Effects of Gamma Irradiation on pH Changes of NaI and Methyl Alkyl Ketone Solutions

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1. Introduction

The pH of pure water would not be changed by the gamma irradiation. However, the pH of solution can be changed when some chemical species are dissolved in the solutions [1,2]. Since the solution pH is an important factor determining chemical reactions, in order to evaluate and predict the chemical phenomena occurring under gamma irradiation conditions, it is necessary to understand the pH changes under these conditions.

In present work, we investigated the pH changes of NaI and methyl alkyl ketone (MEK, MIBK) mixed solutions under gamma irradiation. From these experiments, we confirmed that the pH changes were mainly affected by the reactions occurring in the solutions, not by the individual chemical components. These results will help to understand and to predict the pH changes of solutions and associated chemical behavior of iodine under gamma irradiation conditions.

2. Experimental and Results

2.1 Chemicals and Devices

All chemical reagents were analytical-grade. NaI (≥ 99.5 wt%, Sigma-Aldrich), MIBK (4-methyl-2-pentanone, ≥ 99.5%, Sigma-Aldrich), MEK (2-butanone, ≥ 99.7%, Sigma-Aldrich) were used to prepare the gamma irradiation solutions. A pH meter (Metrohm model 827) calibrated with two different buffer solutions was used for pH measurements.

Gamma irradiation experiments were carried out at the same irradiation system (MDS Nordion, Canada) as previously used [3,4]. The gamma dose was controlled by adjusting the distance of the sample from the ^{60}Co source and the irradiation time. The gamma dose rates were controlled in the range of 0-10 kGy h^{-1}. The irradiation experiments were conducted at a temperature of 25±2°C.

2.2 pH Changes of NaOH Solutions under Gamma Irradiations

Water molecules are decomposed by gamma irradiation into many unstable species such as radicals. The decomposition reaction generally does not change the solution pH. However, on exposure to air, the pH of a solution may change due to the reactions associated with air radiolysis. NO_2, a main product of air radiolysis, dissolves in the solution and hydrolyzes into strong acids such as HNO_2 and HNO_3.

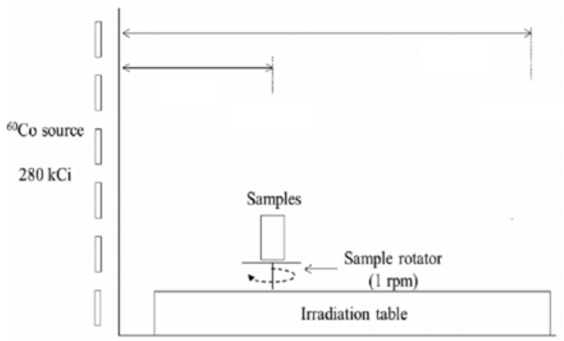

Fig. 1. Schematic diagram of gamma irradiation system [3,4]

NaOH solutions of different pHs were irradiated and the pH changes were measured. Fig. 2 shows the changes in solution pH after irradiation. The pH varied within the alkaline range for the solutions having initial pHs of 7.8 and 10.7 before irradiation, with the initial pH of 10.7 exhibiting a distinct change. No distinguishable changes were observed for initial pHs of 11.9 and 13 after gamma irradiations.

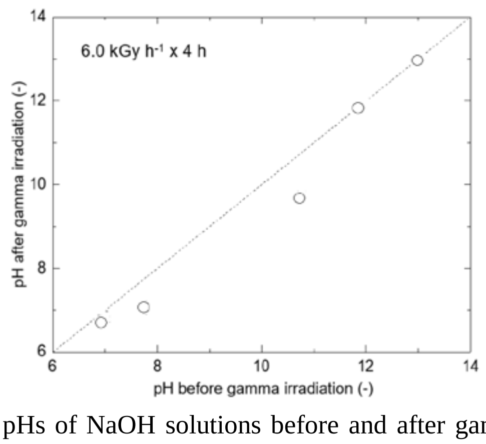

Fig. 2. pHs of NaOH solutions before and after gamma irradiation. The gamma doses were 24 kGy [5].

At a pH of 7.0 (before irradiation), the pH change was insignificant under our experimental conditions. It is understood that a small amount of NO_2 can dissolve in the solution and be in equilibrium at a neutral pH. Unlike in neutral pH, in alkaline solutions with initial pHs of 7.8 and 10.7 (before irradiation), acid-base neutralization reactions occurred between NaOH and the acidic species formed by the radiolysis of air and aerated water. The neutralization reactions under irradiation continued as long as the solution was alkaline. Therefore, the decrease in pH observed for solutions with initial pHs 7.8 and 10.7 resulted from the neutralization reactions. Neutralization reactions are expected to occur much easily at a high pH. However, in the high pH range, it was difficult to distinguish the contribution of pH decrease on the pH scale because a pH unit is based on the logarithmic scale of proton ion concentration.

