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Particle Diffusion Kinetics Of Alkaline Metal Ions In Granular Stannic Phosphotungstate



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ABSTRACT

The sorption kinetics and intraparticulate diffusivity of alkaline earth cations from aqueous solution using granular stannic phosphotungstate was investigated. The amount adsorbed increased as time increased, reaching equilibrium at about 60 minutes. The mechanism of sorption was found to be particle diffusion controlled. The effect of concentration of the exchanging ion, and the effects of particle size on the kinetics of ion exchange for different cations were studied. The results show that Stannic phosphotungstate is an efficient sorbent for the alkaline earth cations with particle diffusion as the predominant mechanism.

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KEYWORDS

Stannic phosphotungstate;
Adsorption;
Kinetics;
Intraparticle diffusivity;
Alkaline earth cations;
Hydrated raddi.

INTRODUCTION

The importance of a cation-exchanger is associated with the rate at which it can exchange ions from the test solution. A fast exchange would increase its applicability while slow exchange would keep its use limited. A solution to the problem of synthesizing high quality ion-exchangers, as well as rational approach to the selection of optimum operating conditions for the ion-exchange units and the regeneration of ion-exchangers lies with a detailed knowl-

edge of both equilibrium and kinetic data. While most of the studies have been concerned with the statics of the ion-exchangers, kinetics has been studied to a lesser extent.

The study of the exchange kinetics for the systems like metal ion-exchanger phase had been limited only to the organic resins^[1,2]. In case of phosphatic clay, precipitation and surface sorption reactions may occur simultaneously due to presence of both apatite and clay minerals^[3]. Pb sorption kinetics in phosphatic clay are biphasic, initially rapid re-

action followed by slow continuous sorption reaction most likely resulting from precipitation, followed by ion exchange, complexation and slow diffusion^[4]. Sorbents consisting of a metal chelating ligand which interacts with the heavy metal ions specifically, and a carrier matrix which may be an inorganic material (e.g. activated carbon, alumina, silica, or glass) or polymer micro spheres (e.g., polystyrene) have also been reported^[5,6] in use for Arsenic removal by diffusion. Few references^[7-8] are available for kinetic studies on inorganic ion-exchangers, like zirconium phosphate, zirconium arsenophosphate, tin(IV) arsenophosphate, tin(IV) antimonophosphate etc, probably due to the sluggish ion-exchange kinetics of such materials.

However, studies on the thermodynamic treatment on zeolites are available and reveal that there are distinct inter-planar spaces available for exchange. The application of high pressure kinetic techniques in the study of inorganic, organometallic and bioinorganic reaction mechanisms in solution, has received significant attention from numerous groups over the past decade^[9]. The kinetic sorption of cesium and strontium ions were investigated and revealed that the intraparticle diffusion was the rate limiting step for the sorption of cesium and strontium^[10]. Active carbon is a good adsorbent for lead ions, and the kinetics of the adsorption are rapid in the initial stage followed by a slow rate^[11].

Rates of ionic diffusion have been correlated with activity factors and state of hydration of the diffusing cations^[12-14]. Activation energies for self-diffusion processes have been correlated with polarizability of the cations^[1]. Mekhail et al^[15] observed that the mechanism of exchange of Cs⁺ ions on $\text{KCu}[\text{Co}(\text{CN})_6]$ varies from film diffusion to particle diffusion and finally becomes chemically controlled as Cs⁺ ion concentration increases. The self-diffusion coefficients, energies of activation and entropies of activation were calculated for the forward and reverse Na⁺-H⁺ and K⁺-H⁺ exchanges on tin arsenophosphate by Varshney et al^[16].

With this background and in the absence of sufficient literature on exchange kinetic studies, it becomes necessary to study the exchange mechanism in synthetic inorganic ion-exchangers. The present

work is a study of exchange kinetics of alkaline-earth metal ions under different conditions of temperature, exchanging ion concentration and particle size of the exchanger on stannic phospho tungstate. This material has been characterized as a weakly acidic, monofunctional cation-exchanger synthesized in the laboratory.

