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ION EXCHANGE EXPERIMENTS WITH POLONIUM

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ION EXCHANGE EXPERIMENTS WITH POLONIUM

Edward R. Tompkins

May 11, 1951

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ION EXCHANGE EXPERIMENTS WITH POLONIUM*

Edward R. Tompkins
Radiation Laboratory

May 11, 1951

ABSTRACT

The state of polonium in aqueous solutions was investigated by means of ion exchange equilibrium studies. The distribution of the polonium between the solid and liquid phases was determined for solutions of various compositions using both a cation and an anion exchanger. These studies show that in the absence of a complexing agent polonium is hydrolyzed to such a degree that it forms monovalent cations and anions whose charge was not investigated in this study. On the basis of these results and previous work it appears that these ions may be $PoO(OH)^+$ and PoO_3^{-2}. The addition of a complexing anion such as chloride decreases both the cationic and anionic form of polonium up to a chloride concentration of about 0.01 M. At higher chloride concentrations the cation concentration continues to decrease while the percentage of polonium in the anionic state increases. In the absence of a complexing anion, no effect of hydrogen ion on the state of hydrolysis of the polonium could be noted. In the presence of chloride the hydrogen ion concentration is very important in determining the fractions of polonium in the cationic, neutral and anionic states.

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ION EXCHANGE EXPERIMENTS WITH POLONIUM

Edward R. Tompkins
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May 11, 1951

Electrodeposition studies have shown that polonium can exist in aqueous solutions either as a cation or an anion, the relative amount in each state varying with conditions. Also, it is probable that it is present as neutral particles, particularly in the presence of complexing agents, since it can be extracted into non-polar liquids. This series of ion exchange equilibrium experiments was performed to study these states of polonium in aqueous solutions.

Because of the tendency of polonium to form co-ordination bonds, it does not exist in aqueous solutions as simple polonium ions. It forms complexes with anions such as nitrate, chloride, sulfate, etc. and in their absence or in dilute solutions, is hydrolyzed. Depending upon the degree of hydrolysis, one may postulate for Po(IV) such particles as: $Po(OH)^{+3}$, $Po(OH)_2^{+2}$, PoO^{+2}, $PoO(OH)^+$, $Po(OH)_3^+$, $PoO(OH)_2$, PoO_2, $PoO_2(OH)^-$, PoO_3^{-2}, etc. and for Po(II), $Po(OH)^+$, $Po(OH)_2$, PoO, $PoO(OH)^-$, PoO_2^{-2}, etc. By determining the equilibrium distribution of polonium between a cation exchanger and perchlorate solutions of various concentrations, it should be possible to obtain some information about the cations. A similar study employing an anion exchanger should give information about polonium in the anionic state. If the hydrogen ion concentration is varied, information concerning the hydrolysis may be obtained.

Technically, there are certain inherent difficulties in performing experiments of this kind. Because of the large tendency of the polonium to exchange from perchlorate solutions, a large percentage of it may collect on the walls of the vessels, even in the absence of any exchanger. Special polystyrene vials with polyethylene caps were obtained for these experiments but the exchange with them was still large and variable. Presumably, this was due to a mold release compound used in their manufacture. By washing them with alcohol or hexane, their exchange capacity could be reduced to a small and relatively constant value.

In the cation exchange experiments with hydrogen form Dowex-50, the equilibrium favored the exchanger to such an extent that a very small quantity of resin had to be used if the polonium was to be distributed evenly between the two phases. The quantity of resin needed decreases as the concentration of the competing ion is reduced. Exchange resins are not very homogeneous and so it is necessary to use enough particles to get a representative sampling. Therefore, the study could not be extended to low perchlorate concentrations. Ammonium perchlorate, the most soluble salt of perchloric acid, can have a maximum concentration of about 1.7 M at room temperature. This is about the minimum concentration which can be studied accurately, using a cation exchanger.

