KINETICS OF CESIUM REACTIONS WITH SOME INORGANIC CATION EXCHANGE MATERIALS

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ABSTRACT

The kinetics of cesium exchange for sodium were studied in the film diffusion region for several cation exchange materials, including an alumina-silica gel, Type A synthetic zeolite, clinoptilolite, phillipsite, erionite and vermiculite. Existing techniques, including the "shallow bed" used to investigate cation exchange kinetics of organic resins, were applied to the above inorganic exchange materials. Results for the effects of temperature, flow rate, cesium concentration and competing sodium on film diffusion loading rates are given, as well as particle diffusion data. Cesium diffusion film thickness was computed by two methods with comparable results. Loading rates of inorganic cation exchangers can be predicted through use of fundamental kinetic data.

INTRODUCTION

Two diffusion mechanisms affecting the rates of cation exchange reactions are known (Boyd *et al.*, 1947). Exchange rates are controlled either by diffusion in and through the adsorbent or by diffusion across a thin concentration gradient or film surrounding the particle, depending upon the cation concentration in the contacting solution. A review of particle diffusion was presented previously (Ames, 1961). For the film diffusion region, diffusion within the particle is very fast relative to diffusion of the cation from the solution, across a concentration gradient surrounding the zeolite particle, and to the particle-solution interface. When diffusion of the cations across the surrounding film is slower than cation diffusion within the particle, liquid diffusion becomes the rate-controlling cation exchange mechanism. Liquid diffusion coefficients are a known quantity at the temperature and concentration of incoming cation used, and can be obtained from the literature (Harned *et al.*, 1953). For simplification of film diffusion data treatment, several assumptions are normally made:

1) film thickness is small compared to particle radius, and the film is spherical in shape,
2) film thickness is the same for the diffusion of cations in both directions, and
3) the exchange rate is controlled entirely by film diffusion.

These assumptions lead to the simple expression, $\ln(1 - F) = -Rt$ (Boyd *et al.*, 1947), for loading curves where the incoming cation is a microcomponent of the system. "F" is equal to the fraction of loading and "t" is the time elapsed since loading began. The constant "R" is equal to $3D^1/(r_0)(\Delta r_0)(\kappa)$, where

$D^1 =$ diffusion coefficient in the liquid,
$r_0 =$ particle radius, assuming a spherical shape,
$\Delta r_0 =$ film thickness, assuming uniformity in depth, and
$\kappa =$ an equilibrium distribution factor for the given cation system.

The value for the constant "R" is the quantity sought, which includes the liquid diffusion coefficient. A value for Δr_0 or κ may be computed if either one or the other is known. Adapting the techniques used to study the organic zeolites seemed to offer a fruitful approach to the study of inorganic cation exchange materials. It should be emphasized, however, that the present use of Boyd's equation is purely empirical. The equation was not originally derived to cover the experimental conditions of this study. Reichenberg's expression for initial loading rates (Reichenberg, 1953) more closely fits the experimental conditions.

It is the purpose of this paper to demonstrate that the same techniques used to describe the kinetics of organic ion exchange resins may also be utilized to describe the kinetics of inorganic cation exchangers.

METHODS OF INVESTIGATION

The kinetics of several zeolites were investigated during this study. The clinoptilolite used in this study was obtained from National Lead Company's Hector, California, leases. The erionite and phillipsite were from Nevada. The standard, six-to-one silica-to-alumina gel (hereafter referred to as gel) was purchased from the Permutit Company, and vermiculite from Libby, Montana, was purchased from Ward's Natural Science Establishment. Sodium-based pelletized Type A synthetic zeolite, containing 20 per cent by weight attapulgite, was obtained from the Linde Company. The natural zeolites erionite, phillipsite, and clinoptilolite were contaminated with 5 to 15 per cent unaltered glass, quartz and feldspar. The Libby vermiculite contained local interlayered biotite. The synthetic Type A zeolite and gel were composed of relatively pure materials. The approximate surface areas/gram of the inorganic exchange materials used in this study are given in Table I. Surface areas were determined by the standard B.E.T. nitrogen adsorption method (Brunauer *et al.*, 1938).

