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PROCESSING OF PLUTONIUM BY ION EXCHANGE-VI.

**PLUTONIUM(IV) SORPTION KINETICS ON DOWEX LX4 FROM
NITRATE SOLUTIONS**

by

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ABSTRACT

The kinetics of the sorption of plutonium(IV) on Dowex 1x4 from nitrate solutions are presented. Sorption rates from various nitric acid and mixed aluminum nitrate-nitric acid solvents were studied. The particle-diffusion controlled reaction proceeds with an apparent average diffusion coefficient which decreases exponentially with increasing plutonium sorption. The results agree reasonably well with a computer solutions of Fick's Law with the local, intra-particle diffusion coefficient proportional to the local, intra-particle fraction of unreacted exchange sites. The trace-sorption diffusion coefficient is strongly dependent upon the composition of the aqueous phase, and is empirically shown to be roughly inversely proportional to the product of the trace -sorption distribution coefficient and the ratio of the hydronium ion to water concentrations. These kinetic results and previously reported equilibrium parameters may be coupled with the fundamental partial-differential equation which describes the operation of a fixed-bed, anion-exchange column to allow computer optimization of plant-scale processing equipment. The effects of the variation of such parameters as volume and mass flow rate, temperature, plutonium feed concentration, and macro concentrations of aluminum nitrate in the feed are discussed.

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INTRODUCTION

Previous papers in this series have dealt with the sorption of plutonium(IV) by the nitrate form of Dowex 1x4 anion-exchange resin from nitrate solutions.⁽¹⁻⁵⁾ Ryan⁽⁶⁾ demonstrated that plutonium(IV) is sorbed as the hexanitrate anion, $\text{Pu}(\text{NO}_3)_6^{=}$. The trace-sorption distribution coefficient,

$$\lambda_o = \frac{\text{amount Pu/g dry resin}}{\text{amount Pu/ml of solution}}, \quad (1)$$

is 10^3 to 10^4 depending on the aqueous composition.^(1,6) This indicates that the hexanitrate anion has a very high affinity for the resin phase in spite of the high nitrate ion concentration in the aqueous phase.

It has been verified previously⁽¹⁾ that for the case of sorption from $7M \text{ HNO}_3$ the equilibrium degree of sorption of plutonium(IV) for various aqueous concentrations of plutonium follows a simple mass-action treatment, which assumes a constant exchange quotient and constant activity coefficient ratios between phases. The isotherm takes the form,

$$\bar{x}^* = \bar{x}_m \{1 + U - \sqrt{U(U+2)}\}, \quad (2)$$

$$U = \bar{x}_m / 2C_{\text{Pu}} \lambda_o, \quad (3)$$

over the entire range of resin loading. In these equations

$\bar{x}^*$ = equilibrium concentration of plutonium in the resin phase in millimoles per oven-dry gram,

$\bar{x}_m$ = maximum concentrations of plutonium in the resin phase (half the equivalent capacity for anions),

C_{Pu} = total molar concentration of plutonium in the aqueous phase,

$$\lambda_o = \frac{\bar{x}^*}{C_{Pu}} \text{ when } \bar{x}^* \rightarrow 0.$$

Also described previously⁽³⁾ is a method for estimating λ_o for any mixed aluminum nitrate-nitric acid aqueous phase.

However, the kinetics of this system have received much less attention. Ryan and Wheelwright⁽⁷⁾ demonstrated that the rate of sorption by Dowex 1x4 from 7M nitric acid is controlled by diffusion coefficient, $\bar{D}^o$ which is about 1×10^{-9} cm²/sec but decreases rapidly with increasing plutonium sorption. James and Cooper⁽²⁾ showed that this sorption could be empirically described by the rate equation,

$$\frac{\partial \bar{x}}{\partial t} = \frac{\pi^2 \bar{D}^o e^{-k\bar{x}/\bar{x}_m}}{2R^2} \frac{(\bar{x}^*)^2 - (\bar{x})^2}{\bar{x}}, \quad (4)$$

where,

$\bar{x}$ = average nonequilibrium concentration of plutonium in the resin phase in millimoles per oven-dry gram,

t = time in seconds,

R = average radius of the resin particles in cm,

k = empirical constant.

Cooper and James⁽⁴⁾ give a computer code for the calculation of fixed-bed column performance from these kinetic and equilibrium parameters.

The object of the work reported here was to investigate the kinetics of this sorption from various concentrated nitrate media in order to attempt to describe the physical mechanism and to allow column performance calculations from various aqueous nitrate solutions.

