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ION-EXCHANGE KINETICS IN SYSTEMS WITH NON-LINEAR EQUILIBRIUM ISOTHERMS

SORPTION OF URANIUM(VI) ON STRONG ACID CATION EXCHANGERS

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SUMMARY

The kinetics of sorption of uranium(VI) from aqueous solutions on the strong acid cation exchangers Amberlite IR-120 and 200 was studied. The influences of the concentration of $\text{UO}_2(\text{NO}_3)_2$ in the range 10^{-3} – 10^{-1} M and of the temperature (298–332°K) were examined. The results were evaluated by means of an “ash model” modified for systems with non-linear equilibrium isotherms. It has been found that the applicability of the kinetic model depends not only on the solution concentration, but also on the type of cation exchanger used.

INTRODUCTION

In contrast to strong base anion-exchange resins, there is very little information about ion-exchange kinetics of U(VI) on strong acid cation exchangers. For example, the study of Florence and Bantley¹ concentrated on the electron exchange U(VI)–U(IV), but it also concerned the ion-exchange kinetics H^+ – UO_2^{2+} on the cation-exchange resin Dowex AG 50W (100–200 mesh). Boyd² diffusion models were used for the evaluation of the rate measurements.

Ion-exchange studies often involve the use of a suitable model to describe the given processes and for the evaluation of the experimental data. Besides classical diffusion models based on the Fick rules and the Nernst–Planck equation³, the “ash model” has been published^{4,5}. This model implies three types of rate-determining steps: liquid-film diffusion, diffusion through the so-called inert layer of the sorbent and chemical reaction taking place at the boundary of an unreacted nucleus. However, in the earlier papers^{4,5}, the “ash model” was derived for cases in which irreversibility of the corresponding chemical reaction or mass transfer can be assumed. This, of course, is only exceptionally true in ion-exchange systems. A generalization of this model for both irreversible and reversible systems (also for systems with non-linear equilibrium isotherms) and for batch and shallow-bed reactors was achieved by Štamberg and Cabicar⁶.

In this paper the generalized "ash model" is used in a more extensive study dealing with the U(VI) sorption kinetics on strong acid cation-exchange resins having gel and macroreticular structures, *i.e.*, Amberlite IR-120 and 200 respectively.

EXPERIMENTAL

Materials

Commercial samples of the strong acid cation exchangers Amberlite IR-120 and 200 were used. Samples were transformed by 0.1 M HCl solution into the hydrogen form and were then washed with water. The desired fractions, *i.e.*, 0.4–0.6 mm, were obtained by sieving in water.

Kinetic measurements

The volume, V_0 , of the U(VI) solution was brought to the desired temperature in a stirred reaction vessel (250 ml, 800 rpm) which was thermostatically heated in a water-bath ($\pm 0.1^\circ\text{K}$). When the desired temperature had been reached, the resin (H^+) was added. The samples of the resin were swollen in water, centrifuged (800 g) and weighed. Small aliquots of solution (*ca.* 2 ml) were removed at specified time intervals and the concentrations of U(VI) in them were determined by a spectrophotometric method using AZO 1⁷. The conditions of the experiments, *i.e.*, the volume V_0 , the weight of the resin, m , temperature and starting concentration of $\text{UO}_2(\text{NO}_3)_2$ solution, are summarized in Table I; the results are illustrated in Figs. 1 and 2.

TABLE I
CONDITIONS OF THE KINETIC EXPERIMENTS

Sorbent		$\text{UO}_2(\text{NO}_3)_2$ solution		Temperature ($^\circ\text{K}$) [*]
Type	Weight, m (g)	Starting volume, V_0 (ml)	Starting concn., c_{A_0} (M)	
Amberlite IR-120	1.7530	236.60	0.001	298
	0.9623	125.10	0.01	298
	0.5700	70.00	0.01	312
	0.5940	70.00	0.01	331.6
	2.6793	41.00	0.1	298
Amberlite 200	1.1390	150.30	0.001	298
	0.7410	88.90	0.01	298
	0.7781	93.40	0.01	312
	0.5830	70.00	0.01	331.6
	2.7450	41.10	0.1	298

* The influence of the temperature was studied for $C_{A_0} = 0.01$ M

Determination of the equilibrium isotherms

The ion-exchange equilibria were determined using the batch method. Samples of resin, *i.e.*, 0.1–1.0 g centrifuged resin in the swollen state and in the hydrogen form, were added to flasks containing different amounts of uranyl nitrate solution (10–100 ml) at the starting concentration 10^{-1} M, 10^{-2} M and 10^{-3} M respectively, and were contacted at 298°K, 312°K and 332°K for 10–15 h. The equilibrium concentrations