These cation exchange materials were crushed and a 0.25 to 0.50 mm diameter size range selected. The size range was eluted with several

TABLE I. SURFACE AREAS

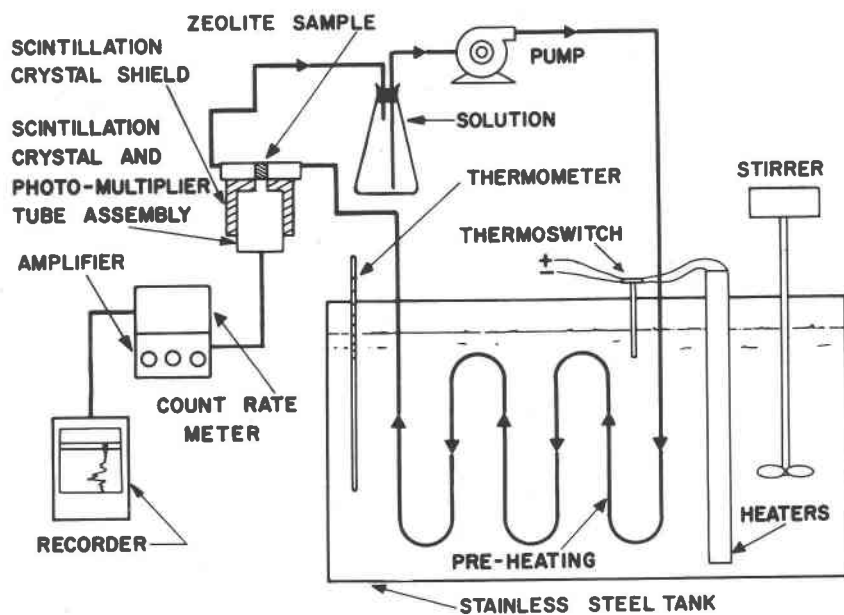| Exchanger	Surface area, m^2/g
Erionite	400–450
Clinoptilolite	15–20
Gel	125–150
Type A	10–15
Phillipsite	450–550

FIG. 1. Experimental apparatus used to obtain kinetic data.

volumes of one molar sodium chloride solution followed by a distilled water rinse and air-drying.

One-hundred and five-hundred milligram columns were used in the "shallow bed" apparatus shown in Fig. 1. The shallow-bed technique was reviewed previously (Ames, 1961). An influent solution containing a gamma-emitting, tracing radioisotope was pumped through the shallow bed of cation exchanger. As the exchanger was loaded with the radio-isotope, the resulting increase in radioactivity was recorded by means of a sodium iodide crystal and multiplier photo tube in conjunction with a gamma spectrograph and count-rate meter.

To obtain "background" for a given influent, a bed of quartz of the same size range and volume as the zeolite bed was filled with influent and counted. This procedure gave the number of radioisotope counts to subtract from the zeolite loading curve obtained with the same in-fluent, and represents the constant counts contributed by influent solu-tion in the voids between zeolite particles. Counts from void solution contribute a significant per cent of the total bed radioactivity only in the first few seconds of bed loading.

