Studies on Extraction of Polonium(IV) by Hexone from Acid Solution

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(Received June 10, 1960)

Solution chemistry of polonium(IV) with a weighable quantity of polonium was developed by Bagnall et al.1) for several years past. However, one of the present authors found that polonium(VI), having a higher oxidation potential with regard to polonium(IV), was not stable, owing to its own α radiation2). Accordingly, it is necessary to employ a minute quantity of this element (which does not cause any radiolysis) in order to distinguish the results from self radiolysis. The extraction study of polonium(IV) was undertaken, therefore, with quantities of less than one microcurie of polonium per millilitre. In the course of the present studies on polonium extraction with hexone (methyl isobutyl ketone,) some peculiarities in the extraction characteristics were observed in a certain range of acidity, suggesting that there will be one or more unestablished complex species of polonium other than PoX_6^{2-}3,4). These phenomena appeared to be closely related with the history of employed polonium sources as well as with the acid nature of the aqueous phase from which polonium was extracted3,5-7). In order to find out new species of polonium(IV) responsible for this peculiarity in aqueous medium, the experiments were carried out under well defined conditions concerning the history of polonium source and the acidity of the extraction system.

Experimental

1) **Materials.**—Polonium received from Amersham, England, dated June 1959, was in the form of nitrate in 1 N nitric acid. It was used after purification in our laboratory as described below:

A portion of polonium solution was converted into 0.3 N hydrochloric acid solution from which

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1) K. W. Bagnall, "Chemistry of the Rare Radioelements", Butterworths Scientific Publications, London, (1957), pp. 3—94.

2) N. Matsuura and M. Haissinsky, *J. chim. phys.*, **55**, 475 (1958).

3) M. Guillot, ibid., **28**, 107 (1931).

4) K. W. Bagnall, R. W. M. D'Eye and J. H. Freeman, *J. Chem. Soc.*, **1955**, 3959.

5) G. Hevesy, *Phys. Z.*, **14**, 49, 1202 (1913).

6) K. W. Bagnall and D. S. Robertson, *J. Chem. Soc.*, **1957**, 509.

7) T. Ishimori, This Bulletin, **27**, 520 (1954).

polonium was deposited on a silver foil by electrochemical displacement. The deposited polonium was redissolved in 1 N nitric acid together with metallic silver and was freed from silver by precipitating silver as chloride. The supernatant liquid thus obtained was evaporated to dryness, while the residue was extracted with hot dilute hydrochloric acid. After this purification procedure was repeated several times, the extracted polonium solution was stored in 6 N hydrochloric acid. The resulting solution was the usual starting source of our experiments, though other solutions of different kinds of acid and acidities were sometimes used as well.

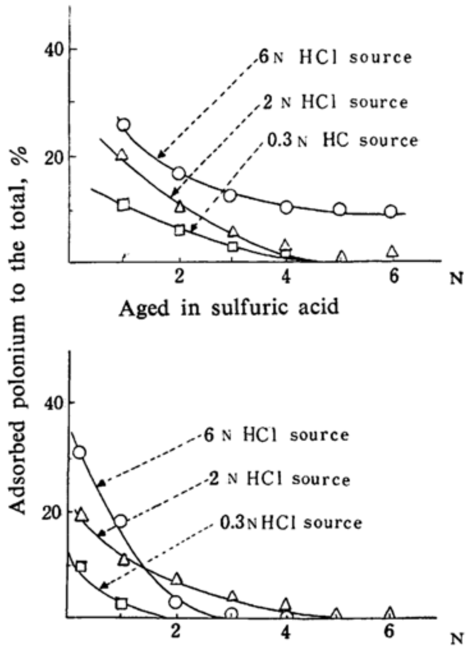
2) **Activity Measurement.**—Twenty microlitres of the solution, containing polonium, was pipetted by a glass micro-syringe furnished with a micrometer. In order to obtain the homogeneity of the samples for the α counting of polonium, two different methods were applied, one by evaporating the pipetted sample directly on a glass plate and the other depositing the polonium on a silver foil by the electrochemical displacement. The simple evaporation method was not suitable for obtaining consistent α activity of polonium, especially when some non-volatile material was present. In the electrochemical method it was desirable to make preliminary extraction with hexone from acid solution in the presence of an excess amount of potassium iodide. By this method all polonium activities could be transferred to an organic phase as hexa-iodo polonium complex, PoI_6^{2-}. The hexone solution thus obtained was placed on a silver foil, while polonium was deposited electrochemically for activity measurement. The discharge rate of electroscope, 5.575 div./min. was standardized against the counting rate of 4π flow counter for the same sample under the same condition of measurement. This yielded 977 counts/min. against 5.575 div./min., i. e., 1 div./min. corresponds to 4.7×10^{-3} microcurie of ^{210}Po.