EXPERIMENTAL

Synthesis of tin(IV) phosphotungstate

Sodium tungstate solution (1M) was added to stannous chloride solution (1N) in the presence of sulphuric acid (5N), hydrogen peroxide (0.3%) and phosphoric acid (5N). Flocculating agent (1.5ppm) was added to the reaction mixture. The whole process of synthesis is carried out at pH 0-1. Reaction time of 1hr was allowed for complete formation of gel and then the gel precipitates were washed with dematerialized water till acid free. The resulting precipitates were left in water at room temperature for 24 hours for growth of the particle size. Supernatant liquid was decanted and washed the precipitates with DM water. Then the precipitate was centrifuged at 900R.P.M. for 30 minutes and dried in hot air circulated oven at 45°C. The whole mass of precipitates became compact solid after about 72 hours of drying. The dried product broke down to small granules when immersed in water. The granular particles of the compound were again air dried at 45°C in oven and collected the material. The product was found compatible for fixed bed column operations. Five such samples were synthesized at different intervals of time for various studies.

Characterization

The absorption band in the infrared spectrum of SnPW is of medium and weak intensities at 470cm⁻¹, 490cm⁻¹ and 506cm⁻¹ respectively and shows the presence of Sn-O group. High intensity band at 1050cm⁻¹ indicate the compound has PO₄³⁻ groups. The spectrum has a medium intensity band at 1398cm⁻¹ that shows the presence of P=O groups attached to the compound. The spectrum shows that coordinated water molecules are present with the compound as indicated by a medium intensity band at 1636cm⁻¹.

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Medium intensity band at 2360cm^{-1} and a weak intensity band at 3389cm^{-1} indicate the presence of O-H groups.

X-Ray diffractogram of the compound shows no sharp peaks. The compound seems to be amorphous in nature. Ion-exchange characteristics like ion-exchange capacity and composition were confirmed before proceeding for the exchange kinetic studies.

Exchange kinetic studies

The ion-exchange was fractionated into different particle sizes (18/30, 30/52.52/72 and 72/100 mesh size). Mesh size 72/100 was used for all kinetic studies, while the remaining fractions were used for the particle size effect. The hydrated salts of MgCl_2 , CaCl_2 , SrCl_2 and BaCl_2 were used as electrolytes.

The exchange kinetic studies were conducted by carrying out isothermal batch-wise experiments at

selected temperatures, concentrations and particle sizes by shaking 0.2g of the exchanger material with 20mL of the exchanging electrolyte solution. The cation concentrations in the aqueous phase before and after the exchange were determined by complexometric titrations with standard EDTA solution.

RESULTS

F values for Cd^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} at different temperature are given in TABLE 1. Plots of F (i.e. fraction of total amount of ions undergoing exchange) vs t (time) are drawn for all the exchanging cations at different temperature and are shown in figure 1. The effect of concentration of the exchanging ion on the exchange kinetics was studied. The results for Ca^{2+} - H^+ exchange are given in TABLE 2. The effect of particle size on the kinetics of ion-

TABLE 1: F values as a function of time for alkaline earth metal ion H^+ ion exchange on stannic phosphotungstate at different temperatures

t (Seconds)	Cd^{2+}				Ca^{2+}				Ba^{2+}				Sr^{2+}			
	298 K	303 K	308 K	313 K												
5	0.21	0.28	0.24	0.18	0.33	0.43	0.4	0.38	0.09	0.18	0.22	0.18	0.24	0.31	0.26	0.2
10	0.28	0.45	0.42	0.4	0.38	0.58	0.53	0.56	0.14	0.23	0.32	0.35	0.35	0.42	0.42	0.36
15	0.37	0.59	0.58	0.52	0.48	0.68	0.62	0.64	0.16	0.25	0.34	0.36	0.42	0.51	0.45	0.42
30	0.46	0.71	0.69	0.59	0.53	0.8	0.71	0.75	0.23	0.27	0.39	0.39	0.51	0.62	0.52	0.45
60	0.58	0.8	0.77	0.67	0.63	0.84	0.8	0.84	0.27	0.3	0.41	0.45	0.59	0.7	0.55	0.52
120	0.65	0.85	0.82	0.74	0.68	0.86	0.83	0.9	0.3	0.35	0.45	0.5	0.62	0.73	0.58	0.55
180	0.73	0.88	0.84	0.78	0.7	0.88	0.86	0.92	0.34	0.36	0.45	0.53	0.65	0.77	0.58	0.61
300	0.77	0.9	0.86	0.8	0.72	0.9	0.88	0.95	0.35	0.41	0.48	0.55	0.67	0.78	0.61	0.61
600	0.85	0.94	0.9	0.82	0.74	0.9	0.92	0.95	0.36	0.43	0.5	0.57	0.67	0.8	0.67	0.65

