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A Cation-exchange Study of the Hydrolysis of Tracer Concentrations of Polonium(IV)

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A cation-exchange method was used for determining the average cationic charge of polonium species present in hydrolytic equilibrium in solutions. This method is based on measurements of the distribution ratio of polonium at a constant internal hydrogen-ion concentration of the cation-exchanger phase. In 1.0 mol dm^{-3} (H,Na)ClO$_4$ and 1.0 mol dm^{-3} (H,Na)NO$_3$ solutions at $-\log[\mathrm{H}^+]=1.0$, tracer concentrations of polonium(IV) were found to exist in the mean chemical forms of $\mathrm{Po(OH)}_{3.43}^{0.53+}$ and $\mathrm{Po(OH)}_{2.83}(\mathrm{NO}_3)_{0.60}^{0.57+}$, respectively. The formation of cationic polymerized species was also estimated in region of $4\leqslant-\log[\mathrm{H}^+]$ in a 1.0 mol dm^{-3} (H,Na)ClO$_4$ solution.

In polonium compounds, it has been reported that the oxidation numbers of plonium are ±2, +3, +4, and +6.[1] The quadrivalent state was assigned to a large portion of polonium in every pH region.[2–4] With respect to polonium in solution, the solvent-extraction study of polonium in strongly acidic solutions has been reported by several workers.[5–9] The present authors have investigated the hydrolysis of polonium(IV) ions in the pH region through solvent extraction with dithizone–CCl$_4$ solutions.[10–12] The dependence of the chemical behavior of polonium on the pH of the solution clearly showed the importance of the hydrolytic processes. Paper chromatography was also used to study the chemical state of polonium in nitrate solutions.[13,14] The results showed appreciable variations in chemical species with the storage time and with the hydrogen-ion concentrations of the polonium solutions. Koch and Schmidt have studied the hydrolysis of polonium in perchlorate solutions by the cation-exchange method.[2] There have been some other reports of ion exchange on polonium,[15–19] but the results, derived from the ion-exchange behavior of polonium, have not indicated the well-defined chemical species for polonium in each solution. In continuation of the preceding work on polonium,[10–12,14] we have now studied the mean chemical species of polonium in 1.0 M (H,Na)ClO$_4$ (1 M=1 mol dm^{-3}) and 1.0 M (H,Na)NO$_3$ solutions at $-\log[\mathrm{H}^+]=1.0$ with the cation-exchange method.

Experimental

Reagents. The water and reagents used were all purified to the highest degree, especially to overcome the difficulties hitherto experienced as a result of contamination. Bio-Rad AG 50W-X8 was the cation-exchange resin employed in this study. The H-form resin, 100—200 mesh, was washed three times alternatively with 1 M HCl and 1 M NaCl to remove impurities (finally converted to the Na-form), washed with water sufficiently, and dried in air. A part of the polonium (^{210}Po) imported from the Radiochemical Centre, Amersham, England, was used by diluting it to the appropriate concentration with a 1.0 M (H, Na)ClO$_4$ or 1.0 M (H, Na)NO$_3$ solution.

Measurements of the Distribution Ratio. Twenty ml (1 ml=1 cm^3) of a 1.0 M (H, Na)ClO$_4$ or 1.0 M (H, Na)NO$_3$ solution containing definite amounts of polonium was mixed with 0.3 g of a cation exchanger in a test tube with a stopper and then shaken at room temperature until the partition equilibrium was attained. A 5-ml portion of the aqueous phase was pipetted into a scintillation vial containing 5 ml of a scintillator (Dotite Scintisol 500, Dojindo Lab.), shaken sufficiently, and then subjected to measurements of its α-activity. Because it is difficult to count the activity of the resin phase with the same counting efficiency as the aqueous phase with a liquid scintillation counter, the α-activity of the resin phase ($\bar{A}$) was calculated using $\bar{A}=A_{\mathrm{aq}}^{\circ}-A_{\mathrm{aq}}$, where A_{aq}° is the initial activity of the aqueous phase before shaking and where A_{aq} is the activity of the aqueous phase after shaking. The distribution ratio of polonium, D, is given as follows:

$D=(\bar{A}/\text{gram of air-dried resin})/(A_{\mathrm{aq}}/\text{ml of aqueous phase})$.