In view of the above considerations, most of the cation exchange experiments were carried out in 2 to 8 M perchloric acid. An aliquot of the equilibrium solution was evaporated in a platinum dish and counted, the amount of polonium on the resin being calculated by subtracting the amount in solution from the quantity added in setting up the experiment. Because of the uncertainty regarding the activity coefficients of ions in the resin phase, concentrations rather than activities were used in calculating the values of the exchange constant for the reaction:

$$PoO_x(OH)_y^{+n} + nHR \rightleftharpoons PoO_x(OH)_yR_n + nH^+$$

where $PoO_x(OH)_y^{+n}$ is the predominant polonium cation and HR is the hydrogen form of the resin. An approximate value for the exchange constant may be calculated by assuming that the activities of the components of the binary solid solution are equal to their mole fractions. In cases where one component is present in trace concentrations:

$$K \cong \frac{PoO_x(OH)_yR_n}{(HR)^n} \cdot \frac{(H^+)^n}{\left(PoO_x(OH)_y^{+n}\right)} \text{ or } \frac{C_R}{C_S} \cdot \frac{(H^+)^n}{(HR)^n}$$

in which C_R and C_S are the counts per minute of polonium in the resin and solution phases, respectively.

By independently varying the quantity of resin employed and the hydrogen ion concentration of the solution, an approximate value for n may be obtained. In Table 1 are given the results of varying (A) the quantity of resin, and (B) the concentration of perchloric acid and the quantity of resin. The relative constancy of K_d in the first case and K in the second indicate that n is one. Thus, it appears that polonium exists as monovalent cations in 4 to 8 M perchloric acid solutions.

Electrodeposition experiments indicate that polonium is reduced by hydrogen peroxide to the lower valence state. The results shown in Table 1B indicate that the exchange constant for the reduced state is about one-third of that for the oxidized state. However, in both cases the cations appear to be monovalent.

Several series of experiments were performed using anion exchange resins and perchloric acid to determine the effect of the acid concentration on the distribution. In all cases the results were erratic but the distribution coefficient was only about 0.01 of that observed with the cation exchanger, indicating that polonium is largely cationic in perchloric

Table 1

A. Effect of the Quantity of Exchanger on K_d in 3.7 M $HClO_4$ (3 ml)

Dowex-50 Resin (mg)	Counts per Minute		K_d*
	Solution	Resin	
2.7	7380	6960	1.05×10^3
4.4	4920	9420	1.31×10^3
6.2	4140	10200	1.19×10^3
8.4	2970	11370	1.37×10^3
9.9	2160	12180	1.71×10^3

B. Effect of the Concentration of $HClO_4$ and of the Presence of H_2O_2 on the Exchange Constant

Dowex-50 Resin (mg)**	$HClO_4$ (3 ml)	Counts per Minute		K***
		Solution	Resin	
4.4	4 M	3800	3120	1.9×10^5
5.0	5 M	2510	3960	4.0×10^5
6.1	6 M	3630	3320	2.3×10^5
6.6	7 M	2780	3720	3.6×10^5
8.6	8 M	1990	2560	3.0×10^5
5.0	4 M + 0.1 M H_2O_2	5990	2680	0.9×10^5
5.6	5 M + 0.1 M H_2O_2	4980	2190	1.0×10^5
5.6	6 M + 0.1 M H_2O_2	5220	1740	0.9×10^5
7.5	7 M + 0.1 M H_2O_2	4250	3100	1.7×10^5
9.9	8 M + 0.1 M H_2O_2	2060	5930	0.6×10^5
5.5	5 M + 0.05 M H_2O_2	3970	2390	1.4×10^5
5.5	5 M + 0.2 M H_2O_2	6090	2420	0.9×10^5

*$K_d = (C_R/C_S)$ (ml solution/g resin).

**Equivalent weight of Dowex-50, H-form, air dried is 254 g.

***Calculated for first power dependence of (H^+) concentration.

acid solutions. When hydrogen peroxide is added, less than 1% of the polonium is found in the resin phase when 50 mg of Dowex-2 is equilibrated with 2 ml of 4 M perchloric acid containing the polonium. These results are consistent qualitatively with electrodeposition studies which show that about 10% of the polonium is deposited on the anode and about 90% on the cathode from perchloric acid solution while over 99% is deposited cathodically when hydrogen peroxide is added.

CHLORIDE COMPLEXES OF POLONIUM

The effect of the chloride concentration on the distribution of polonium between the resin and solution phases was studied with both a cation and an anion exchanger. A preliminary experiment in which the quantity of resin was varied showed that this did not affect the values of K_d as may be seen in Table 2.

