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Application of Atmospheric-pressure Non-equilibrium Microwave Discharge Plasma Jet for Linear Alkylbenzene Sulfonates in Aqueous Solution

Toshifumi Yuji [1], Kenichi Nakabayashi [1], Wittawat Poonthong [1] and Yoshifumi Suzaki [2]
[1]University of Miyazaki
1-1, Gakuenkibanadai-nishi, Miyazaki, 8892192, Japan
First.yuji@cc.miyazaki-u.ac.jp; Second. nakabys@cc.miyazaki-u.ac.jp; Third. poonthong.golf2538@gmail.com
[2]Kagawa University
1-1, Saiwai-cho, Takamatsu-city, Kagawa, 7608521, Japan
Fourth. suzaki.yoshifumi@kagawa-u.ac.jp

***Abstract* -** Many of synthetic detergents such as dish detergents and laundry detergents contain anionic surfactant and are released into rivers and oceans as drainage water together with different detergent, soap, and fabric softener. In such drainage water, anionic surfactant and cationic surfactant bond and are difficult to decompose in aqueous solution when released as drainage water, leading to possible ecological and environmental destruction. In order to overcome such challenges, we studied atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation to prompt decomposition of surfactant through chemical reaction between radical species released from atmospheric-pressure non-equilibrium microwave discharge plasma jet and surfactant in aqueous solution. We found out and report herein that the atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation could decompose surfactant in the aqueous solution containing anionic surfactant.

***Keywords*:** Microwave Discharge Plasma, Linear Alkylbenzene Sulfonate, Methylene Blue Absorptiometric Method, Plasma Irradiation

1. Introduction

In recent years, many synthetic detergents such as dish detergents and laundry detergents have been used in households. Such synthetic detergents contain a good amount of surfactant for cleaning effect. Taking an example of a use case doing laundry using surfactant, it is now quite common to use cleaning detergent together with washing beads acting as fabric softener/refresher. The anionic surfactant in the laundry detergent and cationic surfactant in the softener and washing beads bond, offsetting the cleaning effect and softening/refreshing effect and making them difficult to decompose in aqueous solution. The drainage water after laundry flowing into rivers in such state will leave the surfactant not decomposed, becoming a possible cause of environmental destruction and pollution in the ecosystem, oceans, and rivers [1-3]. It is an urgent need to decompose and process anionic and cationic surfactant in the laundry drainage water to conserve the water quality of rivers and oceans.

We have been studying to urge the decomposition of surfactant in aqueous solution with OH radicals generated from the atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation on the aqueous solution containing Sodium Dodecyl Sulfate (SDS) [4] used in body wash. In the methylene blue absorptiometric method, a method to evaluate decomposition of surfactant in aqueous solution, we used anionic surfactant and methylene blue, which is the cationic pigment, to produce ionic associates and extracted them in the organic solvent such as chloroform. This revealed that irradiation with atmospheric-pressure non-equilibrium microwave discharge plasma jet promoted the decomposition of anionic surfactant in the solution containing anionic surfactant [5].

In this report, we evaluated the decomposition ability of surfactant through irradiation with atmospheric-pressure plasma on aqueous solution containing anionic surfactant, using typical Linear Alkylbenzene Sulfonate (LAS), major surfactant used in a good volume in the dish detergents for household use as our anionic surfactant [6]. The methylene blue absorptiometric method, a method to evaluate the pH change in the aqueous solution and decomposition of surfactant in aqueous solution after atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation, revealed remarkable changes in the absorbance measured with spectrophotometer, indicating the possibility to decompose surfactant in aqueous solution containing anionic surfactant with atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation.

