The Removal and Solidification of Halogenide Ions Using a New Inorganic Compound

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The present paper discusses a new method for removing and solidifying halogenide ions from solution by a reaction with $Bi_5(NO_3)O_7$. Since this compound is isostructural with $Bi_5(I)O_7$ or $Bi_5(Br)O_7$, an ion exchange of the halogen ions with NO_3^- is expected.

$Bi_5(NO_3)O_7$ was reacted with aqueous halogenide ions at 25, 50, and 75 °C. The iodide ion was removed almost perfectly at 50 and 75 °C. The reactions were completed after 15 h. The bromide ion was also removed almost perfectly at 25, 50, and 75 °C. The reactions at 50 and 75 °C were completed after 24 h. The chloride ion was also removed by reactions at 50 and 75 °C, which were almost completed after about 48 h. The fluoride ion was not removed.

The iodide and bromide ions reacted with $Bi_5(NO_3)O_7$ to form $Bi_5(X)O_7$ (X=I or Br), provided that their concentrations were below 2.0 and 1.0 $mol\,dm^{-3}$, respectively. The chloride ion formed other types of compounds, such as $Bi_{12}(Cl_2)O_{17}$ or $Bi_3(Cl)O_4$.

The ion-exchange capacities of iodide, bromide and chloride ions were observed at 50 and 75 °C.

The removal of halogenide ions from waste water is a very important problem. For example in the atomic power industry, various radioactive halogenide ions are produced. Among them, the removal and solidification of iodine-129 is a very important problem, because iodine is released to a great extent during dissolution of spent nuclear fuel, and it has a very long half life of 16 million years. Besides iodine-129, the removal and solidification of chlorine-36 is another important problem, because it has a half life of 0.3 million years.

Two kinds of main methods have already been developed for iodine removal: dissolution of iodine in an alkaline solution (wet method) and the reaction of iodine with inorganic materials (dry method). The dry method has a more promising future than does the wet method.

For the dry method, various materials have been studied. For example, various adsorbents, such as metal zeolites,[1,2] silver silica gel which contains 12% Ag and silver impregnated alumina,[3] have been developed. Besides them, Bi_2O_3 was also studied as a candidate material for the immobilization of radioactive iodine.[4,5] These materials, however, still have some development problems regarding their stability, reactivity, and production cost.

Recently, a new compound, $Bi_5(NO_3)O_7$, has been synthesized by the thermal decomposition of basic bismuth nitrate $(4Bi(NO_3)(OH)_2 \cdot BiO(OH))$ or bismuth nitrate pentahydrate.[6] From the viewpoint of removing and immobilizing radioactive iodide ions, this new compound is very favorable. This is because it has been reported that $Bi_5(I)O_7$ is a candidate material for the immobilization of radioactive iodine.[4] The compositions of $Bi_5(NO_3)O_7$ and $Bi_5(I)O_7$ are represented by $Bi_5(O)_7X$ (X is I or NO_3); it has also been reported that their structures are isostructural.[6] We can thus expect an ion exchange of NO_3^- and I^-. If this ion exchange is

possible in solution, the compound $Bi_5(NO_3)O_7$ would be expected to be a new useful ion exchanger for removing and solidifying radioactive iodide ions.

From the viewpoint of the immobilization of iodide ions, it is important to keep the composition of the product as $Bi_5(I)O_7$ in the ion-exchange reaction. Until now, five kinds of bismuth iodide oxides (Bi(I)-O, $Bi_7(I)_3O_9$, $Bi_5(I)O_7$,[7] $Bi_4(I)_2O_5$,[8] and β-$Bi_5(I)$-O_7[9]) have been repored. Among them, $Bi_5(I)O_7$ is the most stable at high temperature,[8,10] and it is seven orders of magnitude more stable than BiI_3 toward hydrolysis.[11,12]

In the present paper, not only the removal of the iodide ion, but also the removal of fluoride, chloride, and bromide ions from aqueous solution was studied using $Bi_5(NO_3)O_7$. In a NaBr solution, the ion exchange of NO_3^- with Br^- is also expected, since $Bi_5(Br)O_7$ is also isostructural with $Bi_5(NO_3)O_7$. Thus, although the presence of $Bi_5(Cl)O_7$ has not been known, many other bismuth chloride oxides have been reported.[13,14] These compounds are comparatively stable toward hydrolysis.[15] As was reported, although the basic bismuth nitrate had an anion-exchange property for halogenide ions,[16] it would also be very interesting to study the exchange property of $Bi_5(NO_3)O_7$ to chloride or fluoride ions.