TABLE 2: F values as a function of time for Ca^{2+} - H^+ exchange at different concentrations of the electrolyte at 308K

t (seconds)	Concentration of Ca^{2+} Ions (M)			
	5×10^{-3}	1×10^{-2}	1.5×10^{-2}	2×10^{-2}
5	0.42	0.38	0.32	0.24
10	0.48	0.44	0.4	0.38
15	0.62	0.60	0.54	0.42
30	0.68	0.66	0.62	0.48
60	0.78	0.70	0.64	0.54
120	0.82	0.76	0.7	0.56
180	0.84	0.8	0.72	0.6
300	0.86	0.82	0.74	0.62
600	0.9	0.84	0.74	0.62

TABLE 3: F values as a function of time for Ca^{2+} - H^+ exchange for different particle sizes of exchanger at 308K

t (seconds)	Particle size (cm)			
	1.5×10^{-2}	2.1×10^{-2}	3×10^{-2}	5×10^{-2}
5	0.42	0.36	0.32	0.3
10	0.48	0.44	0.38	0.36
15	0.56	0.5	0.44	0.4
30	0.66	0.62	0.56	0.52
60	0.76	0.68	0.62	0.58
120	0.8	0.78	0.7	0.62
180	0.85	0.8	0.74	0.64
300	0.86	0.8	0.78	0.66
600	0.86	0.82	0.8	0.7

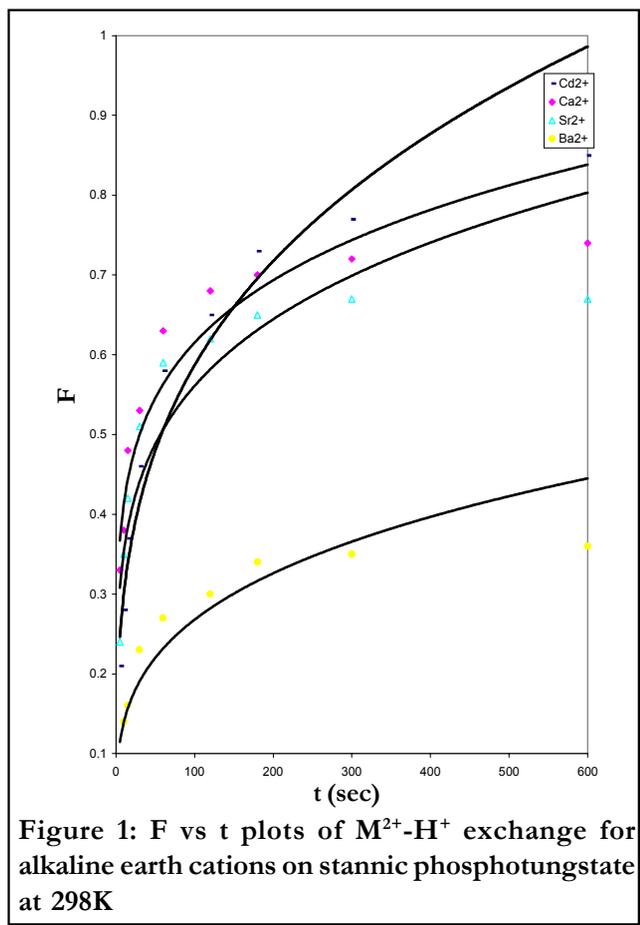


Figure 1: F vs t plots of M^{2+} - H^+ exchange for alkaline earth cations on stannic phosphotungstate at 298K

exchange for different cations was studied and the results for Ca^{2+} - H^+ exchange are given in TABLE 3.

