Atomic Energy of Canada Limited

THE ABSORPTION OF PLUTONIUM BY ANION RESINS

CEI-62 (Revised)

by

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SUMMARY

Equilibrium experiments have shown Pu^{+4} to be absorbed from nitric acid onto an anion resin as a complex anion $Pu(NO_3)_6^{-2}$. The amount of absorption is dependent on the plutonium and nitric acid concentrations in the equilibrium solution with a maximum at 7N to 8N HNO_3. A low cross-linked resin has a higher capacity and reaches equilibrium more rapidly than the normally supplied resin. Saturation capacity of one per cent cross-linked Nalcite SBR (Dowex 1), 50 - 100 mesh, is 385 mg Pu/gram dry resin.

INTRODUCTION

In a previous report (1) data were given for the concentration and purification of dilute nitric acid solutions of plutonium by cation exchange. Such solutions produced during the partitioning stage of a TBP extraction process would be expected to contain a relatively high concentration of Fe^{+2} when ferrous sulphamate is used to back-extract Pu^{+3} from the solvent phase. As Fe interferes with the absorption of Pu^{+3} by cation resins, the possibility of absorbing anionic nitrate complexes of Pu^{+4} by anion resins was explored. Studies of the migration of Pu^{+4} in the presence of various anions had shown that above 10N in nitric acid a negatively charged complex appeared (2) and spectrophotometric absorption work suggested that this was $Pu(NO_3)_6^{-2}$ (3). From these results it was expected that concentrations of nitric acid above 10N would be required to obtain appreciable absorption of plutonium, and there was some doubt therefore that an anion resin could be found that would be stable under these conditions. Dowex 1, however, showed only a darkening in colour when contacted with 10N nitric acid for several days and no impairment of its exchange capacity. The absorption of Pu^{+4} onto Dowex 1 was therefore investigated over a range of nitric acid concentrations.

The data obtained from equilibrium experiments are given in this revision of the original report of the work along with an attempt to interpret from them the equilibria existing between resin and nitrate complexes of Pu^{+4} in nitric acid solution.

EXPERIMENTAL RESULTS

Equilibrium experiments were carried out to get information on the uptake of plutonium by Dowex 1 for several nitric acid

concentrations. A weighed amount of resin of known moisture

content in the nitrate form was shaken for several days with a

known volume of a standard plutonium solution. The solutions

and resin were shaken in 50 ml stoppered Erlenmeyer flasks

sealed with paraffin wax which successfully withstood the

action of the concentrated nitric acid. The resulting

solutions were then analyzed. In this way the amount of

plutonium taken up by unit weight of dry resin in equilibrium

with a solution containing the final concentrations of

plutonium and nitric acid was found. The standard plutonium

solutions were made 0.05^M in sodium nitrite in order to ensure

that the plutonium was all in the Pu^{+4} state.

In preliminary experiments the regularly supplied resin

was used which is 20 - 50 mesh size and 8% cross-linked. These

experiments showed that the absorption is dependent on the

plutonium concentration for a given nitric acid concentration

up to a limit which is defined by the capacity of the resin

for the absorbed anion. This saturation capacity is 90 mg

Pu per g of dry resin. It was found during the course of

these experiments that the rate of exchange of the nitrato-

plutonium complex with the resin is very slow; even after

three weeks' shaking the resin was still taking up plutonium

from the solution. This is consistent with the general

observation that slow exchange rates occur when large cations

and anions are absorbed onto relatively high cross-linked resins.

To speed the exchange rate, 1% cross-linked, 50 - 100

mesh size resin was used for the experiments reported here.

Complete equilibrium was reached with only two days shaking and

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also the resin capacity was four times that of the 8% cross-linked resin.

The results are listed in Table I and the absorption versus Pu concentration at constant nitric acid concentration is plotted in Fig. 1. The curves for 7 and 8N and 5 and 9N are drawn coincident as the results for each pair of concentrations agreed within the experimental error.

