Application of chemical dosimetry to hydroxyl radical measurement during underwater discharge

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Abstract. The pulsed streamer discharge was generated in the liquid by using point-to-sphere electrode geometry. In this study, the OH radicals were measured indirectly by a chemical dosimetry. Terephthalic acid (TA) was used as an OH radical scavenger and fluorescence of the resulted 2-hydroxyterephthalic acid (HTA) was measured. Instead of the use of conventional fluorescence spectrophotometer, a novel fluorescence observing system by using a light-emitting diode (LED) as a light source and a simplified spectrometer as a detector was developed. As a result, the fluorescence intensity increased with time elapsed during the discharge process. The production rate of OH radicals in the liquid was estimated to be of the order of $10^{-10}$ M s$^{-1}$ to $10^{-9}$ M s$^{-1}$ under the present experimental conditions. As an advantage of terephthalate dosimetry, it was found that the discharge system in the small reactor used in our experiment was a useful means for in-situ evaluating formation of OH radicals in an underwater discharge.

1. Introduction

The discharges in liquids or on the liquid surfaces are of great interest both from the point of view of discharge phenomena and their various applications [1-4]. A dynamics of streamers in liquid has been investigated by many researchers [5-9]. It was found that the streamers in liquid was composed of primary streamer with the velocity in the range of 100 m s$^{-1}$ - a few km s$^{-1}$, followed by secondary streamer with the velocity greater than 10 km s$^{-1}$ when positive pulsed high voltage was applied to the needle electrode. Streamers in liquid generate ultraviolet rays, shock waves, microbubbles and reactive oxygen species (ROS) such as the hydroxyl radical (OH) and free radical oxygen. Especially, the OH radical plays an important role in plasma chemistry and plasma medicine due to a higher oxidation potential and stronger disinfection power compared to other oxidative species. The identification of OH radicals in water has been observed mainly by optical emission spectroscopy (OES) [10, 11]. Recently, the optical absorption technique has been employed to investigate the density of the OH radicals in liquid solutions [12]. However, a precise measurement of OH radical density in liquid is still in a line of research.

In this study, the OH radicals were measured indirectly by a chemical dosimetry. Terephthalic acid (TA) was used as an OH radical scavenger and fluorescence of the resulted 2-hydroxyterephthalic acid (HTA) was measured. Instead of the use of conventional fluorescence measurement equipment, a novel fluorescence observing system by using a light-emitting diode (LED) as a light source and a

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simplified spectrometer as a detector was developed. This paper also describes the merit of this method compared to other detection methods.

2. Experimental

2.1. Underwater discharge system

Figure 1 shows schematic diagram of the experimental setup. A pulsed high-voltage circuit with a self-trigger spark gap switch was used to generate streamers in liquid. A needle-to-sphere discharge electrode system was inserted into terephthalic acid (TA) solution, filling a cylindrical silica-glass tube reactor (20 mm in inner diameter and 23.8 mm in outer diameter). A stainless-steel needle (0.14 mm in inner diameter and 0.32 mm in outer diameter) with an insulating cover was used as the stressed electrode, while a stainless-steel sphere (15 mm in diameter) was used as the grounded electrode. The gap distance between the needle and sphere electrodes was set to be 20 mm.

The applied voltage and the current were measured by a high voltage probe (Iwatsu, HV-P30) and a current probe (Pearson Electronics, 2877), respectively. A spectrometer (Ocean Optics, USB2000) was used to measure the emission spectra of the streamers in liquid.