3) **Partition of Polonium between Two Liquid Phases.** — For determining the distribution of polonium between hexone and aqueous acid solution the sample solution was shaken at room temperature in a stoppered glass test tube with the same volume of solvent, preliminarily saturated with the acid of the same concentration. The correction of volume change after extraction was needed when the extraction was made from concentrated acid solution. Although in our measurements only several ten micro microlitres of the sample was taken, the errors fell within the limit of 10%. The equilibrium of partition was established in less than 5 min. at the temperature of 20±5°C.

4) **Aging of Polonium Solution.**—About 80 microlitres of the stock solution which contained a known amount of polonium was taken in 4 ml. of hydrochloric, sulfuric or nitric acid. Just after mixing a portion of polonium was extracted with hexone from the mixture. This provided the data at time 0. The rest of the polonium solution was boiled in a glass flask with reflux condenser for several hours on a steam bath, before it was cooled to room temperature. This aged solution was used as a sample for extraction of polonium.

Results and Discussion

1) **Adsorption of Polonium on Glass Wall.**—Polonium is generally adsorbed strongly on a number of substances. For example, the adsorption on ion-exchange resins, either cationic or anionic, is so strong that polonium is hardly eluted even by an eluant of high ionic concentration. In this respect, ion-exchange technique did not give any reliable data for studying the complex chemistry of polonium. It seemed to us that the partition method was rather preferable. In the extraction method, however, the adsorption on a glass wall caused another difficulty in the accurate determination of polonium activity. In order to obtain a correct partition coefficient, it is necessary to know the loss of polonium by adsorption from the extraction system. In Fig. 1 the actual adsorption loss was shown in (Po lost/Total Po used)×100% as the function of acidity of the medium from which polonium was extracted. In the hydrochloric acid vs. hexone system the adsorption on a glass wall was very small, if the acid was stronger than 2 N. On the other hand in sulfuric acid-hexone system several hundredths of polonium was left on the surface of the glass wall regardless of the acidity so far as we examined it. Therefore, the adsorption loss cannot be neglected for the correct extraction data.



Aged in sulfuric acid

Aged in hydrochloric acid

Fig. 1. Adsorption of polonium(IV) on the wall of 1 ml. glass stoppered vessel for hexone extraction.

2) Aging Effect on Nitric Acid.—The amount of polonium extracted from nitric acid solution was nearly constant, 80% being found in the organic phase. This constant value of extraction coefficient can be obtained if the polonium source stored in 6 N nitric acid is employed for extraction after immediate dilution to a given concentration of the acid. Much lower extraction coefficients were observed, on the other hand, if polonium in 0.4 N nitric acid was extracted. In Fig, 2, the extraction coefficient curve 1 for polonium source in 0.4 N nitric acid fell with decreasing acidity. The aging before extraction by heating under reflux for 1, 2 and 12 hr. at 80°C increased the extraction coefficients up to 80% as shown in corresponding curves 2, 3 and 4 in Fig. 2. This fact suggests that polonium(IV) nitrate complex $Po(NO_3)_6^{2-}$ or $Po(NO_3)_5^{-}$ [8,9], which is stable in 6 N nitric acid, can be readily extracted by hexone, whereas the hydrolysed complex produced in weak nitric acid below