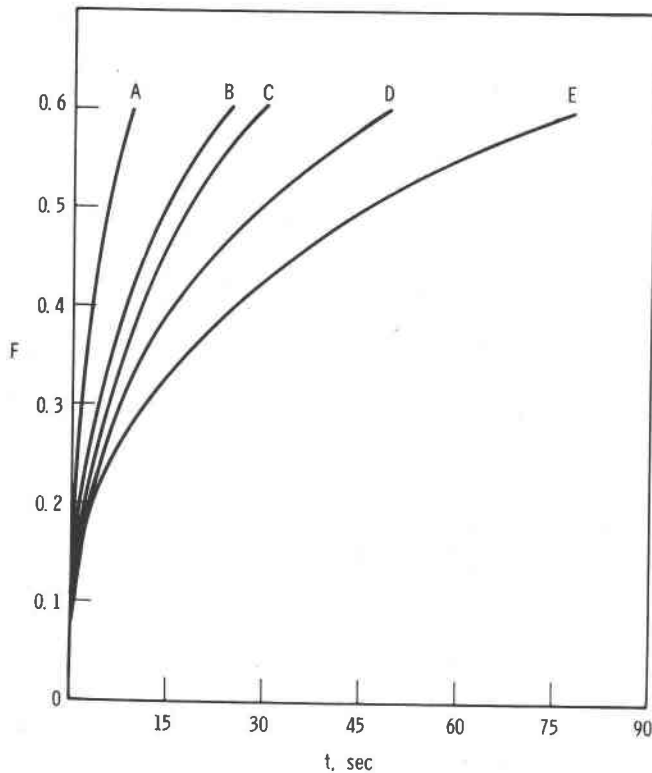Cesium-134, obtained from Oak Ridge, was used as a cesium tracer.

FIG. 2. Curves of cesium loading fraction *vs.* time in the particle diffusion region. Experimental conditions and loading rates for the lower temperatures below are listed under Table II.

Designation	Exchanger	Temperature, °C.
A	Erionite	35
B	Phillipsite	31
C	Type A	29
D	Clinoptilolite	29
E	Gel	29

Cesium-137 has a barium-137 daughter that changes the apparent shape of the cesium-137 loading curve in some instances. Reagent grade chemicals in distilled water solutions were used throughout as influents. Compositions of solutions and other experimental conditions are listed wherever results are given. All zeolite beds were fully loaded as indicated by the leveling-out of the continuous recording of radioisotope loading. Certain of these beds were then analyzed for radioactivity-gram and compared to radioactivity/milliliter of influent to obtain a loading curve.

TABLE II. PARTICLE DIFFUSION DATA FROM FIG. 2

Exchanger	Temperature, C.	B, sec^{-1}	D^i, cm^2/sec	Ea, kcal/mole
Phillipsite	31	0.02222	7.88×10^{-7}	
Phillipsite	45	0.02380	8.44×10^{-7}	1.1
Erionite	35	0.04666	1.65×10^{-6}	
Erionite	55	0.06001	2.13×10^{-6}	2.6
Type A	29	0.01777	6.30×10^{-7}	
Type A	52	0.02933	1.04×10^{-6}	4.3
Clinoptilolite	29	0.01095	3.88×10^{-7}	
Clinoptilolite	30	0.01435	5.09×10^{-7}	5.0
Gel	29	0.00710	2.52×10^{-7}	
Gel	50	0.01435	5.09×10^{-7}	6.5
Vermiculite	47	1.41×10^{-5}	5.3×10^{-10}	>15

Influent solution—0.3N CsCl plus $1.0 \times 10^{-7} N$ Cs^{131}
Influent pH   —6.0
Flow rate   —12.8 l/hr/cm^2
Temperature   —as indicated
Shallow beds   —500 mg, 0.25 to 0.50 mm, sodium based exchangers
B   —Loading rate, sec^{-1}
D^i —Apparent particle diffusion coefficient, cm^2/sec

Since the cesium content of the influent is known, the cesium load on the zeolite can be readily computed from the radioactivity ratio. The loading curve relationships (mg cesium/g zeolite $vs.$ time) may not be similar to kinetic curve relationships (fraction of loading $vs.$ time). If the zeolites all have about the same cation exchange capacities, the two sets of curves will have nearly the same slopes.

Activation energies were computed by ascertaining the effect of temperature on the loading rate of the exchanger (Daniels and Alberty, 1955).