2.3 pH Changes of NaI and RCOCH$_3$ Solutions

The pH changes of NaI and CH_3COR (MIBK or MEK) mixed solutions after 40 kGy of gamma radiation were measured. Before gamma irradiation (0 kGy), the pHs of all the solutions were stayed around 6.8. Under gamma irradiation, the oxidation of iodide ions ($2I^- + 2HO\cdot \rightarrow I_2 + 2HO^-$) causes to increase the solution pH [3], whereas $RCOCH_3$ molecules generally decrease the pH of the solution by decomposing themselves into formic and acetic acids [6].

The pH changes of the irradiated mixed solutions are shown in Fig. 3 as a function of NaI concentration. After irradiation, the pHs of the solutions without NaI were 4.5 or lower and increased with increasing NaI concentration. The pHs of the CH_3COR solutions containing 1 mM NaI were measured between 4.5 and 5.5, while the pHs of the 1 mM CH_3COR + 5 mM NaI solutions were 6 or higher. Moreover, the pHs of the 5 mM CH_3COR + 5 mM NaI solutions ranged from 4.5 to 5.5.

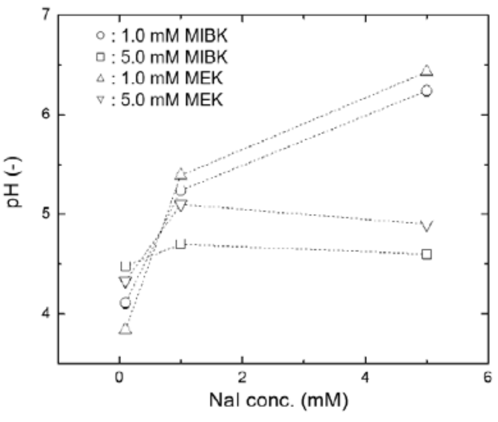

Fig. 3. pHs of NaI and methyl alkyl ketone (MIBK and MEK) mixed solutions after irradiation with 40 kGy gamma radiation [5]

3. Conclusions

While the pH of neutral water changed only slightly after gamma irradiation, the pH of alkaline NaOH solutions decreased after irradiation with 24 kGy of gamma radiation. The result indicates that the pH decrease is attributed by the acid-base neutralization reactions between the OH^- and the acidic species (HNO_2, HNO_3 and $HO_2\cdot$) formed by the radiolysis of air and aerated water.

After gamma irradiation, the pH of the NaI + CH_3COR mixed solutions (pH ~6.89 before irradiation) changed according to the concentration ratio of the two compounds. The pHs of the mixed solutions were complexly affected by the gamma oxidation of I^-, decomposition of CH_3CORs, and formation of CH_3I.

Acknowledgments

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REFERENCES

[1] L. Bosland, F. Funke, N. Girault, and G. Langrock, Paris Project: Radiolytic Oxidation of Molecular Iodine in Containment during a Nuclear Reactor Severe Accident. Part 1. Formation and Destruction of Air Radiolysis Products. Experimental Results and Modeling, Nucl Eng Des., Vol.238, p. 3542, 2008.

[2] EC. Beahm, RA. Lorenz, and CF. Weber, Iodine Evolution and pH Control, Oak Ridge National Laboratory, Tennessee, 1992.

[3] S-H. Jung, J-W. Yeon, SY Hong, Y. Kang, and K. Song, The Oxidation Behavior of Iodide Ion under Gamma Irradiation Conditions, Nuclear Science and Engineering. Vol.181, p. 191, 2015.

[4] SY. Hong, S-H. Jung, and J-W. Yeon, Effect of Aluminum Metal Surface on Oxidation of Iodide under Gamma Irradiation Conditions, Journal of Radioanalytical and Nuclear Chemistry. Vol.308, p. 459, 2016.

[5] M. Kim, SY Hong, T. Kim, S-H Jung, and J-W Yeon, Change in the pH of NaI and methyl alkyl ketone solutions under gamma irradiation, Journal of Radioanalytical and Nuclear Chemistry, in press (https://doi.org/10.1007/s10967-020-07346-8).

[6] M. Kim, T. Kim, and J-W Yeon, Formation of CH_3I in a NaI and methyl alkyl ketone solution under gamma irradiation conditions, Journal of Radioanalytical and Nuclear Chemistry, Vol.316, p. 1329, 2018.