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Equilibrium Anion Exchange of Uranium(VI)
on Dowex 1X4 from Nitric Acid Solutions

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Equilibrium Anion Exchange of Uranium(VI)
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by

D. B. James

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ABSTRACT

Equilibrium exchange isotherms for uranium(VI) sorbed on Dowex 1X4 anion-exchange resin from nitric acid solutions were determined for 5, 7, and 8.3M nitric acid at 24°C and for 7M nitric acid at 40 and 60°C. The results were numerically fitted by a least-squares technique to mass-action theory, assuming sorption as $\text{UO}_2(\text{NO}_3)_3^-$ and $\text{UO}_2(\text{NO}_3)_4^{2-}$.

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INTRODUCTION

The anion exchange of uranium(VI) from nitrate solutions has been investigated by a number of authors.⁽¹⁻⁶⁾ The resin predominantly sorbs the tetranitrato anion, $\text{UO}_2(\text{NO}_3)_4^{-2}$, along with lesser amounts of the trinitrato complex, $\text{UO}_2(\text{NO}_3)_3^{-}$. The relative amount of each was shown to be independent of the composition of the aqueous phase, but dependent upon resin-phase properties, such as fractional uranium loading and equivalent exchange capacity.⁽⁶⁾

Foreman, et al.⁽²⁾ compared trace-loading distribution coefficients from nitrate solutions of various metal nitrates and nitric acid with a constant, total-nitrate concentration of 6M. Googin, et al.⁽⁵⁾ investigated equilibrium sorption isotherms for various nitrate solutions.

It was the purpose of this work to study the sorption of uranium(VI) from nitric acid solutions, and to compare these results to mass-action theory.

EXPERIMENTAL

The resin used in this work was Dowex 1X4(100-200) NO_3^- . Its equivalent capacity was determined as described before⁽⁷⁾ to be 3.82 milliequivalents per gram of oven-dry, nitrate-form resin.

A weighed amount of resin, previously equilibrated with the appropriate nitric acid solution, was contacted with a measured volume of uranyl nitrate-nitric acid solution for 10 days. The aqueous uranium concentration, determined colorimetrically before and after equilibration, was used to calculate the amount of uranium sorbed by the resin.

RESULTS AND CONCLUSIONS

If one assumes that both $\text{UO}_2(\text{NO}_3)_3^-$ and $\text{UO}_2(\text{NO}_3)_4^{2-}$ are sorbed by the resin, then we may write the exchange expressions:

R^+ represents the resin-phase, fixed cation, and the overbar denotes a species in the resin phase. These are indicated as ion pairs, but this is more for convenience than to suggest structure. Of course, these exchange equilibria could be written by starting with any of the certainly several uranyl nitrate complexes that are present in the aqueous phase. The choice of the neutral complex is also for convenience and in no way restricts the discussion.

The expressions (1) and (2) yield equilibrium coefficients,

$$K_1 = \frac{\left[\overline{\text{R}^+ \text{UO}_2(\text{NO}_3)_3^-} \right]}{\left[\text{UO}_2(\text{NO}_3)_2 \right] \left[\overline{\text{R}^+ \text{NO}_3^-} \right]} \quad , \quad (3)$$

$$K_2 = \frac{\left[\overline{\text{R}_2^{+2} \text{UO}_2(\text{NO}_3)_4^{2-}} \right]}{\left[\text{UO}_2(\text{NO}_3)_2 \right] \left[\overline{\text{R}^+ \text{NO}_3^-} \right]^2} \quad , \quad (4)$$

the brackets indicating moles per liter in the aqueous phase and moles per equivalent in the resin phase. Activity coefficients are incorporated in K_1 and K_2 . With a given, high, nitric acid concentration in the aqueous phase,

activity coefficients for aqueous species are certainly constant; and with the high penetration of nitric acid into the resin phase this may be true there also.

Defining x as the total moles of uranium per equivalent of resin and y as the total moles of uranium per liter of aqueous, it can be easily verified that by summing over both uranium species and the total exchange sites,

$$x = y \left(K_1 F_2 \left[\overline{R^+ NO_3^-} \right] + K_2 F_2 \left[\overline{R^+ NO_3^-} \right]^2 \right), \quad (5)$$

$$x = 1 - \left[\overline{R^+ NO_3^-} \right] - K_2 F_2 y \left[\overline{R^+ NO_3^-} \right]^2, \quad (6)$$

where $F_2 = \left[UO_2(NO_3)_2 \right] / y$ is the fraction of uranium as the neutral complex in the aqueous phase, a quantity assumed to be independent of $\left[UO_2(NO_3)_2 \right]$. Defining $\beta_1 = F_2 K_1$ and $\beta_2 = F_2 K_2$ and eliminating $\left[\overline{R^+ NO_3^-} \right]$ we obtain

$$\beta_1^2 (1 - x)y^2 - \left[\beta_1 + \beta_2 (1 - 2x)^2 \right] y + x = 0. \quad (7)$$

The results of experimental determinations of x and y for five systems are shown in Figures 1 through 5. For each system these data were analyzed numerically by a least-squares technique. Best values of the two parameters, β_1 and β_2 , were obtained by first assuming all the error to be in y and then assuming all the error to be in x . The lines in these figures represent equation (7) with these best values, the upper line the result with all the error in y . Values of β_1 and β_2 are shown in Figures 6 and 7 and given in Table I. The quantities in parentheses are percent standard deviation. The columns labeled x and y are values determined with all the error in x and y , respectively.

For small x (and therefore small y) we see from equation (7) that

$$\frac{x}{y} = \beta_1 + \beta_2, \quad (x \rightarrow 0), \quad (8)$$

where the quantity x/y is the trace-loading, equivalent distribution coefficient. It is interesting to note that β_1 and β_2 is not a linear function of T^{-1} in $^{\circ}\text{K}^{-1}$, and this appears to be due to a maximum in β_2 . The expected maximum in $\beta_1 + \beta_2$ with increasing nitric acid concentration is present, but this is in spite of an apparent minimum in β_2 .

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Table I
U(VI) EQUILIBRIUM SORPTION PARAMETERS

Temperature (°C)	C_{HNO_3} (M)	β_1		β_2	
		x	y	x	y
60	7	0.41(64)	0.44(64)	2.13(23)	1.85(34)
40	7	0.75(76)	0.93(36)	2.18(34)	2.46(6)
24	7	1.78(9)	1.71(17)	1.15(16)	1.32(14)
24	5	0.82(52)	1.02(46)	1.29(40)	1.29(28)
24	8.3	1.41(26)	1.46(27)	1.56(28)	1.62(18)

Figure 1. $7.0M$ HNO_3 , $24 \pm 1^\circ C$

Figure 2. $7.0M$ HNO_3 , $40 \pm 1^\circ C$

Figure 3. 7.0M HNO_3 , $60 \pm 1^\circ\text{C}$

Figure 4. 5.0M HNO_3 , $24 \pm 1^\circ\text{C}$

Figure 5. $8.3M$ HNO_3 , $24 \pm 1^\circ C$

Figure 6. β_1 and β_2 vs. reciprocal temperature

Figure 7. β_1 and β_2 vs. concentration of nitric acid