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THE PROCESSING OF PLUTONIUM BY ION EXCHANGE - V.  
EQUILIBRIUM ANION-EXCHANGE SORPTION FROM  
MIXED NITRIC ACID-ALUMINUM NITRATE SOLVENTS

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**LOS ALAMOS SCIENTIFIC LABORATORY**  
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THE PROCESSING OF PLUTONIUM BY ION EXCHANGE - V.  
EQUILIBRIUM ANION-EXCHANGE SORPTION FROM  
MIXED NITRIC ACID-ALUMINUM NITRATE SOLVENTS

by

D. B. James

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#### ABSTRACT

A method is described for calculating the trace-loading equilibrium distribution coefficient,  $K_D^\circ$ , for the sorption of plutonium (IV) on Dowex 1x4 anion-exchange resin from mixed aluminum nitrate-nitric acid solutions. Published data for sorption from salt solutions and from acid solutions are used to obtain the dependence of  $K_D^\circ$  upon the molar concentration of nitrate ion and upon the mole ratio of hydronium ion to water. These parameters are calculated according to a published technique for twenty-two mixed solutions. Values of  $K_D^\circ$ , calculated from theoretical equations, were compared to experimental measurements of  $K_D^\circ$  for these solutions.

#### ACKNOWLEDGMENTS

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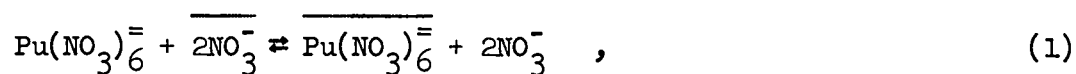
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## INTRODUCTION

Previous papers<sup>(1-3)</sup> have dealt with the sorption of plutonium(IV) on Dowex lx4 anion-exchange resin from 7M nitric acid. While this is probably the best universal solvent for plutonium processing by anion exchange, previous processing operations frequently introduce the aluminum ion into nitric acid feed solutions. The aluminum ion is not sorbed by anion-exchange resin from nitric acid,<sup>(1,4)</sup> but studies by Ryan and Wheelwright<sup>(4)</sup> indicate that considerable quantities of nitrate salts in the aqueous phase may drastically affect both the kinetics and equilibria of the system. It was the purpose of this work to investigate the equilibrium sorption of plutonium(IV) on Dowex lx4 from mixed nitric acid-aluminum nitrate solvents.

Plutonium(IV) is sorbed as the hexanitratoplutonate(IV) ion.<sup>(5)</sup>



where the bar indicates a species associated with the resin phase. An equilibrium quotient for this reaction could be written,

$$K_{\text{Pu}} = \frac{[\text{Pu}(\text{NO}_3)_6]_{\text{R}} [\text{NO}_3^-]_{\text{A}}^2}{[\text{Pu}(\text{NO}_3)_6]_{\text{A}} [\text{NO}_3^-]_{\text{R}}^2} = \frac{K_{\text{D}}^{\circ} [\text{NO}_3^-]_{\text{A}}^2}{\text{FC}^2} \quad (2)$$

The brackets indicate molar concentrations in the aqueous phase and millimoles per "oven-dry" gram of resin in the resin phase. In these high ionic strength solvents there is considerable resin invasion by both acid and salt. However, with the above definition the non-exchange nitrate within the resin phase does not contribute to  $[\text{NO}_3^-]_{\text{R}}$ . The trace-level loading distribution coefficient,  $K_{\text{D}}^{\circ}$ , is the amount of plutonium per gram of oven-dry resin divided by the amount of plutonium per liter of solution; C is the equivalent capacity of the resin for anions; and F is the fraction of plutonium present as  $\text{Pu}(\text{NO}_3)_6^-$  in the aqueous phase.

$$\frac{1}{F} = \frac{[\text{H}_2\text{Pu}(\text{NO}_3)_6] + [\text{HPu}(\text{NO}_3)_6^-] + [\text{Pu}(\text{NO}_3)_6^-] + [\text{HPu}(\text{NO}_3)_5] + [\text{Pu}(\text{NO}_3)_5^-] + \dots + [\text{Pu}^{+4}]}{[\text{Pu}(\text{NO}_3)_6^-]} \quad (3)$$