DISCUSSION

Rate controlling step

In an ion-exchange process, an ion from the electrolyte can either undergo an exchange process due to the electrostatic forces between the fixed anionic groups of the exchanger and the electrolytic cation or through a pure diffusion process. If the exchange rate is dependent on the particle size of the exchanger, it clearly indicates a diffusion controlled process and not the one controlled by chemical interaction of the exchanging ions. So, the rate controlling step is the diffusion controlled process which may or may not be followed the electrostatic exchange of ions. With this objective, the effect of particle size on the exchange kinetics was studied. The extent of an ion-exchange reaction, F is expressed as

$$F = \frac{\text{The amount of exchange at any time, } t}{\text{The amount of exchange at infinite time, } t_{\infty}} \quad (1)$$

F is plotted as a function of time t in figure 1. It indicates that particle diffusions of ions within the exchanger constitute the rate controlling mechanism. The solution in contact with the exchanger is always rich in alkaline earth cations. If particle diffusion is the rate controlling step, the composition of the bulk solution is same as that of the thin film adhering the exchanger particles. Hydrogen ions emerging from the exchanger are instantly replaced by the alkaline earth cations in the thin film of the solution.

Although the rates of exchange are measured in limited bath experiments, the conditions are effectively those of an infinite bath. The theory of Boyd et al^[15](Equation-2) describing diffusion into spherical particles of radius r , is applicable for the system.

$$F = 1 - \frac{6}{\Pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2 Bt)}{n^2} \quad (2)$$

Where $B = \Pi^2 D_i / r^2$, D_i is the effective diffusion coefficient for M^{n+} - H^+ exchange within the exchanger. F vs t plots (Figure 1) for all the alkaline earth cations show that exchange takes place by an initial fast exchange, followed by a slow step, both being independent of the concentration of incoming ions and are particle diffusion controlled. This may be due to the reason that surface protons are responsible for initial fast exchange and later on the exchange rate slows down as the counter ions enter the matrix of the ion-exchanger.

Interdiffusion mechanism

A change in the mode of the ion-exchange process is observed at a point where about 75% of the exchange is complete (Figure 2-4). So, the exchange process can be divided into two steps:

- (1) Initial fast exchange, when the metal ions exchange with protons at the surface of the exchanger particles,
- (2) Subsequent slow exchange process in the inner matrix of the exchanger particles.

The shapes of F vs $t^{1/2}$ plots (Figure 2-4) as well as that of McKay plots (Figure 7) suggest two interdiffusion processes; a faster one corresponding to the residual curve and the later linear portion of the McKay plot. This overall process indicates that the effective diffusion coefficient consists of two components, representing the interdiffusion of counter

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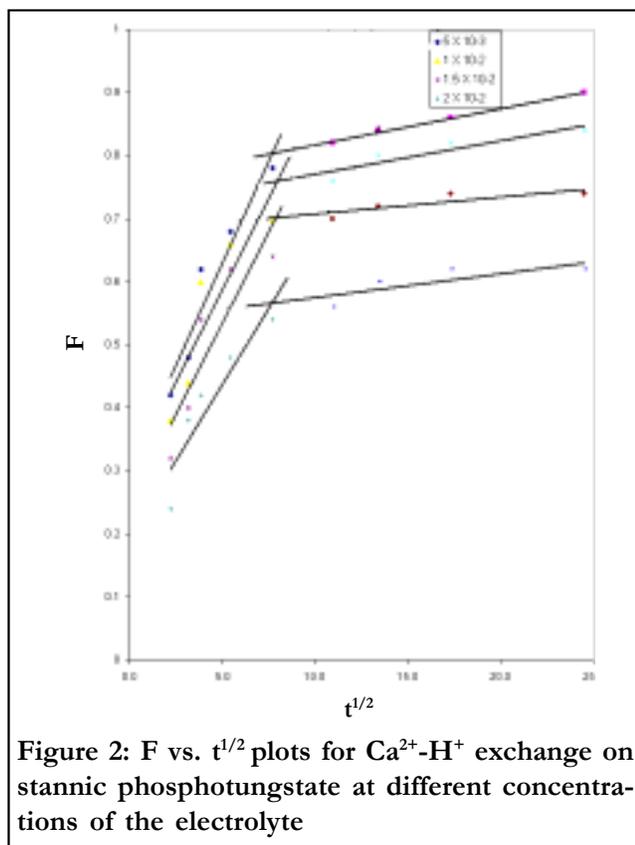


Figure 2: F vs. $t^{1/2}$ plots for Ca^{2+} - H^{+} exchange on stannic phosphotungstate at different concentrations of the electrolyte