TABLE I

Equilibrium Absorption of Plutonium from Nitric Acid Solution by Dowex 1 1% Cross-Linked and 50 - 100 Mesh Particle Size

HNO_3 conc'n Normal	Molal	α	γ_{HNO_3}	Final Pu conc'n mg./l	Pu absorbed mg. Pu/g dry resin
10N	(14.9m)	0.50	1.79	123	38.5
				127	51.5
				147	54.8
				178	71.7
				190	76.3
				196	92.0
				313	212.
9N	(12.7m)	0.56	1.68	69.9	56.9
				73.0	68.8
				99.3	91.0
				105	91.6
				118	158
				126	133
				139	176
				157	243
				603	385
				632	376
8N	(10.8m)	0.63	1.55	35.4	53.6
				41.7	81.9
				44.4	84.4
				52.4	92.6
				58.5	141
				65.6	183
				128	327
				149	334
				175	345
				184	351
				262	349
				486	373
				538	382
7N	(9.0m)	0.68	1.41	36.5	52.3
				42.6	78.8
				50.4	124
				106	281

| HNO$_3$ conc'n Normal	Molal	α	γHNO$_3$	Final Pu conc'n mg/l	Pu absorbed mg Pu/g dry resin
7N	(9.0m)	0.68	1.41	116	306
				186	364
				286	342
				506	385
				624	410
5N	(5.9m)	0.81	1.15	75.6	55.8
				87.1	87.9
				95.7	115
				106	159
				214	296
				259	306
				273	318
3N	(3.3m)	0.90	0.91	226	58.3
				254	64.9
				295	85.4
				314	98.4

DISCUSSION

General:

Inspection of the results shows two characteristics of the system which may help in interpreting the equilibria existing between resin and solution. First, for a given low concentration of Pu, the uptake by the resin increases with increasing HNO$_3$ concentration to a maximum at 7 to 8N and then falls off. Secondly, the maximum uptake of Pu is 385 mg/gm dry resin.

If the exchanged anion is Pu(NO$_3$)$_6^{-2}$, this maximum uptake corresponds to 3.2 equivalents per kg of dry resin. As this is the expected exchange capacity of the resin, a reasonable assumption is that this anionic complex is the sole exchanged Pu species.

It has been found that at high electrolyte concentrations considerable quantities of electrolyte diffuse into the resin (4); the amounts vary markedly depending on the specific electrolyte, degree of cross-linking of the resin and composition of the resin

salt. At the high concentrations of HNO_3 used in the present
work the exchange equilibrium may be represented by

$$Aqueous \rightleftharpoons \left[H^+, \quad Pu(NO_3)_6^{-2}, \quad NO_3^-, \quad H_2O \right] \rightleftharpoons Resin$$
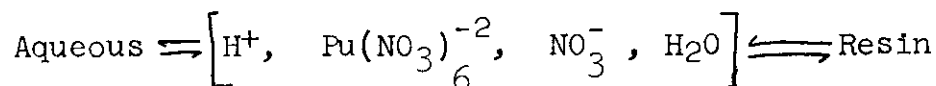
where the species inside the brackets can transfer between
resin and aqueous phases. Also present in the solution will
be all the possible nitrate complexes of Pu^{+4} that may exist via
the following equilibria,

$$Pu(NO_3)_n^{4-n} + (6-n) NO_3^- \rightleftharpoons Pu(NO_3)_6^{-2} \qquad (1)$$
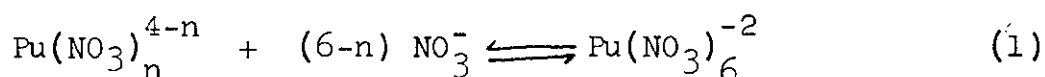
The presence of $Pu(NO_3)_4$, i.e. $n = 4$, has been established by
TBP extraction studies from nitric acid in the concentration
range 0.15 to 13.5 M (5).

Donnan Equilibrium:

The representation of ion exchange equilibrium as a Donnan
membrane equilibrium involving osmotic pressure was first given
by Gregor (6) and elaborated by Glueckauf (7). This approach has
achieved considerable success in correlating ion exchange behaviour
and resin properties such as selectivity with cross-linking (8).
The resin phase is considered as a concentrated solution of a strong
electrolyte where the exchangeable ions plus diffusible ions are
in solution in the imbibed water. The organic matrix expands with
the imbibition of water but the amount of expansion is limited by
the resin cross-linking. Thus the resin in tension produces a
pressure on the internal solution which increases its Gibbs free
energy. This pressure obviously decreases with decreasing cross-
linking and in the limit is zero for a solution of a polyelectrolyte.