By defining,

$$K_n = \frac{[\text{H}_n\text{Pu}(\text{NO}_3)_6^{n-2}] [\text{H}_2\text{O}]}{[\text{H}_{n-1}\text{Pu}(\text{NO}_3)_6^{n-3}] [\text{H}_3\text{O}^+]} \quad , \quad n = 1, 2, \quad (4)$$

$$k_n = \frac{[\text{Pu}(\text{NO}_3)_n^{4-n}]}{[\text{Pu}(\text{NO}_3)_{n-1}^{5-n}] [\text{NO}_3^-]} \quad , \quad n = 1, 2, \dots, 6, \quad (5)$$

and assuming that the contribution of  $[\text{HPu}(\text{NO}_3)_5]$  is insignificant in comparison with the other terms in the numerator of equation (3), we obtain,

$$\frac{K_{\text{Pu}} C^2}{K_{\text{D}}^{\circ} [\text{NO}_3^-]^2} = K_1 K_2 \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{O}]^2} + K_1 \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} + \quad (6)$$

$$+ 1 + \frac{1}{k_6 [\text{NO}_3^-]} + \frac{1}{k_6 k_5 [\text{NO}_3^-]^2} + \dots + \frac{1}{k_6 k_5 \dots k_1 [\text{NO}_3^-]^6} \quad .$$

$$\frac{1}{K_{\text{D}}^{\circ} [\text{NO}_3^-]^2} = \phi_{\text{H}} + \phi_{\text{N}} \quad , \quad (7)$$

where  $\phi_{\text{H}}$  and  $\phi_{\text{N}}$  are functions only of  $[\text{H}_3\text{O}^+] / [\text{H}_2\text{O}]$  and  $[\text{NO}_3^-]$  respectively. This linear dependence of  $K_{\text{D}}^{\circ}$  on the aqueous concentrations requires not only the assumption above, but also that  $K_{\text{n}}$  and  $k_{\text{n}}$  are not functions of these variables and that  $K_{\text{Pu}}$  is a constant. Certainly these are very rough approximations, but any more detailed treatment would introduce a labyrinth of complications.

#### EXPERIMENTAL

Reagents: The resin used in these experiments was from a single batch of Dowex 1x4 (100 - 200 mesh)  $\text{NO}_3^-$ . It was converted from the chloride to the nitrate form and its equivalent capacity for anions,



3.82 milliequivalents per gram of oven-dry resin, was determined as described before.<sup>(1)</sup> The impurities in the plutonium were less than 0.01 weight percent. All other reagents were analytical grade or better.

Batch Equilibration Experiments: A measured weight of resin was equilibrated with solvent containing no plutonium and filtered "dry" with vacuum. The resin was added to a measured volume of aluminum nitrate-nitric acid solution containing a known amount of these compounds and plutonium(IV) nitrate. Amounts of resin and plutonium were controlled so that the resin was loaded to less than 1 percent of its capacity, yet the concentration change in the aqueous phase was at least 90 percent. The mixture was shaken for 48 hours with a wrist-action shaker at room temperature, and then the concentration of plutonium in the aqueous phase was again measured by  $\alpha$ -counting with a correction for americium present, determined by  $\alpha$ -counting.

If the rates of sorption from these mixed solvent systems are no slower than an order of magnitude of that measured for 7M nitric acid,<sup>(2)</sup> then equilibrium should have been reached in this time with this very low degree of resin loading. Preliminary kinetic experiments with these solvents indicate that this is a valid assumption. Several measurements were made with one system by removing a measured volume of the aqueous phase and adding a measured volume of either aluminum nitrate or nitric acid solution between equilibrations. These

sequential experiments allowed equilibrium to be approached from above and below, and the results were always consistent with equilibrium behavior.

#### RESULTS AND CONCLUSIONS

The results of 22 batch measurements of  $K_D^\circ$  in various aluminum nitrate-nitric acid solvents are given in the column labeled  $(K_D^\circ)_{\text{exp}}$  of Table I. Also shown are values of  $K_D^\circ$  calculated by two different methods.

In the absence of anything better, one might estimate  $K_D^\circ$  for a mixed aluminum nitrate-nitric acid solvent from a weighted average of the distribution coefficients for salt solutions and for acid solutions of appropriate concentrations.