Table 2

The Effect of Varying the Quantity of Exchanger on the K_d of Polonium in 6 M Perchloric Acid in the Presence of Chloride

Dowex-50 Resin (mg)	HCl Conc. (M)	K_d
100	0.01	26.9
200	0.01	26.8
300	0.01	25.2
400	0.01	24.2
500	0.01	27.8
300	0.03	4.7
400	0.03	4.3
500	0.03	4.5
600	0.03	4.0
700	0.03	4.4

In one series, 4 M perchloric acid was used as the bulk electrolyte, the chloride concentration being varied from 10^{-4} to 0.1 M. The results of these studies are plotted in Fig. 1. It will be noted that the polonium is largely cationic in perchloric acid. As the concentration of hydrochloric acid is increased, the percentage in the cationic form decreases more and more rapidly. Up to a concentration of about 0.01 M chloride, there is little change in the percentage of the anionic form although there is an indication that it also decreases slightly in this region. This indicates that a neutrally charged complex is most stable under these conditions, being formed from both the cationic and anionic polonium. As the chloride concentration is increased further, the distribution coefficient of polonium on anion exchange resin increases. In the chloride concentration range of about 0.008 to 0.1 M, this increase seems to have a first power dependence on the chloride concentration. At higher chloride concentrations the slope appears to increase, as may be seen from the data in Table 3. The results of the two series of experiments shown in Fig. 1 and Table 3, respectively, cannot be compared directly. In the first series a constant concentration of perchloric acid was used and the concentration of hydrochloric acid was low enough until both the ionic strength and hydrogen ion concentration were nearly constant. Therefore, the change in K_d in this series is due largely to the change in chloride concentration. In the second series, the ionic strength and hydrogen ion concentration were kept constant at 1 M acid by varying the ratio of perchloric to hydrochloric acid in the solution. Subsequent measurement of the exchange constant for the reaction:

$$RClO_4 + Cl^- \rightleftharpoons RCl + ClO_4^-$$

gave a value of about 0.02 for:

$$\frac{RCl}{RClO_4} \cdot \frac{(ClO_4^-)}{(Cl^-)} \cdot$$

If the values of K_d are corrected on the basis of the perchlorate concentration in the various vials, assuming a first power dependence upon the perchloric acid concentration, the dependence of K_d upon chloride concentration in the range of 0.03 to 0.7 M is about $(HCl)^{1.7}$ as against $(HCl)^{1.8}$ for the uncorrected curve. Correction on the basis of a second power dependence of the perchloric acid concentration gives a curve whose minimum slope is greater than one. Thus it appears that chloride ion is forming both monovalent and divalent anions with the polonium in this range of hydrochloric acid concentration.

THE EFFECT OF HYDROGEN ION CONCENTRATION ON K_d IN THE PRESENCE OF CHLORIDE

A series of experiments were performed to determine the effect of varying the perchloric acid concentration at constant chloride concentration on the distribution coefficient of polonium for both a cation and an anion exchanger. On the basis of previous experiments a chloride concentration of 0.01 M was chosen and the perchloric acid concentration was varied from 1.0 to 8.0 M. The results of these experiments are shown in Fig. 2. It will be noted that the cations in solution appear to decrease rapidly as the acid concentration is increased. At perchloric acid concentrations above 3 M there appears to be a fourth power dependence on the hydrogen ion concentration. A minimum in the anion exchange curve occurs in the range of 2 to 4 M perchloric acid. At higher concentrations of perchloric acid the curve rises sharply with a slope of approximately 5.

Table 3

The Effect of Chloride Concentration on the K_d's of RaD, E and F

A. When the Following Solutions are Equilibrated with Dowex-2 Anion Exchanger

Concentration		K_d			Separation Factors	
HCl	$HClO_4$	RaD (Pb)	RaE (Bi)	RaF (Po)	K_dRaE/K_dRaD	K_dRaF/K_dRaE
0.00	1.00	0.2	4.1	8.6	20.5	2.1
0.01	0.99	0.5	10.7	2.9	19.8	2.7
0.03	0.97	0.3	1.8	5.8	7.2	3.2
0.1	0.9	0.6	3.3	57	5.5	17.3
0.3	0.7	0.8	11.1	360	13.2	32.4
1.0	0.0	2.1	1,080	8,500	507	7.9
B. When the following solutions are equilibrated with Dowex-50 Cation Exchanger						
0.00	1.00	740	3,860	3,200	5.2	0.8
0.01	0.99	650	1,700	1,500	2.6	0.9
0.03	0.97	580	510	214	0.9	0.4
0.1	0.9	380	36	10	0.1	0.3
0.3	0.7	134	3	--	0.02	--
1.0	0.0	17	1	7.5	0.07	6.3

One is not justified in drawing any definite conclusions from this series of experiments without considering the effect of the perchloric acid concentration on the activities of the other ions. However, as in Fig. 1, these curves do indicate that a neutrally charged complex is forming in the lower acid concentration range. Above a perchloric acid concentration of 4 <u>M</u>, the rate of decrease of cations appears to remain constant but the anion concentration seems to be increasing rapidly.