In each case, the multiple ion-exchange procedures were repeated by using the same test tube on a solution with a definite hydrogen-ion concentration and definite amounts of polonium; the data obtained in the first half were discarded, and only the reproducible data in the other half were taken. As D is influenced by the extent of the dehydration of air-dried resin, a definite water content must be kept in the series of experiments.

Results and Discussion

Adsorption of Polonium onto Test Tube. The inside surfaces of the test tubes used were, in advance, sufficiently and repeatedly equilibrated with respect to the adsorption of polonium with 20 ml of a 1.0 M (H,Na)-ClO$_4$ solution containing polonium (1.56×10^5 cpm) at $-\log[\mathrm{H}^+]=1.2$. After the test tube containing a freshly prepared 1.0 M (H,Na)ClO$_4$ solution (20 ml, 1.56×10^5

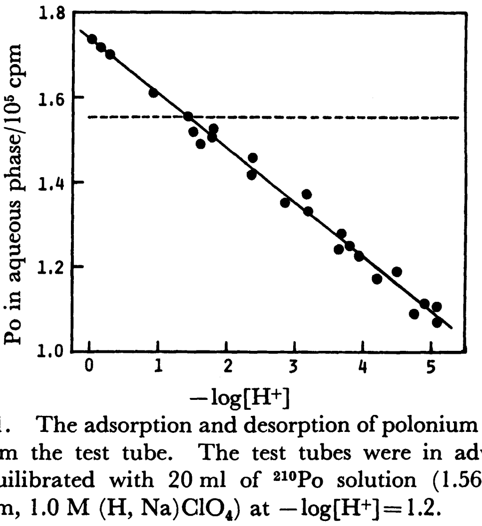

Fig. 1. The adsorption and desorption of polonium onto/from the test tube. The test tubes were in advance equilibrated with 20 ml of ^{210}Po solution (1.56×10^5 cpm, 1.0 M (H, Na)ClO$_4$) at $-\log[\mathrm{H}^+]=1.2$.

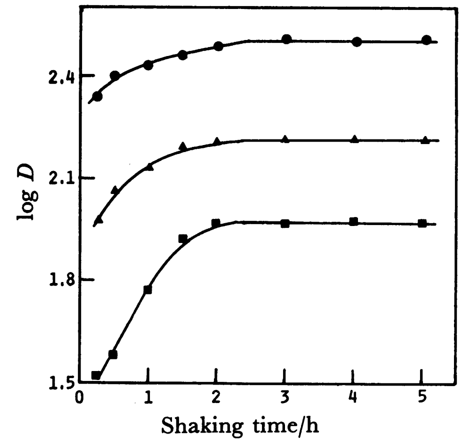

Fig. 2. The effect of shaking time on the cation-exchange equilibrium. ●; 1.0 M $HClO_4$ solution, ▲; 1.0 M (H, Na)ClO_4 solution ($-\log[H^+]=1.95$), ■; 1.0 M (H, Na)ClO_4 solution ($-\log[H^+]=3.95$).

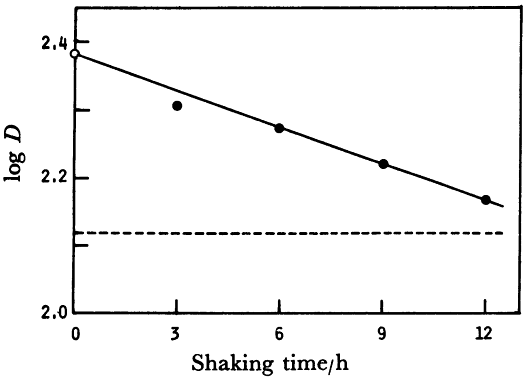

Fig. 3. The time-dependence of desorption from the resin (Bio-Rad AG 50W-X8, 100—200 mesh).
After the partion system (20 ml of ^{210}Po solution of 1.0 M (H, Na)ClO_4 at $-\log[H^+]=3.54$, 0.3 g resin) attained equilibrium, the time-dependence of desorption was measured in the solution whose quarter volume was replaced by the fresh solution free from polonium. (The broken line indicates the D in the equilibrium state.)

