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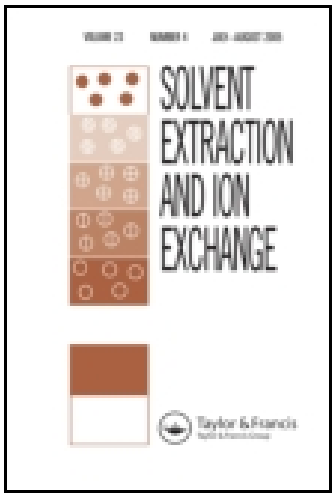

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Kinetic Studies of Some Actinide Ions Exchange on Al-13-Phosphatoantimonic Acid

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ABSTRACT

The kinetics of exchange of thorium and uranyl ions on Al-13-phosphato-antimonic acid (Al-13-PAA) was studied in nitrate solution at pH 1. The investigations were carried out under particle diffusion mechanism and the limited batch technique. The effects of particle size, concentration, and temperature have been studied. The effective diffusion coefficient, activation energy, and entropy of activation have been evaluated. The exchange capacity was evaluated and found to be 0.9 and 0.7 meq g^{-1} for uranyl and thorium ions respectively.

Key Words: Kinetic; Actinides; Thorium; Uranyl; Al-13-phosphato-antimonic acid; Ion exchange.

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INTRODUCTION

The importance of uranium arises from its use as fuel in nuclear reactors. However, thorium is industrially important because it is widely used in incandescent gas mantles. It is also used to prepare the ^{233}U isotope through the irradiation in the outer part of a nuclear reactor, which is used in breeder-type reactors. The need for recovery of actinides from active waste and other solutions will be in the point of interest as long as it is in use. The hazards due to the use of organic solvent extractors force the scientist to find suitable inorganic ion exchangers,[1] for removal of radioactive species in spite of their low capacity and slow kinetic of exchange.

The Al-13-phosphatoantimonic acid (Al-13-PAA), Al-13-$Sb_3P_2O_{14} \cdot xH_2O$, has been prepared by the interaction of the layered phosphatoantimonic acid,[2,3] and the Al-13 Keggin ion.[4] The capacity of the alkali metal ions Li^+, Na^+, and K^+ on Al-13-PAA acid has been evaluated and found to be 4.08, 4.32, and 7.2 meq g^{-1}, respectively. The stability, surface area, and ion exchange properties have also been evaluated.[4]

In this work the kinetics of extraction of thorium and uranium has been studied at pH = 1 from nitrate solution. The batch technique has been utilized under conditions of particle diffusion control.

EXPERIMENTAL

All reagents were of analytical grade (Aldrich) and used without further purification. The Al-13-PAA acid was prepared as described previously.[4]

The phosphatoantimonic acid was prepared by solid state reaction of ammonium phosphate, potassium nitrate, and antimony oxide at 950°C. The obtained antimonic acid, in the hydrogen form, is reacted with 0.2 mM Al-13 Keggin[5] ion at room temperature. The product was heated at 200°C overnight. The solid product was ground, sieved, and differentiated to different particle size. The particle diameters 0.1, 0.2, and 0.4 mm have been utilized to study the effect of particle size, and the particle diameter 0.1 mm was used for all other kinetic studies.

Kinetic studies were performed under particle diffusion control, and the limited batch technique was utilized.[6] Samples of 0.1 g of the exchanger were added to 10 mL of 1×10^{-3} M or 1.5×10^{-3} M metal nitrate solution; the different solution concentrations were used to study the concentration effects on the exchange rate. The V/m ratio, the ratio of the solution phase to the solid exchanger phase, of 100 $cm^3\,g^{-1}$ was utilized. The kinetics was studied at different temperatures 30, 40, and 60°C ± 0.5°C in a water shaker thermostat. At each predetermined period of time, the supernatant solution was quickly

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removed, and the metal ion concentrations were measured spectrophotometrically using the arsenazo III method.[7] A half mL of arsenazo III is added to 1 mL of the ion solution at equilibrium; then 1 mL of 0.1 M HNO_3 was added. The mixture was completed to 10 mL with deionzed water, left for 10 min, then measured spectrophotometrically against the reference at a wave length of 655 nm. A great deal of care must be followed in the case of thorium ion to avoid its adsorption on the walls of the glassware. Accordingly, polypropylene vessels were used.

The radius of the exchanger particles was determined by measuring the diameter of 100 particles with the aid of an optical microscope. The particles were assumed to be spherical, and a mean equivalent radius was calculated.

The saturation capacity was carried out by repeated equilibration of the solid phase with a new portion of element solution 1×10^{-3} M until no further uptake was detected at pH = 1. The concentration of the metal ions in the solution phase was analyzed and the uptake amount was calculated.