Experimental

Synthesis of $Bi_5(NO_3)O_7$: $Bi_5(NO_3)O_7$ was synthesized by the thermal decomposition of basic bismuth nitrate as follows.[4] Basic bismuth nitrate (about 20 g) was charged in a platinum crucible and heated in air at 450 °C for 9 h. After the heating, decomposed products were quenched and characterized by an X-ray powder diffraction analysis. The NO_3 content was determined by mass spectrometry and a thermogravimetric analysis. The data were obtained at the same time on a computer-interfaced MAC & VG TG-DTA/MS system.

Reaction with Halogenide Ions: The stability of $Bi_5(NO_3)O_7$ in water was examined. This compound (233 mg) was heated in 1 cm^3 of pure water at 50 °C for 20 h. A concentration change of NO_3^- was then observed. Since it changed from 0 to 6.5×10^{-5} mol dm^{-3}, $Bi_5(NO_3)O_7$ is sufficiently stable in water toward hydrolysis.

Powdered $Bi_5(NO_3)O_7$ was equilibrated with NaF, NaCl, KBr, and NaI solutions. The reaction was carried out without any agitation in a plastic test tube stopped tightly with a lid and placed in a thermostatic container. The test tube was confirmed to be airtight by measuring its mass both before and after the reaction. After the reaction, any solids were separated from the solution and identified by their X-ray powder diffraction patterns. The concentration of the halogenide ions was determined by means of ion chromatography, using a DIONEX 4500i instrument.

Results and Discussion

Extent of the Ion-Exchange Reaction with Halogenide Ion: The extent of the ion-exchange reaction of $Bi_5(NO_3)O_7$ with halogenide ions was examined as a function of time at constant temperatures. The experimental conditions were as follows: mass of $Bi_5(NO_3)O_7$, 244 mg; concentration of sodium halogenide solution, 0.1 mol dm^{-3}; volume of sodium halogenide solution, 1 cm^3.

Figure 1 shows the result of the reaction in NaI solution. Three curves correspond to the results with the temperature at 25, 50, and 75 °C respectively.

As shown in Fig. 1, the reaction at 25 °C was very slow compared with the reactions at higher temperatures; 79% of the iodide ion still remained after 15 h. On the other hand, the reaction at 50 and 75 °C were comparatively fast; coming to completion within almost 15 h; more than 99.9% of the iodide ion was removed after 15 h.

Figure 2 shows the results of the reaction in KBr solution; it gives almost the same result as in Fig. 1. The reactions at 50 and 75 °C were comparatively fast,
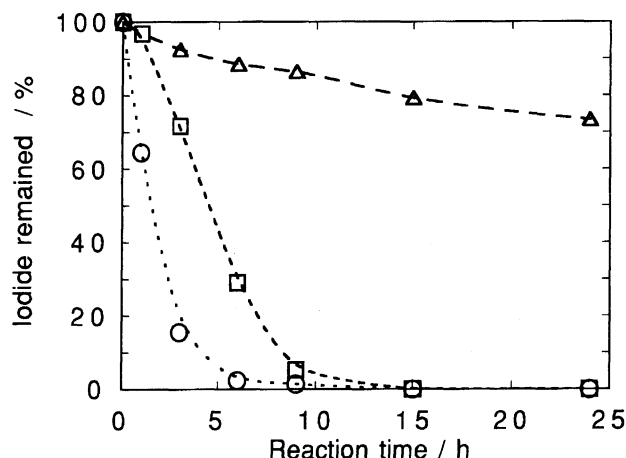
and came to completion within almost 24 h; about 99% of the bromide ion was removed after 24 h. The reaction at 25 °C was slow compared with the other reactions, but not as slow as in a NaI solution; 6.9% of the bromide ion remained after 24 h.

Figure 3 shows the result of the reaction in a NaCl solution. As shown in Fig. 3, although the chloride ion was also removed very well, the reactions proceeded more slowly compared with the reaction in a NaI or KBr solution, not only at 25 °C, but also 50 and 75 °C. The reactions at 50 and 75 °C came to completion within 48 h. In the reaction at 25 °C, about 14% of the chloride ion, and in the reactions at 50 and 75 °C, about 97 and 98% of chloride ion were removed after 48 h.

