Chemical forms of rhodium ion in pure water and nitric acid solution studied using ultraviolet-visible spectroscopy and first-principles calculations

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Abstract. We have investigated chemical forms of rhodium (Rh) ion in nitric acid solution by using spectroscopic and first-principles methods, in order to develop the disposal of high-level radioactive nuclear liquid wastes (HLLW). The electronic structure of Rh complexes in both pure water and nitric acid solutions was investigated using ultraviolet-visible (UV-vis) absorption spectroscopy. Comparison with many-electron calculations indicates that Rh ion forms an octahedral bidentate complex coordinated with three nitrate ions, [Rh(NO3)3], in both pure water and nitric acid solutions. This is consistent with thermodynamic prediction. Since the overall feature of UV-vis spectra of the Rh complex remained unchanged in a range of 0–3 M nitric acid solutions, the structure of the Rh complex was found to be stable in the range. In addition, since no significant changes in UV-vis spectra of Rh complex were observed under γ-ray radiation, the Rh complex, [Rh(NO3)3], can be expected to be stable in actual HLLW.

1. Introduction
High-level radioactive liquid wastes (HLLW in 2M nitric acid solution), which are obtained after recovery of uranium and plutonium from the spent nuclear fuels for reuse of new fuels, are vitrified at a reprocessing plant. In the vitrification processes, platinum-group metals [PGMs: ruthenium (Ru), rhodium (Rh) and palladium (Pd)] and molybdenum (Mo) cause serious problems: PGMs are accumulated on the sidewall of the glass melter, whereas Mo tends to form so-called “yellow phase” in vitrified objects (VOs). These issues result in not only the degradation of VOs but also an increase in cost and disposal space by flushing the glass melter. To solve these serious issues, we have proposed a process for efficiently simultaneous removal of PGMs and Mo from HLLW prior to being introduced into the glass melter, using metal hexacyanoferrates (HCF) as a sorbent [1]. In this process, chemical forms of PGMs and Mo in nitric acid solution are one of the important information for designing a high-performance sorbent, because the stability of those metal ion complexes in the solution is expected to affect the sorption rate of HCFs against each ion. We have already examined the chemical form of Mo and Pd ions in nitric acid solution [2-3]. In the present study, we report on the chemical form of Rh ion in nitric acid solution.

The different results on the chemical form of Rh complex in nitric acid solution have been reported so
far. For examples, Samuels et al. concluded from theoretical and spectroscopic results that a bidentate octahedral structure, \([\text{Rh(NO}_3\text{)}_3]^{3-}\), is the most stable chemical form of the Rh ion in nitric acid solution [4], whereas Vasilchenko et al. concluded from the results of \(^{103}\text{Rh-}\) and \(^{15}\text{N-NMR}\) and Raman spectroscopy that monodentate octahedral structures, trans-\([\text{Rh(NO}_3\text{)}_4(H_2\text{O})_2]^+\) and \([\text{Rh(NO}_3\text{)}_6]^{3-}\), are the stable chemical forms in nitric acid solution [5]. Although they pointed that the Rh concentration and the starting materials are able to affect the chemical form of Rh complex in nitric acid solution, they did not examine the influence of \(\gamma\)-ray radiation on the chemical form of Rh complex in nitric acid solution yet. In this study, we examined the thermodynamic stability and electronic structure of Rh complex in pure water and nitric acid solution with and without \(\gamma\)-ray radiation, using UV-vis spectroscopy and first-principles calculations in order to expect the chemical form of Rh ion in actual HLLW.

2. Methods

2.1. Experimental methods
Rh complex in nitric acid solution were prepared by dissolving the \(\text{Rh(NO}_3\text{)}_3\cdot x\text{H}_2\text{O}\) (RARE METALLIC Co., LTD., 3 N) powder into 0–3 M nitric acid solutions. The concentration of Rh ion in the solutions were adjusted to be \(5 \times 10^{-3}\) M. UV-vis absorption spectra of these samples were measured using JASCO V-630. The absorption signal of nitric acid was subtracted from the nitric acid solution in the same concentration as the background.

\(\gamma\)-ray irradiation to the samples (Rh in 1.5 M HNO\(_3\) solution) for a total dose of 0.5 and 1.0 MGy was performed using a \(^{60}\text{Co}\) radiation source with a dose rate of 3.44 kGy/h. This dose rate includes an absorbed dose by air, and the total dose was controlled by the irradiation time. Thereafter, UV-vis absorption spectra of the \(\gamma\)-ray irradiated samples were also obtained in a similar manner to those of the samples without irradiation.