2. Experiment & Setup

Fig. 1 shows the experimental equipment. In our experiment, aqueous solution containing 15 mL of linear sodium alkylbenzene sulfonate (Wako, molecular weight: 348.48) is set at the distance of 5.0 mm from the nozzle of the cylindrical electrode (6 needle electrodes; ADTEC Plasma Tech., Co.) at atmospheric pressure. We irradiated the interface of the aqueous solution with atmospheric-pressure non-equilibrium microwave discharge plasma jet in an attempt to decompose the aqueous solution with plasma irradiation of the surfactant solution. As the conditions to generate the atmospheric-pressure non-equilibrium microwave discharge plasma jet, we used 2.45 GHz microwave power supply (150 W； Mugge Co.) as the plasma-starting power, and Ar gas (10 L/min) as the gas for generating plasma. We used an oil rotary vacuum pump (G-15ULVAC: Co.) at 0.7 Torr to exhaust the heat generated in the electrodes to cool the plasma jet nozzles.

Fig. 2 shows the chemical structure of the LAS surfactant. The LAS surfactant consists of hydrophilic moiety and oil. The LAS solution used in the experiment was prepared by dissolving the LAS powder into deionized water to the concentration of 10^{-3} mol/L and 10^{-4} mol/L. In order to verify the decomposition mechanism of surfactant solution using plasma, we used methylene blue absorptiometric method (JIS K 0102) [7] to study the mechanism. The anionic surfactant produces ionic associates together with cationic pigment to be extracted into organic solvent such as chloroform. Using this property, we used methylene blue, a cationic pigment, to extract the ion associates of LAS, the anionic surfactant, and the methylene blue (3.0×10^{-3} mol/L) with chloroform and measured the absorbance.

Fig. 3 shows the chemical equation describing the chemical reaction between LAS surfactant and methylene blue. We removed 12 mL of the 15 mL of surfactant after plasma irradiation and put them together with 4.0 mL of methylene blue solution and 8.0 mL of chloroform into a screw bottle. After shaking the bottle for 3.0 minutes, the bottle was left for a while. Then we removed 1.0 mL of the chloroform layer, added 9.0 mL of chloroform to dilute the solution, and measured the absorbance using the spectrophotometer (SHIMADZU; Multispec-1500) for evaluation. In addition, we used liquid chromatography to study the decomposition of the surfactant in the solution containing the LAS surfactant after the irradiation with atmospheric-pressure non-equilibrium microwave discharge plasma jet, and evaluated the property and concentration of the ingredients in the liquid.

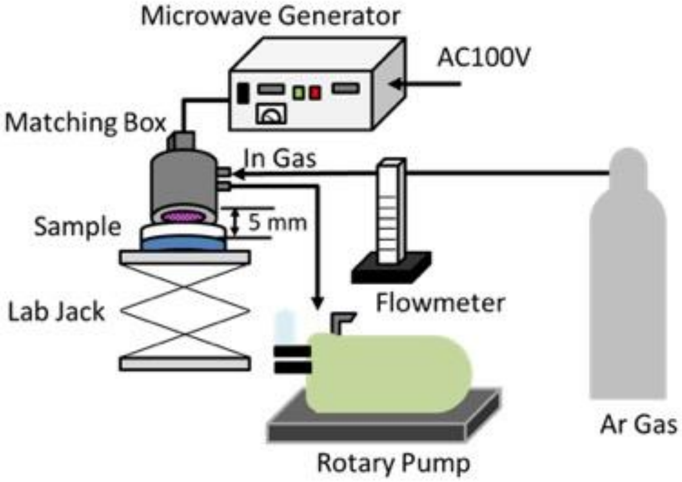


Fig. 1: Experimental equipment.

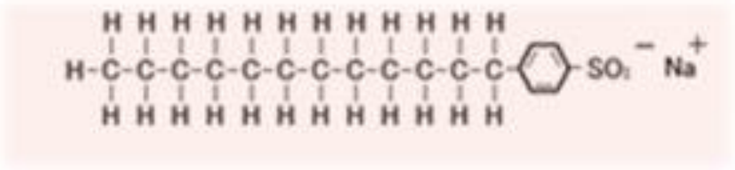


Fig. 2: Chemical structure of LAS.