The reaction $Bi_5(NO_3)O_7$ with the fluoride ion was examined in a NaF solution as a function of time at 50 °C. The result showed that only a few fluoride ions were removed and that only about 3% of the flouride ions was removed after 6 h. This value is almost same
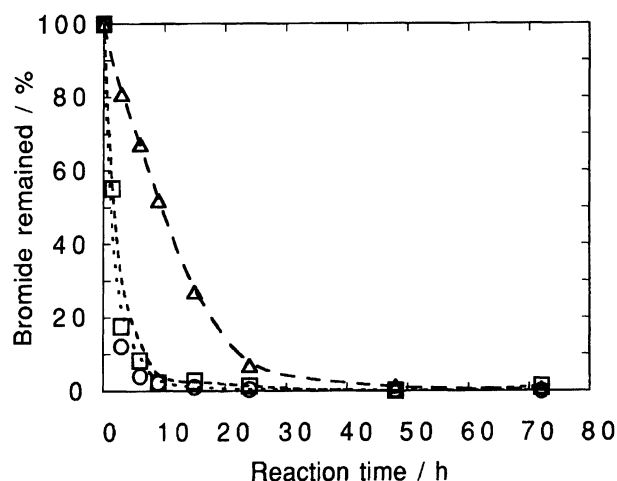
Fig. 2. Extent of reaction, bromide remained vs. reaction time. △: a curve observed at 25 °C, □: a curve observed at 50 °C, ○: a curve observed at 75 °C.

Fig. 1. Extent of reaction, iodide remained vs. reaction time. △: a curve observed at 25 °C, □: a curve observed at 50 °C, ○: a curve observed at 75 °C.
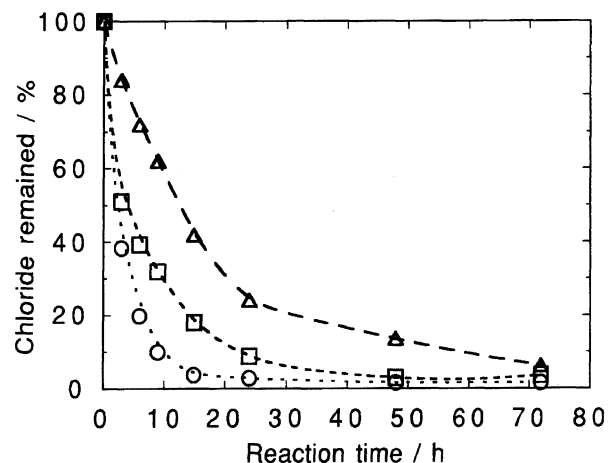
Fig. 3. Extent of reaction, chloride remained vs. reaction time. △: a curve observed at 25 °C, □: a curve observed at 50 °C, ○: a curve observed at 75 °C.

as that after the reactions for 9, 15, 24, and 48 h.

Ion-Exchange Reaction: The ion-exchange reaction of $Bi_5(NO_3)O_7$ with halogenide ions was studied in 0.05, 0.005, and 0.0005 $mol\,dm^{-3}$ NaI, KBr, and NaCl solutions.
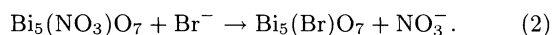
In an experiment concerning a reaction in NaI solutions, powder $Bi_5(NO_3)O_7$ (1.00 g) was placed in a 10 cm^3 solution at 50 °C for 20 h. The iodide ion was removed from all of the solutions. After the reaction with a 0.05 $mol\,dm^{-3}$ NaI solution, 99.99% of the iodide ions was removed; when 3 g of $Bi_5(NO_3)O_7$ was subsequently reacted under the same conditions, no iodide ion was detected in the solution. After a reaction with a 0.005 or 0.0005 $mol\,dm^{-3}$ NaI solution, no iodide ion was detected. The concentration of the remaining iodide ions in the solution was below the limit of detection (5×10^{-7} $mol\,dm^{-3}$).

