Kinetics of Binary Ion Exchange on Titanium Vanadophosphate

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Kinetics of ion exchange of Rb+, Cs+ and Ag+ with H+ on titanium vanadophosphate employing the limited bath technique have been investigated. The slow step which determines the rate of exchange of these ions is the diffusion through the exchanger particle. The values for the inter-diffusion coefficients, energy of activation and entropy of activation have been calculated. The data obtained have been compared with those for organic resins and other inorganic ion exchangers. The rates of exchange on titanium vanadophosphate seem to approach to those on some inorganic ion exchangers and organic resins.

Boyd et al. were the first to report the rate-controlling step in ion exchange to be diffusion either in the exchanger particle itself (particle diffusion) or in an adherent liquid layer (film diffusion), and in an intermediate range of conditions both the mechanisms governing the rate. Particle diffusion-controlled exchange has been studied thoroughly and has found adequate theoretical understanding. In the process of ion exchange, say ion \( A \) is exchanged for ion \( B \) in solution, there occurs an electric coupling of the opposite fluxes of the two ions, so that the rate of inter-diffusion is dependent on the state of conversion of the exchanger from form \( A \) to form \( B \), and diffusion coefficient in the exchanger is not constant with time. An approximate indication of the rate may, however, be obtained if an average constant mobility is assumed (constant-diffusivity model). In isotopic diffusion this assumption is of course very nearly correct. The particle diffusion equation developed by Boyd et al. for isotopic diffusion was found to be valid for binary ion exchange too at higher concentrations in which the composition of the external solution is assumed to be constant and not time dependent.

Most of the studies on the kinetics of ion exchange deal with organic resins, leaving the inorganic counterparts still to be exploited. Mention must be made of the work on zeolites, hydrous zirconium oxide, zirconium phosphate, zirconium antimonate, tantalum arsenate and iron antimonate. These studies have been directed towards the investigation of the diffusion coefficients, since it can describe the mobility of ions in the exchanger and in addition to this it might give a clue to the degree of openness of the channels through which diffusion takes place.

Recently, titanium vanadophosphate (TVP) was synthesized in our laboratory and the material showed good ion exchange properties. Titanium vanadophosphate (TVP) possesses appreciable resistance towards high temperature, chemical attack and ionizing radiations. The practical utility of the material has been shown by achieving a number of metal ion separations of analytical and radiocronical interest. The present paper deals with the kinetics of Rb+/H+, Cs+/H+ and Ag+/H+ exchange systems on the material.

Titanium vanadophosphate \([2\text{TiO}_3 \cdot \text{V}_2\text{O}_5 \cdot 2.5\text{P}_2\text{O}_3 \cdot 13.5\text{H}_2\text{O}]\) was prepared by adding 0.1 M solution of TiCl\(_4\) (Riedel, Germany) to a mixed solution of 0.1 M NH\(_4\)VO\(_3\) (Riedel, Germany) and 0.1 M Na\(_2\)HPO\(_4\) (S. Merck, India) in a volume ratio of 1:1:4, respectively. The granular exchanger was ground and sieved to give two fractions of different particle sizes. Each fraction was converted into hydrogen form by treatment with 2N HCl or HNO\(_3\) in a chromatographic column, then rinsing with demineralized water and finally drying at 70° ± 2°C. The diameters of the particles of the two fractions were measured with a micrometer microscope for hundred particles of each fraction. The mean radii were 2.16 × 10\(^{-4}\)m and 6.35 × 10\(^{-4}\)m (within ~ 4% error). The exchange capacity values determined radioactively by batch method for Rb\(^+\), Cs\(^+\) and Ag\(^+\) are 1.31, 1.43 and 1.26 meq/g., respectively.

Radiotracers, \(^{86}\text{Rb}, ^{110m}\text{Ag}\) and \(^{134}\text{Cs}\) were procured from Bhabha Atomic Research Centre, Bombay. The radiometric assays were made using a gamma-ray spectrometer (ECIL, India).