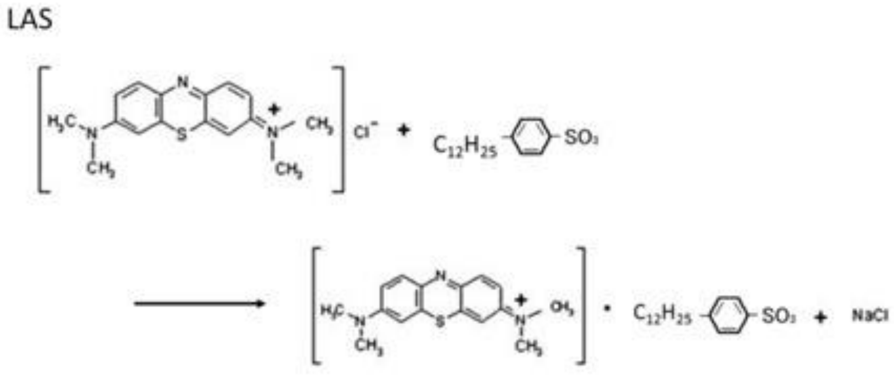


Fig. 3: Chemical bond of LAS + methylene blue.

3. Experiment Results & Discussions

Fig. 4 shows the measurement result of pH in the LAS solution by the plasma irradiation time when Ar gas was used to generate atmospheric-pressure non-equilibrium microwave discharge plasma jet. The figure shows a tendency that as the atmospheric-pressure irradiation time gets longer, the pH gets more acidic. Similarly, as the LAS concentration gets lower, the pH gets more acidic too. The atmospheric-pressure plasma irradiation time of 10 minutes showed the largest difference in absorbance from the untreated sample and thus is considered to be optimum. During the irradiation with atmospheric-pressure non-equilibrium microwave discharge plasma jet, radical species from the plasma react chemically on the interface of the solution. The H radicals generated from water molecules react with the air in the atmosphere, producing nitrate ion in the solution. This reaction suggests the tendency described above.

Fig. 5 shows the difference between the absorbance of associates (656 nm) of LAS and methylene blue without irradiation and that of ion associates of LAS and methylene blue by the Ar gas irradiation time. The figure compares the difference of absorbance between non-irradiated samples and plasma-irradiated samples by the irradiation time (value of non-irradiated samples subtracted by the value of samples after atmospheric-pressure irradiation). The difference between the non-irradiated samples and plasma-irradiated samples being positive means that the absorbance decreases after plasma irradiation. The reason why it decreases can be because the concentration of the ion associates of LAS and methylene blue in the chloroform extract is low. It suggests that the LAS surfactant decomposed with the plasma irradiation. The absorbance difference is the greatest at 10 minutes of plasma irradiation time with both LAS of 10^{-3} mol/L and 10^{-4} mol/L, suggesting that it saturates at this point. From that, we can say that the optimum irradiation time is 10 minutes.

Fig. 6 shows the measurement result of the spectrum obtained with liquid chromatography on the associates of LAS and methylene blue without plasma irradiation and on the ion associates of LAS and methylene blue after plasma irradiation using Ar gas. Comparing three large peaks observed before/after atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation in this figure, we can see difference in peak ratio. This can be due to change in chemical structure caused by the decomposition of LAS surfactant with plasma. Considering C and C' in the spectrum as 1, the peak area of A' was larger than that of A. Similarly, the peak area of B' was larger than that of B.

Fig. 7 shows the measurement result obtained with the liquid chromatography after the LAS decomposed with irradiation. As for the peak of undecomposed residue, we referred to ref [8]. The peak 3 in this graph is from residue which we assume to correspond to peak C after plasma irradiation. With the tendency, we can assume that the 1 and 2 of radiolytic products correspond to peaks A and B after plasma irradiation. We can consider the chemical described in the equation (1) shown below. As a result, we can estimate that the radical species produced in the plasma atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation react with LAS surfactant, unbinding the benzene ring and sulfo group.