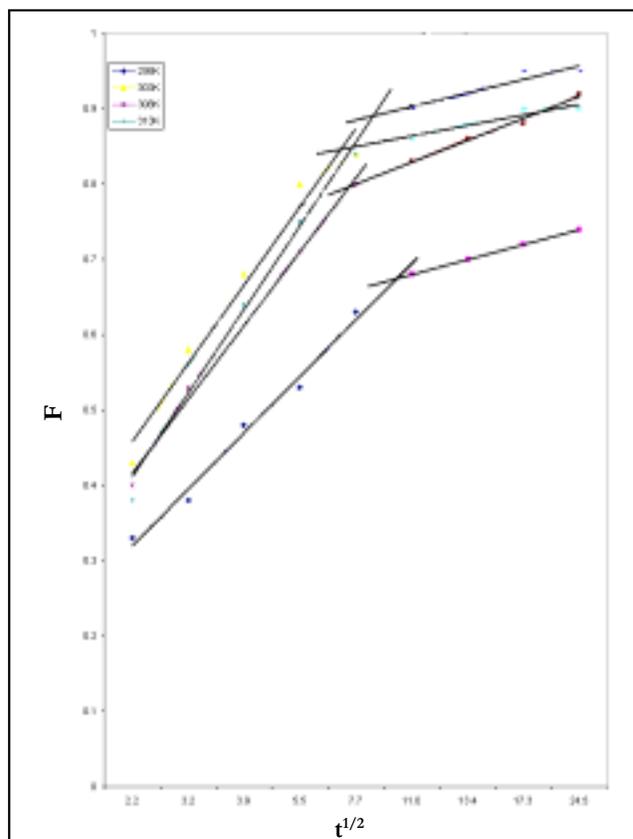


Figure 4: F vs. $t^{1/2}$ plots for Ca^{2+} - H^{+} exchange on stannic phosphotungstate at different temperatures

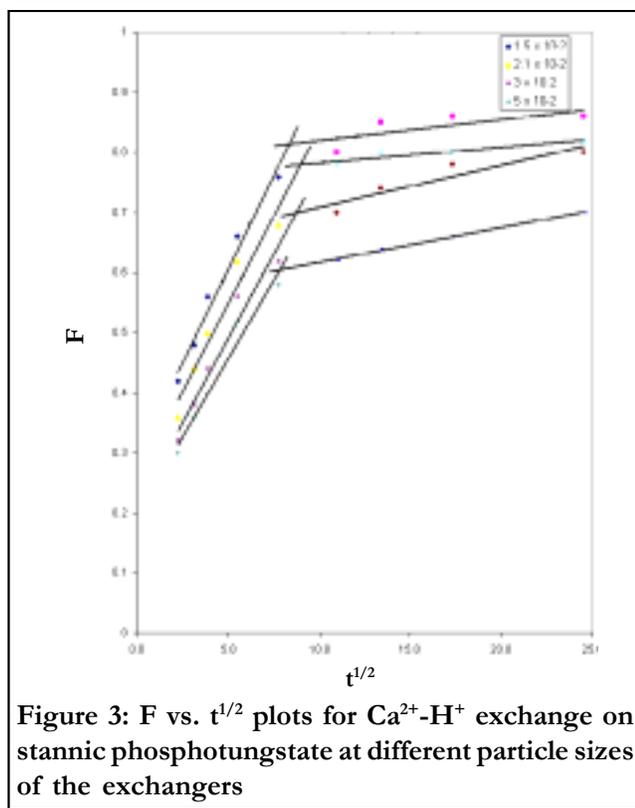


Figure 3: F vs. $t^{1/2}$ plots for Ca^{2+} - H^{+} exchange on stannic phosphotungstate at different particle sizes of the exchangers

ions through the pores of the exchanger matrix. Shapes of McKay plots can be explained on the basis

