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Dissolution of the Gaseous H₂O₂, HNO₂, and O₃ Species in the Bulk Water and Electrospray

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Background: Cold (non-thermal) atmospheric air plasma creates in contact with water what so-called "plasma-activated water (PAW)". The PAW solutions contain various dissolved reactive oxygen and nitrogen species (RONS) e.g., hydrogen peroxide (H₂O₂), nitrate (NO₃⁻) and nitrite (NO₂⁻) anions, and ozone (O₃), as well as other short-lived species [1]. The PAW solutions have potential applications in biomedicine and agriculture without causing undesired side effects or environmental burdens [2]. The solubility potential of the gaseous RONS into liquids e.g., water is described by Henry's law coefficients k_H . The k_H of long-lived plasma RONS: H₂O₂, HNO₂, and O₃ are $\approx 10^3$, 10^{-1} , 10^{-4} mol/m³ Pa, respectively. It means that the solubility of different gaseous RONS into water varies markedly [3].

Method: H₂O₂, HNO₂, and O₃ are generated by external sources. Bubbler glass tubes contained separately 9.8 M of H₂O₂ or 20 mM of HNO₂ solutions, which delivered ~100 ppm of gaseous H₂O₂ or HNO₂. O₃ generator was used with an output of 300 mg/h O₃ and mixed with air to reach ~450 ppm of gaseous O₃. The solvation of gaseous H₂O₂, HNO₂, and O₃ as representative high, medium, and low solubility species, respectively, in bulk water and electrosprayed (ES) water aerosol droplets is investigated. Figure 1 shows the experimental setup where deionized water (conductivity <3 μ S/cm) is delivered using a syringe pump through a needle (anode) placed opposite to a ground wire, more details in [4].



Figure 1. Experimental setup to investigate solvation of gaseous H₂O₂, HNO₂, and O₃ species into ES water.

In the bulk experiment, the ES reactor is replaced with a bulk reactor filled with deionized water with different volumes and a fixed surface area exposed to gaseous species. Other than H_2O_2 and O_3 , HNO_2 is dissolved in water as a dominant source of NO_2^- . UV-vis spectroscopy colorimetric methods were used for the chemical analysis of the dissolved species in the aqueous phase. TiOSO₄, Griess, and indigo blue II reagents were used for H_2O_2 , NO_2^- , and O_3 with an absorption

maximum at 407, 540, and 600 nm, respectively. In the gas phase, the concentration of H_2O_2 and O_3 is measured using electrochemical gas sensors. For HNO₂, the UV-Vis absorption spectroscopic technique is used through a 32 cm double light path cell.

Results: The total surface area of water droplets is increased with increasing applied voltage during the ES, which starts at 7.5 kV. Thus, the solvation of gaseous H₂O₂, HNO₂, and O₃ into water is enhanced due to the increase of the gas-water interface surface area, leading to an increase in the number of dissolved moles of H₂O₂, NO₂⁻, and O₃ in ES water compared to the bulk with a fixed surface area, as shown in Figure 2. However, there are some limitations of the solvation of the gaseous species in the ES water due to the very short lifetime (ms) of the generated flying microdroplets. The number of dissolved moles in the water of H2O2 is 4 orders of magnitude higher than that of O_3 despite the 7 orders of magnitude larger Henry's law coefficient of H₂O₂ than that of O₃. This is because of the insufficient amount of gaseous H₂O₂ next to the gas-water interface area, as it is depleted from gas, unlike O3 molecules, which are not depleted. Otherwise, the number of dissolved moles in the water of NO₂⁻ is 3 orders of magnitude higher than that of O₃, which fits well with the ratio of HNO₂ and O₃ Henry's law coefficients. Our results contribute to a better understanding of the solvation process of RONS in water and lead to optimization of water sprays [4].



Figure 2. Dissolution of H_2O_2 , NO_2^- and O_3 species in bulk and ES water.

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References

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