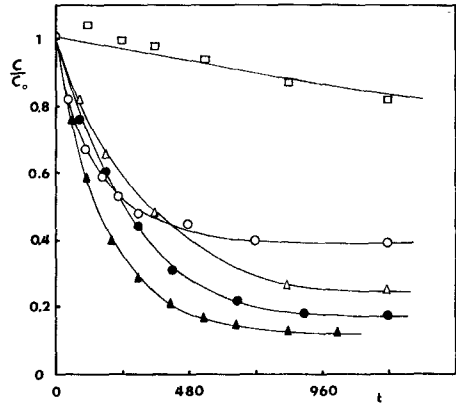
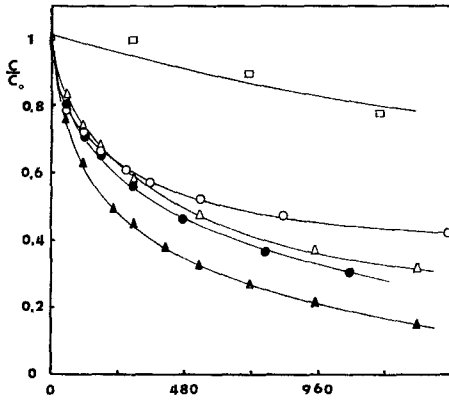


Fig. 1. Sorption kinetics of U(VI) on Amberlite IR-120, shown as dependence of mole fraction, c/c_0 , of $UO_2(NO_3)_2$ on time, t . Starting concentration, c_0 : \square , 0.001 M (298°K); \triangle , 0.01 M (298°K); \circ , 0.1 M (298°K); \bullet , 0.01 M (312°K); \blacktriangle , 0.01 M (331.6°K). Time (t) in seconds.

Fig. 2. Sorption kinetics of U(VI) on Amberlite 200. Details as in Fig. 1.

of U(VI) were determined by the spectrophotometric method using AZO I⁷. The experimental data at 298°K are illustrated in Figs. 3 and 4.

RESULTS AND DISCUSSION

The studied sorption systems differ in concentrations of U(VI) and in cation-exchange resin types. All the equilibrium sorption isotherms show non-linearity (see Figs. 3 and 4) and can be described by the Langmuir adsorption isotherm

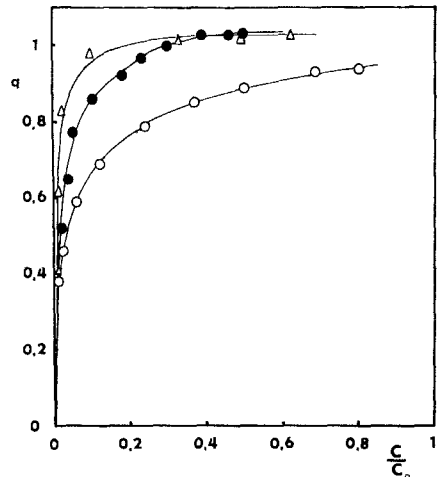
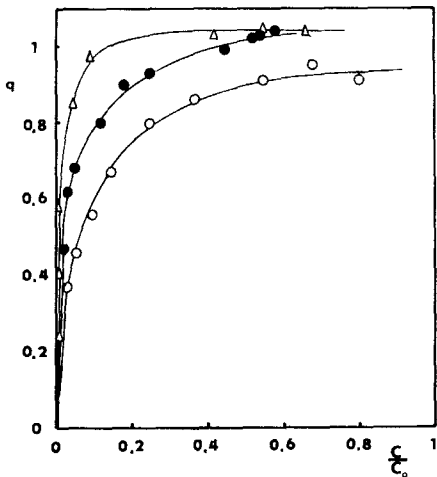


Fig. 3. Equilibrium sorption isotherms on Amberlite IR-120 at 298°K, shown as dependence of concentration of U(VI) in the sorbent, q , on concentration of U(VI) in the solution, c/c_0 . Starting concentration of $UO_2(NO_3)_2$ in the solution, c_0 : \bullet , 0.001 M; \triangle , 0.01 M; \circ , 0.1 M.

Fig. 4. Equilibrium sorption isotherms on Amberlite 200 at 298°K. Details as in Fig. 3.

(eqn. 7). The results of this correlation, *i.e.*, constants *a*, *b* and correlation coefficients, are given in Table II. Because of the non-linearity of the isotherms, the modified "ash model"⁶ was used for the evaluation of the ion-exchange rate curves (Figs. 1 and 2).