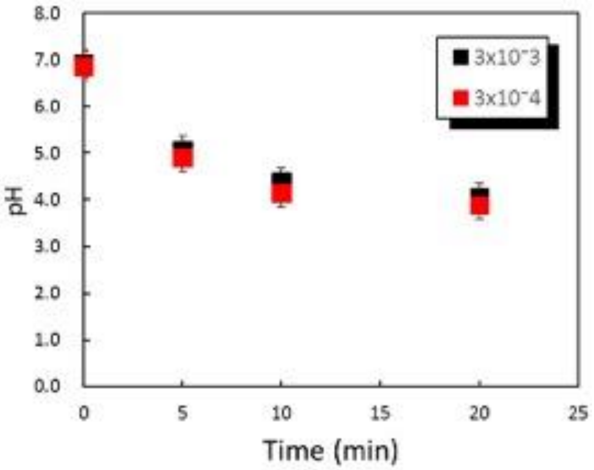


Fig. 4: Measurement of pH in the LAS solution by the plasma irradiation time.

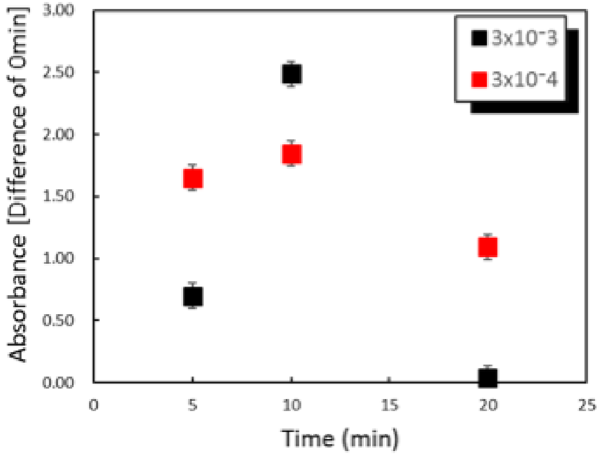
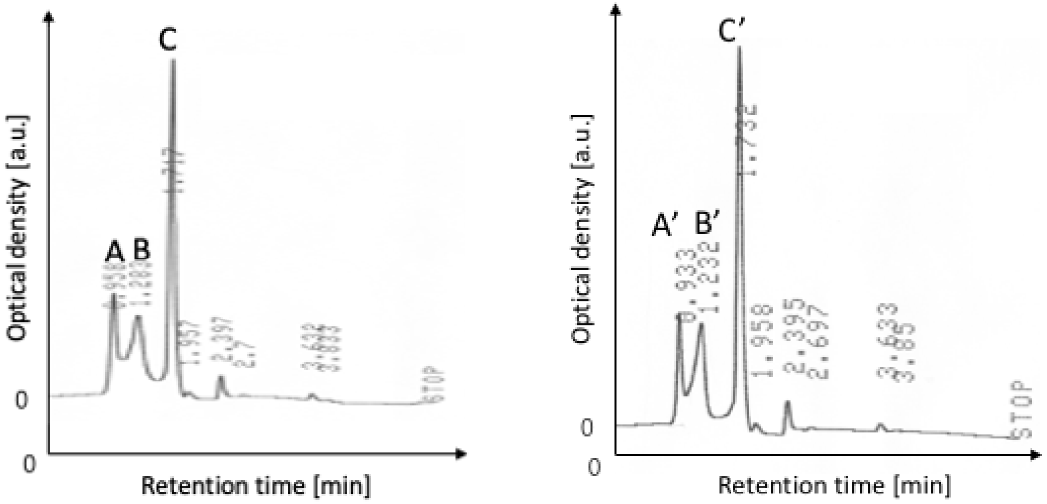
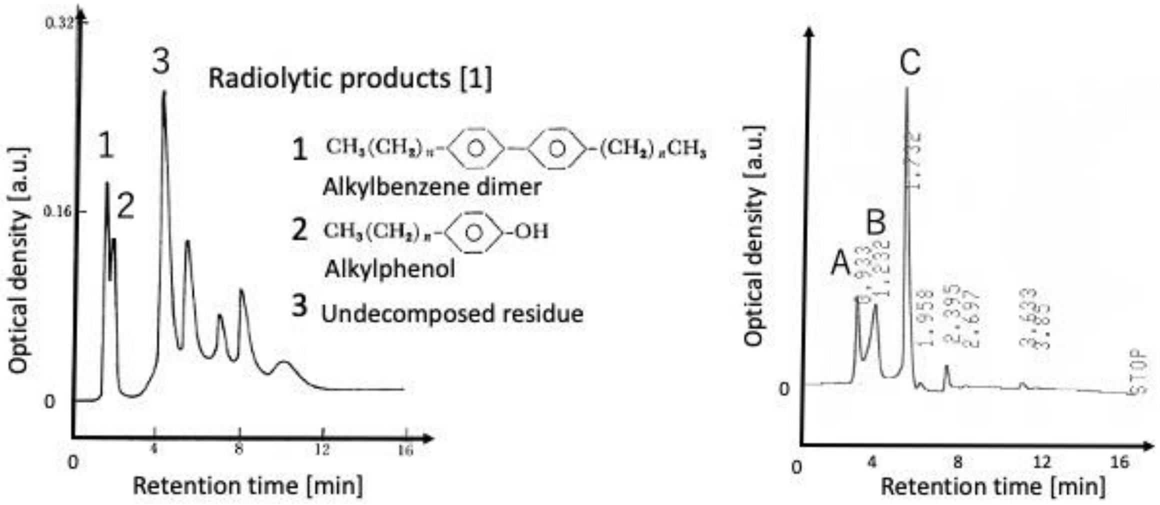