cpm), with pH values varying from 0 to 5, had been shaken for 3 h, the activity of the aqueous phase was measured. The results are shown in Fig. 1. Those results indicate that polonium is leached from the glass wall in a higher acidity than $-\log[H^+]=1.2$ and, moreover, adsorbed onto it in a lower acidity. Therefore, the reproducible results of D should be obtained in the cation-exchange study of polonium only when the distribution equilibrium is set up among the resin phase, the glass wall of the test tube, and the aqueous phase in a definite hydrogen-ion concentration.

Time Required for Partition Equilibrium. As is shown in Fig. 2, the sorption of polonium onto Bio-Rad AG 50W-X8 (0.3 g) reaches equilibrium within 3 h in 1.0 M (H,Na)ClO_4 solutions at $-\log[H^+]=0$, 1.95, and 3.95 respectively. Accordingly, the partition system was shaken for more than 3 h in all the experiments in order to attain equilibrium.

Time Dependence of Desorption from the Resin. After the partition system (20 ml of ^{210}Po solution and 0.3 g resin) had attained equilibrium at $-\log[H^+]=3.54$, the time dependence of the desorption was measured in a solution whose quater volume had been replaced by a newly prepared solution containing no polonium. From the results shown in Fig. 3, we can see that the distribution ratio decreases slowly toward equilibrium again in 1.0 M (H,Na)ClO_4 at $-\log[H^+]=3.54$ and that the rate of desorption of polonium from the resin is smaller than that of sorption onto the resin. At any rate, it seems that the sorption reaction of polonium with the resin proceeds reversibly.

Dependence of Selectivity Coefficients of Polonium Species on the Hydrogen-ion Concentration. We have previously reported that polonium was present in the chemical forms of $Po(OH)_3^+$ and $Po(OH)_4$ in a 1.0 M (H,Na)-ClO_4 solution in region of $0\leq-\log[H^+]\leq 6$.[10] In general, as the ionic strength in the resin phase is higher than in a solution equilibrated with it, the less hydrolyzed species, such as $Po(OH)_2^{2+}$, should be present in the resin, when the hydrolysis reaction on polonium is suppressed. Therefore, the distribution ratio, D, is expressed as follows:

$$D=\frac{([Po^{4+}]_R+[Po(OH)^{3+}]_R+[Po(OH)_2{}^{2+}]_R+[Po(OH)_3{}^+]_R+[Po(OH)_4]_R)}{([Po(OH)_3{}^+]+[Po(OH)_4])} \tag{1}$$

$$=K_{H^+}^{Po(OH)_3{}^+}\times\frac{[H^+]_R}{[H^+]}\times\frac{(\bar{K}_{-3}[OH^-]_R{}^{-3}+\bar{K}_{-2}[OH^-]_R{}^{-2}+\bar{K}_{-1}[OH^-]_R{}^{-1}+1+\bar{K}_1[OH^-]_R)}{(1+K_1[OH^-])}, \tag{2}$$