EXPERIMENTAL

Reagents: The resins used were Dowex 1x2, x4 and x10, 50-100 and 100-200 mesh, nitrate form. They were converted from the chloride to the nitrate form and their equivalent capacity for anions determined as described before.⁽¹⁾ These capacities are given in Table 1.

Table 1
Capacity of Resins Used

<u>Resin</u>	<u>Capacity (meg/oven-dry gram)</u>
Dowex 1x2	4.02
Dowex 1x4	3.82
Dowex 1x10	3.26

The impurities in the plutonium used were less than 100 ppm.

Measurement of λ_0 : The measurement of λ_0 was described before.⁽³⁾

Kinetic Batch Sorption Experiments: The sorption of plutonium(IV) was followed in a round, four-liter flask with the two phases being rapidly stirred mechanically. A coarse frit at the end of a small tube allowed one-ml samples of the aqueous phase to be withdrawn in about 10 seconds at timed intervals. A weighted amount of moist resin (the conversion factor to oven-dry weight having been determined with a small separate sample), equilibrated with the nitrate solution of interest, and filtered "dry" with vacuum, was contacted with one-liter of the nitrate solution of measured plutonium concentration at time zero. The mixing time was less than 30 seconds. In each experiment the amount of resin was adjusted so that the aqueous-phase concentration of plutonium, which indicated the degree of sorption, was reduced by a factor of five to ten during the experiment. The alpha counting analytical technique described earlier⁽¹⁾ is probably better than two percent. The concentration change in the first few samples was about 10 to 20 percent, hence the early results could be in error by as much as 10 to 20 percent.

For each sample $\bar{x}$ was determined from the concentration change and $\bar{x}^*$ from equations (2) and (3). Defining

$$Y = \bar{x}/\bar{x}^* , \quad (5)$$

equation (4) becomes

$$\frac{dY}{dt} = \frac{\pi^2 \bar{D}_{0e} -k\bar{x}/\bar{x}_m}{2R^2} \frac{1 - Y^2}{Y} \quad (6)$$

Plots of Y vs $\ln t$ were differentiated graphically to obtain dY/dt . Then plots of $\ln \{ (dY/dt) Y/(1-Y^2) \}$ vs. $\bar{x}/\bar{x}_m$ have a slope of $-k$ and an intercept of $\pi^2 \bar{D}_{0e}/2R^2$.

The temperature of the glove-box enclosure in which all the experiments were conducted was $23 \pm 1^\circ\text{C}$. The elevated-temperature batch sorption experiments employed a semi-spherical heating mantle, which controlled the temperature of the reaction mixture to $\pm 1^\circ\text{C}$.

Resin Bead Radii Measurements: The average and range of bead radii in the resin used was measured photomicrographically with samples containing 100 to 200 beads. Very little change was observed between nitrate-form resin in contact with water and nitrate-form resin in contact with concentrated nitrate solutions; however, the values for wet nitrate-form resin were considerably lower than that reported by the manufacturer for wet chloride-form resin. The results are shown in Table II.

Table II
Bead Radii for Resin Samples

Resin	Average Radii (cm)	Range (cm)
Dowex 1x4 (100-200)NO ₃ ⁻	4.9×10^{-3}	$2.4 \rightarrow 7.0 \times 10^{-3}$
Dowex 1x4 (50-100)NO ₃ ⁻	9.9×10^{-3}	$5.1 \rightarrow 14.6 \times 10^{-3}$
Dowex 1x2 (100-200)NO ₃ ⁻	6.9×10^{-3}	$4.9 \rightarrow 9.8 \times 10^{-3}$
Dowex 1x10 (100-200)NO ₃ ⁻	5.6×10^{-3}	$3.7 \rightarrow 8.2 \times 10^{-3}$

Column Experiment: A plant-scale anion-exchange column was assembled from a 40-cm, 3-inch inside-diameter, glass pipe, fitted with stainless steel end sections employing teflon screens, supported by perforated stainless steel plates, to retain the resin. The leveled column was completely filled with 634 oven-dry grams of Dowex 1x4 (100-200)NO₃⁻, which was backwashed with 7M HNO₃ several times to insure uniform packing of the column. From the pycnometrically determined "specific gravity" (7M HNO₃ volume/oven-dry weight) the void fraction of the packed resin bed was calculated to be 0.508. The volume of the piping from the bottom screen to the sampling valve was about 100 ml.

