Exchange kinetic studies on zirconium antimonophosphate

S K Mittal* & Pritpal Singh
Department of Chemical Engineering, Thapar Institute of Engg & Technology (Deemed University), Patiala 147 004, India
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Exchange kinetics of the alkaline earth metal ions with labile protons of the synthetic ion exchanger zirconium antimonophosphate has been studied, using the limited batch technique. Effect of concentration, particle size and temperature on the extent of exchange at the solution-solid interface are reported. The Boyd method for studying the kinetics of spherical particles is used to explain the results. Distinction between particle diffusion and film diffusion has been made by interruption test. The overall studies indicate that the effective diffusion coefficient consists of two components, an initial fast exchange and later a slow exchange, representing the inter-diffusion of counter ions through the pores of the exchanger matrix. With increase in temperature, the contribution of the faster component decreases, probably because the metal ions diffuse as dehydrated ions and the dehydration of the metal ions is easy at lower temperature. The effect of concentration and particle size on the exchange rate are also discussed.

The importance of an ion 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. Initially, exchange kinetics studies for the systems like metal ion-exchanger had been limited to the organic resins. Recently, there has been a lot of interest in the systems with synthetic inorganic ion-exchangers. Studies on the thermodynamic treatment of zeolites reveal that there are distinct inter-planar spaces available for the exchange. Rates of ionic diffusion have been correlated with activity factors and state of hydration of the diffusing cations. Activation energy for self diffusion processes has been correlated with polarizability of the cation. Physical parameters like diffusion coefficients, activation energies and entropies of activations have been calculated from the forward and reverse exchange kinetic studies on antimony based 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 zirconium antimonophosphate.

Materials and Methods
Zirconium(IV) antimonophosphate was prepared by adding an equimolar solution of zirconyl oxychloride(0.1M) to a continuously stirred mixture of potassium pyraantimonate(0.1M) and phosphoric acid solution(0.1M) kept at 20°C, in a volume ratio of 2:1:1. The gelatinous precipitate so obtained was filtered, washed to remove excess co-ions and air dried at 40°C. The dried material was converted to H⁺-form by keeping in HCl (0.1M) for 24 h, washed again to remove excess acid and later dried at 40°C in an air oven and stored over fused silica in a desiccator. IR spectra of the material show sharp bands at 247, 277, 338, 394, 415, 527 and 612 cm⁻¹ conforming to Sb-O-P and other M-O stretching bands besides broad bands of co-ordinated water in the region 1620 cm⁻¹ and 3400 cm⁻¹.

XRD studies on the exchanger show sharp lines indicating the crystalline nature of the material. Alkali metal ion exchange shows reduction in the sharpness of the d-lines which further indicate that a weak Van der Waal based crystallinity exists in the structure. Ion-exchange characteristics like ion exchange capacity and composition were confirmed before proceeding for the exchange kinetic studies.

The ion-exchanger was fractionated into different particle sizes (18/30, 30/52, 52/72 and 72/100 mesh size). Mesh size 30/52 was used for all kinetic studies, while the remaining fractions were used for the particle size effect. The hydrated salts of MgCl₂, CaCl₂, SrCl₂ and BaCl₂ 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 0.2 g of the exchanger material with...
20 mL 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 and Discussion

Rate controlling step

In an ion exchange process, the exchanging ions from the electrolyte can either undergo an exchange process resulting from 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. Therefore, the rate controlling step is the diffusion controlled process which may or may not be followed by 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:

\[ F = \frac{\text{The amount of exchange at anytime, } t}{\text{The amount of exchange at infinite time, } t_\infty} \]  

(1)

A plot of F as a function of time t, in Fig. 1 indicates that particle diffusion of ions within the exchanger constitutes 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 solution at any instant would be same throughout the thin film adhering the exchanger particle to that in the bulk of the solution. 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 (Eq.2) describing diffusion into spherical particles of radius r, is applicable for the system:

\[ F = 1 - \frac{6}{\Pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2 B r)}{n^2} \]  

(2)

where, \( B = \frac{\Pi^2 D_i}{r^2} \), \( D_i \) is the effective diffusion coefficient for \( M^{n+} - H^+ \) exchange within the exchanger. The validity of Eq. 2 has been tested by F vs B plots for each exchanging cation, which is a straight line and passes through the origin. F vs t plots (Fig. 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 confirms the availability of two different hydrogen ions available for exchange within the exchanger. This fact is also supported by potentiometric titration of the exchanger against a base showing successive release of two protons by the exchanger.