$Bi_5(I)O_7$ was the sole product in all of the reactions in these and Fig. 1; this means that the ion exchange can be represented by

$$Bi_5(NO_3)O_7 + I^- \rightarrow Bi_5(I)O_7 + NO_3^-. \qquad (1)$$
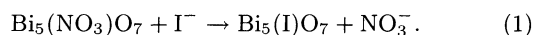
In experiments concerning the reaction in KBr solutions, powder $Bi_5(NO_3)O_7$ (1.00 g) was placed in 10 cm^3 solutions at 50 °C for 24 h. After the reaction, 99.6—97.7% of the bromide ions were removed.

$Bi_5(Br)O_7$ was the sole product in these reactions and Fig. 2; this means that the ion exchange can be represented by

$$Bi_5(NO_3)O_7 + Br^- \rightarrow Bi_5(Br)O_7 + NO_3^-. \qquad (2)$$

In experiments concerning the reaction in NaCl solutions, powder $Bi_5(NO_3)O_7$ (1.00 g) was placed in 10 cm^3 solutions at 75 °C 48 h. After the reactions, 99.7—93.3% of the chloride ions were removed.

The products in these reactions and Fig. 3 were $Bi_{12}(Cl)_2O_{17}$ and $Bi_3(Cl)O_4$. In these cases, the formation of $Bi_5(Cl)O_7$ is not expected, because its presence has not been reported in the literature. $Bi_{12}(Cl)_2O_{17}$, $Bi_3(Cl)O_4$, $Bi_{24}(Cl)_{10}O_{31}$, $Bi_4(Cl)_2O_5$, and $Bi(Cl)O$ are the reported compounds in this system.[12]

Ion-Exchange Capacity: The ion-exchange capacity was measured with solutions (1 cm^3) having various concentrations of NaI, KBr, and NaCl (0.2, 0.3, 0.4, and 0.5 $mol\,dm^{-3}$). Accurately weighted $Bi_5(NO_3)O_7$ (244 mg) was reacted with NaI for 20 h, with KBr for 24 h and with NaCl for 48 h at 50 and 75 °C.

The ion-exchange capacities of $Bi_5(NO_3)O_7$ for the iodide ion were 0.46, 0.29, 0.17, and 0.14 $mequiv\,g^{-1}$ at 50 °C and 0.76, 0.82, 0.80, and 0.76 $mequiv\,g^{-1}$ at 75 °C (the values are written in accordance with the order of the concentrations described above). The reaction products in these experiments were not only $Bi_5(I)O_7$, but the formation of $Bi(I)O$, in addition to $Bi_5(I)O_7$, which was observed at concentrations above 0.3 $mol\,dm^{-3}$ at 50 and 75 °C. This indicates that the

ion-exchange reaction is not expressed only by Eq. 1 when the concentration of iodide ions is higher than 0.2 $mol\,dm^{-3}$.

The ion-exchange capacities for the bromide ion were 0.79, 1.12, 1.33, and 1.28 $mequiv\,g^{-1}$ at 50 °C and 0.76, 0.96, 1.08, and 1.14 $mequiv\,g^{-1}$ 75 °C. The reaction products in these experiments were not only $Bi_5(Br)O_7$, but the formation of $Bi_3(Br)O_4$, in addition to $Bi_5(Br)$-O_7, which was observed at the concentrations of 0.2 and 0.3 $mol\,dm^{-3}$ at 50 °C, and at all concentrations at 75 °C. At concentrations of 0.4 and 0.5 $mol\,dm^{-3}$ at 50 °C, the reaction product was only $Bi_3(Br)O_4$ and the formation of $Bi_5(Br)O_7$ was not observed. This indicates that the ion-exchange reaction is not expressed only by Eq. 2 when the concentration of the bromide ion is higher than 0.1 $mol\,dm^{-3}$.

If the ion-exchange reaction proceeds according to Eqs. 1 or 2, the calculated maximum value of the ion-exchange capacity is 0.82 $mequiv\,g^{-1}$.

The ion-exchange capacities for the chloride ion were 0.76, 1.02, 1.17, and 1.23 $mequiv\,g^{-1}$ at 50 °C and 0.77, 0.88, 1.89, and 0.94 $mequiv\,g^{-1}$ at 75 °C. The reaction products in these experiments were a mixture of $Bi_{12}(Cl)_2O_{17}$ and $Bi_3(Cl)O_4$ at all concentration at 50 and 75 °C. The content of the $Bi_3(Cl)O_4$ increased with an increase in the concentration of the chloride ion.

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