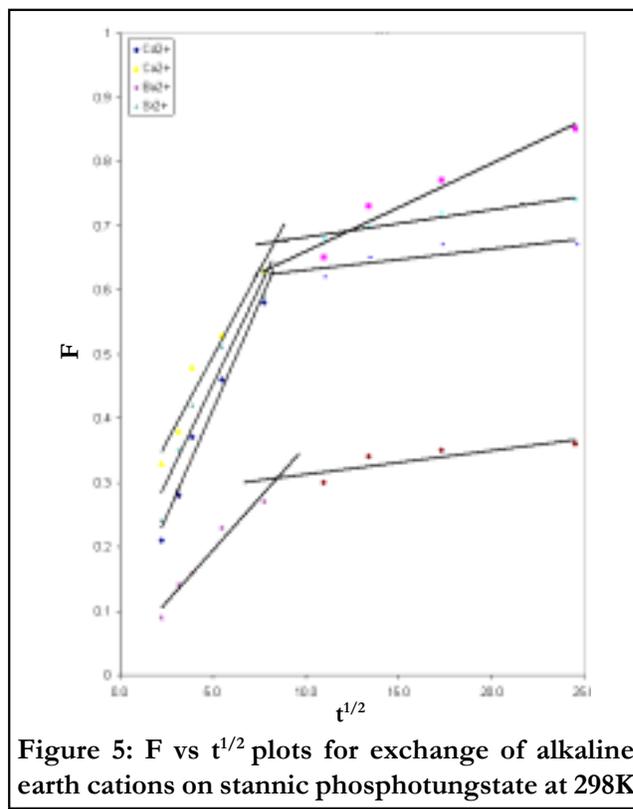


Figure 5: F vs. $t^{1/2}$ plots for exchange of alkaline earth cations on stannic phosphotungstate at 298K

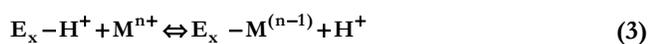
of the heterogeneity of the functional groups, as tungstates and phosphates are incorporated in the exchanger. Similar observations are reported by Singh et al^[16].

Effect of concentration

Diffusion coefficients do not change much (Figure 2) within the concentration range of 5×10^{-3} to 2×10^{-2} M, since the number of fixed ionic sites does not change.

Effect of particle size

The rate of exchange increases as the particle size of the exchanger decreases (Figure 3), probably due to the reason that an increased surface area becomes available with particle of small size, showing that the exchange is taking place through a particle diffusion process. It is quite interesting to note that ion exchange rate increases with decreasing diameters of the particles. The particles with diameter $(5-17) \times 10^{-2}$ cm have about 35% more ion exchange rate than the particles with diameter $> 17 \times 10^{-2}$ cm. The particles with diameters $(3-5) \times 10^{-2}$ cm and $(2.1-3) \times 10^{-2}$ cm have only about 10% more ion exchange rate than the particles with diameters $(5-17) \times 10^{-2}$ cm and $(3-5) \times 10^{-2}$ cm respectively. Below the particle sizes with diameter 2.1×10^{-2} cm the rate of exchange becomes almost constant. With decreasing particle size, the ion exchange equilibrium shifts more and more to the right in the following equation (3).



Where E_x^- is one of the many fixed anionic sites in the exchanger matrix and Mn^+ is the exchanging metal ion.

Effect of temperature

The shape of F vs $t^{1/2}$ plots (Figure 4) indicate

TABLE 4: Magnitude of exchange (meq/g) of cations in stannic phosphotungstate with in initial 2 minutes of contact time

Temperature ^o C	Mg ²⁺ (0.65 Å)	Ca ²⁺ (0.99 Å)	Sr ²⁺ (1.13 Å)
25	0.06	0.14	0.2
30	0.065	0.15	0.195
35	0.05	0.11	0.16

that with increase in temperature, contribution of faster component decreases which is in contrast to observation by other workers^[11]. This may be attributed to the fact that at lower temperature, the metal ion diffuses as dehydrated ions. The probability of diffusion of dehydrated ions is more at lower temperature since the excess energy available at successive higher temperature is preferably used in keeping the hydration shell intact. The hypothesis of diffusion of metal ions as dehydrated ions is supported by the observations (TABLE 4) that the magnitude of exchange in the initial stage of diffusion decreases in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ ion. Bare Ionic radii of the alkaline earth metal ions increase in the reverse order to that of hydrated radii. Moreover, the ion-exchange capacities for these metal ions (TABLE 5) are in the order $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, suggesting that the exchange of metal ions is taking place as hydrated ions. Interdiffusion coefficients also depend on the electropotential gradient along the diffusion path.

Following observation can be made from the F vs $t^{1/2}$ plots (Figure 5) for the exchange of alkaline earth metal ions at a given temperature.