TABLE II

CONSTANTS OF THE SORPTION EQUILIBRIUM ISOTHERMS

The fit of the Langmuir isotherm equation was statistically evaluated by means of the Student's *t*-test. The differences between the calculated and measured points are not statistically significant: the level of significance is greater than 10% and the standard deviations of the differences are 6×10^{-6} – $5 \cdot 10^{-5}$.

Sorbent type	Starting concn. of $UO_2(NO_3)_2$ solution (M)	Temperature ($^{\circ}K$)	Constants of eqn. 7		Correlation coefficient
			<i>a</i>	<i>b</i>	
Amberlite IR-120	0.001	298	$3.083 \cdot 10^{-5}$	0.921	0.99
	0.01	298	$7.139 \cdot 10^{-5}$	0.948	0.99
	0.01	312	$7.130 \cdot 10^{-5}$	0.948	0.99
	0.01	331.6	$9.720 \cdot 10^{-5}$	0.918	0.99
	0.1	298	$4.389 \cdot 10^{-3}$	1.024	0.98
Amberlite 200	0.001	298	$2.349 \cdot 10^{-5}$	0.920	0.99
	0.01	298	$4.136 \cdot 10^{-5}$	0.969	0.99
	0.01	312	$4.130 \cdot 10^{-5}$	0.969	0.99
	0.01	331.6	$1.640 \cdot 10^{-5}$	0.964	0.99
	0.1	298	$3.806 \cdot 10^{-3}$	1.030	0.98

The following differential equations were used for the description of the three types of rate-determining processes.

Liquid-film diffusion:

$$\frac{dc_A}{dt} = -\frac{m}{V} \cdot \frac{3k_A}{Rq} (c_A - c_{AS}) \quad (1)$$

Inert-layer diffusion ("ash-layer" diffusion):

$$\frac{dc_A}{dt} = -\frac{m}{V} \cdot \frac{3D}{R^2q} \cdot \frac{(c_A - c_{AC})}{\left(1 - \frac{q_A}{Q_A}\right)^{-1/3} - 1} \quad (2)$$

Chemical reaction:

$$\frac{dc_A}{dt} = -\frac{m}{V} \cdot \frac{3}{Rq} \cdot r_A \left(1 - \frac{q_A}{Q_A}\right)^{2/3} \quad (3)$$

Also, for a reversible first-order monomolecular reaction:

$$r_A = k'_A(c_A - c'_A) \quad (4)$$

The meanings of the symbols in eqns. 1–4 are:

c_A = concentration of U(VI) in the solution at time *t*

t = time

m = mass of the centrifuged sorbent

V = volume of the solution

k_A = mass-transfer coefficient

R = radius of the sorbent particles

ρ = sorbent density

c_{AS} = concentration of U(VI) in the solution at the sorbent particle surface at time t , which is in equilibrium with the concentration in the sorbent

D = diffusion coefficient

c_{AC}, c'_A = concentration of U(VI) in the solution at the surface of the "non-reacted nucleus" at time t , which is in equilibrium with the concentration in the sorbent

r_A = rate of the chemical reaction

q_A = concentration of U(VI) in the sorbent which corresponds to the concentration c_A at time t

Q_A = equilibrium concentration of U(VI) in the sorbent which corresponds to the concentration c_A

The concentration q_A and equilibrium values c_{AS}, c_{AC}, c'_A and Q_A were calculated using eqns. 5-7

$$q_A = (V/m)(c_{A_0} - c_A) + q_{A_0} \quad (5)$$

$$c_{AS} \equiv c_{AC} \equiv c'_A = aq_A/(1 - bq_A) \quad (6)$$

$$Q_A = c_A/(a + bc_A) \quad (7)$$

where

c_{A_0} = starting concentration of U(VI) in the solution ($t = 0$)

q_{A_0} = starting concentration of U(VI) in the sorbent (equal to zero in all cases)

a, b = constants of the Langmuir isotherm

As analytical solutions are difficult, except for eqn. 1, numerical solutions of the differential eqns. 1-3 were obtained by means of an Hewlett-Packard 9830 calculator. The results of the calculations were evaluated by plotting $I_t = f(t)$,