Interrupted test

An interruption test was performed to ascertain the nature of diffusion process. After allowing the exchange for three minutes, the exchange process was interrupted for one minute and the exchanger was put again in the same electrolyte solution. Another experiment was performed without interruption by keeping all the conditions of temperature, particle size and concentration the same. It was found (Fig. 2) that

![Fig. 1—F vs t plots of M^{n+}H^+ exchange for alkaline earth cations on zirconium antimonophosphate at 25°C](image1)

![Fig. 2—Exchange of Ca^{2+} ions in zirconium antimonophosphate with and without interruption](image2)
the exchange rate increases immediately after interruption, probably due to the reason that during interruption, exchanging ions get sufficient time for diffusion through the exchanger matrix. It is possible if a particle diffusion process is operational. Hence, the particle diffusion controlled process is established. Studies \(^6\) on potassium copper hexacyanocobaltate(III) have indicated that initial film diffusion process is followed by particle diffusion.

**Interdiffusion mechanism**

A change in the mode of ion exchange process is observed at a point where 65-75\% of the exchange is complete (Fig. 3). So, the exchange process can be divided into two steps:

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

The shapes of F vs \(t^{1/2}\) plots (Fig. 3) as well as that of Mckay plots (Fig. 4) 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 ions through the pores of the exchanger matrix. Shapes of Mckay plots can be explained on the basis of the heterogeneity of the functional groups, as antimonates and phosphates are incorporated in the exchanger. Singh et al. \(^17\) have also reported similar observations.

**Effect of concentration**

Diffusion co-efficients do not show any significant change and remain almost same (Fig. 3) within a concentration range of \(5 \times 10^{-3}\) to \(2 \times 10^{-2}\) M, because the number of fixed ionic sites on the exchanger do not change.

**Effect of particle size**

An increase in the rate is observed with decrease in the particle size which shows that the exchange is taking place through a particle diffusion process. This is due to the increase in available surface area with the decrease in particle size. It is quite interesting to note that for fine particles of the size \(2.5 \times 10^{-4}\) m, the exchange rate is twice as fast as for the particles of diameter \(4.0 \times 10^{-4}\) cm. A further increase in size to \(6.75 \times 10^{-4}\) cm decreases the rate by 20\% and thereafter becomes constant. A possible explanation can be that with decreasing particle size, the ion exchange equilibrium shifts more and more to the right in the following Eq. (3):

\[
E_x - H^+ + Mn^{n+} \rightarrow Ex-M(n-x)+ + H^+
\]

where \(E_x\) is one of the many fixed anionic sites in the exchanger matrix and \(M^{n+}\) is the exchanging ion.

**Effect of temperature**

The shapes of F vs \(t^{1/2}\) plots indicate that with increase in temperature, contribution of faster component decreases which is in contrast to observation by other workers \(^18,19\). This may be attributed to the fact that at lower temperatures, the metal ions diffuse as dehydrated ions. The probability of diffusion of dehydrated ions is more at lower temperature, since the...
excess energy available at successive higher temperatures is preferably used in keeping the hydration shell intact. The hypothesis of diffusion of metal ions as dehydrated ions is supported by the observation (Table 1) that the magnitude of exchange in the initial stage of diffusion decreases in the order \( \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} \). Results for \( \text{Ba}^{2+} \) are not in any order, probably due to its exchange as partially hydrated 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 2) decrease in the order \( \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} \), suggesting that the exchange of metal ions is taking place as dehydrated ions. Interdiffusion coefficients also depend on the electronegativity gradient along the diffusion path.

