

Decomposition of Sodium Dodecyl Sulfate Aqueous Solution Using Atmospheric-Pressure Non-Equilibrium Microwave Plasma Jet

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Abstract- Typical households use dish detergents, laundry detergent, and other synthetic detergents containing large amounts of surfactants. For example, in the case of laundry, it is common to use a combination of laundry detergent and fabric softener, and the anionic surfactants contained in laundry detergent and the cationic surfactants contained in fabric softener bond together to create a state where the surfactants do not easily decompose in an aqueous solution. As a result, surfactants that are drained to waterways without decomposing can cause environmental damage and pollution to ecosystems, oceans, and waterways. In this study, an aqueous solution containing anionic surfactants was treated by an atmospheric-pressure non-equilibrium microwave plasma jet using an Ar gas and an Ar + H₂ mixture gas to enable decomposition of the surfactants in the aqueous solution by the OH and H₂ radicals given off in the plasma.

I. INTRODUCTION

Today, typical households use many synthetic detergents, such as dish detergents and laundry detergents. These synthetic detergents contain large amounts of surfactants as the main ingredient for their cleansing action in removing dirt [1]. For example, in typical households, it is common to use a combination of laundry detergent and fabric softener that contains surfactants. The anionic surfactants contained in laundry detergent and the cationic surfactants contained in fabric softener will bond together to form a state where their enhanced cleansing action and softening action cancel each other out, and the surfactants do not easily decompose in an aqueous solution. As a result, when surfactants are drained to waterways, they have not decomposed and can cause environmental damage and pollution to ecosystems, oceans, and waterways. Most surfactants are sources of water pollution in rivers, streams, lakes, oceans, and other bodies of water, and this water pollution adversely affects aquatic life and harms the environment [2]. For this reason, the

development of a method for easily decomposing surfactants from aqueous solutions containing surfactants is vital for reducing the future environmental impact on oceans and rivers.

Previously, the authors of this study conducted research where an atmospheric-pressure non-equilibrium plasma could be used to treat an organic matter aqueous solution containing pigments, and they were able to successfully control color changes of the pigments in the aqueous solution itself and the pH value within the aqueous solution by using the radicals (OH, O*, O₂, etc.) given off from the plasma [3].

In this study, an aqueous solution containing anionic surfactants was treated by an atmospheric-pressure non-equilibrium microwave plasma jet using an Ar+H₂ mixture gas. The OH and H₂ radicals given off by the gases in the plasma caused a chemical reaction with the surfactants in the aqueous solution. It was found that this chemical reaction generated nitric acid within the aqueous solution, which facilitated decomposition of the surfactants and shifted the pH to a more acidic state.

II. HELPFUL HINTS

Figure 1 shows a diagram of the experimental equipment. In the experiment, a glass petri dish containing sodium dodecyl sulfate (SDS; CH₃(CH₂)₁₁O

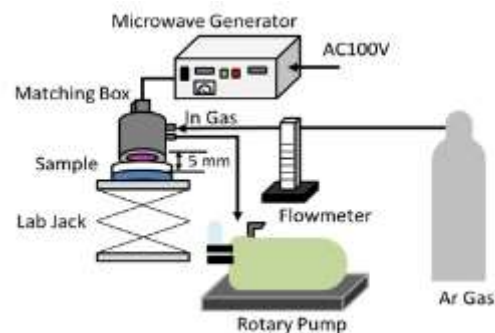


Fig. 1. Experimental setup

SO₃Na) aqueous solution (30 mL) classified as an anionic active agent was placed at a position 5.0 mm from the nozzle of the atmospheric-pressure non-equilibrium microwave plasma jet (ADTEC Plasma Tech. Co.). At the surface of the aqueous solution, plasma was emitted to test whether the surfactants were decomposed by the plasma treatment for the aqueous solution containing surfactants.

The atmospheric-pressure plasma was generated using a plasma jet torch electrode, and a steady discharge was maintained using a microwave power supply (2.45 GHz) for generating plasma. The transmission route of the microwaves used a coaxial cable (RG-393). The atmospheric-pressure non-equilibrium microwave plasma jet torch electrode had a basic structure where the main material of the entire torch was aluminum, the torch discharge tube used quartz glass that was 13 mm in diameter and 170 mm in length, and the antenna used aluminum that was 7.0 mm in diameter and 23 mm in length [4-7]. The plasma input power for generating the plasma was 100-150 W, and the plasma used an Ar gas or an Ar + H₂ mixture gas (10-20 L/min).

