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Partitioning of hydrogen peroxide between the gas and liquid phases in the presence of surfactant

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Abstract

Gas–liquid phase partitioning is a key physical property that can predict the environmental fate of a compound between two phases. Several environmental factors have been known to affect the gas–liquid phase partitioning. We investigated the influence of surfactant on the gas–liquid phase partitioning of hydrogen peroxide (H_2O_2). The surfactant used was ammonium perfluorooctanoate (APFO). H_2O_2 solution containing the surfactant was equilibrated in a closed system and gas phase H_2O_2 concentration was measured by the peroxyoxalate chemiluminescence (PO-CL) method. Gas phase H_2O_2 concentrations remained constant below the critical micelle concentration (CMC) and increased linearly with surfactant concentration above the CMC, which indicated that surfactant micelles influenced the gas–liquid phase partitioning of H_2O_2. This result showed that H_2O_2–micelle interactions are less favorable than H_2O_2–H_2O interactions. Surfactant monomers did not affect the gas–liquid phase partitioning of H_2O_2 due to the absence of micelles. Solvent (methanol) effect was also investigated and showed that gas phase H_2O_2 concentrations increased with the addition of solvent. This indicated the unfavorable interaction of H_2O_2 with hydrophobic medium compared to hydrophilic one. It is consistent with the result that H_2O_2–micelles has a weaker interaction than H_2O_2–water because surfactant micelles are hydrocarbon-like organic phase rather than aqueous phase.

Keywords: Gas–liquid phase partitioning; Micelle; Monomer; Solvent; Ammonium perfluorooctanoate (APFO); Chemiluminescence

1. Introduction

Hydrogen peroxide (H_2O_2) is clear, colorless, and completely miscible with water (Schumb et al., 1955). It can act as an oxidizing (Larson and Weber, 1994) or reducing agent (Strukul, 1992). H_2O_2 has a strong tendency to partition from the gas phase to the liquid phase, which can be expected from its very low Henry's law constant (HLC). The gas–liquid phase partitioning is a key physical property that predicts the direction and fate of a compound between two phases. It is described by HLC, which can be expressed in different units and their relation as follows:

$$H\,(\mathrm{atm}) = H' C_{\mathrm{H_2O}} \tag{1}$$

where H is the Henry's law constant in atmospheres, and $C_{\mathrm{H_2O}}$ is the molar concentration of water (55.5 mol l^{-1}).

$$H'(\mathrm{atm M^{-1}}) = \frac{V_\mathrm{p}}{[\mathrm{H_2O_2}]_\mathrm{l}} \tag{2}$$

where H' is Henry's law constant in the unit of atm M^{-1}, V_p (atm) is the vapor pressure of H_2O_2 and $[\mathrm{H_2O_2}]_\mathrm{l}$ is the molar concentration of H_2O_2 dissolved in the liquid phase.

$$H''\,(\mathrm{mol_g^{-1}}/(\mathrm{mol_l^{-1}}) = \frac{H'}{RT} = \frac{[\mathrm{H_2O_2}]_\mathrm{g}}{[\mathrm{H_2O_2}]_\mathrm{l}} \tag{3}$$

where H'' is the dimensionless Henry's law constant, R is the gas constant (0.082 atm $\mathrm{M}^{-1}\,\mathrm{K}^{-1}$), T is the absolute temperature (K), and $[\mathrm{H_2O_2}]_\mathrm{g}$ is the molar concentrations of H_2O_2 in the gas phase. The HLC for H_2O_2 is generally

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reported to be about 4×10^{-7} in dimensionless unit at 25 °C (Larson and Weber, 1994), although several environmental factors such as temperature, pH, and dissolved salts can affect the gas–liquid partitioning of a compound (Alaee et al., 1996; Staudinger and Robers, 1996).

