detergency of contaminated cloth immersed in different aqueous solutions was determined. Evaluated synthetic surfactants included SDoS, DBS and SDeS, which are typical anionic surfactants commonly used as house or skin cleansers (Table 1).

The 10% S-100 aqueous solution, which is currently used as a cleaning agent for precision machinery, has a comparable cleaning power to that of various surfactants generally used in residential detergents (Figure 1). Furthermore, in order to investigate the concentration dependence of S-100 cleaning efficiency in more detail, the cleaning efficiencies for 10, 30, 50, 80 and 100% concentrations were also determined. The cleaning efficiency of S-100 increased in a concentration-dependent manner (Figure 2). These results clarified that S-100 has a cleaning power comparable to that of various synthetic surfactants. In order to further investigate the mechanism of this cleaning, pH, surface tension and ORP were measured as physicochemical properties of the S-100 aqueous solution, and compared with that of various synthetic surfactant solutions (Figures 3, 4 and 5).

In general, as a mechanism by which pH contributes to cleaning, alkaline agents negatively charge the surface charge of the dirt and the adhesion surface, thereby increasing the electrostatic repulsion force, and making it easier for the dirt to detach from the adhesion surface. This mechanism is known to contribute to cleaning by preventing reattachment (*13*). Therefore, the pH values of S-100 and various synthetic surfactants were measured (Figure 3). S-100 shows alkalinity because, in the water electrolysis process, water molecules are reduced at the cathode to generate hydrogen (H_2) and subsequently hydroxide ions (OH^-) (reaction formula 1). Various aqueous surfactant solutions are almost neutral possibly because the degree of dissociation of the sulfone and sulfate groups in each surfactant is large and does not affect pH.

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad \text{(reaction formula 1)}$$

As a mechanism by which the surface tension contributes to cleaning, for example, a surfactant with a surface tension-reducing action is adsorbed on the cleaning liquid and adhesion surface, and this contributes to cleaning by removing the dirt and dispersing the dirt in the cleaning liquid. Therefore, the surface tensions of S-100 special electrolytic reduced water and various synthetic surfactants at various concentrations were measured (Figure 4). Higher S-100 concentration corresponded to lower surface tension. In contrast, the surface tensions of various synthetic surfactants showed values lower than that for S-100. S-100 showed a lower surface tension than purified water because water molecules are reduced at the cathode to generate hydrogen (H_2) in the water electrolysis process (reaction formula 1).

If dissolved hydrogen is present, the ORP may be low. Therefore, ORP was measured to estimate the dissolved hydrogen concentration in S-100 electrolyzed reduced water and various synthetic surfactants (at 25°C and at each concentration) (Figure 5). The low ORP in S-100 may be due to the dissolved hydrogen generated at the cathode in the water electrolysis process to produce S-100. The ORP of dissolved hydrogen approaches that of purified water with dilution, but the hydrogen concentration does not decrease with dilution. In other words, even in a 10% solution in which S-100 is diluted 10-fold, the reducing power estimated from the reduction potential of S-100 is not simply reduced to 1/10; this can be explained by assuming that there is hydrogen dispersed in addition to the dissolved hydrogen.

Kikuchi *et al*. (*14*) found that dissolved hydrogen in electroreduction water obtained by electrolyzing an electrolyte solution contains dissolved hydrogen and colloidal nanobubbles (micro hydrogen bubbles) that are dissolved in molecular form above the saturation concentration. Therefore, if nanobubbles of hydrogen gas are also present in S-100, even if the dissolved hydrogen is diluted when the S-100 stock solution is diluted, then the hydrogen in the nanobubbles dissolves in the water. The hydrogen concentration may be higher than the concentration obtained by simply diluting S-100. Subsequently, according to the method of Takenouchi *et al*. (*15*), the particle size and particle size distribution were measured using a zeta-potential and particle size analyzer system. S-100 was confirmed to contain particles with an average particle size of 1 -

3 nm (average particle size 1.3 nm) (Figure 6). These particles are likely to be hydrogen nanobubbles. Based on these results, the cleaning mechanism of S-100 compared with each surfactant is discussed below. The two main cleaning mechanisms for the three types of surfactants (SDoS, DBS and SDeS) used in this experiment are as follows. One is that the surfactant is dissolved in the water, and the interfacial tension between the dirt or its attached surface and water is lowered, thereby removing the dirt from the attached surface. The other is that the surfactant is adsorbed on the dirt surface and the adhesion surface, such that the sulfonate ions or sulfate ions in the structure negatively charge both surfaces and creates an electrostatic repulsive force between the dirt and the adhesion surface.

On the other hand, the cleaning mechanism of S-100 electrolytically reduced water on stains may cause separation of the dirt from the adhesion surface, as well as repelling between the dirt and the adhesion surface, due to a mechanism different from that of the surfactant. The reason for this is that hydrogen dissolves in water, or the presence of hydrogen nanobubbles reduces the surface tension of the solution, which reduces the interfacial tension between the dirt or its attached surface and water, and removes the dirt from the attached surface. The pH of S-100 solution becomes extremely high due to electrolysis, the dirt surface and adhesion surface are negatively charged, and electrostatic repulsion is generated between the dirt and the adhesion surface.

The cleaning efficiency of S-100 is concentration-dependent and linear at concentrations from 10 to 100%. However, compared to purified water (the control), the relationship is not completely proportional, and cleaning efficiency is not proportional to the dilution rate (Figure 2). In a 10% aqueous solution, in which S-100 is diluted 10 times, the cleaning efficiency of S-100 is not simply reduced to 1/10. The effect of alkalinity may have a stronger influence on the cleaning power than the effect of surface tension reduction. Therefore, cleaning efficiency was measured for NaOH aqueous solution with the same pH 12 as S-100 in the same experimental system, and found to be 6.4 ± 0.58%, thus confirming the cleaning effect due to the alkaline cleaning solution.

In conclusion, S-100 special electrolyzed reduced water has the same detergency as other electrolytically reduced waters already on the market, and the 10% aqueous solution of S-100 was confirmed to have a cleaning power comparable to that of various surfactants such as SDoS and DOS that are mixed in general detergents. In addition, the cleaning mechanism considered from the various physicochemical properties of S-100 are mainly due to the effect of surface tension reduction by dissolved hydrogen or hydrogen nanobubbles in S-100 and the alkalinity generated by electrolysis. Furthermore, the peeling effect may have been produced by charging the surface of the oil stains.

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Conflict of Interest: Special electrolytic-reduction ion water (S-100) used in this study was manufactured by A. I. System products, Corp. Masahiro Okajima and Yoshinao Okajima are employees of A. I. System products, Corp.

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