2.2. Computational methods
The geometry optimization of \([\text{Rh(NO}_3\text{)}_n(H_2\text{O})_{6-n}]^{3-n}\) (monodentate) and \([\text{Rh(NO}_3\text{)}_n(H_2\text{O})_{6-2n}]^{3-n}\) (bidentate) complexes were performed using Gaussian09 based on density-functional theory (DFT) [6]. The change in the Gibbs’s free energy (\(\Delta G\)) for anation reactions at 298.15 K, 1 atom were also estimated using the optimized structures. All DFT calculations were performed with B3LYP/def2-TZVP level [7, 8]. The effective core potential was used for the Rh atom [9], whereas all electrons were explicitly considered for hydrogen, nitrogen and oxygen atoms. The polarizable continuum model was employed to consider the solvent effects of water by using the integral equation formalism variant [10].

Theoretical absorption spectra arising from the 4d-4d transitions of the optimized Rh complex were obtained using the relativistic configuration-interaction (CI) method (DVME) [11-12]. Since the Rh\(^{3+}\) ion has the 4d\(^6\) electronic configuration, we considered the 6 electrons in 10 molecular spinors as the active space of CI calculations. One-electron approximation calculations were performed with the relativistic formalism in the framework of local density approximation proposed by Vosko, Wilk and Nusair [13]. For the many-electron calculations, we adopted the Dirac-Coulomb-Brite Hamiltonian. The calculated oscillator strength was convoluted with 0.3 eV full-width-at-half-maximum Gaussian functions.

3. Results and Discussion
Figure 1 shows the \(\Delta G\)s of the anation reactions for (a) mono and (b) bidentate Rh complexes. The anation reactions for the mono and bidentate Rh complexes proceed by the following equations (1) and (2), respectively.

\[
\text{Monodentate: } [\text{Rh(NO}_3\text{)}_n(H_2\text{O})_{6-n}]^{3-n} + \text{NO}_3^- \rightarrow [\text{Rh(NO}_3\text{)}_{n+1}(H_2\text{O})_{5-n}]^{2-n} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Bidentate: } [\text{Rh(NO}_3\text{)}_n(H_2\text{O})_{6-2n}]^{3-n} + \text{NO}_3^- \rightarrow [\text{Rh(NO}_3\text{)}_{n+1}(H_2\text{O})_{4-2n}]^{2-n} + \text{H}_2\text{O} \quad (2)
\]
The results of the monodentate complex system indicate that trans-\([\text{Rh(NO}_3\text{)}_4(\text{H}_2\text{O})_2^-]\) complex is the most stable among ten chemical species. In addition, cis-\([\text{Rh(NO}_3\text{)}_4(\text{H}_2\text{O})_2^-], [\text{Rh(NO}_3\text{)}_5(\text{H}_2\text{O})_1]^{2-}\), and \([\text{Rh(NO}_3\text{)}_6]^{3-}\) complexes are also thermodynamically stable chemical species. The energy difference between these complexes (cis-\([\text{Rh(NO}_3\text{)}_4(\text{H}_2\text{O})_2^-], [\text{Rh(NO}_3\text{)}_5(\text{H}_2\text{O})_1]^{2-}\), and \([\text{Rh(NO}_3\text{)}_6]^{3-}\)) and the most stable complex (trans-\([\text{Rh(NO}_3\text{)}_4(\text{H}_2\text{O})_2^-]\)) was 4.40, 0.87 and 15.96 kJ/mol, respectively. As shown in Fig. 1(a), the anation reaction proceeds for monodentate coordination complexes and the complex with \(n > 4\) is considered to form stably. This result is consistent with the previous report described above [4].

![Figure 1. \(\Delta Gs\) of the anation reactions for mono (a) and bidentate (b) Rh complexes](image)

On the other hand, the results of the bidentate complex system indicate that \([\text{Rh(NO}_3\text{)}_3]\) was the most stable complex among five chemical species. Since the energy difference when compared to other species was relatively large by more than 70 kJ/mol, it is considered that this chemical specie was the dominant component in the bidentate system. In other words, the anation reactions of Rh complex proceed smoothly for the bidentate system.

![Figure 2. Experimental (a) and theoretical (b) absorption spectra of Rh complexes](image)

Figure 2 shows the UV-vis absorption spectra (top) of Rh complexes in pure water and 0–3 M nitric acid solutions along with theoretical spectrum (bottom) calculated by the CI method. Although the absorption peaks originating from ligand-metal charge transfer (LMCT) and ligand \(\pi-\pi^*\) transitions
were observed around 202 nm for Rh complexes [5], the strong absorption due to nitric acid itself was overlapped in this wavelength region, and thus we could not distinguished between them. Therefore, we focused on the absorption originating from the 4d-4d transitions of Rh ion in a wavelength region longer than 400 nm.