where $K_{H^+}^{Po(OH)_3{}^+}$ (selectivity coefficient) $=\frac{[Po(OH)_3{}^+]_R[H^+]}{[Po(OH)_3{}^+][H^+]_R}$ for the reaction, $Po(OH)_3{}^++\overline{H^+}=\overline{Po(OH)_3{}^+}+H^+$, $K_n=[Po(OH)_{3+n}{}^{1-n}]/\{[Po(OH)_3{}^+][OH^-]^n\}$ for the reaction, $Po(OH)_3{}^++nOH^-=Po(OH)_{3+n}{}^{1-n}$, and $\overline{K_n}=[Po(OH)_{3+n}{}^{1-n}]_R/\{[Po(OH)_3{}^+]_R[OH^-]_R{}^n\}$ for the reaction, $\overline{Po(OH)_3{}^+}+n\overline{OH^-}=\overline{Po(OH)_{3+n}{}^{1-n}}$, where $\overline{\text{species}}$ and $[\text{species}]_R$ refer to the species in the resin phase and its concentration respectively. It is difficult to determine the selectivity coefficients between hydrogen ions in macro amounts and a definite polonium species in trace amounts. The constancy of its selectivity coefficients was, therefore, examined by replacing that of the selectivity coefficients between Na^+ and H^+, both present in macro amounts in solution. The selectivity coefficient ($K_{Na^+}^{H^+}$) was evaluated from the exchange capacity of the resin (2.581 mequiv./g) and the hydrogen-ion concentration of solutions before/after the ion-exchange reaction. The hydrogen-ion concentration was determined by titration with a standard solution (0.1 M NaOH) for $-\log[H^+]<1.1$ and by measuring with a pH meter for $-\log[H^+]>1.1$. The results are shown in Fig. 4. Taking into account the activity coefficient for the hydrogen-ion concentration in case of the titration,[20] it seems that $K_{Na^+}^{H^+}$ is constant in the region of $0.3<-\log[H^+]<3$.

Dependence of the Distribution Ratio on the Hydrogen-ion Concentration. The distribution ratio of polonium is plotted in Fig. 5 as a function of the hydrogen-ion concentration in a 1.0 M (H,Na)ClO_4 solution. As is shown in the figure, the $\partial\log D/\partial(-\log[H^+])$ slope is negative for $0<-\log[H^+]<3$, naught for $3<-\log[H^+]<4$, and positive for $4<-\log[H^+]<5$. As the condition

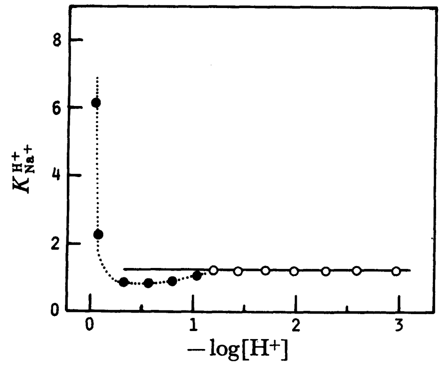

Fig. 4. The dependence of the selectivity coefficient ($K_{Na^+}^{H^+}$) on the hydrogen-ion concentration in 1.0 M (H, Na)ClO_4 solution. The hydrogen-ion concentration was determined by the titration method (●) or with a pH meter (○).

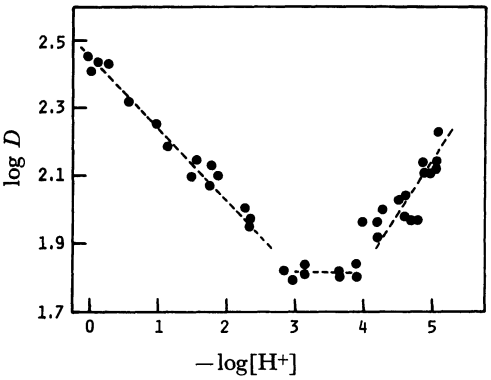

Fig. 5. The dependence of the distribution ratio of polonium on the hydrogen-ion concentration in 1.0 M (H, Na)ClO_4 solution after shaking for 4 h.