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

- The size of the exchanging ion is an important but not the only factor controlling the extent of exchange.
- Ion exchange process in case of \( \text{Mg}^{2+} \) is continuous, unlike that of \( \text{Ca}^{2+} \), \( \text{Sr}^{2+} \) and \( \text{Ba}^{2+} \) which undergo a two-step 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.\(^{18}\) which say that conduction by surface protons is 1000 times faster than the protons in the inner matrix of the exchanger. In case of \( \text{Ba}^{2+} \) 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 \( \text{Ba}^{2+} \) 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.,

\[
\frac{Q_t}{Q_e} = \left( \frac{2A}{V} \frac{D_i t}{\Pi} \right)^{1/2}
\]

where \( Q_t \) and \( Q_e \) are the amounts of exchange at time \( t \) and at an equilibrium, respectively. \( A \) and \( V \) are the surface area and volume of the exchanger particles and \( D_i \) is the effective or apparent diffusion coefficient. Assuming the exchanger particles to be spherical with radius \( r \), the relation (i) can be written as:

\[
F = \frac{Q_t}{Q_e} = 6 \left( \frac{D_i t}{r^2} \frac{1}{\Pi} \right)
\]

Linearity of \( F \) vs \( t^{1/2} \) plots for an initial exchange of 65-75\% (Fig. 3) confirms the validity of Eq. 5 vis-a-vis the particle diffusion mechanism for the exchange. From the slopes of these curves, apparent diffusion coefficients have been calculated and are given in Tables 3 and 4. Although the diffusion coefficients calculated from the slopes represent the interdiffusion coefficients of the two exchanging ions i.e., for the \( \text{M}^{n+} - \text{H}^+ \) exchange (where \( \text{M}^{n+} \) represents \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \),

**Table 1** — Magnitude of exchange of cations in ZrSbP within initial 2 min of contact time

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>( \text{Mg}^{2+} ) (0.65 Å)</th>
<th>( \text{Ca}^{2+} ) (0.99 Å)</th>
<th>( \text{Sr}^{2+} ) (1.13 Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.13</td>
<td>0.082</td>
<td>0.080</td>
</tr>
<tr>
<td>30</td>
<td>0.13</td>
<td>0.065</td>
<td>0.065</td>
</tr>
<tr>
<td>35</td>
<td>0.057</td>
<td>0.052</td>
<td>0.037</td>
</tr>
</tbody>
</table>

**Table 2** — Ion exchange capacities of ZrSbP for alkaline earth metal ions

<table>
<thead>
<tr>
<th>Metal ion (0.5 M)</th>
<th>Salt used</th>
<th>Hydrated ionic radius (Å)</th>
<th>Ion exchange capacity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}^{2+} )</td>
<td>Magnesium chloride</td>
<td>3.10</td>
<td>0.36</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} )</td>
<td>Calcium chloride</td>
<td>2.00</td>
<td>0.24</td>
</tr>
<tr>
<td>( \text{Sr}^{2+} )</td>
<td>Strontium chloride</td>
<td>1.80</td>
<td>0.20</td>
</tr>
<tr>
<td>( \text{Ba}^{2+} )</td>
<td>Barium chloride</td>
<td>1.50</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Figure 5 — \( F \) vs \( t^{1/2} \) plots for \( \text{Ca}^{2+}-\text{H}^+ \) exchange on zirconium antimonophosphate at different temperatures.
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 3 for the diffusion coefficients as a function of temperature shows that at a given concentration and particle size, the diffusion coefficient decreases with increase in temperature because the ions are present in hydrated form at successive higher temperatures. This is supported by the observation that entropy decreases with increase in temperature (Table 5) indicating that the additional energy is used up in keeping the hydration shell intact. Our observation is in sharp contrast to that of other researchers.