The feed solution, 0.1022M in Pu and 6.98M in HNO₃, was gravity fed. The flow rate of 2.58 l/hr. was held constant by a regulating valve below the column and a flow meter above the column and was measured by the exit volume and the running time.

RESULTS AND CONCLUSIONS

The strong dependence of λ^0 upon the concentration of nitric acid is shown in Fig. 1. The dark circles are data from this work, and the open circles are from reference (6). Measurements in 7M nitric acid as a function of temperature are given in Table III. It is easily shown⁽¹⁾ that with constant activity coefficient ratios between phases the equilibrium quotient for sorption is,

$$K = \frac{\lambda^0 C_{\text{NO}_3}^2}{4 f \bar{x}_m^2} \quad , \quad (7)$$

where C_{NO_3} is the molar concentration of the nitrate ion in the aqueous phase and f is the fraction of plutonium as the sorbable hexanitrate complex in the aqueous phase. The plot of $R \ln (\lambda^0 C_{\text{NO}_3}^2)$ vs. reciprocal temperature in Fig. 2 has a slope of -4.1 kilocalories per mole which is the sum of the enthalpies of hexanitrate complex formation and of sorption. Values of C_{NO_3} in Table III were taken from the nitric acid dissociation data of Axtman et. al.⁽⁸⁾

Fig. 1. Distribution Coefficients in Nitric Acid.

Fig. 2. Temperature Dependence of Equilibrium Sorption

Table III
 λ° in 7M Nitric Acid as a Function of Temperature

T (°K)	λ°	$C_{\text{NO}_3^-}$ (M)
295	2900	5.00
313	2260	4.68
333	1550	4.56

The kinetic experiments with nitric acid are described in Table IV. The results are shown in Fig. 3. As described in the experimental section, smooth curves through the data in Fig. 3 were differentiated graphically to yield the results in Fig. 4. The slope of these lines gives a value to k in equation (6) of 3.1, and this value appears to be independent of the composition of the aqueous phase or the size of the resin beads.

Table IV
 Kinetic Experiments with Nitric Acid

Data Points Figs. 3,4	C_{HNO_3} (M)	C_{Pu} (g/l)	$\bar{x}^*/\bar{x}_m$	Dry Mesh Range
•	7.0	1.0-0.2	0.66-0.42	100-200
○	7.0	47-11	0.95-0.89	100-200
⊙	7.0	5-0.6	0.81-0.62	100-200
◦	7.0	23-7.0	0.92-0.86	50-100
△	4.0	46-16	0.88-0.82	100-200
□	5.5	23-1.0	0.89-0.61	100-200
■	7.5	30-7.2	0.93-0.86	100-200
▽	9.0	23-1.7	0.91-0.79	100-200

Fig. 3. Plutonium Sorption from Nitric Acid.

Fig. 4. Estimation of $\bar{D}^0$ and k

Values of $\bar{D}^0$ were calculated from the intercepts in Fig. 4 and are shown in Table V.

Table V
Apparent Trace-Loading Diffusion Coefficient

C_{HNO_3}	λ^0	$\bar{D}^0 \times 10^{10}$ (cm ² /sec)	Dry Mesh Range
4.0	680	26.0	100-200
5.5	1600	10.7	100-200
7.0	2900	7.0	50-100
7.0	2900	7.0	100-200
7.5	3450	6.0	100-200
9.0	2370	5.4	100-200

Of course this is not exactly the self-diffusion coefficient of plutonium but an interdiffusion coefficient which is physically and electrostatically coupled to the diffusion of other ions and the migration of water within the beads. As described by Helfferich⁽⁹⁾ these effects are minimized in ion-exchange systems where there is a high concentration of co-ions within the resin phase. However, equation (6), upon which this treatment is based, is entirely empirical, so the values of $\bar{D}^0$ in Table V can have no basis in physical reality for local intra-particle phenomena. As $\bar{x}/\bar{x}_m$ approaches zero equation (6) becomes,

$$\frac{dy}{dt} = \frac{\pi^2 \bar{D}^0}{2R^2} \frac{1-y^2}{y} \quad (8)$$

This is a very good approximation suggested by Vermeulen⁽¹²⁾ to the exact solution of Ficks Law for diffusion into spherical particles with a constant diffusion coefficient.⁽¹⁰⁾ The apparent average diffusion coefficient of plutonium is exponentially decreased as the average plutonium concentration is increased. While these average values can have no physical significance, equation (6) may be used to calculate sorption rates from any nitric acid solution if values of λ^0 , $\bar{D}^0$ and R are known.