The experimental UV-vis spectral features of Rh ion in 0–3 M nitric acid solutions seemed to be almost same and thus were independent of nitric acid concentration. This indicates that the chemical form of Rh complexes in 0–3 M nitric acid solutions were the same. In addition, for Rh(NO\textsubscript{3})\textsubscript{3}·xH\textsubscript{2}O dissolved into pure water, the coordination number of nitrate ion does not increase. Accordingly, the Rh complex in pure water was coordinated with three or less NO\textsubscript{3} ions, and in a similar manner, the Rh complex was assumed to be coordinated with three or less NO\textsubscript{3} ions in 1–3 M nitric acid solution. Figure 2 (b) shows theoretical absorption spectrum of [Rh(NO\textsubscript{3})\textsubscript{3}] complex to confirm the assumption. The [Rh(NO\textsubscript{3})\textsubscript{3}] complex has the D\textsubscript{3} symmetry with a slightly distorted octahedral field. The ground state (GS) is 1\textit{A}\textsubscript{1} with a low spin state, which corresponds to the (t\textsubscript{2g})\textsuperscript{6}(e\textsubscript{g})\textsuperscript{0} electronic configuration in the O\textsubscript{h} symmetry notation. As shown in Fig. 2, the theoretical absorption spectrum well reproduced the experimental one in the wavelength region longer than 400 nm. Thus, the chemical species of Rh complex in pure water and nitric acid solution can be assigned to [Rh(NO\textsubscript{3})\textsubscript{3}]. Since the strong absorption band appearing in less 400 nm wavelength is attributed to the LMCT or ligand π−π* transitions [4], and it was not considered in the present many-electron calculations. The absorption band in the range 400–450 nm is due to the transitions from 1\textit{A}\textsubscript{1} (GS) to 1\textit{A}\textsubscript{2} and 1\textit{E} excited states, which corresponds to the transition from (t\textsubscript{2g})\textsuperscript{6}(e\textsubscript{g})\textsuperscript{0} to (t\textsubscript{2g})\textsuperscript{5}(e\textsubscript{g})\textsuperscript{1} electronic configuration. These absorption bands are assigned to the 4d-4d transitions of Rh\textsuperscript{3+}, and their intensities were relatively week when compared to those of the LMCT or ligand π−π* transitions. Since the previous study focused on the strong absorptions such as LMCT and ligand π−π* transitions [4], these weak absorptions may not have been observed.

Although the present results were consistent with those reported by Samuels et al, the theoretical results of the Δ\textit{G}s suggest that the monodentate coordination complexes could exist in the strong nitric acid solution, which depends on the Rh metal concentration or the initial materials.

![Figure 3](image_url) Figure 3. The absorption spectra of the γ-ray irradiated samples with a total dose of 0 (black), 0.5 (red) and 1.0 (blue) MGy.

Considering the actual HLLW, it is important to examine whether γ-ray radiation affects the chemical form of the Rh complex or not in nitric acid solution. We next investigated the influence of the absorption spectra of Rh complex in 1.5 M nitric acid solution by γ-ray irradiation. Figure 3 shows the absorption spectra of the γ-ray irradiated samples with a total dose of 0 (black), 0.5 (red) and 1.0 (blue) MGy. The overall features of these spectra were the almost same. This indicates that there were
no changes in the chemical form of the Rh complex against the γ-ray radiation. In other words, [Rh(NO$_3$)$_3$] complex structure exhibits a radiation resistant, and is considered to be dominant chemical species even in the actual HLLW.

4. Conclusion
We have investigated the chemical forms of Rh ion in pure water and nitric acid solution, using UV-vis spectroscopy and first-principles calculations, in order to develop the disposal of HLLW.

[Rh(NO$_3$)$_3$] complex was the most stable among the five bidentate Rh chemical species thermodynamically, whereas trans-[Rh(NO$_3$)$_4$(H$_2$O)$_2$]$^+$ complex was the most stable among ten monodentate ones. In addition, in case of the monodentate system, cis-[Rh(NO$_3$)$_4$(H$_2$O)$_2$]$^-$, [Rh(NO$_3$)$_5$(H$_2$O)$_1$]$^{2-}$, and [Rh(NO$_3$)$_6$]$^{3-}$ complexes were also stable chemical species.

Comparison between UV-vis spectra and many-electron calculations indicated that Rh forms an octahedral bidentate complex coordinated with three nitrate ions, [Rh(NO$_3$)$_3$], in both pure water and nitric acid solution. However, the monodentate coordination complexes still existed in the strong nitric acid solution, which depended on the Rh concentration or the initial materials.

We further examined the influence of γ-ray radiation to the Rh complex, using UV-vis spectroscopy, and revealed that the Rh complex, [Rh(NO$_3$)$_3$], exhibits a radiation resistant and is considered to be the dominant chemical species even in the actual HLLW.

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