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Original Article

Effects of temperature and solution composition on evaporation of iodine as a part of estimating volatility of iodine under gamma irradiation

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ABSTRACT

As a part of evaluating the volatility of iodide ions subjected to gamma irradiation, I_2 evaporation experiments were performed with I_2 and I^- mixed solutions in the temperature range 26–80°C in an open, well-ventilated space. The evaporation of I_2 was observed to follow primarily first order kinetics, depending on the I_2 concentration. The evaporation rate constant increased rapidly with increase in temperature. The presence of I^- slightly reduced the evaporation rate of I_2 by forming relatively stable I_3^-. The effect of Cl^- at <1.0 wt% on I_2 evaporation was insignificant. The evaporation rate constants of I_2 were 1.3×10^{-3} min^{-1} cm^{-2}, 2.4×10^{-2} min^{-1} cm^{-2}, and 8.6×10^{-2} min^{-1} cm^{-2}, at 26°C, 50°C, and 80°C, respectively.

1. Introduction

The volatility of radioactive iodine has been mainly of interest in the study of severe accidents at nuclear power plants, because radioactive iodine is a major radionuclide to determine the total air radioactivity around the accident area during the first number of weeks [1–3]. Therefore, many studies [4–23] have been carried out in order to understand the behavior of radioactive iodine and to minimize the impact of severe accidents. In reactor containment buildings during accidents, the radioactive iodine becomes dissolved in the cooling water directly from irradiated fuels or indirectly by the emergency spray. Iodide, which is one of the major iodine species dissolved in cooling water, is easily diffused into the gas phase after being oxidized to gaseous I_2 by gamma irradiation [4–6,11]. Next, I_2 can be converted to more volatile organic iodides, such as CH_3I, after reacting with various organic materials such as paints under high gamma irradiation [12–16]. Overall, the behavior of I_2 which is main precursor of organic iodide, is an important component used to evaluate and predict the radioactivity at an early stage of severe accidents.

To date, most iodine volatility tests were carried out with iodide solution under a high dose rate (~ k Gy/h) of gamma rays [4–6,11]. The evaporated I_2 from the I^- solution was directly measured by radiation counting or chemical analysis. This type of direct method generally provides highly reliable data about the volatilization of iodine under gamma irradiation, because the test condition was very similar to that of a real accident.

By contrast, as shown in Fig. 1, the volatilization of iodine can be divided into two connected steps. The first step (1) is the oxidation reaction of I^- to I_2 by oxidizing species such as HO·generated from water radiolysis [22,23]. The second step (2) is the evaporation of dissolved I_2 to gaseous I_2. When we predict the volatilization of iodine under various environmental conditions, it is advantageous to evaluate separately the effects of environmental factors on each step. For example, temperature is one of the main factors that affects these two steps. With increasing temperature, the rate of I^- gamma oxidation (1) decreases, while the rate of the I_2 evaporation (2) increases. Therefore, by separating the effect of temperature on these steps, we can evaluate the volatility of iodide at various temperatures more accurately. For the first step (1), which is gamma oxidation reaction of I^- to I_2(aq), considerable experimental data have been obtained on various factors, such as gamma dose, iodide concentration, and solution pH [4–6,22,23]. For the second step (2) which is evaporation of I_2(aq), various experiments and tests were carried out based on the two-film model and its extended ones [16,24]. However, relatively few experimental data have been reported [25] to date.

In the current work, we investigated the effects of temperature, concentration of I_2, and presence of I^- and Cl^- on the evaporation of

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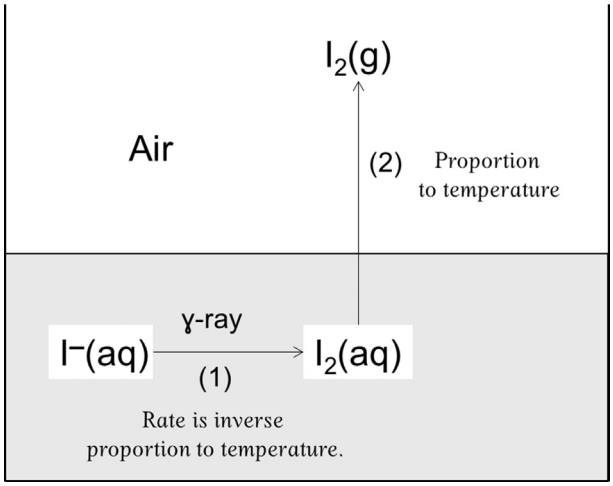

Fig. 1. Paths of iodine from I^- ion dissolved in solution to $I_2(g)$ in the air.

I_2 in I_2 and I^- mixed solutions in an open and well-ventilated space. From the experiments, we confirmed that the evaporation rate of I_2 increased exponentially as the solution temperature increased, showing a similar trend with temperature dependence of the saturated vapor pressure of I_2. We obtained the evaporation rate constant of I_2 under the temperatures of 26°C, 50°C, and 80°C. The presence of I^- was observed to slightly decrease the evaporation rate, but there was no prominent effect of Cl^- below 1.0 wt% NaCl on the evaporation of I_2. Our results will contribute to the understanding of the I_2 evaporation reaction under various environmental conditions.