These results were extended to provide for variable temperature with experiments at 40 and 60°C from 7M nitric acid. These data were treated as before. A slight decrease in k for 60°C was noted, but this may not be real. If we assume that

$$\bar{D}^0 = A e^{-\Delta E/RT}, \quad (9)$$

then the slope of the plot in Fig. 5 of 8.7 kilocalories/mole is the activation energy for diffusion. While this is rather high compared to aqueous solutions (3 to 6 kcal/mole) it is not unexpected since the retarding effect of the plutonium-resin interaction is probably lessened by increased temperature.

While nitric acid is probably the best universal solvent for plutonium processing by anion exchange, previous processing operations frequently introduce macro-quantities of the aluminum ion into nitric acid feed solutions. An earlier paper⁽³⁾ gives a method for estimating λ^0 for mixed aluminum nitrate-nitric acid solutions of plutonium. It would be a formidable research program to verify that equations (2) and (3) hold for these systems, but considerable random, indirect unpublished experience in this laboratory gives no indication that these equations are seriously invalid.

In order to extend kinetic calculations to these mixed systems, several batch kinetic experiments were conducted with mixed aluminum nitrate-nitric acid solvents. The results are shown in Table VI. Within experimental error k in equation (6) was 3.1 for all of these experiments. The exponential decrease in the apparent diffusion coefficient with the average fraction of exchange sites occupied by plutonium, $\bar{x}/\bar{x}_m$, is independent of the composition of the aqueous phase and also independent of the changes in the composition of the resin phase which these aqueous changes must invoke.

However, $\bar{D}^0$ is apparently very sensitive to the composition of the aqueous phase. Boyd, et. al.⁽¹³⁾ have suggested that in systems with high λ^0 most of the counterions are bound to the resin matrix, leaving only a very few free to diffuse in the liquid within the bead. Therefore, since λ^0 is a measure of the affinity of the counterion for the resin, $\bar{D}^0$ should be inversely proportioned to λ^0 . The product, $\lambda^0 \bar{D}^0$ is given in Table VI for the nine mixed experiments.

Fig. 5. Temperature Dependence of Plutonium Sorption

Table VI
Trace-Sorption Diffusion Coefficients for Mixed
Aluminum Nitrate-Nitric Acid Solvents

Data Points Fig. 7	$C_{Al(NO_3)}$ (M)	C_{HNO_3} (M)	λ^0	$\bar{D}^0 \times 10^{10}$ (cm ² /sec)	$\lambda^0 \bar{D}^0 \times 10^8$ (cm ² /sec)
▼	2.0	1.0	13,500	3.8	5.1
▲	1.6	0.7	9,160	15	13.7
▽	1.4	0.7	4,470	23	10.3
△	1.2	1.1	2,690	23	6.2
□	1.0	0.7	1,010	13	13.1
◇	1.0	2.3	4,350	7.5	3.3
◇	0.91	3.7	7,730	1.4	1.1
□	0.50	4.5	3,890	4.2	1.6
□	0.55	6.3	4,350	2.8	0.9
○	0.10	6.6	3,120	6.2	1.9

A previous paper⁽³⁾ showed that when the mole ratio of hydronium ion to water in these systems reaches about 0.07, the protonation of the hexanitrato complex becomes significant. The resulting lowered affinity for the resin is already discounted in λ^0 , but if $H_2Pu(NO_3)_6$ is sufficiently less mobile than $Pu(NO_3)_6^{=}$, an increased acid concentration could also have a retarding effect. A plot of $\bar{D}^0$ vs $C_{H_2O}/\lambda^0 C_{H_3O}^+$ is shown in Fig. 6. A means of estimating the ratio $C_{H_2O}/C_{H_3O}^+$ according to the dissociation data of Axtmann, et. al.⁽⁸⁾ was given earlier.⁽³⁾ While the correlation is certainly insufficient to establish the above argument, it may provide a method for estimating $\bar{D}^0$ which is sufficiently accurate for most applications.

The conditions of the experiments described in Table VI were controlled so that $\bar{x}^*/\bar{x}_m$ varied from about 0.94 to 0.86 in all the experiments. A computer integration⁽⁴⁾ of equation (6) with the boundary conditions of these batch sorption experiments and $k = 3.1$ is given by the dash-dot line in Fig. 7. The ordinate is a dimensionless time parameter which normalizes the effect of the different initial diffusion coefficients, $\bar{D}^0$, for the different experiments.