of resin in the partition system of cation exchange is changed by varying the hydrogen-ion concentration of the aqueous phase, the variation in $\log D$ does not always indicate a change in the chemical species. However, if the selectivity coefficient between polonium species and H^+ is invariant, it can be assumed that the variation in D indicates the change in the chemical species of polonium. The increase in D for $4<-\log[H^+]$ implies the variation in the selectivity coefficient and/or the increase in the cationic polonium species. From the results of the paper chromatography on polonium in nitrate solutions stored for a month or more,[14] it has been indicated that hydrolyzed polynuclear cationic species of polonium might exist for $-\log[H^+]=4.7$—6.6. Consequently, the formation of cationic polymers of polonium after shaking for 4 h can be assumed in the region of $4<-\log[H^+]<5$. On the other hand, the decrease in D for $0.3<-\log[H^+]<3$ indicates a decrease in the cationic polonium species, by analogy with the results of solvent extraction and paper chromatography.[10,14]

The Mean Charge of Polonium Species in 1.0 M (H,Na)-ClO_4 Solutions at $-\log[H^+]=1.0$. As the constancy of $K_{H^+}^{Po(OH)_3^+}$ in the region of $0.3<-\log[H^+]<3$ has been assumed from $K_{Na^+}^{H^+}$ as is shown in Fig. 4, the distribution ratio, D, was determined under the condition of a constant hydrogen-ion concentration in the resin phase. If the hydrogen-ion concentration in the resin phase is constant, D in Eq. 2 may be simplified as follows:

$$D = \text{constant} \times ([H^+]+K_1Q_W)^{-1}, \tag{3}$$

where $Q_W=[H^+][OH^-]$.

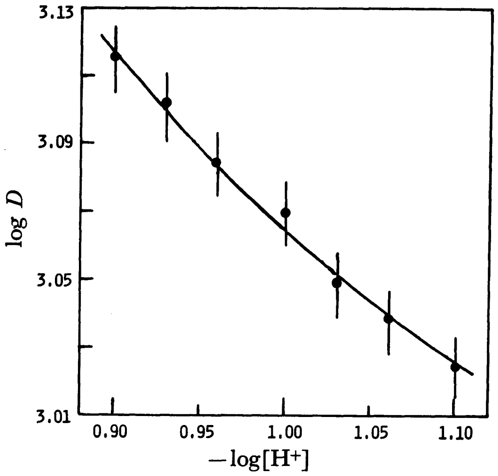

Fig. 6. The dependence of the distribution ratio of polonium on the hydrogen-ion concentration measured at a constant resin acidity.

TABLE 1. COMPOSITIONS OF THF EQUILIBRATING SOLUTION IN 100 ml

$-\log[H^+]$ of aqueous phase	1.00 M $HClO_4$ (ml)	1.00 M $NaClO_4$* or 1.80 M $NaClO_4$** (ml)	H_2O (ml)	$[ClO_4^-]$ of aqueous phase/M
0.90	12.59	66.81*	20.60	0.794
0.93	11.75	73.35*	14.90	0.851
0.96	10.96	80.23*	8.81	0.912
1.00	10.00	90.00*	—	1.000
1.03	9.33	54.36**	36.31	1.072
1.06	8.71	58.94**	32.35	1.148
1.10	7.94	65.53**	26.53	1.259

To determine the charge of the polonium species from the distribution ratio at $-\log[H^+]=1.0$ under the condition of a definite ionic strength in (H,Na)ClO_4 solutions, D was, in practice, determined by using the equilibrating solutions shown in Table 1.[21] In Fig. 6, we plot $\log D$ as a function of $-\log[H^+]$ in solution. The slope of a tangent line as the mean charge of polonium, that is, the value of -4 plus n_{OH} (number of OH^- ligands combining to a polonium atom), was obtained as -0.45 ± 0.08 at $-\log[H^+]=1.0$. The value of n_{OH} was calculated to be 3.55, slightly larger than 3.43, the value obtained by solvent-extraction study at $-\log[H^+]=1.0$.[10] It is assumed that the true tangential slope at $-\log[H^+]=1.0$ in the cation-exchange method should be larger than the value obtained, for the ionic strength in a higher acidity should be slightly lower than that at $-\log[H^+]=1.0$ (to promote the hydrolysis) and higher in a lower acidity (to depress it). The value of n_{OH}, judging from these facts, may be close to 3.43, result from solvent extraction;[10] hence, the mean chemical form can be estimated to be $Po(OH)_{3.43}{}^{0.57+}$.