RESULTS

Figure 2 shows several curves of loading fraction $vs.$ time in the particle diffusion region. Data derived from these curves are presented in Table II. Reaction rates and apparent diffusion coefficients for clinoptilolite and erionite were reported previously, but were rerun for this study since loading rates are a function of particle radius (Ames, 1961). The apparent discrepancy in the two reported loading rates is due to the dif-
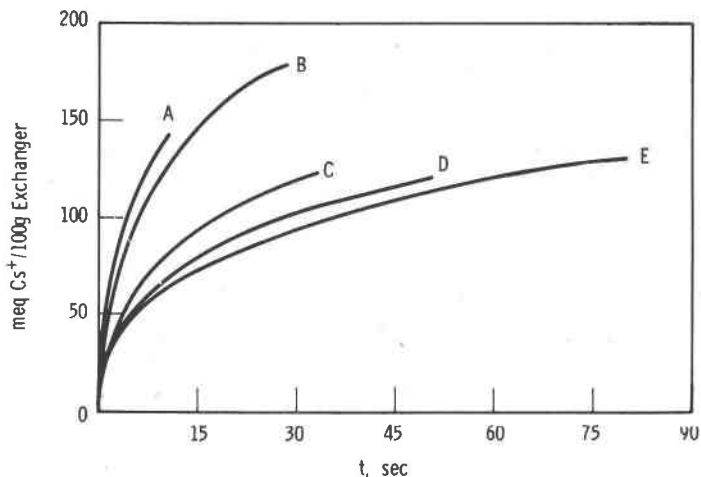
FIG. 3. Cesium loading curves in the particle diffusion region,
representing a replot of the data from Fig. 2.

Designation	Exchanger	Cesium capacity, meq/100 g
A	Erionite	226
B	Phillipsite	287
C	Type A	200
D	Clinoptilolite	200
E	Gel	217

ferences in the average grain size of the two samples. Note that activation energies for the sodium-cesium exchange reaction are generally quite low except for vermiculite, whose loading fraction curve could not be conveniently presented in Fig. 2. In the latter case, the activation energy of the rate-controlled diffusion mechanism is of the same order of magnitude as that of many chemical reactions. Figure 3 gives the loading curves of the exchange materials for which the kinetics were presented in Fig. 2. Table III shows the results of an attempt to fit Boyd's film diffusion equation to two points on a set of curves obtained in the film diffusion region of cesium concentration. The fit obtained in most cases is as good as that obtained by Boyd, using organic cation exchange resins. Figure 4 presents the curves from which the data of Table III were computed. These curves may be compared with those for particle diffusion shown in Fig. 2.

Table IV shows the effect of temperature on loading rates for some of the exchange materials. The magnitude of these temperature effects are of the same order as temperature effects on the liquid diffusion coeffi-

TABLE III. TEST OF EQUATION-CURVE FIT

Exchanger	Sec. at 0.2 F	R at 0.2 F, sec⁻¹	Sec at 0.3 F	R at 0.3 F, sec⁻¹
Erionite	90	0.00248	141	0.00252
Phillipsite	138	0.00161	213	0.00167
Type A	168	0.00132	255	0.00139
Clinoptilolite	184	0.00120	276	0.00129
Gel	195	0.00114	294	0.00121

Influent solution—$1.0\times10^{-3}N$ CsCl plus $1.0\times10^{-8}N$ Cs^{134}
Influent pH   —6.0
Temperature   —25C
Flow rate   —12.8 l/hr/cm²
Shallow beds   —500 mg, 0.25 to 0.50 mm, sodium-based exchangers