Fig. 6. Empirical Relation between $\bar{D}^0$ and Aqueous Composition.

Fick's law for diffusion into spheres is described by

$$\frac{dx(r,t)}{dt} = \frac{1}{r^2} \frac{\partial}{\partial r} \frac{1}{r^2} \bar{D}(x) \frac{\partial x}{\partial r}, \quad (10)$$

where $x(r,t)$ is the local intra-particle concentration of plutonium, r is the radial dimension and $\bar{D}(x)$ is the local intra-particle diffusion coefficient. Equation (10) was integrated numerically with various functional dependence of $\bar{D}(x)$ upon x . The dotted line represents the solution with $\bar{D}(x)$ constant throughout the sorption.⁽¹¹⁾ The slopes are such that all solutions using the form $\bar{D}(x) = \bar{D}^0 \exp(-kx/\bar{x}_m)$ cannot be correlated with the data with positive values of k . The result using $\bar{D}(x) = \bar{D}^0(1-x/\bar{x}_m)$ is given by the dashed line in Fig. 7. The solid line is the same result corrected for the effect of the distribution of particle radii. This proportionality of $\bar{D}(x)$ to the fraction of unoccupied exchange sites is reasonable if one assumes that the large sorbed $\text{Pu}(\text{NO}_3)_6^-$ ion blocks the diffusional paths. Of course, there are probably a large number of other functional relations between $\bar{D}(x)$ and x which are not too unreasonable physically and produce as good agreement with these data (e.g. $\bar{D}(x) = \bar{D}^0 \exp(-kx^2/\bar{x}_m^2)$ is almost as good). Hence, we should not conclude that this agreement with a linear function establishes the diffusional mechanism. For any practical application of these results to the calculation of the performance of a sorption system, it will probably be better to use equation (6) rather than equation (10), which introduces another dimension to the problem and does not provide as good a fit to the experimental data.

The effect of resin crosslinkage was investigated briefly using 7M HNO_3 . The results are shown in Table VII and the data points in Fig. 7. The results for x10 appear to differ from x4 only in the magnitude of $\bar{D}^0$, which is consistent with the above mechanism. However the results for x2 fit the constant diffusion coefficient curve. The data points begin to deviate from the theory for $Y > 0.8$. Dowex 1x2 shrinks markedly as it

Fig. 7. Plutonium Sorption from Nitrate Solutions

becomes loaded with plutonium. It may be that above $Y = 0.8$ ($\bar{x}/\bar{x}_m = 0.73$) the intra-particle diffusion "pores" have shrunk to the point that the sorbed plutonium complex begins to block them.

Table VII
Effect of Resin Crosslinkage on the
Kinetics of Pu Sorption

<u>Data Points</u> <u>Fig. 7</u>	<u>Nominal</u> <u>Crosslinkage</u>	<u>λ^0</u>	<u>$\bar{D}^0 \times 10^{10}$</u> <u>(cm²/sec)</u>
■	x2	3050	55
○	x4	2900	7.0
■	x10	2480	2.4

NUMERICAL DUPLICATION OF PLANT-SCALE COLUMN PERFORMANCE

The fundamental equation which describes the fixed-bed ion-exchange column is

$$\epsilon \frac{\partial C_{Pu}}{\partial t} + v \frac{\partial C_{Pu}}{\partial z} = - \frac{\partial \bar{x}}{\partial t}, \quad (11)$$

where

ϵ = fractional interstitial void space about the resin beads,

z = distance along the column in centimeters,

v = linear flow rate of the aqueous phase in centimeters per second.

Because of the slow diffusion rate of plutonium the quasi-steady state, which has well-known solutions,⁽¹²⁾ is not established in the time of normal processing operations. A computer solution to equations (2), (3), (6) and (11) was described earlier.⁽⁴⁾ This code also includes a correction for diffusion in the static film which surrounds the beads and longitudinal diffusion across the column. These are very minor corrections in most applications. A value for the film thickness was

calculated according to Glueckauf's empirical relation,⁽¹⁴⁾ and values for the aqueous diffusion coefficient were extrapolated from the data of Starik, et. al.⁽¹⁵⁾

In order to demonstrate the reliability of these calculations a plant-scale column was loaded with plutonium well past breakthrough. The exit plutonium concentrations are given by the points in Fig. 8. The solid line gives the exit concentration as calculated by the computer. The slight difference in the slopes of the breakthrough curves of computer and experiment could be caused by physical mixing of the exit solution in the small volume between the bottom of the resin bed and the sampling port.