These data indicate that up to about 4 M perchloric acid a neutral complex is being formed but that above this concentration the amount of anion increases rapidly with perchloric acid concentration.

DISCUSSION

On the basis of these experiments it is evident that both Po(IV) and Po(II) are highly hydrolyzed in aqueous solutions. They both form monovalent cations in perchloric acid solutions but only the higher valence state appears to form anions. As the chloride concentration is increased in the presence of 4 M perchloric acid, the oxide and hydroxide groups seem to be replaced by the chloride to form at first another cation then a neutrally charged particle and finally one or more anions. Although the degree of hydrolysis does not seem to change with perchloric acid concentration in the absence of a complexing agent, the change is very rapid in 0.01 M hydrochloric acid. The oxygen and hydroxide groups seem to be successively replaced by chloride to form first a neutrally charged particle and finally, in higher perchloric acid concentrations, anions. The following reactions have been postulated to explain these observations:

$$\mathrm{Po(IV)} + 2\,\mathrm{H_2O} \rightleftharpoons \mathrm{PoO(OH)^+} + 3\mathrm{H^+}$$

$$\mathrm{Po(IV)} + 3\,\mathrm{H_2O} \rightleftharpoons \mathrm{PoO_3^{-2}} + 6\mathrm{H^+}$$

$$\mathrm{Po(II)} + \mathrm{H_2O} \rightleftharpoons \mathrm{Po(OH)^+} + \mathrm{H^+}$$

$$\mathrm{PoO(OH)^+} + \mathrm{Cl^-} \rightleftharpoons \mathrm{PoOCl^+}$$

$$\mathrm{PoOCl^+} + \mathrm{Cl^-} \rightleftharpoons \mathrm{PoOCl_2}$$

$$\mathrm{PoOCl_2} + \mathrm{Cl^-} \rightleftharpoons \mathrm{PoOCl_3^-}$$

$$PoOCl_3^{-} + Cl^{-} \rightleftharpoons PoOCl_4^{-2}$$

$$PoOCl_4^{-2} + 2Cl^{-} + 2H^{+} \rightleftharpoons PoCl_6^{-2} + H_2O$$

$$PoOCl_2 + Cl^{-} + H^{+} \rightleftharpoons Po(OH)Cl_3$$

$$Po(OH)Cl_3 + Cl^{-} + H^{+} \rightleftharpoons PoCl_4 + H_2O$$

$$PoCl_4 + Cl^{-} \rightleftharpoons PoCl_5^{-}$$

$$PoCl_5 + Cl^{-} \rightleftharpoons PoCl_6^{-2}$$

$$PoO_3^{-2} + 2Cl^{-} + 4H^{+} \rightleftharpoons PoOCl_2 + 2H_2O$$

The fraction of the total polonium that is present in any one of these forms will depend upon the conditions. In exchange equilibrium experiments one can determine only the effect of changing conditions on the quantity of polonium adsorbed on either the cation or anion exchanger. If the log-log plot of K_d vs. concentration were a straight line over the entire concentration range studied for both exchangers, it would be possible to calculate the concentrations of cations, anions and neutral particles, respectively, at any concentration of competing ions. When the relationships are more complicated it is possible to draw qualitative conclusions only. Therefore, while the results of this study leave much to be desired in interpreting the chemistry of polonium, it is possible to derive a limited amount of interesting results. Continuation of the study using nitric or acetic acid so that hydrogen peroxide could be employed in connection with a complex forming anion should yield additional data regarding the two valence states of polonium. Further studies with anion exchange resin in the alkaline range in the presence of oxidizing and reducing agents should lead to further conclusions in regard to the anions of polonium.

