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

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Kinetics of the Anion Exchange of Uranium(VI)
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by

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ABSTRACT

The kinetics of the sorption of uranium(VI) from nitric acid solutions on Dowex 1X4 anion-exchange resin were studied. The system is controlled by diffusion within the resin phase and described by a constant-diffusion-coefficient theory. Diffusion coefficients for 5, 7, and 8.3M nitric acid at 24°C are 7.4×10^{-8} , 5.2×10^{-8} , and 4.0×10^{-8} cm²/sec, respectively, and for 7M nitric acid at 40 and 60°C are 1.2×10^{-7} and 3.3×10^{-7} cm²/sec, respectively. The diffusional activation energy is 13 kcal/mole.

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INTRODUCTION

The equilibrium anion exchange of uranium(VI) on Dowex 1X4 from nitric acid solutions was discussed in a previous paper.⁽¹⁾ Exchange isotherms from 5, 7, and 8.3M nitric acid at 24°C and from 7M nitric acid at 40 and 60°C were numerically fitted by a least-square technique to mass-action theory, assuming sorption as $\text{UO}_2(\text{NO}_3)_3^-$ and $\text{UO}_2(\text{NO}_3)_4^{2-}$ as established by Ryan.⁽²⁾ The qualitative work of Googin, et al.⁽³⁾ provides the only information as to the kinetics of the sorption of uranium(VI).

It was the purpose of the work reported here to study the rate of sorption of uranium(VI) by Dowex 1X4 in order to provide a more quantitative description of this system.

EXPERIMENTAL

The resins used were Dowex 1X4, 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 to be 3.82 milliequivalents per oven-dry gram as described before.⁽⁴⁾

The sorption of uranium(VI) was followed in a round, 4-l flask with the two phases being rapidly stirred mechanically. A coarse frit at the end of a small pipette allowed 1-ml samples of the aqueous phase to be withdrawn in about 10 sec at timed intervals. A weighed amount of moist resin (the conversion factor to oven-dry weight having been determined with a small separate sample), equilibrated with the nitric acid solution of interest, and filtered "dry" with

vacuum, was contacted with 1 ℓ of the nitric acid solution of measured uranium concentration at time zero. The mixing time was less than 30 sec.

From each sample the amount of uranium sorbed was determined from the concentration change. As the concentration of uranium decreased in the aqueous phase the equilibrium level of uranium sorption that the system was seeking changed according to the equilibrium isotherm as described before.⁽¹⁾ From this calculated equilibrium sorption, the fraction of equilibrium, Y, was calculated for each sample.

RESULTS AND CONCLUSIONS

The results of several experiments for sorption from 7M nitric acid on Dowex 1X4 (50-100) are shown in Figure 1. For the open circles the concentration of uranium in the aqueous phase varied from 2×10^{-3} to 0.8×10^{-3} M, for the dark circles from 2×10^{-2} to 0.7×10^{-2} M, and for the open squares from 0.2 to 0.09 M. The dark squares are results from an experiment from 7M nitric acid with Dowex 1X4(100-200). The values of time for these data were multiplied by a factor of 4.08, which is the ratio of the squares of the average particle radii for 50-100 mesh to 100-200 mesh resins.⁽⁵⁾ The uranium concentration change was 8×10^{-2} to 3×10^{-2} M.

The independence of the sorption on the aqueous uranium concentration and the dependence upon the square of the bead radius establishes that the kinetics of the system are controlled by diffusion within the resin phase. With a constant diffusion coefficient, resin-phase diffusion is described by⁽⁶⁾

$$Y = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-D t \pi^2 n^2 / R^2) , \quad (1)$$

where $\bar{D}$ is the diffusion coefficient in square centimeters per second, t is time in seconds, and R is the bead radius in centimeters. Equation (1) holds for systems with an infinite solution volume or, as with this work, when the effects of aqueous concentration changes are corrected.

The fractional attainment of equilibrium, Y , is seen to depend only on the dimensionless time parameter, $\tau = \bar{D}t/R^2$. Equation (1) is tabulated in reference (6) as Y versus τ . The solid line in Figure 1 represents Y versus t with $\bar{D} = 5.2 \times 10^{-8}$ cm²/sec and $R = 4.9 \times 10^{-3}$ cm.⁽⁵⁾ The simple, constant-diffusion-coefficient theory seems to fit the data within the experimental scatter.

The results of experiments with the aqueous uranium concentration changing from 2×10^{-2} to 0.8×10^{-2} M with Dowex 1X4(100-200) are shown in Figures 2 and 3. Again the lines represent a fit of constant-diffusion-coefficient theory by adjusting $\bar{D}$. The values of $\bar{D}$ so determined are presented in Figures 4 and 5. The slope of the data in Figure 5 yields a diffusional activation energy of 13 kcal/mole. While this is rather high compared to aqueous solutions (3 to 6 kcal/mole) it is not unexpected since the retarding effect of the uranium-resin interaction is probably lessened by increased temperature.

These results, coupled with the equilibrium parameters reported in a previous paper,⁽¹⁾ should allow the numerical simulation of the performance of anion-exchange columns and other equipment for the processing of uranyl nitrate solutions. These computer techniques were developed for plutonium anion-exchange simulation and are described in previous work.^(5, 7)

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Fig. 1. Variation of Y with time [Dowex 1X4(50-100)]

Fig. 2. Variation of Y with time at various temperatures
[Dowex 1X4(100-200)]

Fig. 3. Variation of Y with time at various HNO_3 concentrations
[Dowex 1X4(100-200)]

Fig. 4. Dependence of $\bar{D}$ on HNO₃ concentration

Fig. 5. Dependence of $\text{Log}_e \bar{D} T^{-1}$