Kinetic measurements — The rates of exchange were determined by ‘limited bath technique’, employing the method reported earlier. The labelled metal ion solutions \((M^+ = 0.01, 0.05, 0.10 \text{ and } 0.20\text{ M})\) and \(H^+ = 0.01\text{ M}\) were used. The experiments were carried out at 25°, 35°, 45°, and 55°C (±...
Different metal solutions were analysed radio-metrically and the amount exchanged at different time intervals is given by Eq. (1),

\[ F = \frac{S_0 - S_t}{S_0 - S_m} \quad (1) \]

where \( F \) is the fraction exchanged at time \( t \), \( S_0 \) = the counting-rate at \( t = 0 \), \( S_t \) = the counting-rate at \( t = t \), and \( S_m \) = the counting-rate after \( \sim 100\% \) exchange.

The experimental data were analysed by the least squares method. The estimated error was within 5\% for each obtained value of inter-diffusion coefficient, and other thermodynamic parameters.

Results and Discussion

The present investigation was confined to the particle diffusion mechanism only. As the studies were made by 'limited bath technique', the equation given by Boyd et al. and latter modified by Riechenberg has been employed. If the rate-determining step is the diffusion through the exchanger particles, Eq. (2) is valid.

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

In Eq. (2) \( F \) is the fractional attainment of equilibrium at time \( t \), \( n \) is an integer and \( B \) is given by Eq. (3)

\[ B = \pi^2 D_1 / r^2 \quad (3) \]

where \( D_1 \) is the inter-diffusion coefficient for exchanging ion inside the exchanger particle and \( r \), the radius of exchanger particle. The experimental data can be tested to determine whether or not they conform to Eq. (2) by plotting \( Bt \) values (corresponding to experimentally determined \( F \) values from Reichenberg's table (ref. 14) against time. The plots of \( F \) and \( Bt \) versus time for \( \text{Rb}^+ / \text{H}^+ \) exchange as a typical system are presented in Fig. 1.

The plot of \( Bt \) versus \( t \) is linear passing through the origin, with constant value of inter-diffusion coefficient (within experimental error) only at concentration \( > 0.10 \) M. Similar curves (not included in the text) were also obtained for \( \text{Cs}^+ / \text{H}^+ \) and \( \text{Ag}^+ / \text{H}^+ \) systems. From the shape of \( Bt \) versus \( t \) curves an inference can be made that for concentrations 0.01 and 0.05 M in the initial stage of the exchange the diffusion is not controlled by particle diffusion alone, while at concentrations \( > 0.10 \) M, the slow step which determines the rate of exchange is particle diffusion.

The effect of varying temperature and particle size on the rate of exchange for \( \text{Rb}^+ / \text{H}^+ \) system is illustrated in Fig. 2. As can be expected from Eq. 3, the ratio of radii is 11.5 which agrees within experimental error with the inverse ratio of \( B \) values (12.0) for \( \text{Rb}^+ / \text{H}^+ \) exchange at 25°C (Table 1). This applies fairly well to \( \text{Cs}^+ / \text{H}^+ \) and \( \text{Ag}^+ / \text{H}^+ \) exchange systems also. The rate of exchange increases with increase in temperature. This may be attributed to an increase in ionic mobility of exchanging...
ion with temperature. The plots of log $D_i$ versus $1/T$ (Fig. 3) have been drawn to calculate the values of pre-exponential constant ($D_0$) and energy of activation ($E_a$) employing Arrhenius type equation (4).

$$D = D_0 \exp \left( -\frac{E_a}{RT} \right)$$  \hspace{1cm} (4)

The values of entropy of activation ($\Delta S^\ddagger$) are calculated by substituting $D_0$ in equation (5) proposed by Barrer et al.14

$$D_0 = 2.72 \left( k_B T d^2/h \right) \exp \left( \frac{\Delta S^\ddagger}{R} \right)$$  \hspace{1cm} (5)

where $k_B$ = Boltzmann constant, $T = 273$ K, $d$ = ionic jump (distance between two successive positions of ion in the process of diffusion) taken as equal to $5 \times 10^{-10}$ m, $h$ = Planck's constant and $R$ = gas constant.