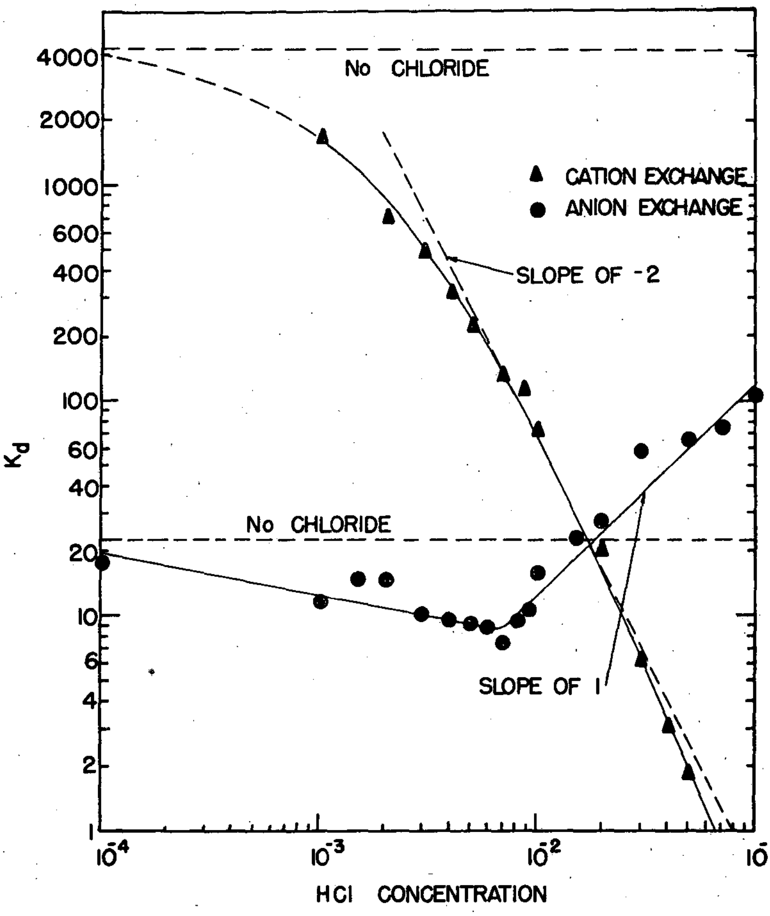

FIG. 1 - THE EFFECT OF THE CHLORIDE CONCENTRATION ON THE K_d OF POLONIUM IN 4 MOLAR PERCHLORIC ACID

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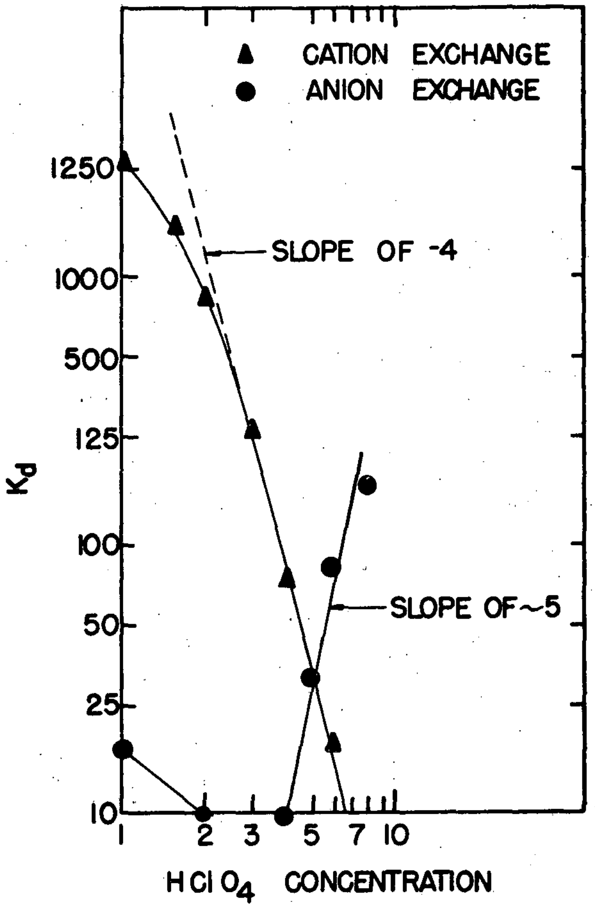

FIG. 2 - THE EFFECT OF PERCHLORIC ACID CONCENTRATION ON THE K_d OF POLONIUM IN 0.01 MOLAR HYDROCHLORIC ACID

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