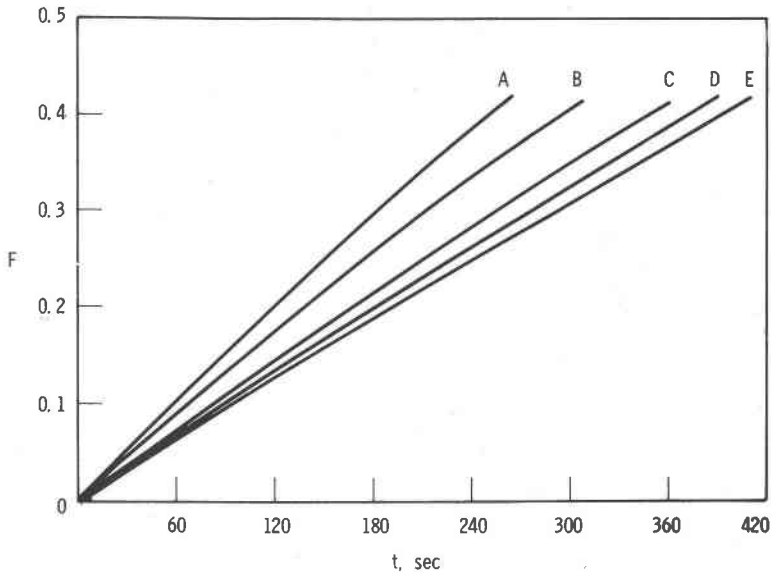

FIG. 4. Curves of cesium loading fraction vs. time in the film diffusion region. Experimental conditions are listed under Table III.

Designation	Exchanger
A	Erionite
B	Phillipsite
C	Type A
D	Clinoptilolite
E	Gel

TABLE IV. EFFECT OF TEMPERATURE ON LOADING RATES

Exchanger	R at 27 C, sec^{-1}	R at 50 C, sec^{-1}
Erionite	0.0024	0.0051
Clinoptilolite	0.0012	0.0031
Vermiculite	0.0013	0.0033
Type A	0.0013	0.0031

Influent solution—$1.0 \times 10^{-3} N$ CsCl plus $1.0 \times 10^{-8} N$ Cs^{134}
Influent pH   —6.0
Temperature   —as indicated
Flow rate   —12.8 l/hr/cm^2
Shallow beds   —500 mg, 0.25 to 0.50 mm, sodium based exchangers

cients. For example, Garrels *et al.* (1949) list the diffusion coefficient for K$^+$ as 1.69 cm^2/day at 25 C. and 5.6 cm^2/day at 100 C.

Table V illustrates the effect of flow rates on the loading rate of erionite. Note that within the flow rate range studied, R is proportional to flow rate change as reported earlier for organic resins.

Reichenberg (1953) presented a more generalized expression for the loading curve in the film diffusion region that showed the initial exchange rate directly proportional to the concentration of incoming cation. Table VI, the effect of cesium concentration on loading rates, shows that a variation of ten in the cesium concentration causes approximately a factor of ten variation in the loading rate.

The quantity R was found to vary inversely with particle radius, as predicted by the equation. Table VII illustrates the effect of particle size on R of Type A. Temperature also changed R by altering the liquid diffusion coefficient for the cation.

TABLE V. EFFECT OF FLOW RATE ON THE LOADING RATE OF ERIONITE

Exchanger	Flow rate, l/hr/cm^2	R, sec^{-1}
Erionite	19.2	0.00317
Erionite	12.8	0.00224
Erionite	4.4	0.00077
Erionite	0.6	0.00017

Influent solution—$1.0 \times 10^{-3} N$ CsCl plus $1.0 \times 10^{-8} N$ Cs^{134}
Influent pH   —6.0
Temperature   —24C
Flow rate   —as indicated
Shallow beds   —500 mg, 0.25 to 0.50 mm, sodium-based erionite

TABLE VI. EFFECT OF CESIUM CONCENTRATION ON LOADING RATES

Exchanger	Cesium normality	R, sec⁻¹ 1.0×10⁻⁴N CsCl	Cesium normality	R, sec⁻¹ 1.0×10⁻³N CsCl
		R, sec⁻¹		R, sec⁻¹
Erionite	1.0×10^{-4}	0.00043	1.0×10^{-3}	0.0051
Clinoptilolite	1.0×10^{-4}	0.00034	1.0×10^{-3}	0.0031
Vermiculite	1.0×10^{-4}	0.00034	1.0×10^{-3}	0.0033
Type A	1.0×10^{-4}	0.00033	1.0×10^{-3}	0.0031