![Figure 1: Schematic of experimental setup.](image1)

![Figure 2: Formation of HTA through the reaction of TA and OH radical.](image2)

2.2. Chemical dosimetry

In order to measure the OH radicals dissolved in the liquid, we used chemical dosimetry [13] based on terephthalic acid (TA). Terephthalic acid is a well known OH scavenger which does not react with other radicals, such as $O_2^-$, $HO_2$ and $H_2O_2$. As shown in figure 2, the OH radical can convert terephthalic acid to 2-hydroxyterephthalic acid (HTA), which can be detected by fluorescence measurement. When the solution containing TA and HTA molecules is irradiated by UV light ($\lambda=310$ nm), HTA molecules emit light at $\lambda=425$ nm, while TA molecules do not. The fluorescence intensity of HTA is independent of pH in the range of 6-11. Since TA (Aldrich) does not dissolve in acidic/neutral liquid, aqueous solution of TA was prepared by dissolving TA in the distilled water containing NaOH (Wako). The initial concentrations of TA and NaOH were 2 and 5 mM except for the case of fluorescence imaging, respectively. The initial values of pH and conductivity of the solution were 10 and 368 $\mu$S cm$^{-1}$, respectively. The solution volume in the cylindrical silica-glass tube reactor was ca. 33 mL. The LED (Sandhouse Design, $\lambda=310$ nm, FWHM 10 nm) was used as a light source to excite HTA. During the discharge, a collimated beam from the LED output is passed...
through the liquid in the reactor, just below the needle electrode. The fluorescence (λ=425 nm, center wavelength) image was captured by an ICCD camera (Andor, i-Star) at various time intervals during the process, liquid was sampled into a cuvette and fluorescence spectrum around λ=425 nm was recorded through an optical fiber by the spectrometer (Figure 1). In order to quantify the OH radical concentration in the liquid, a calibration curve for known OH radicals concentrations was prepared using the standard HTA (Atlantic Research) solution. Typical calibration curve is shown in figure 3. The linear relationship between the peak area of fluorescence spectrum and the concentration of HTA was obtained.

![Figure 3. Calibration curve for hydroxyterephthalic acid (HTA).](image)

3. Results and discussion

Typical voltage and current waveforms for the discharge in TA solution are shown in figure 4. The rise time of the pulsed high voltage used in this study is about 70 ns and pulsewidth is about 10 μs. After a displacement current appears at the rising edge of the pulsed voltage, the discharge current with a 6 A peak and 5 μs pulsewidth flows. The average of pulse repetition rate is about 10 pps. Since the solution conductivity is relatively high, a streamer discharge consists of a few filaments with the length less than 5 mm as shown in figure 5.

![Figure 4. Applied voltage and current waveforms for the discharge in TA solution.](image)

![Figure 5. Streamer in TA solution. (Applied voltage: 24.5 kV)](image)
Figure 6. Optical emission spectrum of underwater discharge: (a) discharge in TA solution and (b) discharge in distilled water. (Applied voltage: 24.5 kV)

Figure 6 shows the typical emission spectra of the streamers in TA solution and in distilled water. In both spectra, we found the emissions of hydrogen atomic lines (Hα, Hβ, Hγ) and OH radicals from the excited state (A^2Σ^+). Also the atomic line of oxygen (OI) was found. A strong emission was observed for the discharge in TA solution. This is due to the higher conductivity of TA solution. The line broadening of hydrogen atomic lines such as Hα, Hβ indicates higher electron density plasma for underwater discharge, especially in the case of TA solution, compared to other discharge-induced plasmas in contact with liquids.

Figure 7 shows time-dependent fluorescence images under the illumination of the LED light source during the underwater discharge. Each image is an accumulation of 20 captured images. OH radicals are formed along the streamer propagation and trapped by TA molecules. The intensity of the fluorescence due to the HTA formation increased with time elapsed and its part is almost uniform even though no stirring of the liquid was performed, indicating homogeneous HTA diffusion in the solution. The light scatterings by the needle electrode and reactor wall are also observed. For the case of the discharge operating longer than 5 min the fluorescence can be observed by our naked eye. Furthermore, the possibility of the decomposition of HTA by the underwater discharge was investigated. Using a HTA solution we confirmed that HTA decomposition is negligible under the present experimental condition.