Figure 2 shows the chemical structures of the SDS surfactants and methylene blue. The SDS surfactants consist of a hydrophilic region and oil region. Normally, anionic surfactants generate cationic pigments and ionic associates and are extractable into chloroform and other organic solvents. Methylene blue, which is a cationic pigment, uses chloroform to extract SDS, which is an anionic surfactant, and ionic associates of methylene blue, and this absorbance can be measured [8].

From the 30 mL of aqueous solution containing surfactants treated by plasma, 15 mL was extracted and put into a screw cap bottle together with 5.0 mL of methylene blue aqueous solution (5.0 mL) and chloroform (10 mL). This bottle was mixed for 3 minutes and left to sit. Then, a volume of only 1.0 mL was extracted from the chloroform layer that had sunk to the downstream section, 9.0 mL of chloroform was added to this extracted volume to dilute it, and then the absorbance was measured.

In the same way, a pH meter (HORIBA; pH / COND METER D-54) was used to measure the hydrogen ion concentration index in the aqueous solution after plasma treatment for confirming the change in the hydrogen ion concentration index. To find out the decomposition mechanism of the aqueous solution containing surfactants that was treated by plasma, the analysis method used the methylene blue absorptiometric method (JIS K 0102) with spectrophotometer (SHIMADZU; Multispec-1500).

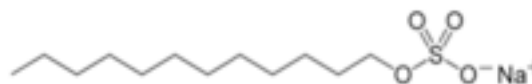


Fig. 2. Chemical structure model of SDS

III. RESULTS AND DISCUSSION

In Figure 3, a calibration curve was created for calculating the SDS concentration after plasma emission. The same figure shows the absorbance of SDS and methylene blue ionic associates based on the concentration of the SDS aqueous solution. To create this figure, SDS aqueous solutions with concentration 1.0×10^{-6} M and 5.0×10^{-6} M, 1.0×10^{-5} M, 5.0×10^{-5} M, and 1.0×10^{-4} M were prepared, and 15 mL of aqueous solution was extracted from each and put into a screw cap bottle together with 5.0 mL of methylene blue aqueous solution and 10 mL of chloroform. Next, a volume of 1.0 mL was extracted from this chloroform layer and 9.0 mL of chloroform was added to this extracted volume to dilute it. Then, a spectrophotometer was used to measure the absorbance of the SDS and methylene blue ionic associates.

In the same way, the remaining concentration of SDS after plasma emission was found. The absorbance after 15 minutes of plasma emission was a value of 0.8 using argon gas, and the remaining concentration of SDS after plasma emission was found to be 4.8 M from the same figure. In the same way, when the argon-hydrogen mixture gas was used, we found an absorbance of 0.08, and the remaining concentration of SDS was found to be approximately 5.0 M.

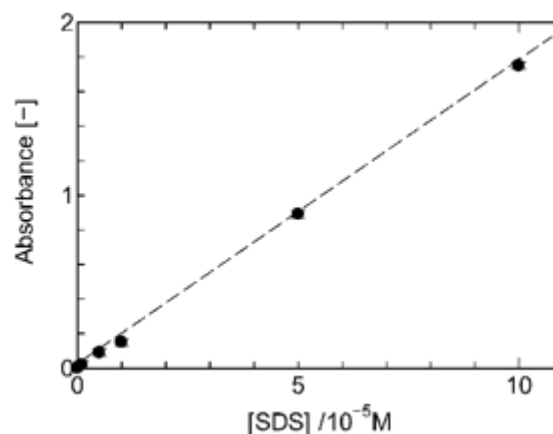


Fig. 3. Measurement of absorbance for concentration of SDS aqueous solution.