The weighted average values,  $(K_D^\circ)_{\text{av.}}$ , were calculated from

$$(K_D^\circ)_{\text{av.}} = \frac{C_{\text{HNO}_3} (K_D^\circ)_{\text{HNO}_3} + 3C_{\text{Al}(\text{NO}_3)_3} (K_D^\circ)_{\text{salt}}}{C_{\text{HNO}_3} + 3C_{\text{Al}(\text{NO}_3)_3}}, \quad (8)$$

where  $C_{\text{HNO}_3}$  and  $C_{\text{Al}(\text{NO}_3)_3}$  are total stoichiometric molar concentrations of nitric acid and aluminum nitrate, and  $(K_D^\circ)_{\text{HNO}_3}$  and  $(K_D^\circ)_{\text{salt}}$  are the distribution coefficients of plutonium(IV) from nitric acid solutions and from calcium nitrate solutions with molar concentrations one and a half that of  $C_{\text{Al}(\text{NO}_3)_3}$ . These distribution coefficient data for nitric acid and calcium nitrate are given in Reference 5. The author

Table I

Distribution Coefficients from Mixed  $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$  Solvents

$C_{\text{HNO}_3}$ (M)	$C_{\text{Al}(\text{NO}_3)_3}$ (M)	$[\text{NO}_3^-]$ (M)	$[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ (M/M)	$\phi_{\text{N}}$ ( $\times 10^6$ )	$\phi_{\text{H}}$ ( $\times 10^6$ )	$K_{\text{D}}^{\circ}$		
						$K_{\text{D}}^{\circ}$ exp.	$K_{\text{D}}^{\circ}$ calc.	$K_{\text{D}}^{\circ}$ av.
6.0	0	4.4	0.109	18.4	3.1			
4.8	0.38	4.7	0.093	11.2	1.6	2000	2400	2400
7.0	0	4.8	0.125	9.9	5.2	2200	3600	4500
3.8	0.67	4.8	0.077	9.4	0.6	2600	2900	2900
3.1	0.91	5.0	0.065	7.0	0.2	4500	4300	6100
						8200	5600	7400
8.0	0	5.0	0.138	7.1	7.6			
5.6	0.38	5.0	0.106	7.1	1.9	2800	2700	2700
2.5	1.11	5.1	0.051	6.2	0.1	2800	4400	6800
9.0	0	5.1	0.148	6.2	10.8	8800	6200	8100
4.5	0.67	5.2	0.092	5.6	1.4	1800	2200	2200
						4700	5300	9000
4.1	0.91	5.3	0.086	4.3	1.1			
6.4	0.38	5.3	0.120	4.3	4.6	8700	6800	13,300
2.9	1.11	5.3	0.059	4.3	0.1	3000	3900	8700
2.3	1.26	5.4	0.050	3.9	0.1	12,400	8000	10,800
4.1	0.91	5.5	0.086	3.3	1.1	14,400	8600	11,200
						9600	7500	13,300
3.3	1.11	5.5	0.069	3.3	0.3			
5.8	0.67	5.7	0.114	2.7	3.7	9800	9100	13,800
3.0	1.26	5.8	0.065	2.4	0.2	3300	4800	14,000
4.6	0.91	5.8	0.097	2.4	1.9	10,000	11,600	16,400
3.7	1.11	5.8	0.079	2.4	0.7	7000	7000	16,400
						8800	9700	16,700
5.6	0.89	6.0	0.114	1.6	3.7			
6.4	0.89	6.3	0.129	1.3	5.9	5800	5200	18,300
						4700	3600	17,500

kindly supplied the original numbers so that precise calculations could be made.