Figure 7. Time evolution of the fluorescence from TA solution during underwater discharge. (Applied voltage: 24.5 kV, TA solution: 0.2 mM, pH 9.6)

Figure 8 shows the fluorescence spectra as a function of treatment time. The fluorescence intensity corresponds to a time integrated OH radical concentration in the liquid. As the time elapsed, the
fluorescence intensity increased, indicating the increase of the total amount of OH radicals trapped by TA. In order to evaluate the density of OH radicals in the solution, using the fluorescence intensity integrated over the wavelength (shown in figure 8) and the calibration curve (figure 3) for known concentrations of OH radicals, we calculated the OH radical density in the solution as a function of treatment time as shown in figure 9. The concentration of OH radicals in the reactor almost linearly increases with increasing the time. The tendency of saturation is probably related to the decreasing TA in the liquid. Besides trapping of OH by TA, however, other reactions that consume OH radicals also occurred. In the present case, the HTA yield was assumed to be 35%, according to [14]. As a result, the production rate of OH radicals in the liquid was estimated to be of the order of $10^{-10}$ M s$^{-1}$ to $10^{-9}$ M s$^{-1}$ under the present experimental condition.

![Figure 8](image1.png)

**Figure 8.** Fluorescence spectra of aqueous TA solutions irradiated by underwater discharge.(Applied voltage: 24.5 kV, TA solution: 2 mM, pH 10.16, volume 32.5 mL)

![Figure 9](image2.png)

**Figure 9.** Formation of OH radicals in aqueous TA solution as a function of treatment time.(Applied voltage: 24.5 kV, TA solution: 2 mM, pH 10.16, volume 32.5 mL)

Under our another experiment, the rates of production of OH radicals are of the order of $10^{-9}$ M s$^{-1}$ for the surface pulsed streamer discharge on the liquid [15] and of the order of $10^{-8}$ M s$^{-1}$ for the plasma jet on the liquid [16], respectively. Sahni et al. [17] have reported that the production rate of
OH radicals was $1.67 \times 10^{-8} \text{ M s}^{-1}$ for the direct discharge in water at an applied voltage of 45 kV and input power delivered to the water of 64 W. Joshi et al. [18] have determined the rate of formation of OH radicals using the free radical scavenging property of carbonate ions. They reported the value of $9.25 \times 10^{-10} \text{ Ms}^{-1}$ for the pulsed streamer corona discharge in an aqueous solution. Recently, Li et al. [19] have estimated OH production rate of the order of $10^{-10} \text{ Ms}^{-1}$ for pulsed discharge in water by using a salicylic acid dosimetry. At the present stage, we attribute these differences to various factors, such as discharge types, reactor size, operating conditions, and different measuring methods.

Finally, other chemical dosimetrries are reviewed in connection with TA dosimetry. There are various dosimetrries which might be used to monitor the OH radicals. The Fricke dosimetry and iodide dosimetry are widely used in sonochemistry and radiation chemistry. However, Fricke or iodide dosimetrries are non-specific since iodide and Fe (II) ions are oxidized not only by OH radicals but also by the H atom, HO$_2$ radical, and H$_2$O$_2$. The salicylic dosimetry based on salicylic acid is similar method to TA dosimetry. In recent years, this method is used to measure the OH radicals generated by the discharges in water [19] or in air [20]. In this case, liquid chromatography was used to detect fluorescent substances. Moreover, the electron spin resonance (ESR) spin-trapping has been also recognized as the radical monitoring technique with high sensitivity and lower detection limits [21]. The ESR requires an expensive instrument and a skillful operator. Taking into account the sensitivity and simplicity in data collection, TA dosimetry seems to be a suitable method for characterizing the discharge-induced OH radicals.

4. Conclusions

A novel method of measuring OH radicals in aqueous solution was developed and applied to the measurement for underwater discharges. In the case of terephthalate dosimetry, the apparatus is simple and cheap, especially chemical reagent of terephthalic acid, compared to other dosimetrries. The time-integrated amount of OH radicals in the reactor was visualized by using fluorescence of TA solution irradiated by the UV LED. The production rate of OH radicals in the liquid was estimated to be of the order of $10^{-10} \text{ M s}^{-1}$ to $10^{-9} \text{ M s}^{-1}$ under the present experimental condition.

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