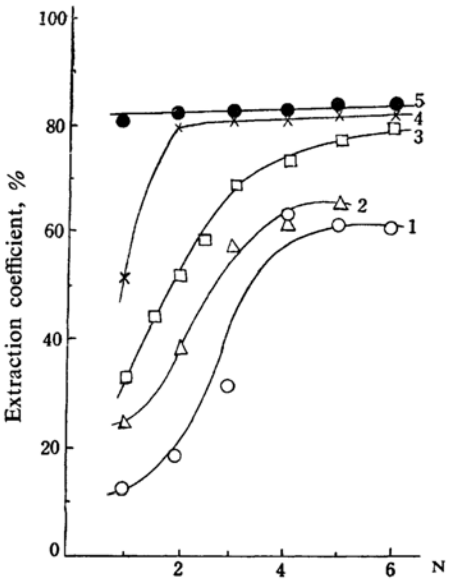


Fig. 2. Aging effect on polonium(IV) extraction with hexone from nitric acid medium for the source stored in 0.4 N (1~4) and in 6 N (5).

-○- 1. Extraction immediately after dilution.
-△- 2. Extraction after 1 hr.'s heating.
-□- 3. Extraction after 2 hr.'s heating.
-×- 4. Extraction after 12 hr.'s heating.
-●- 5. Extraction without aging.

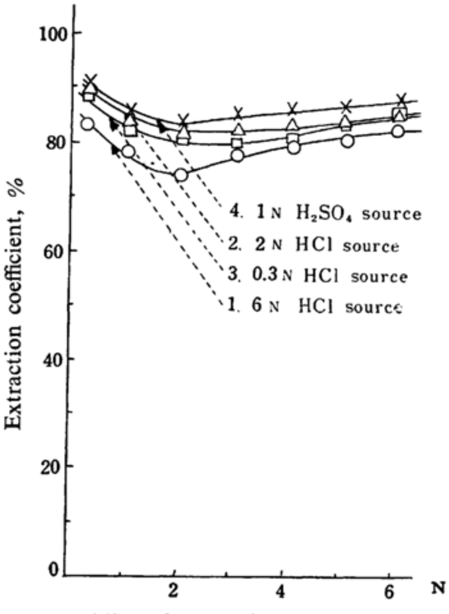


Fig. 3A. Aging effect on extraction coefficients. (Immediately after dilution.) 1. 6 N HCl source 2. 2 N HCl source 3. 0.3 N HCl source 4. 1 N H_2SO_4 source

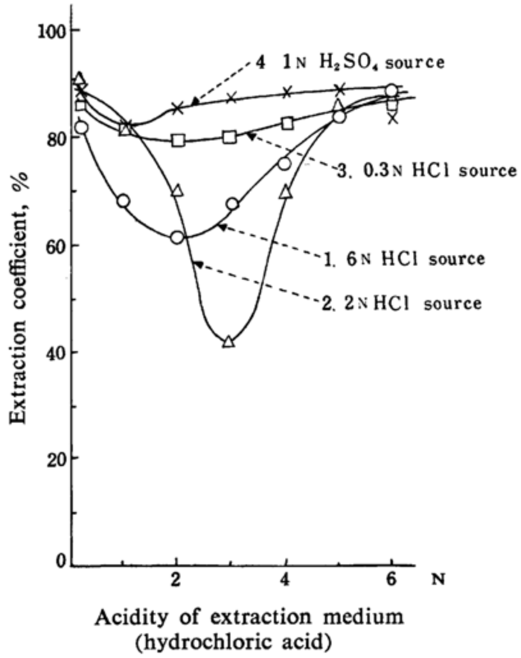


Fig. 3B. Aging effect on extraction coefficients. (Aged for 6 hr. at boiling point.)
1. 6 N HCl source 2. 2 N HCl source 3. 0.3 N HCl source 4. 1 N H_2SO_4 source

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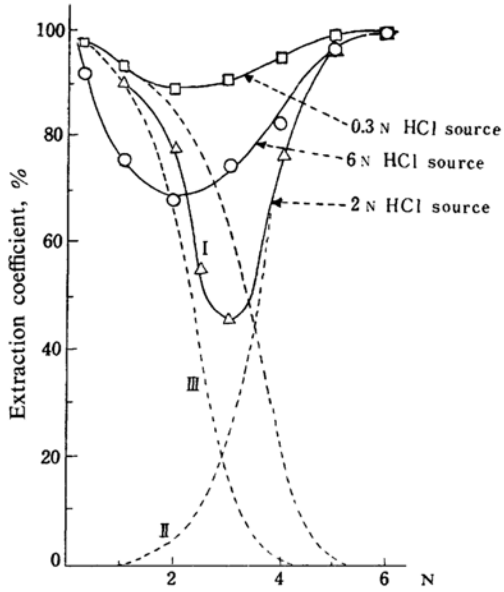
[8] J. Danon and A. A. L. Zamith, *J. Phys. Chem.*, **61**, 431 (1957).