The values of  $K_D^\circ$  in Table 1 under  $(K_D^\circ)_{\text{calc.}}$  were calculated from equation (7). The values of  $(K_D^\circ)_{\text{salt}}$  from Reference 5 were used to calculate  $\phi_N$  according to equation (7), assuming that  $\phi$  makes an insignificant contribution since  $C_{\text{HNO}_3} = 0.5$  in the experimental solutions. A plot of  $\phi_N$  versus  $[\text{NO}_3^-]^3$  is shown in Fig. 1. Then  $\phi_H$  was determined by calculating, at constant  $[\text{NO}_3^-]$ , the difference between  $\phi_N$  and  $1/(K_D^\circ)_{\text{HNO}_3} [\text{NO}_3^-]^2$ , again using Ryan's data<sup>(5)</sup> for  $(K_D^\circ)_{\text{HNO}_3}$ . Values for  $[\text{NO}_3^-]$  and  $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$  in nitric acid solutions were calculated from the degree of dissociation as determined by the proton magnetic resonance method of Axtmann et al.<sup>(6,7)</sup> and the specific gravity of these solutions.<sup>(8)</sup> A plot of  $\phi_H$  versus  $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$  is shown in Fig. 1. Values of  $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$  and  $[\text{NO}_3^-]$  in the mixed aluminum nitrate-nitric acid solutions given in Table I were also calculated by Axtmann's method and the specific gravity of these mixed solutions.<sup>(9)</sup> Then  $\phi_H$  and  $\phi_N$  were extracted from Fig. 1 and  $(K_D^\circ)_{\text{calc.}}$  evaluated according to equation (7).

The average absolute percent deviation of  $(K_D^\circ)_{\text{calc.}}$  and  $(K_D^\circ)_{\text{exp.}}$  in Table I is 24. However, since Axtmann's calculations were only experimentally verifiable to plus or minus 10 percent and  $\phi_N$  changes very rapidly with  $[\text{NO}_3^-]$ , such a deviation is to be expected. Nevertheless, these calculations are more reliable than the simple weighted average, especially for solutions containing large amounts