Influent solutions—Cesium chloride concentrations as indicated plus $1.0\times10^{-8}N$ Cs134
Influent pH   —6.0
Temperature   —$1.0\times10^{-4}N$ CsCl at 42C, $1.0\times10^{-3}N$ CsCl at 50C
Flow rate   —12.8 l/hr/cm²
Shallow beds   —500 mg, 0.25 to 0.50 mm, sodium-based exchangers

DISCUSSION

The average diffusion film thickness, Δr, may be computed by two methods. Both are approximations developed primarily to describe organic resin kinetics (Boyd *et al.*, 1947, and Reichenberg, 1953). To utilize Reichenberg's technique, one first determines the quantity "dθ/dt (initial)" in the expression,

$$d\phi/dt \text{ (initial)} = \frac{3D^1}{(r)(\Delta r)} \text{ [cation]},$$

where

D^1 = the liquid diffusion coefficient for the ingoing cation in cm²/sec,
r = the particle radius in cm,
[cation] = concentration of the incoming cation, and
dϕ/dt = the initial slope of the loading curve in meq/ml/sec.

TABLE VII. EFFECT OF AVERAGE PARTICLE RADIUS ON CESIUM LOADING RATES.
USE OF AN AVERAGE PARTICLE SIZE ASSUMES A NORMAL SIZE
DISTRIBUTION OVER THE RANGE GIVEN

Exchange	Diameter range, mm	Average radius, mm	R, sec⁻¹
Type A	0.50 to 0.75	0.3125	0.0008
Type A	0.25 to 0.50	0.1875	0.0013
Type A	0.10 to 0.25	0.0875	0.0028

Influent solution—$1.0\times10^{-3}N$ CsCl plus $1.0\times10^{-8}N$ Cs134
Influent pH   —6.0
Temperature   —25 C
Flow rate   —12.8 l/hr/cm²
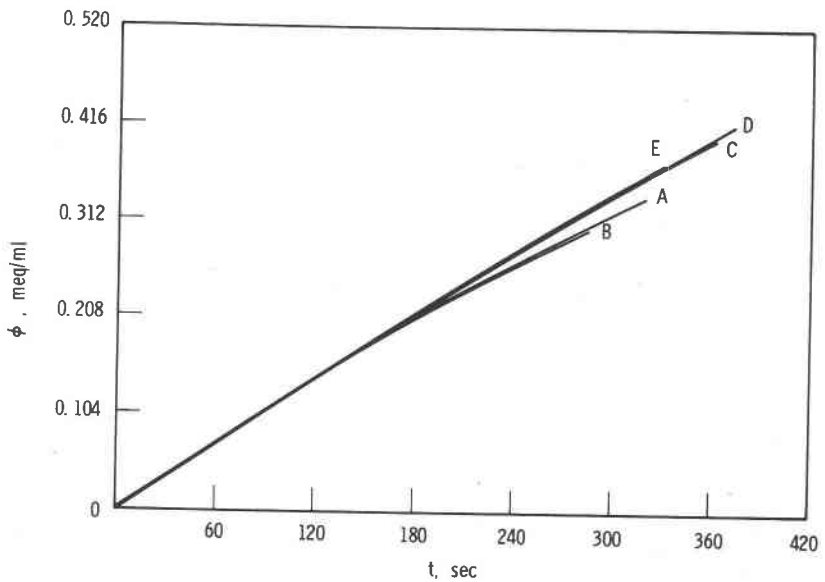Shallow beds   —500 mg, sodium-based Type A

FIG. 5. Curves of ϕ (cesium meq/ml of bed) vs. time in the film diffusion region, representing a replot of the data of Figure 4. Cesium capacities are with a $1.0 \times 10^{-3}N$ CsCl influent.