RESULTS AND DISCUSSION

Under particle diffusion control the following equation of Boyd et al.[8] can be applied.

$$F = \frac{Q_t}{Q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2Bt) \tag{1}$$

where Q_t is the percentage of exchange at time t, Q_e is that at equilibrium, and n is an integer number. $B = \pi^2 D_i/r^2$ where r is the particle radius of the exchanger. D_i, the effective diffusion coefficient, is obtained from Bt–t plots, where Bt is calculable mathematical function of F, and the values of Bt corresponding to each value of F are obtained from Reichenberg table.[9]

When $\ln D_i$ was plotted against $1/T$ straight lines were obtained, enabling the estimation of the energy of activation E_a and the pre-exponential constant D_o in the Arrhenius equation, $D_i = D_o \exp(-E_a/RT)$. The entropy of activation ΔS^* can then be calculated from D_o by applying the equation proposed by Barrer et al.[10]

$$D_o = 2.72\left(\frac{\mathrm{K}Td2}{\hbar}\right)\exp\left(\frac{\Delta S^*}{R}\right) \tag{2}$$

where D_o is a pre-exponential factor representing the hypothical self diffusion coefficient at absolute zero. K is the Boltzmann constant, T is the absolute temperature, d is the average distance between successive positions in the process of diffusion, taken to be 5 Å, $\hbar$ is Planck's constant and R is the gas constant.

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The distribution coefficients (K_d) of uranyl and thorium ions were found to be 89 and 100 mL g^{-1} at pH 1, respectively. The K_d value of uranyl ion on SnSb ion exchanger varies between 45 at pH 1 and 400 at pH 2.8.[11] The slopes of the straight lines are 1.82 and 3.66, which are close to theoretical values of the ion valences 2 and 4 for uranyl and thorium ions, respectively. These somewhat low values of the slopes related to valences may be due to partial hydration of the ions or limited nitrate complex formation.

The equilibrium uptake of 10^{-3} M uranyl and thorium ions as a function of pH are shown in (Fig. 1). The K_d values change linearly with the change in the hydrogen ion concentration. Similar results were obtained for uranyl ion exchanged on SnSbA exchanger as reported.[11]

The capacity measurements show that the Al-13-PAA can be loaded with about 0.9 and 0.7 meq g^{-1} for uranyl and thorium ions, respectively. However, the saturation capacity of uranyl and cobalt ions on tinantimonate ion exchanger are 0.6 and 0.5 meq g^{-1}, respectively, at pH = 2 and 30°C. In comparison, the Al-13-PAA shows higher capacities at lower pH. This increase favors actinides separation from high acid concentration.

The variation of the exchange rate as a factor of time shows that the rate of ion exchange is independent of concentration for the ions under investigation in the concentration range studied (Figs. 2 and 3). Also, the exchange rate is inversely proportional to the square of the reciprocal particle radius (Fig. 4).

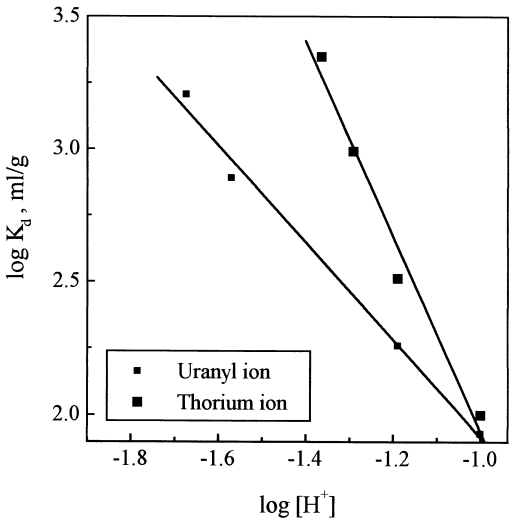

Figure 1. The effect of pH on the distribution coefficients of uranyl and thorium ion.

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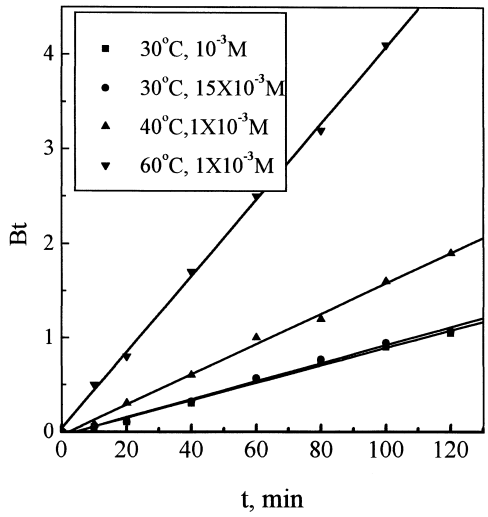

Figure 2. *Bt* vs. time for exchange of uranyl ion on Al-13-PAA at various temperatures and concentration.

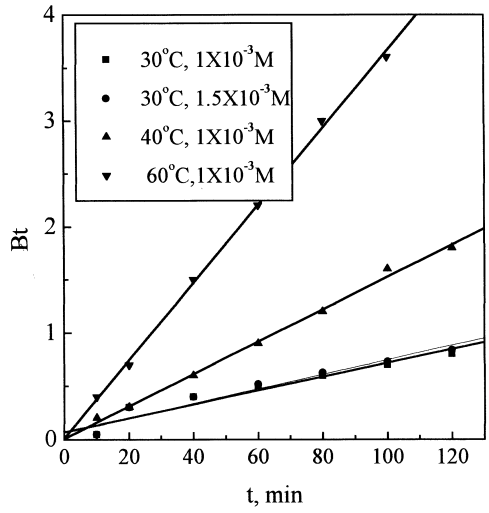

Figure 3. *Bt* vs. time for exchange of thorium ion on Al-13-PAA at various temperatures and concentration.