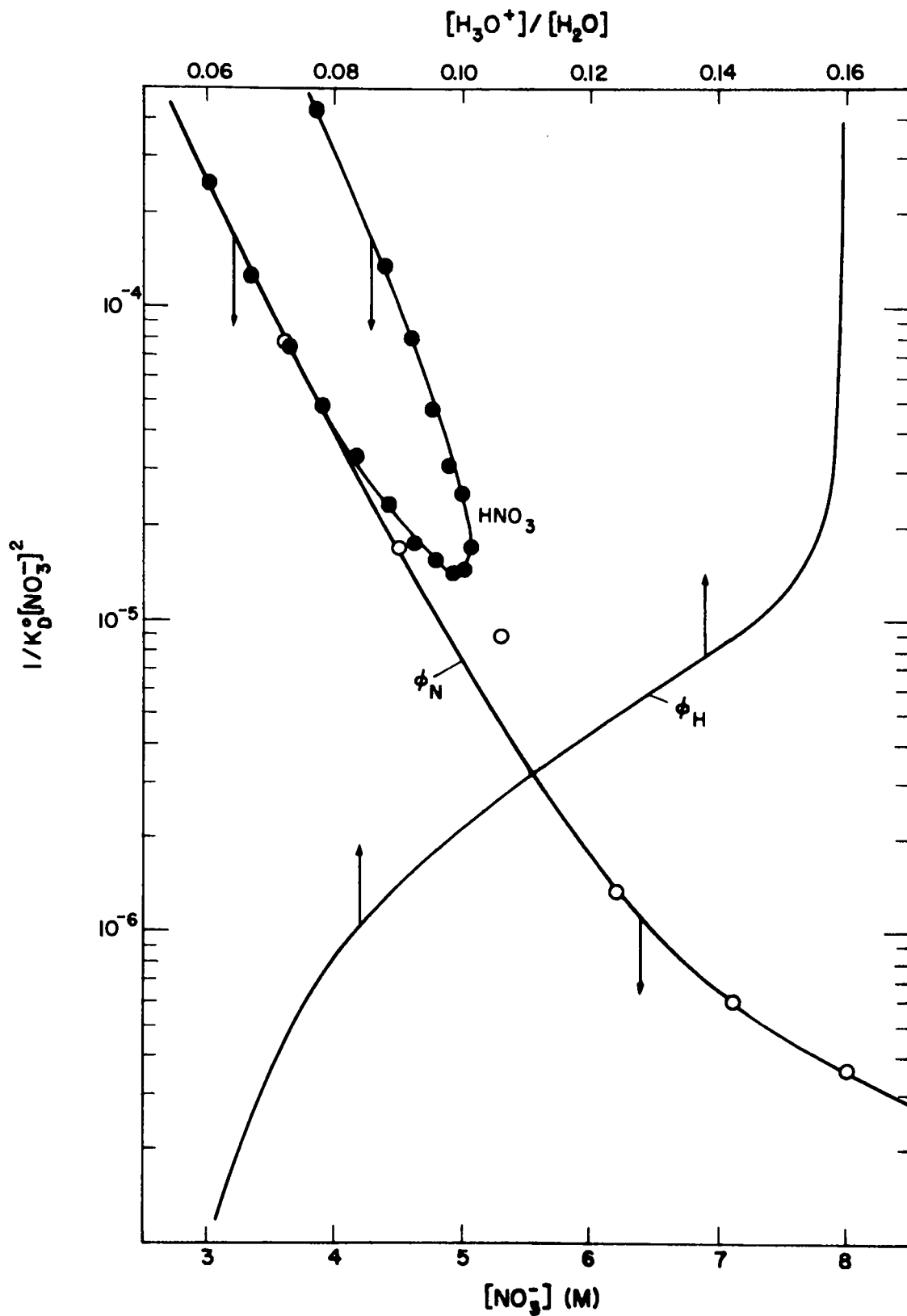


Fig. 1. Equilibrium Sorption of Plutonium from Nitrate Solutions.

of both salt and acid. The variation of  $(K_D^\circ)_{\text{calc.}}$  with total nitrate for various molarities of aluminum nitrate is shown in Fig. 2.

The curves for salt and acid begin to deviate at  $[\text{NO}_3^-] = 3.9$ , which corresponds to  $C_{\text{HNO}_3} = 5$ . Hence, we might speculate that below a total nitrate molarity of 5 the difference between Ryan's acid and salt distribution coefficient curves in Fig. 2 (curves A and H) is due, for the most part, to incomplete dissociation of the acid. The acid solution simply provides less nitrate ion for the formation of the sorbable hexanitrate complex of plutonium(IV).

In nitric acid solutions greater than 5 molar, the difference between curves A and H is augmented by the protonation of the sorbable complex. The formation of  $\text{HPu}(\text{NO}_3)_6^-$  and  $\text{H}_2\text{Pu}(\text{NO}_3)_6$  reduces the fraction of the plutonium(IV) that is in the form of sorbable complex. The absence of this association at lower concentrations indicates that  $\text{HPu}(\text{NO}_3)_6^-$  is at least as strong, if not a stronger acid than nitric acid.

The trace-level loading distribution coefficient for the sorption of plutonium(IV) from a given solvent is a constant only for very low degrees of resin loading, say less than 1 percent. If one assumes that  $K_{\text{Pu}}$  is a constant for any given solvent for all levels of sorption, then from equation (2) it can be shown<sup>(1)</sup> that the equilibrium distribution coefficient for any degree of sorption,  $K_D$ , is given by

$$K_D = K_D^\circ \left( 1 - \frac{2[\text{Pu}(\text{NO}_3)_6^-]^2}{c^2} \right) \quad (9)$$