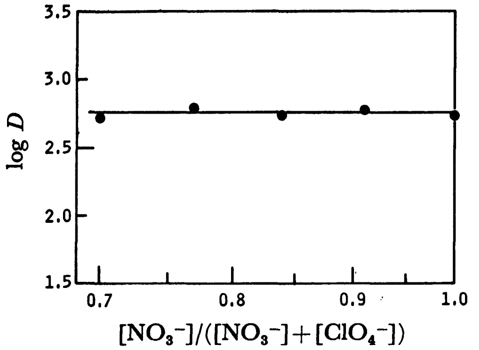

Fig. 7. The effect of the nitrate ion on the distribution ratio of polonium in the cation exchange. The $-\log[H^+]$ of the aqueous phase was kept constant to 1.0.

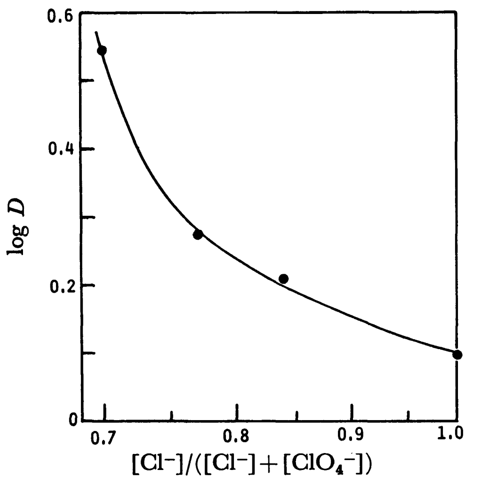

Fig. 8. The effect of the chloride ion on the distribution ratio of polonium in the cation exchange. The $-\log[H^+]$ of the aqueous phase was kept constant to 1.0.

The Mean Charge of Polonium Species in 1.0 M (H,Na)-NO_3 Solutions at $-\log[H^+]=1.0$. In general, the slope of $\log D$ *vs.* $\log\{[NO_3^-]/([NO_3^-]+[ClO_4^-])\}$ in 1.0 M (H,Na)(NO_3,ClO_4) solutions at $-\log[H^+]=1.0$ indicates the difference in the mean charge of the polonium species between 1.0 M (H,Na)NO_3 and 1.0 M (H,Na)ClO_4 solutions at $-\log[H^+]=1.0$. We have determined the slope by varying the mole fractions of the NO_3^- ion, as is shown in Fig. 7. As the slope indicates nearly 0, the mean charge of polonium species in 1.0 M (H,Na)NO_3 at $-\log[H^+]=1.0$ is almost identical with that in 1.0 M (H,Na)ClO_4 at $-\log[H^+]=1.0$. Because it is improbable that the polonium species is polymerized in the shaking period, only the coordination of nitrate ions to polonium should be taken into account. The mean number of NO_3^- combining to a polonium atom being 0.60 at $-\log[H^+]=1.0$,[10,11] the mean chemical form may be $Po(OH)_{2.83}(NO_3)_{0.60}{}^{0.57+}$ in 1.0 M (H,Na)NO_3 solutions. A similar experiment was carried out with 1.0 M (H,Na)(Cl,ClO_4) solutions at $-\log[H^+]=1.0$. The results are shown in Fig. 8. The distribution ratio of polonium rapidly decreases with an increase in the mole fraction of Cl^- ions, reaching a small value in a 1.0 M (H,Na)Cl solution at $-\log[H^+]=1.0$. This result indicates the formation of negatively charged species and is consistent with the results of solvent extraction.[12] The mean charge of the polonium species in 1.0 M (H,Na)Cl solutions must be further determined by using an anion-exchange method.

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