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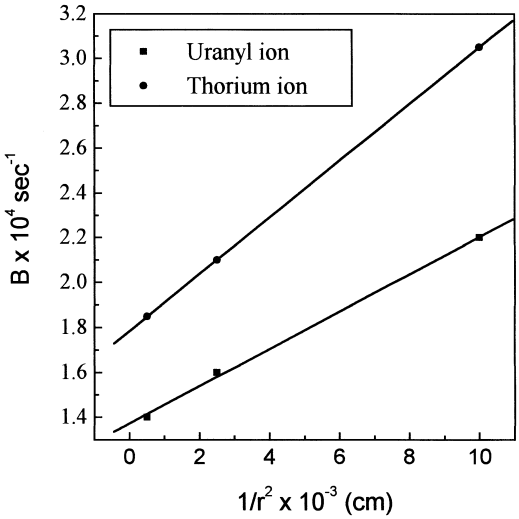

Figure 4. Plots of B vs. $1/r^2$ at 30°C.

Accordingly, the particle diffusion control can thus be deduced to be the mechanism of the exchange in all cases.

The Arrhenius plots show straight lines (Fig. 5), where the diffusion parameters and the activation energy have been calculated. The calculated values of the diffusion coefficient D_i, energy of activation E_a and entropy of activation ΔS^* are given in Table 1. The values of D_i are more than the obtained values for uranyl ion exchanged on tin antimonite SnSbA cation exchanger, $3.5 \times 10^{-9}\,\mathrm{cm^2\,sec^{-1}}$ at 30°C.[12] This may be due to the structure of the ion exchange materials. The Al-13-PAA possesses an open tunnel structure with surface area of about $245\,\mathrm{cm^2\,g^{-1}}$.[13] This nature of the exchanger allows the cations to be exchanged, primarily, in the hydrated form with a certain degree of free mobility, as will be discussed below.

The entropy of exchange depends on the extent of hydration of the ions exchanged along with the change in water content around the ion upon diffusion to the exchange site. The positive values of ΔS^* indicate that the ions are introduced to the exchange site in the hydrated form. This is also supported by the high value obtained for E_a. The values of D_i and ΔS^* for uranyl ion are higher than for the thorium ion. This can be explained in the light of the ionic radii of coordination number 6 for both ions as given in Table 1. The small size of the uranyl ion increases its mobility, accordingly increaseing ΔS^* and D_i. However, as the mobility of the cations increase the activation energy

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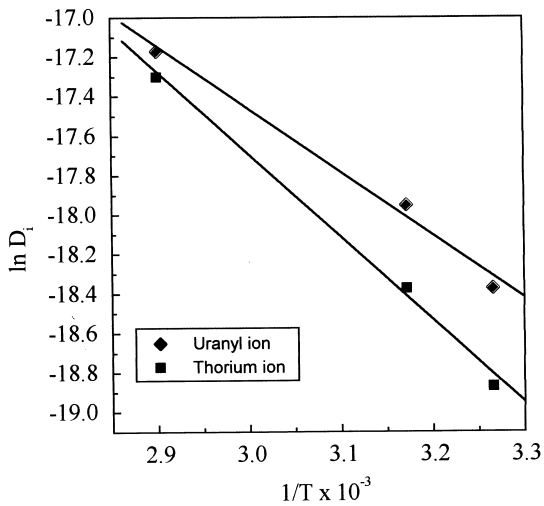

Figure 5. The Arrhenius plot of $1/T$ vs. $\ln D_i$.

decreases, as expected. E_a, also increases due to the higher positive charge of thorium than uranyl ion which increases the energy of activation required to achieve the dehydration inside the exchange sites.

CONCLUSION

The kinetics of the exchange of uranyl and thorium ions has been studied under particle diffusion control on the Al-13-PAA. The capacities for both ions were found to be 0.9 and 0.7 meq g^{-1} for uranyl and thorium ions, respectively. The thermodynamic parameters have been evaluated and interpreted in the light of the exchanger structure and the size of the related coordination

Table 1. Thermodynamic parameters for the diffusion of thorium and uranium on Al-13-PAA at different temperatures.

Exchange system	D_i ($cm^2 s^{-1}$)	D_o ($cm^2 s^{-1}$)	Ionic radii (pm)	E_a ($kJ mol^{-1}$)	ΔS^* ($J mol^{-1} K^{-1}$)
Th^{4+}/H^+	6.32×10^{-9}	7.00×10^{-2}	108*	40.89	4.16
UO_2^{2+}/H^+	1.01×10^{-8}	5.25×10^{-3}	87*	33.08	9.39

*Coordination number 6.

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number for the ions under investigation. The capacity and the rate of the exchange show that these are promising ion exchange materials for actinides separation from high acid concentration.

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