The Donnan equation (9) for the equilibrium involved can
be written

$$\log\left[\frac{m_{6r}\, m^2_{NO_3}}{m^2_{NO_3 r}\, m_6}\right] = \log\frac{\gamma^4_{HNO_3 r}}{\gamma^3_{H_2 6_r}} - \log\frac{\gamma^4_{HNO_3}}{\gamma^3_{H_2 6}} + \frac{P\left(2\bar{V}_{NO_3} - \bar{V}_6\right)}{2.303\ RT} \qquad (2)$$

where subscripts denote the species involved. The subscript r denotes the resin phase, 6 the anion $Pu(NO_3)^{-2}_6$ and $H_2 6$ the stoichiometric acid. Concentrations are expressed in terms of moles per kg of water (molality), and as the Gregor-Glueckauf treatment is thermodynamically rigorous, the activity coefficients in the resin phase are the usual type incurred in aqueous solutions of strong electrolytes, i.e. mean molal stoichiometric. P is the internal pressure and V the partial molar volume of the particular 'resin salt' in nitric acid.

In tnis work, the concentrations in the resin phase have been determined in units of moles per kg dry resin. Equation (2) however requires moles per kg water imbibed. A variable S, kg water per kg dry resin, is therefore necessary. Similarly, F, the fraction of Pu in solution as $Pu(NO_3)^{-2}_6$ and $\emptyset_r$, the ratio of nitrate ion diffused in the resin to exchanged nitrate are quantities required to fit the data to equation (2). Nitrate ion molality in the solution can be obtained using published data (10) for the degree of ionization, α, of nitric acid. Values of γ_{HNO_3} are also available in the literature (11). Substituting in equation (2)

$$\log\left[\frac{m_{6r}(\alpha m\gamma^2)^2_{HNO_3}}{m_{Pu}\, m^2_{NO_3 r}}\right] = \log\frac{F\,(1+\emptyset_r)^2}{S} + \log\frac{\gamma^4_{HNO_3 r}}{\gamma^3_{H_2 6_r}} + \log\gamma^3_{H_2 6}$$

$$+ \frac{P\left(2\,\bar{V}_{NO_3} - \bar{V}_6\right)}{2.303\ RT} \qquad (3)$$

where $m_{NO_3 r}$ is now the difference between the exchange capacity and the Pu loading in equivalents per kg dry resin.

All the measured quantities have been included in the bracketed term which is the familiar 'selectivity coefficient' K. Strictly, the activity coefficient of nitric acid should remain with the other unknowns on the r.h.s. because it is the value obtaining in the mixed electrolyte solution. However, the Pu concentration in solution is so low $(0.4-4 \times 10^{-3}m)$ that it will have a negligible interaction with the nitric acid and the mean molal activity coefficient of pure nitric acid can be used.

In Figure 2 the values of the selectivity coefficient at each nitric acid concentration have been plotted against the equivalent fraction of $Pu(NO_3)_6^{-2}$ on the resin, X_{6r}. A significant difference from usual ion exchange behaviour is that K increases as the loading of the more strongly absorbed anion increases. Gregor et al. (12) suggest this property may be due to non-random absorption of anions on exchange sites. In this work however it may be due to changes in the non-thermodynamic quantities collected into the first term on the r.h.s. of equation (3), which were not measured.

If we consider how each quantity on the r.h.s. varies with loading at constant nitric acid concentration we find first that F and $\gamma_{H_2 6}$ will be constant. The P ΔV term will decrease due to the large size of $Pu(NO_3)_6^{-2}$: however the effect will be very small due to P being small because of the low cross-linking of the resin. The second term on the r.h.s. would also be expected to decrease with increasing X_{6r} in a similar fashion to the results of Boyd et al (8) for the exchange of Br^- for F^- on 0.5% cross-linked Dowex 2. These effects would decrease K as X_{6r} increased.

On the other hand, S, the specific water content of the resin, decreases as X_{6r} increases. Column studies have shown that the resin shrinks about 30% on going from the nitrate form to the $Pu(NO_3)_6^{-2}$ form. At the same time $\emptyset_r$, the ratio of diffusible NO_3^- to exchange NO_3^-, increases, becoming more pronounced as X_{6r} approaches unity. This is noticeable in the marked upswing of K for 8N nitric acid above $X_{6r} = 0.9$. It is important to remember however that the degree of ionization of HNO_3 in the resin phase is probably lower than normal due to the low dielectric constant of polystyrene, and diffusible NO_3^- in the resin may be quite low. The apparent reversal of normal behaviour can therefore be due to an increase in $\dfrac{(1 + \emptyset_r)^2}{S}$ with X_{6r} occasioned by the invasion of the resin by nitric acid at the high concentrations used and the low water imbibition by the resin Pu salt.