Fig. 5: Measurement of difference between the absorbance of associates (656 nm) of LAS and methylene blue without irradiation and that of ion associates of LAS and methylene blue by the Ar gas irradiation time.



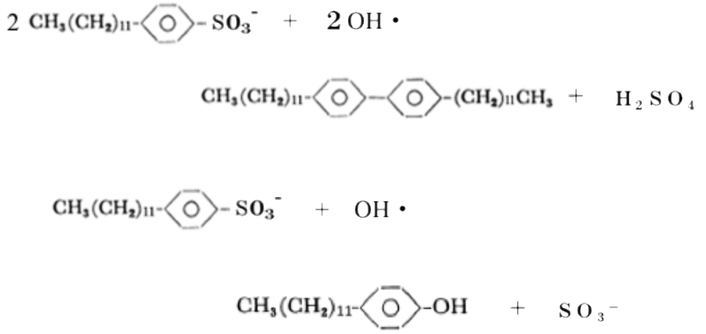
(a) Non-plasma irradiation (b) Plasma irradiation

Fig. 6: Difference between the absorbance of associates of LAS and methylene blue without irradiation and that of ion associates of LAS and methylene blue by the Ar gas irradiation time.



(a) Undecomposed residue (b) Plasma irradiation

Fig. 7: Measurement result obtained with the liquid chromatography after the LAS decomposed with irradiation.



(1)

4. Conclusion

In this study, we tried to decompose surfactants in the aqueous solution by irradiating atmospheric-pressure non-equilibrium microwave discharge plasma jet on the solution containing anionic surfactant. It revealed that irradiating the solution containing LAS surfactant with atmospheric-pressure non-equilibrium microwave discharge plasma jet shifted the pH of the solution toward acidity as the irradiation time got longer. We also found out that the concentration of the associates of LAS surfactant and methylene blue decreases by irradiating the sample with plasma. We assume that the radical species released from the plasma decomposed the LAS surfactant in the solution during the plasma irradiation. For this reason, we reveal that the LAS surfactant in the solution containing LAS surfactant can decompose with atmospheric-pressure non-equilibrium microwave discharge plasma jet irradiation.

In the future, we are going to clarify the decomposition process of the anionic surfactant in the solution containing anionic surfactant with atmospheric-pressure non-equilibrium microwave discharge plasma jet and establish the procedure to decompose anionic surfactant by changing the amount of radicals generated in and released from the plasma.

Acknowledgements

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