[9] K. W. Bagnall, D. S. Robertson and M. A. A. Stewart. *J. Chem. Soc.*, **1958**, 3633.

1 N is hardly extracted at all. The form of the latter hydrolysed ionic species cannot be detected in our experiments, though some authors suggest that the ionic formula is PoO^{2+} or $Po(OH)_2\ (NO_3)_4^{2-}$ 7).

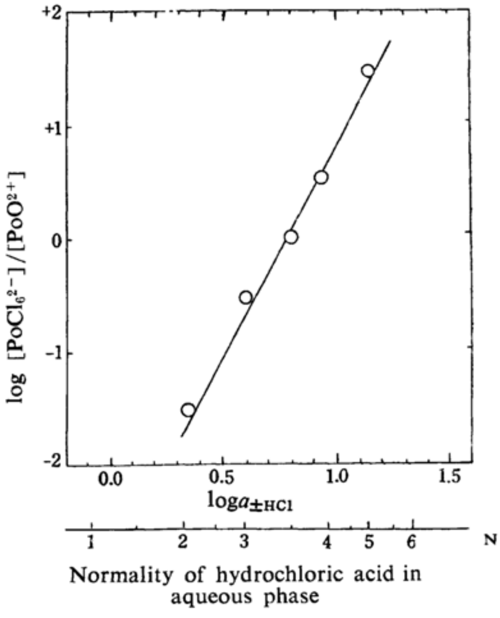
3) Aging Effect in Hydrochloric Acid.—Aging effect on the extraction characteristics of polonium was also observed in hydrochloric acid as well as in nitric acid. The results were represented in Fig. 3 for the several different polonium sources aged and stored in 0.3, 2 or 6 N hydrochloric acid. In this case polonium was extracted from hydrochloric acid of 0.3∼6 N for the samples aged 6 hr. under reflux (A) and non-aged (B). The minimum extraction coefficient was observed at about 2 N hydrochloric acid. This minimum appeared only in the extraction from hydrochloric acid medium. Hence, it was assumed that in hydrochloric acid there would be two different ionic species of polonium complex easily soluble in hexone. A well-established form of polonium(IV) complex in hydrochloric acid is $PoCl_6^{2-}$ which is believed to be formed easily in hydrochloric acid of higher than 6 N and stable even in more dilute acid after it was formed10,11). But by aging in more dilute acid solution for prolonged time, the solubility of polonium in hexone decreased as it formed some kinds of hydrolytic products which were hardly soluble in hexone.

4) Ionic Species of Hydrolytic Product.—It is very interesting to estimate the ratio of insoluble species to soluble species from the data of Fig. 3B. This ratio depends not only on the acidity of the extraction system but also on the history of the polonium source. Then, for example, the curve 2 in Fig. 3B, having a sharp minimum at nearly 2 N, can be analysed into two separated curves, as shown in Fig. 4 with dotted lines. These separated curves indicate two different hexone soluble complex species contributed to the extraction at the same time, though in different ways, in the acidity region, one in the range over 3 N and the other in the acidities less than 2 N. The dependence of each curve on the acidity of the extraction system can be shown in Fig. 5 by the logarithmic plots of Polonium soluble/Polonium insoluble or $E'/(1+E')$ as a function of acidity in linear scale. Here, E' denotes the extraction coefficient for separated species. These plots have linear character with the tangential increment 4. Applying mass action law to this system for the hydrolytic reaction given by (1), an equilibrium relation (2) is obtained between two polonium species, soluble and insoluble, which shows dependence on the fourth power of acidity.



Normality of hydrochloric acid in aqueous phase

Fig. 4. Analysis of the extraction coefficient curve.