Designation	Exchanger	Cesium capacity, meq/g	Bed density, g/ml	Cesium capacity, meq/ml
A	Erionite	1.7	0.41	0.70
B	Phillipsite	2.2	0.35	0.78
C	Type A	1.3	0.73	0.95
D	Clinoptilolite	1.4	0.75	1.04
E	Gel	1.5	0.77	1.16

This is accomplished by plotting bed exchange capacity in milligram equivalents per milliliter vs. the time elapsed since loading began. An example of this type of plot is given in Fig. 5, which represents a replot of the data from Fig. 4. Note that initial $d\phi/dt$ values for these curves are the same. Thus the cesium diffusion film thickness will be the same for curves run under the same experimental conditions including temperature and flow rate. In this instance,

$$r = 0.02 \text{ cm,}$$
$$Cs^+D^1 = 1.03 \times 10^{-5} \text{ cm}^2/\text{sec (Harned } et\ al., 1953),$$
$$Cs^+ = 1.0 \times 10^{-3}N, \quad \text{and}$$
$$d\phi/dt = 0.00116 \text{ meq/ml/sec.}$$

Thus,

$$\Delta r = \frac{3(1.03 \times 10^{-5})}{(0.02)(0.00116)} (1.0 \times 10^{-3})$$

= 13.3µ, average film thickness for cesium diffusion.

To compute Δr_0 (Boyd's notation), a κ term must be determined experimentally, as well as a loading rate, R (Boyd *et al.*, 1947). As an illustrative example,

clinoptilolite $\kappa = 1.04 \times 10^3$, and

clinoptilolite R, from Table III, equals 0.0012 sec⁻¹.

Thus,

$$\Delta r_0 = \frac{3(1.03 \times 10^{-5})}{(0.02)(0.0012)(1.04 \times 10^3)}$$

= 12.4µ, average film thickness for cesium diffusion.

The other exchange materials would have their own characteristic κ and R values. The agreement between the Δr values computed with the two techniques is notable. Boyd *et al.*, and Reichenberg, reported film thicknesses of 4 to 6 μ compared to the 12 to 13 μ value obtained in this study. The latter values are larger, due mainly to the lower temperature
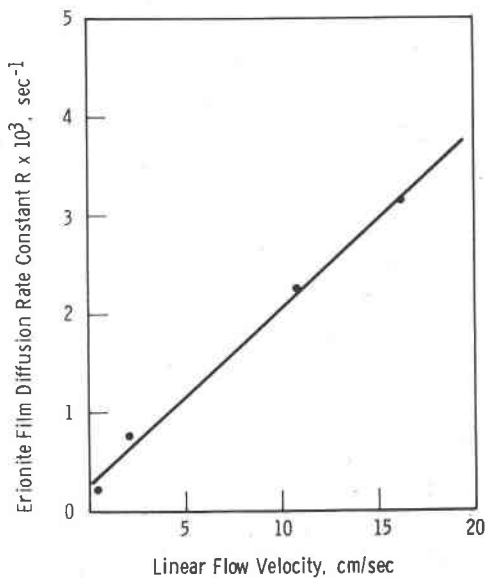

FIG. 6. The variation of erionite loading rate with linear flow velocity. Experimental conditions are listed under Table V.

and slower flow rate used in this study. Figure 6, for example, shows the linear relationship between the loading rate R (and hence Δr) and the linear flow velocity for erionite. Boyd *et al.* used a standard flow rate of 18 l/hr compared to 10 l/hr of this study. Boyd's temperatures were likewise five degrees higher. Another factor in the two different film thicknesses (although found to be a surprisingly small one) is the difference in the degree of roundness between the inorganic exchangers and the organic resins.

By consideration of the two diffusion mechanisms of organic resins, particle and film diffusion, inorganic cation exchange kinetics also can be characterized. Determination of fundamental kinetic quantities, such as particle diffusion coefficients and average film depths, allows computation and prediction of loads and loading rates of the exchange materials under given experimental conditions.

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