- The size of the exchanging ion is an important but the only factor controlling the extent of exchange.
- Ion exchanging process in case of Ba^{2+} is a continuous one, unlike that of Ca^{2+} , Sr^{2+} and Cd^{2+} which undergo a two exchange process.
- Generally, the first stage exchange process is faster, followed by a relatively slower second stage exchange process. It is supported by observations of Clearfield et al^[17] which say that conduction by surface protons is 1000 times faster than the protons in the inner matrix of the exchanger.

TABLE 5: Ion exchange capacities of stannic phosphotungstate for alkaline-earth metal ions

Metal ion	Solution used (0.5M)	Hydrated ionic radii (Å)	I.E. capacity (meq/g)
Mg ²⁺	MgCl ₂	3.1	0.06
Ca ²⁺	CaCl ₂	2	0.17
Sr ²⁺	SrCl ₂	1.8	0.29
Ba ²⁺	BaCl ₂	1.5	0.4

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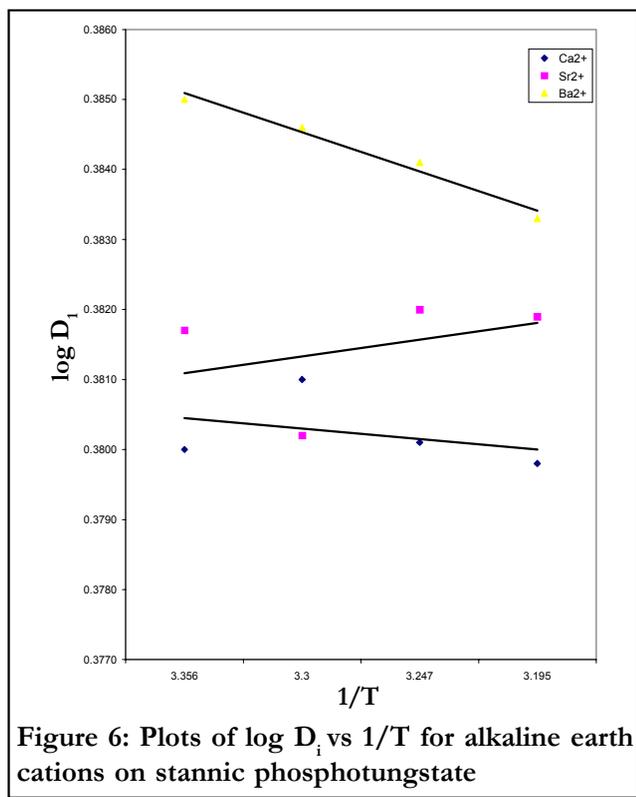


Figure 6: Plots of $\log D_i$ vs $1/T$ for alkaline earth cations on stannic phosphotungstate

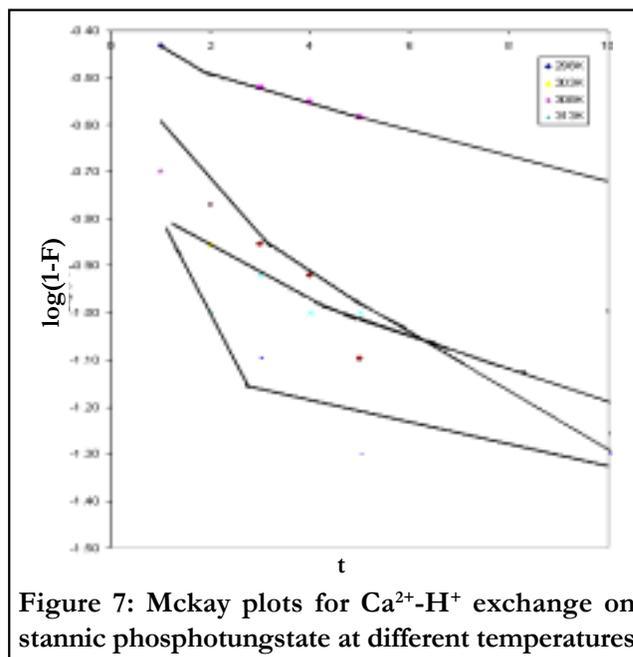


Figure 7: McKay plots for Ca^{2+} - H^+ exchange on stannic phosphotungstate at different temperatures