Normality of hydrochloric acid in aqueous phase

Fig. 5. Logarithmic plots of curve II in Fig. 4.

$$PoCl_6^{2-}+2H_2O=Po(OH)_2Cl_4^{2-}+2H^{+}+2Cl^{-} \quad (1)$$

$$\frac{PoCl_6^{2-}\ \text{soluble in hexone}}{Po(OH)_2Cl_4^{2-}\ \text{insoluble}}=K\cdot[H^{+}]^{2}\cdot[Cl^{-}]^{2}$$

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10) D. J. Hunt, *Amer. Rep.*, MLM, 979 (1954).

11) K. W. Bagnall and J. H. Freeman, *J. Chem. Soc.*, 1956, 2770.

$$\text{or}\quad \frac{\text{Po(IV) soluble}}{\text{Po(IV) insoluble}}=\frac{E'}{1-E'}$$
$$=K\cdot a^2_{\pm\text{HCl}}$$

Where, $a_{\pm\text{HCl}}$ is the mean activity of hydrochloric acid. It seemed from the above consideration that the species of $Po(OH)_2Cl_4^{2-}$ or $PoO^{2+}(H_2O+4Cl^-)$ is responsible for the appearance of minimum extraction from hydrochloric acid medium at the concentration about 2 N.

However, the idea is not entirely excluded that polonium nitrate complex formed in the purification process is partly extracted even from hydrochloric acid. Accordingly, it is possible to assume that the minimum value of extraction appears in the acidity most favorable to hydrolytic reaction succeeded by the following schema:

$$Po(NO_3)_6^{2-}+2H_2O$$
$$=PoO^{2+}+2H^++6NO_3^-+H_2O$$
$$\underline{PoO^{2+}+2H^++6Cl^-+H_2O=PoCl_6^{2-}+2H_2O}$$
$$Po(NO_3)_6^{2-}+6Cl^-=PoCl_6^{2-}+6NO_3^-$$

Here, unconverted nitrate complex contributes to the extraction in the concentration range of hydrochloric acid lower than 2 N. In this hypothesis, an assumption of an uncertain soluble complex of polonium is not necessary.

However, there is no reason to believe that the nitrate complex is more stable than chloro-complex nor that the conversion of nitrate complex into chloro-complex is incomplete.

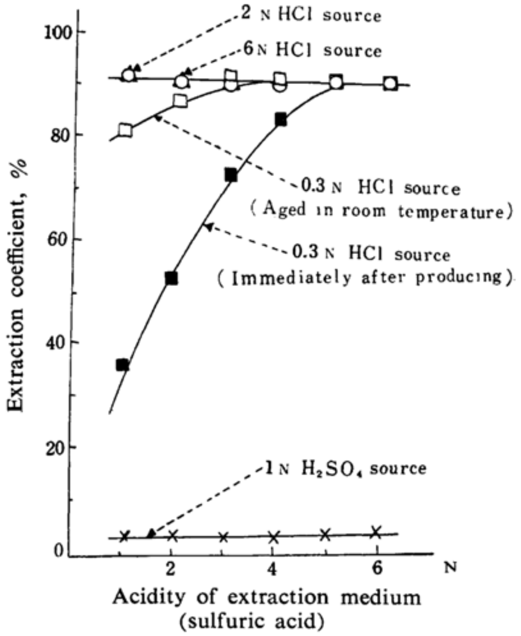

Fig. 6A. Aging effect on extraction coefficient. (Immediately after dilution.)

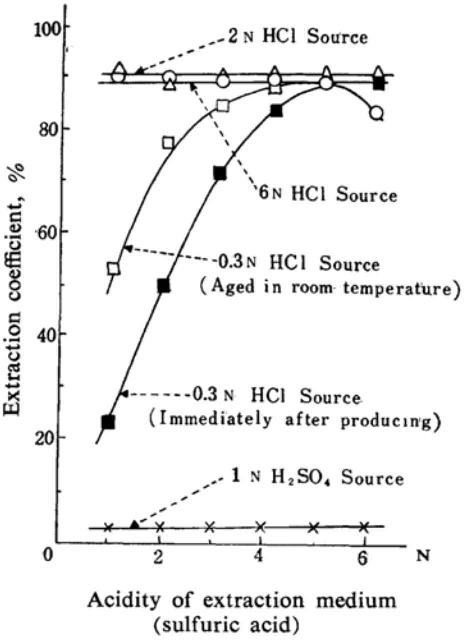

Fig. 6B. Aging effect on extraction coefficient. (Aged for 6 hr. at boiling point.)