2. Materials and methods

We prepared various I_2 and NaI mixed solutions for I_2 evaporation experiments. The chemical reagents used for the experiments were NaI (99.5 wt%, Sigma Aldrich, USA), I_2 (99.8 wt%, Sigma Aldrich, USA), and NaCl (99 wt%, Sigma Aldrich, USA). The I^- ion from NaI is a major chemical form of iodine released from the irradiated fuels and one of the chemical additives used in filtered containment venting system pool scrubbing. The NaCl was used for the consideration of seawater injection. However, the concentration range of each species was not determined by the consideration of any accident conditions, but rather by the detection limits of the measurement techniques we used.

The pH values of all evaporation solutions were in the range 6.1–6.5. This pH range was determined since it is the highest pH range in which I_2 is relatively stable. Above this pH range, the hydrolysis effect of I_2 cannot be ignorable in the concentration we used (~1mM), and H_2O_2 (a radiolysis products of water) starts to reduce I_2 to non-volatile I^- [22,23]. The portion of I_2 hydrolysis is less than 5% (at I_2~1mM) at pH 6.5 [26]. The pH values of all evaporation solutions were measured by a pH meter (Metrohm 654, Metrohm AG, Switzerland) at room temperature before the evaporation experiments. The solution pH definitely depends on the solution temperature, since most equilibrium reactions, even the dissociation of water molecules, depend on the temperature. In addition, the electrochemical reactions including the chemical activity of Cl^- ion working in the pH meter depend on the temperature [27]. However, in this experiment, we did not compensate the temperature effects on the solution pH and chemical reactions.

We used typical 20 mL glass vials as evaporation vessels. During the evaporation experiment, the temperature and relative humidity in the fume hood were in the range of 23 ± 2°C and 75 ± 7% relative humidity, respectively. The temperature of evaporation vessels was controlled in the range 26–80°C by a water bath. The airflow rate measured by the air velocity meter (TSI Velocicalc 8346, TSI Inc., Shoreview (MN), USA) at six points of evaporation vessels was in the range 0.81 ± 0.15 m/s. This flow rate was the maximum airflow of the fume hood, and was not determined from consideration of any reactor building condition. All I_2 evaporation experiments were carried out in the same fume hood. The schematic diagram of the evaporation experimental equipment is shown in Fig. 2.

The mixed solution of 15 mL was contained in the evaporation vessel. The height of the solution was approximately 3.5 cm from the bottom of the vessel, and the exposed area of solution for I_2 evaporation was 4.16 cm^2. In some cases, the exposed area of evaporation solution may affect I_2 evaporation. However, in this work we did not consider the effect of the exposed area on I_2 evaporation. Four or more evaporation vessels were used for a series of experiments at the same temperature. As the evaporation time passed, vessels were collected from the water bath one by one in order to measure the concentration of I_2 remaining in the solution. The I_2 concentration was measured at the ambient temperature using an ultraviolet and visible light spectrophotometer (Biochrom model WPA Lightwave II, Biochrom Ltd., Cambridge, UK) [28].

When an I_2 evaporation experiment was carried out, we placed an additional vessel containing 95.6 wt% of ethyl alcohol in the fume hood at 25 ± 1°C, outside of the water bath and measured the amounts of ethyl alcohol evaporated during each experiment. This was done to compare ventilation conditions in the fume hood. The evaporated amounts of ethyl alcohol were observed to be in the range of 0.81 ± 0.09 g/h at 23 ± 2°C and did not exhibit any dependence. This indicated that the ventilation conditions in the fume hood were almost constant during all evaporation experiments (within a range of 10%). The ethyl alcohol vessels were placed in parallel with the iodine evaporation vessels and airflow direction in order to minimize contamination by the evaporated ethyl alcohol.

3. Results and discussion

3.1. Effects of temperature and concentration on I_2 evaporation

The I_2 evaporation experiments were carried out with four different concentrations (0.05mM, 0.09mM, 0.50mM, and

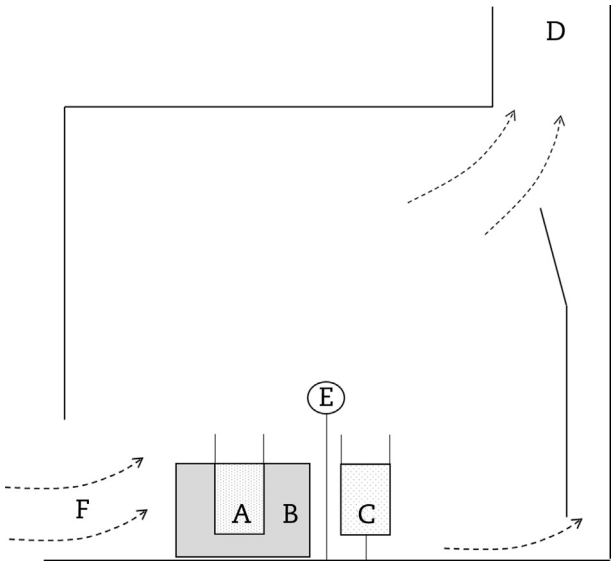

Fig. 2. The schematic diagram of the evaporation experimental equipment. (A) Iodine solution. (B) Water bath. (C) Ethyl alcohol (95.6 wt%). (D) Exhaust plenum. (E) Thermometer and humidity meter. (F) Air flow.

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