The values of inter-diffusion coefficients (Table 1) on TVP are much smaller than those on strongly cationic resins1416 and appreciably higher than those for zeolites17. However, the values are almost of the same order of magnitude as on some inorganic ion exchangers, e.g. on zirconium antimonate18 the reported value for Rb$^+/H^+$ exchange is $4.86 \times 10^{-13}$ m$^2$ sec$^{-1}$ at 30°C which is close to $1.97 \times 10^{-12}$ m$^2$ sec$^{-1}$ observed on TVP at 25°C. For Na$^+/H^+$ on weakly cationic resin, Amberlite IRC-50, Conway et al.19 gave the value $3.9 \times 10^{-12}$ m$^2$ sec$^{-1}$. On crystalline zirconium phosphate, however, for alkali metal ion the value of $D_i$ is of the order of $10^{-16}$ m$^2$ sec$^{-1}$ (ref. 6). Thus a comparison of the $D_i$ values observed herein with those reported earlier suggests that the rates of exchange on TVP are approaching to those on some organic resins and other inorganic ion exchangers.

### Table 1 — Inter-Diffusion Coefficients and Other Thermodynamic Parameters Calculated for the Exchange of Rb(I), Cs(I) and Ag(I) on Titanium Vanadophosphates

<table>
<thead>
<tr>
<th>Exchange system</th>
<th>Particle size (m)</th>
<th>Temp. K</th>
<th>$B$ (sec$^{-1}$)</th>
<th>$10^{13} D_i$ (m$^2$ sec$^{-1}$)</th>
<th>$D_0$ (m$^2$ sec$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J mol$^{-1}$ deg$^{-1}$)</th>
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<tr>
<td>Rb$^+/H^+$</td>
<td>2.16x10$^{-4}$</td>
<td>298</td>
<td>4.16x10$^{-4}$</td>
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<td>Ag$^+/H^+$</td>
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</table>

Fig. 3 — Plot of log $D_i$ versus $1/T$ [(1) Cs$^+$; (2) Rb$^+$; (3) Ag$^+$]

Fig. 4 — McKay plot for Rb$^+/H^+$ exchange on TVP [Particle size, $r = 2.16 \times 10^{-4}$ m]
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The McKay plots\(^1\) (Fig. 4) for Rb\(^+\)/H\(^+\) are similar to those of independently decaying activities. This suggest the occurrence of a complex exchange reaction. This can be explained on the basis of the heterogeneity of functional groups as phosphate and arsenate anionic groups are incorporated in the exchanger. Similar observations have been made by Tandon et al.\(^3-\)\(^8\) on the antimonates of zirconium and tin for Rb\(^+\) and Cs\(^+\) exchange and also by Rahman and Barrett\(^9\) for the isotopic exchange of phosphate groups of zirconium phosphate.

The plots of log \(D_i\) versus \(1/T\) are linear enabling the estimation of energy of activation and pre-exponential constant. The values of \(E_a\) have been found to increase with increasing ionic radii for Rb\(^+\) and Cs\(^+\). An analogous behaviour was observed for the diffusion of alkali metal ions through analcite\(^1\) and of Rb\(^+\) and Cs\(^+\) through antimonates of zirconium and tin\(^6\)\(^8\). The value of energy of activation for Ag\(^+\) is equal to that for Cs\(^+\), but the size of Ag\(^+\) is smaller than Cs\(^+\). This can probably be explained as being due to different degrees of dehydration of cations while entering the exchanger phase.

The values of entropy of activation\(^9\) are in part associated with the change of hydration states of the ions as they leave the aqueous solution and enter the solid phase and vice versa. The negative values of \(\Delta S^\ddagger\) observed may be in part due to an overall increase in the hydration as the hydrogen ions replace larger cations (counterions) in solution, indicating thereby a certain degree of dehydration of cations while diffusing into the solid phase. This is in agreement with the observation of Harvie and Nancollas\(^8\) who pointed out that Li\(^+\) and Na\(^+\) diffuse as hydrated species, with the possibility of K\(^+\) being anhydrous on zirconium phosphate.

References