5) Aging Effect on the Extraction from Sulfuric Acid Medium.—Partition equilibrium of polonium(IV) between hexone and aqueous solution of sulfuric acid was also studied with the different sources of polonium, stored in 6, 2 and 0.3 N hydrochloric acid and 1 N sulfuric acid, respectively. The results were shown in Fig. 6. Among them only the polonium source prepared and stored in sulfuric acid

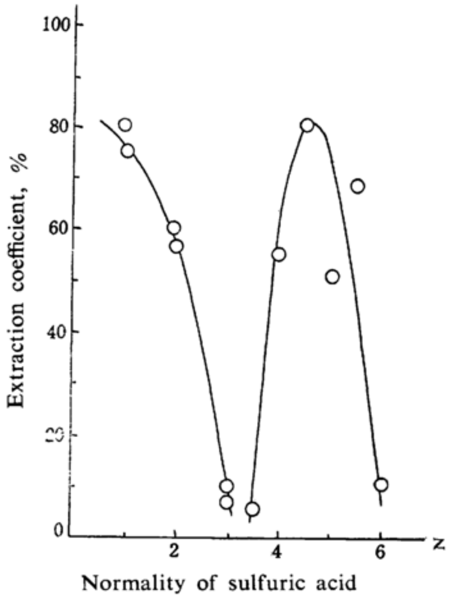

Fig. 7. Extraction of polonium(IV) in sulfuric acid.

gives extraction coefficient nearly nul in the entire range of acidity examined. This indicates that a trace quantity of chloride, if present in sulfuric acid, causes a remarkable increase of extraction yield and that the yield attains the maximum value corresponding to that of hexachloro-polonium(IV) complex, $PoCl_6^{2-}$. It can be said that one of the complex species, $PoCl_6^{2-}$ is readily formed in the presence of a minimum quantity of chloride in sulfuric acid. In our latest publication on polonium the extraction of polonium(IV) from sulfuric acid medium passed through maximum and minimum phases as shown in Fig. 7. This was observed by using the polonium source of 6 N hydrochloric acid after diluting 100 times with sulfuric acid before extraction. In this case the aging was made at 80°C for one hour by heating on a steam bath. A minimum value of extraction that appeared in the proximity of 2 N sulfuric acid is consistent with the results obtained for the extraction from hydrochloric acid by using an aged polonium source as already mentioned in 3). From this consideration the present authors prefer the ionic form PoO^{2+} as the stable species of polonium(IV) in sulfuric acid to that of PoO_3^{2-} which is regarded as stable in less acidic solution according to the analogy of $Te(IV)O_3^{2-}$.

Summary

The ionic state of polonium(IV) in hydrochloric and sulfuric acid solution was studied by the solvent extraction with hexone (methyl isobutyl ketone).

1) The polonium solution stored in 0.4 N nitric acid is strongly hydrolysed by aging. The low extraction coefficient caused by hydrolysis became higher by heating the polonium solution in stronger nitric acid. On the other hand, the polonium stored in 6 N nitric acid can be extracted with constant extraction coefficient, about 80%, through the entire acidity range from 1 to 6 N., if the extraction was carried out without any aging.

2) The aging effect of polonium(IV) in hydrochloric acid is rather complicated. A minimum extraction appeared in the acidity range near 2 N hydrochloric acid. By applying mass action law the probable form of polonium(IV) in that range was $Po(OH)_2Cl_4^{2-}$ or PoO^{2+}, assuming that $PoCl_6^{2-}$ was the stable form of polonium(IV) in 6 N hydrochloric acid which is readily soluble in hexone.

3) Almost no polonium(IV) was extracted by hexone from sulfuric acid solution. Here, the polonium(IV) in sulfuric acid exists probably as PoO^{2+} rather than as PoO_3^{2-}.

The authors wish to express their thanks to Professor T. Shirai and to their colleagues in the laboratory for their helpful discussions. A part of the expenses of these studies was defrayed by a grant from the Ministry of Education.

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