In the case of liquid-film diffusion (model 1):

$$I_t = - \int_{c_{A_0}}^{c_A} dc_A / (c_A - c_{AS}) = K_i t \quad (8)$$

$$K_i = 3 mk_A / VR\rho \quad (9)$$

In the case of inert-layer diffusion (model 2):

$$I_t = - \int_{c_{A_0}}^{c_A} \frac{[(1 - q_A/(Q_A)^{-1/3} - 1)]}{(c_A - c_{AC})} dc_A = K_i t \quad (10)$$

$$K_i = 3 mD / VR^2\rho \quad (11)$$

In the case of chemical reaction (model 3):

$$I_t = - \int_{c_{A_0}}^{c_A} \frac{(c_A - c'_A)^{-1}}{(1 - q_A/Q_A)^{2/3}} dc_A = K_i t \quad (12)$$

$$K_i = 3 mk'_A / VR\rho \quad (13)$$

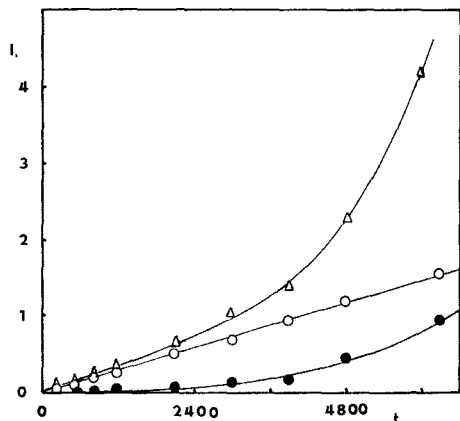


Fig. 5. Evaluation of kinetic model equations on Amberlite IR-120. Starting concentration of $\text{UO}_2(\text{NO}_3)_2$ solution: 0.001 M. Temperature: 298°K. Kinetic models: \circ , liquid-film diffusion (model 1); \bullet , inert-layer diffusion (model 2); \triangle , chemical reaction (model 3). Time (t) in seconds.

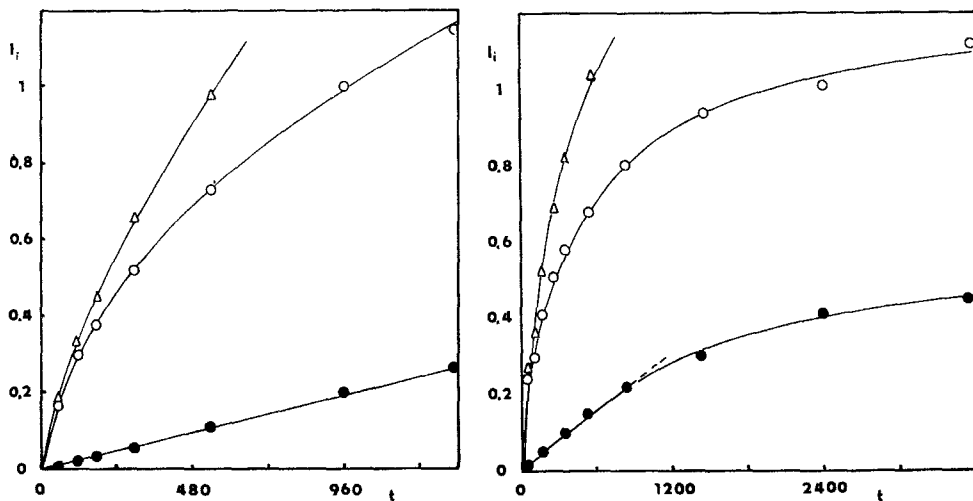


Fig. 6. Evaluation of kinetic model equations on Amberlite 200. Starting concentration of $\text{UO}_2(\text{NO}_3)_2$ solution: 0.01 M. Temperature: 298°K. Kinetic models: \triangle , model 1; \bullet , model 2; \circ , model 3. Time (t) in seconds.

Fig. 7. Evaluation of kinetic model equations on Amberlite 200. Starting concentration of $\text{UO}_2(\text{NO}_3)_2$ solution: 0.1 M. Other details as in Fig. 6.

If the $I_i = f(t)$ plot is linear and goes through the origin then $K_i = \text{constant}$ and the sorption of U(VI) is controlled by the i th process. Figs. 5–7 show the characteristic course of $I_i = f(t)$ for three representative systems. For all systems, the results, *i.e.*, K_i values and kinetic parameters calculated from them, are summarized in Table III.

It can be concluded that the type of the rate-determining process is dependent not only on the concentration of U(VI) in the solution but also on the structure of the strong acid cation-exchange resin. As far as the composition of the solution is con-

TABLE III

RESULTS OF THE KINETIC MEASUREMENTS

LFD = Liquid-film diffusion; ID = inert-layer diffusion; CHR = chemical reaction.