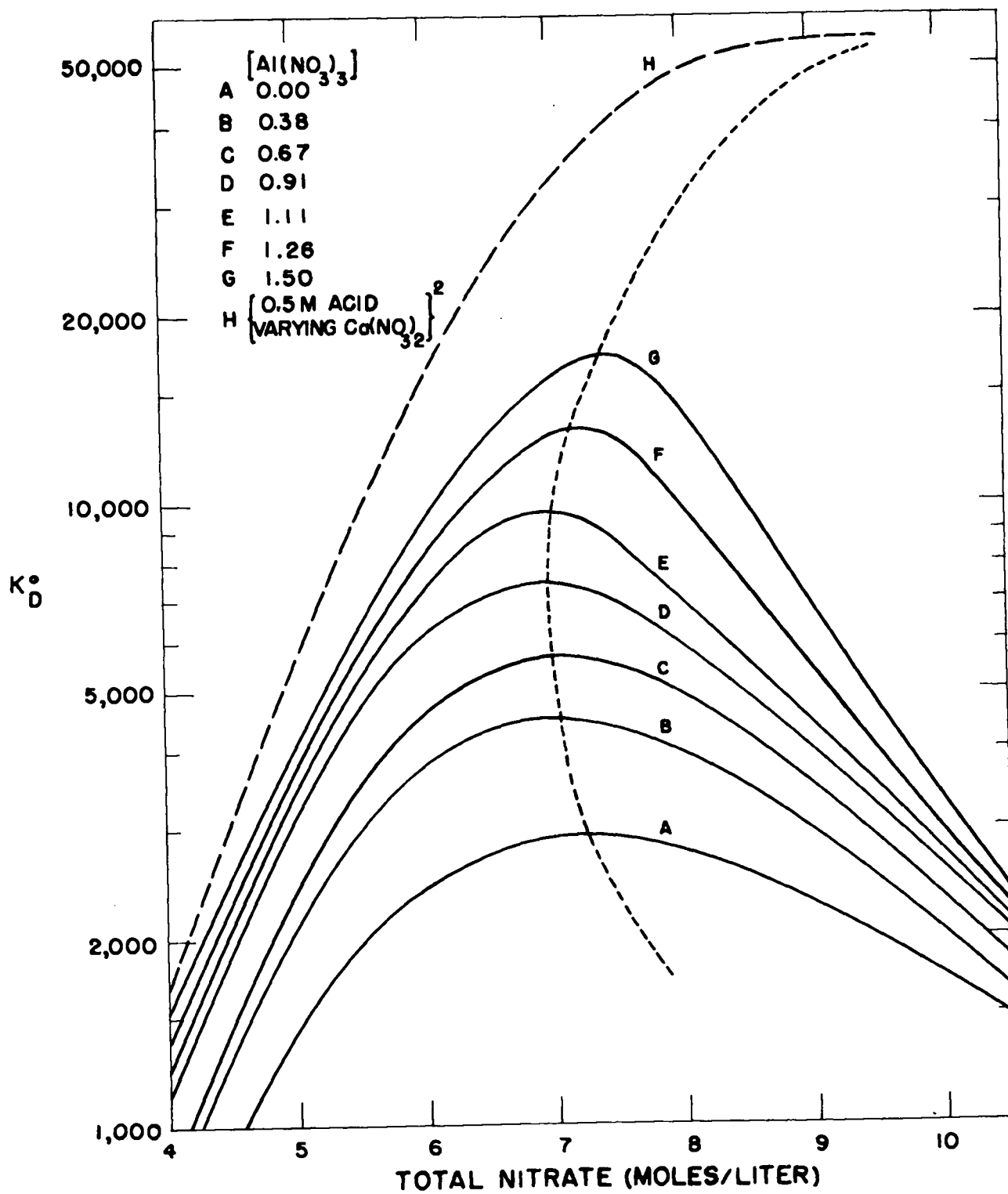


Fig. 2. Distribution Coefficients from Mixed Nitric Acid-Aluminum Nitrate Solvents.

It has been demonstrated<sup>(1)</sup> that this relationship holds for the entire range of resin loading for sorption from 7M nitric acid. To verify equation (9) for  $0 < 2[\text{Pu}(\text{NO}_3)_6]/C < 1$  for a sufficient number of aluminum nitrate-nitric acid solvents to establish its validity for all such mixtures would be a formidable research program. A few equilibrations at higher loadings have not contradicted equation (9).

Written in terms of the aqueous molar concentration of plutonium(IV),  $C_{\text{Pu}}$ , equation (9) takes the form<sup>(1)</sup>

$$K_D = K_D^\circ \left\{ 1 + U - \sqrt{U(U + 2)} \right\} \quad , \quad (10)$$

$$U = \frac{C}{4 C_{\text{Pu}} K_D^\circ} \quad . \quad (11)$$

By using Axtmann's method for calculating  $[\text{NO}_3^-]$  and  $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ , the curves in Fig. 1 for estimating  $\phi_N$  and  $\phi_H$ , and then equations (7), (10), and (11), one can predict the equilibrium sorption behavior of plutonium (IV) on Dowex 1x4 from any aluminum nitrate-nitric acid solution.



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