H_2O_2 has been widely used in environmental engineering processes. In aqueous solution, hydrogen peroxide can oxidize or reduce a variety of inorganic ions. When it acts as a reducing agent, oxygen gas is produced. Potassium permanganate is reduced to Mn^{2+} by H_2O_2 under acidic conditions, releasing oxygen as a by-product. Fe^{3+} can be reduced to Fe^{2+} under alkaline-H_2O_2 conditions (Greenwood and Earnshaw, 1997). Hydrogen peroxide was used to treat a liquid waste containing organic compounds and chromium(VI). In the treatment, H_2O_2 reduced Cr^{6+} to Cr^{3+} which was then precipitated in the solution (Schmitt, 1982). In addition, photolysis combined with H_2O_2 is a well-known oxidation application to treat a wide range of organic contaminants. Photolysis of subsurface contaminants in surfactant solution has been demonstrated as a post-treatment method after surfactant flushing to recover and reuse the surfactant solution (Chu and Jafvert, 1994; Chu et al., 1998). Recently, UV/H_2O_2 process in surfactant solution was also proposed for surfactant recovery because it would be a more general approach compared to direct photolysis for environmental applications (An, 2001). Chemical oxidation of hydrocarbon-contaminated soil using Fenton or a modified Fenton was known that surfactant was produced during Fenton reaction and then accumulated up to the levels of four times of the critical micelle concentration (CMC) (Ndjou'ou and Cassidy, 2006). Behavior of hydrogen peroxide in the presence of surfactant plays an important role in the environmental engineering processes, but it has not received much attention. Previous studies reported that the presence of surfactants affected the gas–liquid phase partitioning of volatile organic compounds (VOCs) (Anderson, 1992; Vane and Giroux, 2000). However, the influence of surfactant on the gas–liquid partitioning behavior of highly water-soluble compounds such as H_2O_2 is not well understood. This study was motivated to provide a better understanding on the interactions between H_2O_2 and surfactants and provide fundamental information for future environmental applications.

The objective of this study was to investigate the effect of surfactant micelles on the gas–liquid phase partitioning of H_2O_2. Surfactant used in this study was ammonium perfluorooctanoate (APFO). The influence of surfactant monomers and solvent was studied to compare the gas–liquid phase partitioning of H_2O_2 in different media. After gas–liquid phase equilibrium of H_2O_2 with and without surfactant in a closed system, the headspace H_2O_2 concentration was measured by peroxyoxalate chemiluminescence (PO-CL) method. A PO-CL reaction is based on the light generated in chemical reactions. It has become a powerful analytical tool for sensitive and selective detection of chemical species. The PO-CL reaction technique has advantages over other detection methods such as UV absorbance and fluorescence. Previously, H_2O_2, used as a reagent in PO-CL reaction (Stigbrand et al., 1994), was quantified using one of the intermediates generated by PO-CL reactions. H_2O_2 in an oil–water emulsion system was determined by *bis*(2,4,6-trichlorophenyl) oxalate chemiluminescence (Hasebe et al., 1996). Gaseous H_2O_2 in the atmosphere was analyzed by 1-1′-oxalyldiimidazole PO-CL reaction test (Stigbrand et al., 1996).

2. Materials and methods

2.1. Materials

H_2O_2 (Aldrich, 50% and 35%), potassium permanganate ($KMnO_4$, Aldrich, 0.1 ± 0.005 N), *bis*(2,4,6-trichlorophenyl) oxalate (TCPO, Aldrich, 97%), perylene (Aldrich, 99+%), and imidazole (Aldrich, 99+%) were received as reagent grade. A stock solution of H_2O_2 was prepared in acetonitrile (EM science, spectrophotometric grade) from the 35% reagent solution and standardized by titration with potassium permanganate. Ammonium perfluorooctanoate ($C_7F_{15}COONH_4$, APFO, 98%) was supplied by Fluka and used without further purification. APFO is an anionic perfluorinated surfactant and its CMC was reported to be 26.6 mM (An, 2001). Water was purified by a Barnstead Nanopure system resulting in a resistivity $>17.8\ M\Omega\ cm^{-1}$.

2.2. Equilibrium experiment

A H_2O_2 solution containing surfactant was equilibrated in a closed system. Clear vials (8 ml VOA vials) were used as batch systems. H_2O_2 and water were added to each vial such that the solution H_2O_2 concentrations varied from 7 to 14 M. Appropriate amounts of surfactants were added to each vial such that the surfactant concentrations were below and above CMC of APFO. Controls were prepared identically to samples except no surfactant was added. Samples were prepared in triplicate for each experiment. Prepared vials were capped with PTFE/silicone septa. They were placed on the shaker table at ambient laboratory temperatures of 24 ± 1 °C and shaken for 24 h. Preliminary trials showed that agitation of 24 h or longer were enough to reach equilibrium. Vials were perpendicularly positioned to prevent the contact of aqueous sample with septa. After equilibrium, a 1 ml aliquot of the headspace gas was carefully withdrawn through the septa by using the gas-tight syringe and transferred into the headspace of the 1.5 ml vial (GC auto sampler vial was used) containing 1 ml of acetonitrile. The vial was then shaken on a vortex mixer to dissolve the gas phase H_2O_2 into the acetonitrile. H_2O_2 dissolved in acetonitrile was analyzed to quantify the gas phase H_2O_2 concentration. These experiments as described above were also performed with the addition of methanol to investigate the interaction of H_2O_2 with methanol, which is extensively used in industrial processes. The methanol