Table 4 for the diffusion coefficients as a function of particle size shows that diffusion coefficient increases with decrease in particle size. This may be due to the reason that more diffusion is possible in smaller particles with large effective surface area. It is clear from Table 4 that the diffusion coefficients increase with increase in concentration of the exchanging ions as more ions become available with increase in concentration of the electrolyte.

**Thermodynamic analysis**

Activation energies for the exchange were calculated from the slopes of the plots between log \(D_i\) and 1/T. Self diffusion coefficients \((D_o)\) and entropy of activation \((\Delta S^a)\) are calculated by employing Arrhenius type equation and equation given by Barrer et al. respectively.

Inter-diffusion coefficients (Tables 3 and 4) are much smaller when compared with those for strongly cationic resins and even those for inorganic ion-exchangers like titanium vanadophosphate and zirconium antimonate, but closer to that for crystalline zirconium phosphate \((\text{of the order of } 10^{-16} m^2 s^{-1})\).

Results indicate negative values of energy of activation for all the cations under study. Such unusual observations are difficult to explain. The reasons for these results can be found in the mechanism of the exchange process which, in the given case, is a sequence of three steps:

1. Dehydration of the metal ion just before entering the exchanger matrix.
2. Ion-exchange process resulting in the release of hydrogen ions from the exchanger phase to the aqueous phase.
3. Hydration of the hydrogen ions released from the exchanger phase.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>(E_a) (kJ mol(^{-1}))</th>
<th>(\Delta S^a) (J deg(^{-1}) mol(^{-1}))</th>
<th>(D_i\times10^{16}) (cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>-155</td>
<td>-119</td>
<td>2.1</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>-174</td>
<td>-118</td>
<td>2.3</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>-171</td>
<td>-177</td>
<td>3.3</td>
</tr>
</tbody>
</table>

The observed activation energy is the resultant of all the above three steps of the exchange process. By definition, activation energy represents only the elementary process. Since the experimental values represent the overall change in energy contents, it will not be proper to call the observed results as energy of activation, rather it may be called ‘apparent energy of activation’ for the sake of analogy.

‘Apparent energies of activation’ for Ca\(^{2+}\) and Sr\(^{2+}\) are comparable, being -155 kJ mol\(^{-1}\) and -174 kJ mol\(^{-1}\), respectively. The hydrated ionic radii are also comparable (2.0 Å for Ca\(^{2+}\), 1.8 Å for Sr\(^{2+}\)). It is very small (61 kJ mol\(^{-1}\)) for Ba\(^{2+}\) (hydrated ionic radii 1.5 Å), probably due to the reason that the ions exchange with different degrees of hydration. Close values for Ca\(^{2+}\) and Sr\(^{2+}\) ions (Table 5), indicate that the entering ions (in the hydrated form) experience almost same amount of resistance while entering the exchanger matrix, while Ba\(^{2+}\) ions, being smaller in size in the hydrated form, face relatively less resistance. Activation energy is not only dependent on size factor, but also on variables such as magnitude of electrostatic attraction between the fixed anionic sites and the incoming ion as well as on the state of hydration. Ef-
fective diffusion coefficients increase in the order \( \text{Ca}^{2+} < \text{Sr}^{2+}, \text{Ba}^{2+} \) (Table 5) which parallels the ionic radii and the ionic mobility. This trend is supported by the observations by El-Naggar et al.\(^{24}\).

Entropy of activation (\( \Delta S^* \)) for the alkaline earth metal ions is reported in Table 5. The negative values of \( \Delta S^* \) may be in part due to the change in the hydration states of the ions as they enter the exchanger matrix. The hydrogen ions released from the exchanger sites being smaller in size result in overall increase in hydration. The resulting decrease in entropy is more than compensated by the excess hydration energy. Singh et al.\(^{17}\) and Harvie and Nancollas\(^{23}\) have reported similar observations for alkali metal ion exchange on zirconium phosphate.

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**References**


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