Figure 4 shows the results when argon gas or argon-hydrogen mixture gas is injected and the absorbance of the ionic associations at a wavelength of 656 nm was measured for each plasma treatment time. This figure shows that the absorbance value decreased noticeably as the plasma treatment time increased. In the same way, when examining the plasma input power and plasma generated gas, increasing the input power and plasma generated gas flow rate resulted in a significant decrease in absorbance by the ionic associates due to the increased generation of radicals and their longer lifetimes [9]. And so, it is thought that the oil component and hydrophilic group itself of the

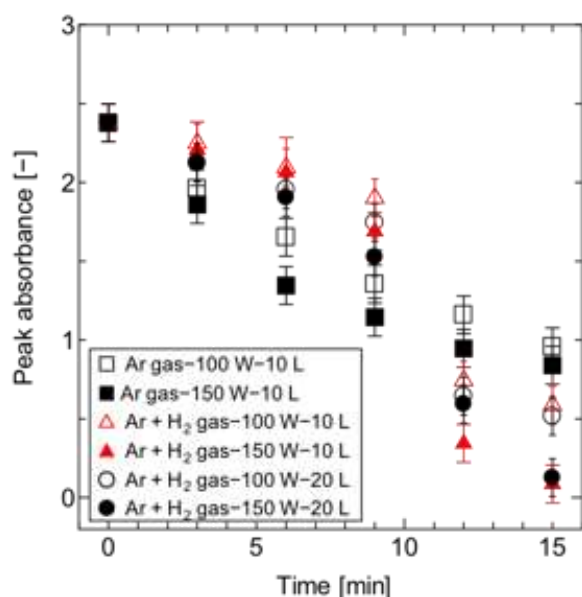


Fig. 4. Relationship between the maximum absorbance of plasma gas flow rate and plasma power and the plasma treatment time of the atmospheric-pressure non-equilibrium microwave plasma jet.

SDS aqueous solution are decomposed by the radicals that contribute to the generation of OH and H₂ [10-13] from the plasma due to the plasma treatment on SDS, which the associates are derived from.

Figure 5 shows the relationship with the pH value of aqueous solution containing surfactants for each plasma treatment time when an Ar gas or Ar+H₂ mixture gas is used. When plasma treatment was performed on purified water using an Ar gas or Ar+H₂ mixture gas, the pH value of the aqueous solution showed 3.0 to 4.0. This figure shows that, as the plasma treatment time increased, the pH value decreased, and the acidity became stronger. In the same way, this shows that, as the plasma input power and plasma gas flow rate increased, the pH value decreased, and the acidity became stronger. The primary reason for this is that the surfactants are decomposed by a chemical reaction with

the aqueous solution due to OH radicals and H₂ radicals generated from the Ar or Ar+H₂ mixture gas. The mechanisms for generating OH radicals and H₂ radicals from the Ar or Ar+H₂ mixture gas are shown in the following three chemical formulas (1)-(4) [14-16]

The shift of the pH to a more acidic state is thought to be due to the generated OH radicals and H₂ radicals reacting with nitrogen in the air for certain types of gases and radicals given off from the plasma so that a chemical reaction occurs between the hydrogen ions and nitrate ions in the aqueous solution to generate nitric acid [17-19].

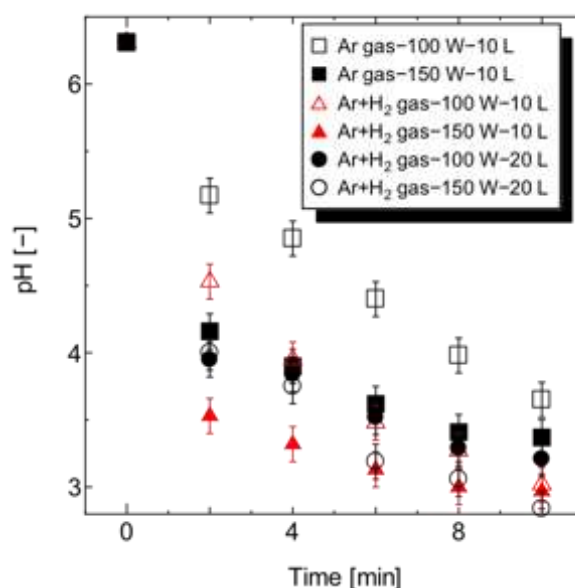
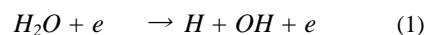
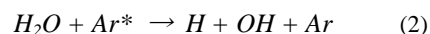


Fig. 5. Relationship between the maximum absorbance of plasma gas flow rate and plasma power and the plasma treatment time of the atmospheric-pressure non-equilibrium microwave plasma jet.