TABLE 6: Diffusion coefficients of Ca^{2+} , Sr^{2+} and Ba^{2+} ion exchange in stannic phospho-tungstate as a function of temperature

Temperature $^{\circ}\text{C}$	$D_i \times 10^9$ (m^2s^{-1})		
	Ca^{2+}	Sr^{2+}	Ba^{2+}
25	2.4025	2.4052	2.4268
30	2.3923	2.3964	2.4241
35	2.3894	2.4060	2.4195
40	2.3859	2.4053	2.4117

TABLE 7: Diffusion coefficients of Ca^{2+} , Sr^{2+} and Ba^{2+} ion exchange in stannic phosphotungstate as a function of particle size and concentration of electrolyte

Particle size (cm)	$D_i \times 10^9$ (m^2s^{-1})	Concentration (M)	$D_i \times 10^9$ (m^2s^{-1})
1.5×10^{-2}	2.3955	5×10^{-3}	2.3919
2.1×10^{-2}	2.3966	1×10^{-2}	2.3956
3×10^{-2}	2.3968	1.5×10^{-2}	2.4021
5×10^{-2}	2.4049	2×10^{-2}	2.4096

(d) In case of Cd^{2+} ions, firstly there is a slow exchange followed by a fast exchange because once the metal ion enters the matrix of the exchanger, its exchange becomes faster. This observation supports the hypothesis that Cd^{2+} ions move as dehydrated (small sized) ions in the exchanger matrix.

Quantitative analysis

Exchange kinetics can be dealt with quantitatively, by applying the particle diffusion equation for zeolite based exchangers, i.e.,

$$\frac{Q_t}{Q_\infty} = \frac{(2A)}{V} \left\{ \frac{D_i t}{\Pi} \right\}^{1/2} \quad (4)$$

Where Q_t and Q_∞ are the amounts of exchange at time t and at equilibrium, respectively. A and V are the surface area and volume of the exchange particles and D_i is the apparent diffusion coefficient. Assuming the exchanger particles and spherical with radius r , the relation (1) can be written as:

$$F = \frac{Q_t}{Q_\infty} = \frac{6}{r} \left(\frac{D_i t}{\Pi} \right)^{1/2} \quad (5)$$

Linearity of F vs $t^{1/2}$ plots for initial exchange of about 75% (Figures 2-4) confirm the validity of equation (5) vis-a-vis the particle diffusion mecha-

nism for the exchange. From the slopes of these curves, apparent diffusion coefficients have been calculated and are given in the TABLES 6 and 7. Although the diffusion coefficients calculated from the slopes represent the interdiffusion coefficients of the two exchanging ions, i.e., for the M^{n+} - H^+ exchange (where M^{n+} represent Cd^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}), the variation of D_i would be the same if D_i were the diffusion coefficient of the entering ion alone, because in each case, the starting exchanger

is in H^+ form.

TABLE 6 for the diffusion coefficients as a function of temperature shows that at a given concentration and particle size, the diffusion coefficients of Ca^{2+} and Ba^{2+} decrease with increase in temperature because the ions may be present in hydrated form at successive higher temperatures.

TABLE 7 for the diffusion coefficients as a function of particle size shows that diffusion coefficient increases with the increase in particle size. This may be due to the reason that more diffusion is possible in larger particles which have more exchangeable hydrogen ions. It is clear from TABLE 7 that magnitude of diffusion coefficients increase with increase in concentration of the exchanging ions as more ions become available with increase in concentration of electrolyte.

CONCLUSION

The exchange of cations with H^+ ions of stannic phosphotungstate is a rate controlling process similar to diffusion. The size of the exchanging ion is an important but the only factor controlling the extent of exchange. Generally, the first stage exchange process is faster, followed by a relatively slower second stage exchange process. In case of Cd^{2+} ions, firstly there is a slow exchange followed by a fast exchange because once the metal ion enters the matrix of the exchanger, its exchange becomes faster. This observation supports the hypothesis that Cd^{2+} ions move as dehydrated (small sized) ions in the exchanger matrix. At a given concentration and particle size, the diffusion coefficients of Ca^{2+} and Ba^{2+} decrease with increase in temperature because the ions may be present in hydrated form at successive higher temperatures. Magnitude of diffusion coefficients increase with increase in concentration of the exchanging ions as more ions become available with increase in concentration of electrolyte.

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