The curves shown in Figs. 9, 10 and 11 are computer calculated breakthrough curves for a 6-inch diameter column, filled to a depth of 40 cm with Dowex 1x4 (100-200) NO_3^- with $\epsilon = 0.31$. The curves in Figs. 9 and 10 are computed with a 7M nitric acid feed solution.

Figure 9 shows the effect of feed concentration and temperature under conditions of a constant volume flow rate of 10.8 l/hr. At 25°C. the more dilute solution breaks through later because the same amount of plutonium has a longer column residence time. The equilibrium capacity of the resin for plutonium sorbed from 0.01M solution is lower by a factor of 1.32 from that from a 0.1M solution, but this effect is more than cancelled by the longer time to be sorbed. The exit concentration from the more dilute feed approaches the input concentration more rapidly because of the exponential decrease in the kinetics as the resin is loaded to a higher degree with the more concentrated feed solution.

This latter effect is still present when the system is run at 60°C. because the exponential decrease is not temperature dependent. However, at this elevated temperature the order of the breakthrough curves is reversed. This is a result of the system becoming less dependent upon the kinetic parameters and more dependent upon the equilibrium parameters. There is about a 1.3 mole increase in the capacity with the elevated temperature for the 0.1M feed solution. The flow of plutonium through the column is so rapid that the temperature enhancement of the kinetics far outweighs the temperature adversity on the equilibrium capacity.

Fig. 8. Breakthrough Curve for Plant-Scale Column Experiment.

Fig. 9. Breakthrough Curves with Constant Volume Flow Rate.

Fig. 10. Breakthrough Curves with Constant Mass Flow Rate.

Fig. 11. Effect of Nitric Acid on Breakthrough Curves.

Figure 10 shows the breakthrough curves for the same variables as with the curves in Fig. 9 but with a constant mass flow rate of 1.0 moles/hr. Now the column residence time for plutonium is the same for each experiment, so the effects of kinetic differences are greatly reduced. The general shapes of the curves are the same and they all reach a high level of loading at about the same point. The improvement with temperature is about the same for all concentrations. This is because the kinetics of the system are still the dominate factor at this mass flow rate, and the improvement is due to the increase in the diffusion coefficient which is not a function of the aqueous concentration for a single temperature; however, the earlier breakthrough for the more dilute feed solution is due, for the most part, to the lower equilibrium capacity of the resin for plutonium.

The curves shown in Fig. 11 are computer calculated breakthrough curves at 25°C. for the same column with a mass flow rate of 1.0 moles/hr, a feed concentration of 0.1M, but with varying concentrations of nitric acid in the feed. Ryan and Wheelwright⁽⁷⁾ chose 7.2M HNO₃ as the optimum feed concentration for plutonium processing because λ^0 is at a maximum (see Fig. 1). However, $\bar{D}^0$ decreases with increasing nitric acid concentration, reaching a minimum at about 8M. That $\bar{D}^0$ is more important than λ^0 in determining column capacity is clearly shown in Fig. 11. Under the conditions of these calculations about 4M appears to be the best solvent if capacity is the only criteria. The higher λ^0 may be of greater importance for plutonium purification processes.

Figures 12 and 13 give λ^0 and $\bar{D}^0$ for mixed aluminum nitrate-nitric acid solvents. The curves A through G are for 0.00, 0.38, 0.67, 0.91, 1.11, 1.26 and 1.5M aluminum nitrate respectively. The values of λ^0 were calculated according to the method described earlier.⁽³⁾ The values of $\bar{D}^0$ were calculated from (see Fig. 6),

$$\bar{D}^0 = 1.6 \times 10^{-10} + 1.4 \times 10^{-7} C_{H_2O} / \lambda^0 C_{H_3O^+} \quad (12)$$

As evidenced by the scatter in Fig. 6 these calculations are probably no better than $\pm 50\%$.

Fig. 13. Diffusion Coefficients for Nitrate Solutions.

If we assume that the temperature coefficients for λ° and $\bar{D}^{\circ}$ for 7M nitric acid may be applied to all nitrate solutions, the curves in Figs. 12 and 13 may be used to calculate the performance of any column for the sorption of plutonium(IV) by Dowex 1x4 from any aluminum nitrate-nitric acid solution.

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