IV. CONCLUSIONS

In this study, we tried to decompose surfactants in aqueous solutions containing anionic surfactants by using an atmospheric-pressure plasma treatment. An atmospheric-pressure non-equilibrium plasma in Ar or Ar + H₂ mixture gas was used to treat an SDS aqueous solution, and the absorbance was measured by a

spectrophotometer. Our results showed that, over time, the peak value dependent on SDS decreased and the pH value changed so that the aqueous solution became more acidic. We found that the nitric acid content increased due to radicals, and this led to decomposition of the surfactant aqueous solution.

In the future, we plan to test atmospheric-pressure plasma treatments for developing an atmospheric-pressure plasma treatment technology for decomposition processes of aqueous solutions containing surfactants where cationic surfactants and anionic surfactants have bonded.

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REFERENCES

- [1] E. Andrews, S. M. Larson, *Environ. Sci. Technol.*, 27, 857 (1993).
- [2] M. Soda, H. Okochi, H. Ogata and H. Okawa, *BUNSEKI KAGAKU*, 62, 589 (2013)
- [3] T. Yuji, *J. Surf. Finish. Soc. Jpn.* 68, 551 (2017).
- [4] T. Yuji, T. Urayama, S. Fujii, N. Mungkung and H. Akatsuka, *Surface and Coatings Technology*, 202, 5289 (2008).
- [5] T. Yuji, S. Fujii, N. Mungkung and H. Akatsuka, *IEEE Trans. on Plasma Science*, 37, 839 (2009).
- [6] T. Yuji, T. Urayama, S. Fujii, Y. Iijima, Y. Suzaki and H. Akatsuka, *Electron. Commun. Jpn.* 93, 42 (2010).
- [7] J. Sukhapan and P. Brimblecombe, *The Scientific World Journal*, 2, 1138 (2002).
- [8] P. Attri, Y. H. Kim, D. H. Park, Ji H. Park, Y. J. Hong, H. S. Uhm, K.-N. Kim, A. Fridman and E. H. Choi, *Scientific Reports*, 5, 9332 (2015).
- [9] S. Samukawa, M. Hori, S. Rauf, K. Tachibana, P. Bruggeman, G. Kroesen, J. C. Whitehead, A. B. Murphy, A. F. Gutsol and S. Starikovskaia, *Journal of Physics D: Applied Physics*, 45, 253001 (2012).
- [10] T. Atsushi, Y. Ono, S. Fukui, S. Ikawa and K. Kitano, *Applied physics letter*, 100, 254103 (2012).
- [11] B. Pateyron, M.-F. Elchinger, G. Delluc, and P. Fauchais, *Plasma Chemistry and Plasma Processing*, 12,421(1992).
- [12] H. Kuwahata and T. Yamaguchi, *e-J. Surf. Sci. Nanotech.* 13, 474 (2015).
- [13] T. Yuji, H. Kawano, S. Kanazawa, T. Ohkubo and H. Akatsuka, *IEEE Transactions on Plasma Science*, 36, 976 (2008).
- [14] H. Inui, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine, H. Kano, N. Yoshida and M. Hori, *Appl. Phys. Express* 3 126101 (2010).
- [15] Y. Ichkawa and N. Mason, *J. Phys. Chem. Ref. Data*, 34, 1 (2005).
- [16] M. Kirkpatrick, B. Dodet and E. Odic, *International Journal of Plasma Environmental Science and Technology*, 1, 96 (2007).
- [17] K. Tachibana and K. Yasuoka, *International Journal of Plasma Environmental Science & Technology* 8,117 (2014).
- [18] A. A. Joshi, B. R. Locke, P. Arce, and W. C. Finney, *Journal of Hazardous Materials*, 41, 3 (1995).
- [19] C. Douat, S. Hübner, R. Engeln and J. Benedikt, *Plasma Sources Science and Technology*, 25, 025027 (2016).

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