In Figure 3 values of K at a fixed Pu loading ($X_{6r} = 0.2$) have been plotted against molality of nitric acid to show the effect on K of changes in solution equilibria. There is in fact a very sharp increase in K up to a maximum at 10.8m (8N) followed by a relatively small decrease between this concentration and 14.9 m (10N), the highest studied. Column studies at zero loading (13) showed no change in resin volume over the range of nitric acid concentrations involved. Coupling this with the fact that the curves in Figure 2 have similar slopes it can be assumed that the PΔV term in equation (3) is constant at constant loading. $\emptyset_r$ will increase with increasing nitric acid concentration in the aqueous phase. (The data of Nelson and Kraus (17) for absorption of HCl by a low cross-linked anion exchanger show $\emptyset_r$ to increase from 1.30 at 4.44m HCl to 4.07

at 16.0m HCl.) At the same time S will decrease as acid replaces water (the value for the HCl data is 20%) and the term $\frac{(1 + \phi_r)^2}{S}$ will therefore increase with increasing nitric acid concentration but not to an extent that would explain the steep slope of Fig. 3.

The resin activity coefficient-ratio term might be expected to increase as the nitric acid concentration increased because the molality of both species will increase. Glueckauf suggested (7) that these activity coefficients should follow the Harned rule (14), i.e. at constant total molality, the log of the activity coefficient of one component is proportional to the molality of the second. Soldano and Chesnut (15) however found the proportionality coefficient to decrease with increasing molality of the resin salts. This effect modifies the increase in $\frac{\gamma^4_{NO_3r}}{\gamma^3_{H_26r}}$ with nitric acid concentration at constant m_{H_26r}. For the Br-F exchange Boyd et al found only 25% increase in $\frac{\gamma_{Fr}}{\gamma_{Br_r}}$ for a 50% decrease in specific water content of the resin at $X_{Br} = 0.5$. The expected increase in this term is obviously too small to account for the large increase in K seen in Fig. 3.

The remaining factors affecting the shape of the curve in Figure 3 are F and $\gamma^3_{H_26}$. As the Pu concentration in solution is very low, γ_{H_26} corresponds to that obtaining at zero concentration in pure nitric acid. Guggenheim's treatment as outlined by Stokes and Robinson (16, p. 436) should then apply to its variation with nitric acid concentration. The relation is

$$\ln \gamma_{AB} = - \frac{\alpha \sqrt{I}}{1 + \sqrt{I}} + (b_{AB} + b_{AC}) m$$

I is the ionic strength of the solution and the b's are specific interaction coefficients for the pairs of ions which have values of 0.1 to 0.004 for the alkali chlorides (16 p. 450). If the b values are similar for the HNO_3 - Pu^{+4} system, then γ_{H_26} should show only a small increase over the range of nitric acid concentrations studied. The major part of the large change in selectivity coefficient K with nitric acid concentration is then due to a change in F, the fraction of total Pu in solution as $Pu(NO_3)_6^{-2}$. The step-wise addition of NO_3^- groups to Pu^{+4} represented by the equilibria of equation (1) increases rapidly until at 10.8m (8N) in HNO_3 a maximum concentration of $Pu(NO_3)_6^{-2}$ is reached. The decrease in F above this concentration is probably due to a decrease in the degree of ionization of the stoichiometric compound $H_2Pu(NO_3)_6$ similar to that of nitric acid.

CONCLUSIONS

It is obvious that insufficient data are available for more than a rough qualitative approach to the equilibria involved in the nitric acid - Pu^{+4} - anion resin system. An investigation of the absorption of water and nitric acid at different concentrations by the resin nitrate and nitrate-plutonium salts, as well as isopiestic measurements of their water activities in the manner of Glueckauf to obtain resin activity coefficients, is needed. With these results more light could be shed on the problem of nitrate complexing of Pu^{+4}.

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Figure I.

Equilibrium Plutonium Absorption as a function of Pu(IV) and HNO₃ Concentration.

FIGURE 2

VARIATION OF SELECTIVITY COEFFICIENT
WITH Pu LOADING

FIGURE 3

VARIATION OF SELECTIVITY COEFFICIENT
AT CONSTANT LOADING WITH NITRIC
ACID CONCENTRATION.