Sorbent	Starting concn. of $UO_2(NO_3)_2$ solution (M)	Temperature ($^{\circ}K$)	Rate-determining step	K_t (sec^{-1})	D ($m^2 sec^{-1}$)	k_A ($m sec^{-1}$)
Amberlite IR-120	0.001	298	LFD	$2.48 \cdot 10^{-4}$ *	—	—
	0.01	298	CHR	$3.43 \cdot 10^{-3}$	—	$4.14 \cdot 10^{-5}$
	0.01	312	CHR	$4.72 \cdot 10^{-3}$	—	$5.15 \cdot 10^{-5}$
	0.01	331.6	CHR	$6.07 \cdot 10^{-3}$	—	$6.17 \cdot 10^{-5}$
	0.1	298	ID	$6.83 \cdot 10^{-4}$	$5.66 \cdot 10^{-9}$	—
Amberlite 200	0.001	298	CHR	$4.20 \cdot 10^{-4}$	—	$4.79 \cdot 10^{-5}$
	0.01	298	ID	$2.13 \cdot 10^{-4}$	$5.72 \cdot 10^{-10}$	—
	0.01	312	ID	$3.03 \cdot 10^{-4}$	$8.07 \cdot 10^{-10}$	—
	0.01	331.6	ID	$5.17 \cdot 10^{-4}$	$1.32 \cdot 10^{-9}$	—
	0.1	298	ID	$2.63 \cdot 10^{-4}$	$2.13 \cdot 10^{-9}$	—

* $k_A = 3.06 \cdot 10^{-5} m sec^{-1}$.

cerned, the complexation of U(VI) can influence the results significantly and must not be neglected⁸. It was our intention to use an uranium(VI) salt with minimal complexation between cations and anions, which is the case of the $UO_2(NO_3)_2$.

According to our results, liquid-film diffusion is the rate-determining step only for sorption of U(VI) on Amberlite IR-120 from solutions having concentrations below $10^{-3} M$ U(VI) (Fig. 5). The chemical reaction appears to be the rate-determining process in the same concentration region for Amberlite 200 and for Amberlite IR-120 at 10^{-3} – $10^{-2} M$ U(VI) even for temperatures in the range 298–332°K. However, it should be pointed out that this "chemical reaction" is approximated by an equation for a reversible first-order monomolecular reaction which conforms with the film-diffusion equation. Therefore this rate-determining step (*i.e.*, model 3) need not be exclusively chemical in nature. The inert-layer diffusion process (model 2) is the most probable rate-determining step for Amberlite IR-120 at 10^{-2} – $10^{-1} M$ U(VI), but near the equilibrium a deviation from model 2 can be observed. The same result was obtained in the case of Amberlite 200 (Fig. 7). Undoubtedly inert-layer diffusion appears to be the rate-determining process for sorption of U(VI) on Amberlite 200 from the solutions with initial concentrations of $10^{-2} M$ U(VI) (Fig. 6) even at temperatures of 312 and 332°K.

The curves in Figs. 1 and 2 and also the values in Table III (see kinetic parameters for initial concentration of $10^{-1} M$) show that Amberlite IR-120 takes up U(VI) faster than Amberlite 200. Evidently, the reason lies in the different physical structure of the cation exchangers: the macroreticular type, even if it is a more selective sorbent for U(VI)⁸ (having a higher driving force for sorption), sorbs U(VI) more slowly than the gel-type resin. It can be also concluded from Figs. 1 and 2 that the sorption of U(VI) on Amberlite IR-120 is a little more temperature dependent than on Amberlite 200.

CONCLUSIONS

The results of the sorption kinetics of U(VI) on the strong acid cation exchangers Amberlite IR-120 and 200 were evaluated by means of liquid-film diffusion, inert-layer diffusion and chemical reaction models, modified for systems with non-linear equilibrium isotherms. It has been found that the applicability of these kinetic models depends not only on the solution concentration, but also on the type of cation exchanger used. In the case of Amberlite IR-120 only the region of the uranium(VI) concentration below $10^{-3} M$ is characterized by the liquid-film diffusion model. The chemical reaction and the "ash-layer" diffusion models are rate-determining for the concentration regions 10^{-3} – $10^{-2} M$ and 10^{-2} – $10^{-1} M$ U(VI), respectively. On the other hand, the inert-layer diffusion is the main rate-determining process in the case of Amberlite 200. The kinetics of the sorption of U(VI) on Amberlite IR-120 is faster than on Amberlite 200.

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